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Seasonal variations of diacids, ketoacids, and α-dicarbonyls in aerosols at Gosan, Jeju Island, South Korea: Implications for sources, formation, and degradation during long-range transport

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[1] Aerosol samples (n = 84) were collected continuously from April 2003 to April 2004 at Gosan site in Jeju Island, South Korea. The samples were analyzed for diacids, ketoacids, and α-dicarbonyls, as well as organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), and water-soluble inorganic ions. Oxalic acid (C_2) was the most abundant followed by malonic acid (C_3) in all the seasons. The mean concentration (784 ng m^{-3}) of total diacids (C_2–C_{12}) and their relative abundances in total organic species detected, OC and WSOC were found to be the highest in summer, whereas those of ketoacids and dicarbonyls were the highest in winter. The annual mean contributions of diacids, ketoacids, and dicarbonyls to WSOC are 12, 1, and 0.4%, respectively. They are several times higher than those reported in East Asia from which air masses are transported to Gosan, indicating an importance of photochemical processing of aerosols during a long-range transport. Diacids and related compounds show different seasonal variations, suggesting their season-specific sources and photochemical processing. This study demonstrates an enhanced photochemical production and degradation of water-soluble organics in summer. In contrast, higher positive correlations between combustion tracers (non-sea-salt K^+ and EC) and diacids and related compounds were observed in the winter, pointing out higher emission of diacids and related compounds or their precursors from fossil fuel/biomass burning.

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1. Introduction

[2] The ubiquitous presence of diacids and related compounds (ketoacids and α-dicarbonyls) in tropospheric aerosols has been well documented in the literature [*Kawamura and Ikushima*, 1993; *Kawamura and Usukura*, 1993; *Li and Winchester*, 1993; *Khwaja*, 1995; *Baboukas et al.*, 2000; *Kerminen et al.*, 2000; *Limbeck et al.*, 2001; *Fraser et al.*, 2002; *Mochida et al.*, 2003a, 2003b; *Ho et al.*, 2007; *Legrand et al.*, 2007; *Miyazaki et al.*, 2009]. They can account for 0.3–4.5% of total carbon (TC) in urban aerosols and more than 10% of TC and water-soluble organic carbon (WSOC) in remote marine aerosols [*Kawamura and Ikushima*, 1993; *Kawamura and Sakaguchi*, 1999; *Kerminen et al.*, 2000; *Kawamura and Yasui*, 2005; *Ho et al.*, 2007; *Wang et al.*, 2006]. These studies demonstrated that diacids are the major organic species in atmospheric aerosols, although their seasonal behaviors are not well understood.

[3] *Pradeep et al.* [2003] reported that oxalic, malonic, and glutaric acids are fully activated to cloud droplets at supersaturation, being consistent with the experiments of *Cruz and Pandis* [1997]. They observed that submicron aerosols of glutaric and adipic acids can act as cloud condensation nuclei at typical atmospheric supersaturations of 0.3% and 1%. Diacids can also affect the heterogeneous chemistry in the atmosphere. For example, *Folkers et al.* [2003] reported that the reactive uptake coefficient of N_2O_5, one of major intermediates for the removal of NO_x in the atmosphere, by uncoated NH_4HSO_4 particles is depressed when NH_4HSO_4 is coated with organics containing diacids and others. This suggests that an organic surface suppresses the transfer of N_2O_5 into the ammonium bisulfate core. The higher levels of N_2O_5 increase the oxidizing capacity of the atmosphere. It is therefore very important to study diacids and related compounds in atmospheric aerosols.

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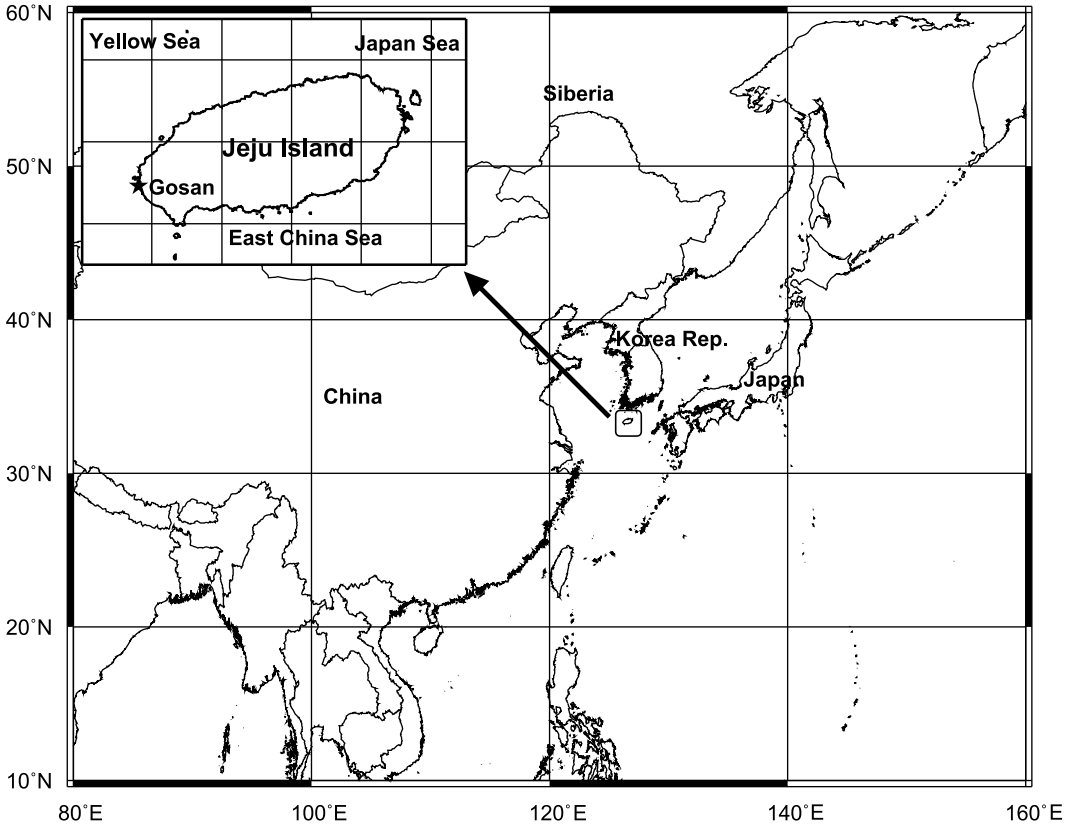

Figure 1. Map showing geographical region where sampling was carried out. The Gosan site is situated in the west coast of Jeju Island, South Korea.

[4] Diacids and related compounds do have primary sources, such as fossil fuel combustion [*Kawamura and Kaplan*, 1987], meat cooking operation [*Rogge et al.*, 1991; *Schauer et al.*, 1999], and biomass burning [*Yamasoe et al.*, 2000; *Mayol-Bracero et al.*, 2002; *Gao et al.*, 2003; *Kundu et al.*, 2010a]. However, it is widely believed, based on laboratory and field observations, that they are overwhelmingly produced due to the oxidation of various organic precursors via different photochemical pathways in the atmosphere.

[5] *Matsunaga et al.* [1999] reported that an irradiated oleic acid-ozone system produces a homologous series of diacids (C_2–C_9) with azelaic acid as dominant species. A cycloalkene-ozone system can produce diacids via the transformation of dialdehydes to oxoacids [*Hatakeyama et al.*, 1985; *Kalberer et al.*, 2000; *Gao et al.*, 2001]. *Warneck* [2003] suggested that cloud processing of glyoxal and glycoaldehyde yields oxalic acid via glyoxylic acid. Glyoxal can be produced from toluene and other aromatic hydrocarbons, ethyne, and isoprene [*Stockwell et al.*, 1997; *Warneck*, 2003; *Ervens et al.*, 2004; *Ieda et al.*, 2006], whereas glycoaldehyde is from ethene and isoprene [*Warneck*, 2003; *Ervens et al.*, 2004; *Ieda et al.*, 2006]. *Lim et al.* [2005] and *Carlton et al.* [2006] suggested that oxalic acid is produced from the oxidation of methylglyoxal via the formation of pyruvic and acetic acids as intermediates. *Fisseha et al.* [2004] reported that photooxidation of 1, 3, 5-trimethylbenzene can produce oxalic, methylmaleic, and pyruvic acids. Phthalic acid is a photodegradation product of naphthalene [*Bunce et al.*, 1997] and possibly other polycyclic aromatic hydrocarbons [*Jang and McDow*, 1997].

[6] Diurnal variations of diacids and related compounds have been reported in aerosol samples with maxima at noontime [*Satsumabayashi et al.*, 1990; *Stephanou and Stratigakis*, 1993; *Kawamura and Yasui*, 2005]. Diacids are enriched in the submicron mode of aerosols [*Mészáros et al.*, 1997; *Kerminen et al.*, 1999, 2000]. *Kawamura et al.* [1995] reported that concentrations of diacids are 5–20 times more abundant in Arctic aerosols during polar sunrise season than those in aerosols during the preceding dark winter months. These studies provide strong evidence for the secondary production of diacids and related compounds.

[7] Gosan site, which is located at the western edge of Jeju Island, South Korea, has been regarded as an ideal place to study the chemical production and transformation of atmospheric organic aerosol from anthropogenic and biogenic (oceanic and continental) precursors, whose emission strengths vary due to the air masses transported from China, Korea, Japan, and the Pacific Ocean. Air mass transport patterns depend on the seasons. Previous studies at the Gosan site have determined inorganics, bulk organics, and trace gases in the atmosphere over short and long timescales [*Carmichael et al.*, 1996, 1997; *Arimoto et al.*, 1997; *Chen et al.*, 1997; *Kim et al.*, 2002, 2007; *Park et al.*, 2004; *Topping et al.*, 2004; *Lee et al.*, 2007; *Miyazaki et al.*, 2007].

Table 1. Concentrations of Diacids, Ketoacids, and α-Dicarbonyls Detected in Atmospheric Aerosols Over Gosan, Jeju Island, South Korea

Compounds	Spring (n = 37)[a]			Summer (n = 13)[a]			Autumn (n = 10)[a]			Winter (n = 24)[a]		
	Range (ng m^{-3})	Average (ng m^{-3})	Median (ng m^{-3})	Range (ng m^{-3})	Average (ng m^{-3})	Median (ng m^{-3})	Range (ng m^{-3})	Average (ng m^{-3})	Median (ng m^{-3})	Range (ng m^{-3})	Average (ng m^{-3})	Median (ng m^{-3})
Saturated n-diacids												
Oxalic, C_2	198–1228	537.0	471.0	201–1293	564.4	478.2	189.2–775	381.9	350.0	92.3–1251	349.2	272.8
Malonic, C_3	12–166	64.8	54.0	7–167	73.3	72.1	20.2–118	54.3	49.0	10.1–129	40.9	32.2
Succinic, C_4	8–190	59.3	43.5	10–187	68.8	62.2	7.1–68.6	30.9	22.0	8.7–118	33.1	26.0
Glutaric, C_5	1.4–65	16.5	12.3	2.1–69	17.9	12.5	0.9–17.5	7.9	6.0	2.8–41	9.5	7.2
Adipic, C_6	0.7–19	5.6	4.8	0.9–18	4.9	2.5	0.6–7	3.7	3.3	1.6–18.1	4.8	3.6
Pimelic, C_7	0.2–8	2.3	1.8	0.1–9.4	2.2	1.0	0.4–2.9	1.4	1.4	0.4–11.2	2.2	1.7
Suberic, C_8	0.7–6	2.2	1.9	0.7–8.3	2.5	1.8	0.6–2.6	1.6	1.5	0.01–9.1	1.9	1.5
Azelaic, C_9	1.3–7.6	4.3	4.1	2–9	4.6	4.1	2.2–6.2	3.9	3.5	0.01–12.6	3.4	3.3
Sebacic, C_{10}	0.02–4.1	0.9	0.8	0.4–2.5	0.9	0.6	0.1–1.1	0.5	0.4	0.1–2.8	0.6	0.5
Undecanedioic, C_{11}	0.4–4.9	1.2	1.0	0.5–9	3.3	3.2	0.7–2	1.2	1.1	0.2–3.3	0.8	0.5
Dodecanedioic, C_{12}	0.01–0.2	0.1	0.1	BDL[a] –0.4	0.1	0.03	0.01–0.1	0.1	0.1	BDL[a]–0.4	0.1	0.1
Branched diacids												
Methylmalonic, iC_4	0.6–4.9	1.7	1.4	0.4–4.6	1.8	1.7	0.3–3.7	1.6	1.3	0.5–4.2	1.3	1.1
Methylsuccinic, iC_5	0.6–10.2	3.7	3.0	0.3–10.6	3.5	2.4	0.2–5.8	2.1	1.8	1.3–11.9	3.6	2.7
Methylglutaric, iC_6	0.1–5.2	1.2	0.8	0.1–4.7	1.0	0.9	0.1–1.4	0.6	0.5	0.5–2.6	0.9	0.8
Unsaturated diacids												
Maleic, M	0.1–10.9	3.7	3.0	0.6–6.6	2.3	1.9	0.5–7.4	3.1	3.1	2.2–12.8	4.9	4.0
Fumaric, F	0.4–9.2	3.2	2.3	0.7–9.9	3.2	2.6	0.5–4.1	2.1	2.1	0.7–11.5	2.7	1.9
Methylmaleic, mM	0.2–5.9	2.6	2.4	0.5–6.1	1.9	1.3	0.3–6	2.6	2.5	0.9–12.1	3.4	2.4
Phthalic, Ph	1–19.9	7.9	7.4	0.5–15.5	4.9	2.9	1.4–38.3	9.6	8.2	0.5–52.4	19.4	15.0
Isophthalic, iPh	0.2–2.7	1.2	1.1	0.1–3.8	0.8	0.4	0.01–2	0.8	0.8	0.3–5.2	1.5	1.1
Terephthalic, tPh	0.01–17	8.0	8.4	1.4–17	6.7	5.5	2.6–13.4	8.6	9.1	3–30	8.9	7.6
Multifunctional diacids												
Hydroxysuccinic, hC_4	BDL[a]–15	3.0	2.2	0.6–21.1	7.4	6.4	0.5–13	4.2	2.7	0.5–11.8	2.6	2.0
Ketomalonic, kC_3	0.1–4	1.2	1.0	0.1–1.7	0.7	0.4	0.1–1.8	0.8	0.9	0.6–6	2.1	1.5
Ketopimelic, kC_7	0.01–20	4.0	2.0	0.6–20.8	6.8	3.9	0.4–5.2	1.9	1.4	0.2–4.9	1.4	1.1
Total diacids	233–1730	735.4	630.4	253–1875	784.0	623.4	245–1062	525.3	461.6	142–1757	499.1	392.4
Ketoacids												
Glyoxylic, ωC_2	7.3–103.4	38.0	31.4	6.3–84.8	28.5	17.7	6.3–63.8	27.8	23.8	11.2–148.2	40.7	34.5
3-Oxopropanoic, ωC_3	0.01–2.0	0.4	0.2	0.02–4.2	1.4	0.5	0.01–0.4	0.1	0.1	0.1–0.6	0.2	0.2
4-Oxobutanoic, ωC_4	0.004–3.7	0.7	0.3	0.1–0.9	0.4	0.4	BDL[a]–2.9	0.6	0.3	0.1–1.6	0.3	0.2
9-Oxononanoic, ωC_9	BDL[a]–5.3	1.9	1.8	BDL[a]–4.7	1.1	0.6	0.8–4.5	2.0	1.9	BDL[a]–5.7	1.3	0.7
Pyruvic acid, Pyr	0.54–13.4	5.0	4.9	0.9–12.1	4.3	2.7	0.8–5.5	3.0	3.0	0.7–15	4.6	3.2
Total ketoacids	9.7–120.3	46.1	39.7	9–103	35.7	22.3	8–73.9	33.5	29.0	12.8–170.4	47.3	39.5
α-Dicarbonyls												
Glyoxal, Gly	1.1–11.6	3.6	3.3	0.5–4.7	2.0	1.2	0.4–6.9	2.2	1.6	2.2–106.3	9.3	4.7
Methylglyoxal, MeGly	0.9–60	14.4	11.0	1.9–15.6	7.1	7.2	4.6–21.7	9.2	7.0	1.7–35.7	13.8	13.5
Total α-dicarbonyls	2–64	17.9	14.4	2.3–20.3	9.1	8.3	6–28.6	11.4	8.9	8.1–108.2	23.1	17.1

[a]Spring, March to May; summer, June to August; autumn, September to November; winter, December to February; n, number of samples; BDL, below detection limit.

However, there are a few studies on molecular composition of atmospheric organic aerosols [*Kawamura et al.*, 2004; *Yang et al.*, 2004; *Wang et al.*, 2009]. These studies, except for the work of *Kawamura et al.* [2004], mainly focused on the spring samples, when the continental outflows are the most intense. *Kawamura et al.* [2004] discussed composition and seasonal variations of diacids and related compounds in atmospheric aerosol samples (n = 48) collected from April 2001 to March 2002. There are a few ground, ship, and aircraft measurements of diacids and related compounds in the regions surrounding the Gosan site, such as East Asian megacities, the Japan Sea, the China Sea, the Pacific Ocean, and Chichi-jima Island [*Kawamura et al.*, 2003; *Mochida et al.*, 2003a, 2003b; *Ho et al.*, 2007].

[8] In this study, we report molecular distributions, abundances, and seasonal trends of diacids and related compounds in atmospheric aerosol samples (n = 84) collected at Gosan from April 2003 to April 2004 and compare our data with previous studies carried out at the same site and its surrounding areas to understand any significant organic composition changes in East Asia. We also discuss the sources and chemical formation and loss of diacids and related compounds during long-range transport.

2. Experiment

2.1. Site Description

[9] The Gosan site in Jeju Island (33°29′N, 126°16′E) is approximately 100 km south of Korean Peninsula, ~500 km east of China (Jiangsu province or Shanghai), ~200 km west of Kyushu Island, Japan, and ~1000 km northeast of Taipei (Figure 1). The site and its surroundings are covered with grasses but no trees. Because of its location and very limited local anthropogenic emissions [*Kim et al.*, 1998], Gosan has been considered as an ideal site to monitor the air quality of the western rim of the North Pacific and the outflows from East Asia [*Carmichael et al.*, 1996, 1997; *Chen et al.*, 1997]. Gosan was used as a supersite of the Asian Pacific Regional

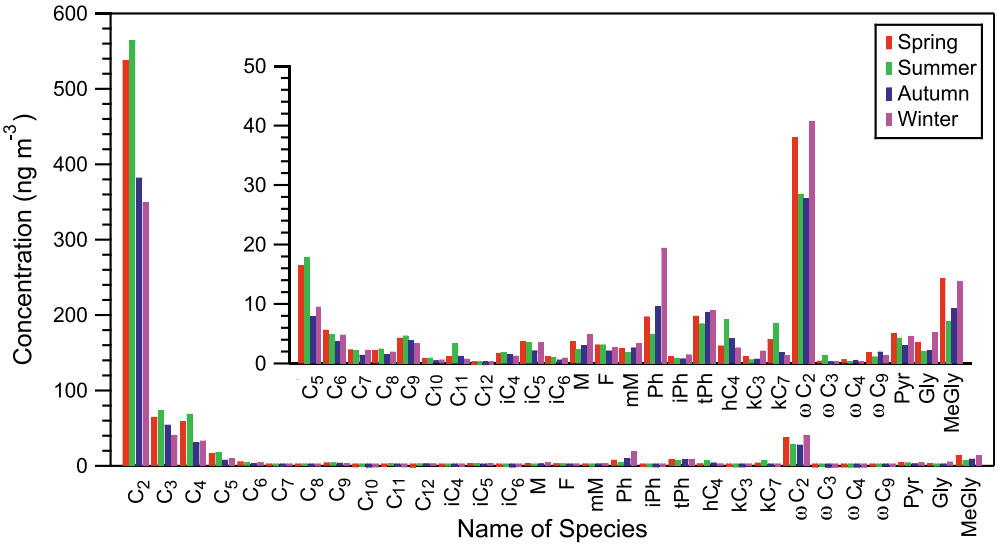

Figure 2. Seasonally averaged molecular distribution of straight chain diacids (C_2–C_{12}), branched chain diacids (iC_4–iC_6), unsaturated diacids (M, F, mM, Ph, iPh and tPh), multifunctional diacids (hC_4, kC_3 and kC_7), ketoacids (ωC_2–ωC_9, and Pyr), and α-dicarbonyls (Gly and MeGly) in aerosol collected at Gosan from April 2003 to April 2004. See Table 1 for abbreviations.

Aerosol Characterization Experiment (ACE-Asia) campaign in 2001 [*Huebert et al.*, 2003] and the Pacific Exploratory Mission (PEM)-West A and PEM-West B programs conducted between 1991 and 1994 [*Hoell et al.*, 1996, 1997]. It is now used as one of superstations of Atmospheric Brown Cloud program [*Lee et al.*, 2007]. A more detailed description of this site is given elsewhere [*Kim et al.*, 1998; *Kawamura et al.*, 2004; *Lee et al.*, 2007].

2.2. Aerosol Sampling

[10] Total suspended particles (TSP) in the atmosphere were collected at the Gosan site over 2–7 days throughout the year from 2003 April to 2004 April. TSP samples (n = 84) were collected onto precombusted quartz fiber filters (20 × 25 cm, Pallflex 2500QAT-UP) using a high-volume air sampler (Kimoto AS-810) at a flow rate of 0.8 m^{-3} min^{-1}. The sampler was placed on the roof of a trailer house (~3 m above the ground). TSP sampling is preferred for collecting adequate aerosol materials in order to measure diacids and related compounds and a wide variety of chemical components (water-soluble inorganic ions, organic carbon (OC), elemental carbon (EC), WSOC, etc.). Before and after the sampling, each filter was placed in a clean glass jar (150 mL) with a Teflon-lined screw cap. Samples were stored immediately in a freezer after the collection, transported to our laboratory in Sapporo at ambient temperatures, and stored in a dark freezer room at −20°C until analysis. High-volume sampling has potential problems: (1) adsorption of gaseous diacids and related compounds onto filter substrates and already collected particles and (2) volatilization of particulate diacids and related compounds during sampling. *Mochida et al.* [2003b] compared the concentrations of diacids (oxalic, malonic, succinic, and glutaric acids) obtained using high-volume and annular denuder samplers. Annular denuder system has negligible adsorption/volatilization problems in the measurement of particulate diacids. An agreement was observed between high-volume and denuder data [*Mochida et al.*, 2003b]. *Limbeck et al.* [2001] observed the dominant fraction of diacids (C_2–C_9) and related compounds (pyruvic and glyoxylic acids) in the aerosol phase. This result has suggested that high-volume data represent real ambient concentration of particulate diacids and related compounds. Field blank filters were collected every month like the real samples except that the pump was not turned on.

2.3. Analytical Method

[11] Filter samples were analyzed for water-soluble diacids, ketoacids, and α-dicarbonyls using the method described by *Kawamura and Ikushima* [1993] and *Kawamura* [1993]. Briefly, aliquots of the filter samples were extracted with organic-free pure water (5 mL × 3, >18 MΩ) by ultrasonic agitation for the isolation of diacids and related compounds. The extracts were passed through a glass column (Pasteur pipette) packed with quartz wool in order to remove filter debris and insoluble particles and then concentrated to almost dryness using a rotary evaporator (~40°C). The concentrates were derivatized with 14% borontrifluoride in n-butanol at 100°C over an hour. The derived dibutyl esters and dibutoxy acetals were extracted with n-hexane (~5 mL) after adding pure water (~5 mL). The hexane layer was concentrated to ~50 μL using a rotary evaporator, transferred to small vial (1.5 mL), dried to almost dryness by N_2 blow down, and dissolved in a known volume of n-hexane (usually 100–400 μL). This analytical technique may provide some artifacts due to chemical treatment of aerosols [*Hallquist et al.*, 2009]. For example, oligomers of glyoxal and methylglyoxal in aerosols can be broken down to monomers during the derivatization step, which results in higher concentrations of α-dicarbonyls than reality. Although this artifact has not been evaluated in the present study, we consider that the reported concentrations of glyoxal and methylglyoxal include their oligomers.

[12] A 2 μL aliquot of the sample was injected into a capillary gas chromatography (GC) system (Hewlett-

Table 2. Relative Abundances of Individual Compounds in Total Diacids, Ketoacids, and α-Dicarbonyls in Aerosols

Compounds	Spring (n = 37)[a]			Summer (n = 13)[a]			Autumn (n = 10)[a]			Winter (n = 24)[a]		
	Minimum (%)	Maximum (%)	Average (%)	Minimum (%)	Maximum (%)	Average (%)	Minimum (%)	Maximum (%)	Average (%)	Minimum (%)	Maximum (%)	Average (%)
Saturated n-diacids												
Oxalic, C_2	53.54	80.95	67.60	64.35	81.00	70.77	56.58	75.62	67.14	53.88	70.97	61.25
Malonic, C_3	4.11	11.12	8.14	1.37	11.03	8.67	6.75	13.11	9.31	5.39	9.17	7.17
Succinic, C_4	3.18	10.78	6.96	3.14	10.81	7.10	2.72	6.68	5.15	4.78	6.54	5.70
Glutaric, C_5	0.48	3.49	1.82	0.72	3.44	1.72	0.35	1.81	1.27	1.19	2.08	1.62
Adipic, C_6	0.30	1.18	0.69	0.25	0.89	0.50	0.23	0.91	0.65	0.49	1.10	0.86
Pimelic, C_7	0.06	0.43	0.27	0.03	0.47	0.22	0.16	0.38	0.25	0.11	0.57	0.36
Suberic, C_8	0.10	0.46	0.27	0.19	0.48	0.29	0.20	0.36	0.28	0.003	0.46	0.33
Azelaic, C_9	0.26	1.20	0.60	0.37	1.20	0.65	0.55	1.15	0.75	0.005	1.20	0.63
Sebacic, C_{10}	0.005	0.42	0.10	0.06	0.20	0.12	0.02	0.13	0.09	0.06	0.18	0.10
Undecanedioic, C_{11}	0.07	0.91	0.17	0.14	0.73	0.43	0.17	0.73	0.26	0.05	0.36	0.13
Dodecanedioic, C_{12}	0.002	0.08	0.01	BDL[a]	0.02	0.01	0.004	0.02	0.01	BDL[a]	0.03	0.01
Branched diacids												
Methylmalonic, iC_4	0.12	0.41	0.22	0.10	0.29	0.21	0.12	0.32	0.25	0.14	0.43	0.24
Methylsuccinic, iC_5	0.24	1.22	0.47	0.09	0.58	0.37	0.08	0.75	0.36	0.46	0.98	0.66
Methylglutaric, iC_6	0.03	0.33	0.14	0.03	0.23	0.10	0.02	0.18	0.11	0.07	0.32	0.19
Unsaturated diacids												
Maleic, M	0.02	2.54	0.51	0.13	0.34	0.26	0.11	1.37	0.60	0.35	2.13	1.04
Fumaric, F	0.10	0.55	0.37	0.18	0.50	0.34	0.16	0.64	0.37	0.23	0.64	0.47
Methylmaleic, mM	0.09	0.96	0.33	0.13	0.30	0.20	0.08	0.87	0.48	0.23	0.88	0.61
Phthalic, Ph	0.15	3.37	1.06	0.20	0.93	0.54	0.41	4.91	1.75	0.08	7.47	3.68
Isophthalic, iPh	0.05	0.38	0.15	0.02	0.19	0.07	0.004	0.42	0.15	0.12	0.42	0.24
Terephthalic, tPh	0.002	2.13	1.07	0.39	1.77	0.79	1.00	3.29	1.71	0.96	2.01	1.60
Multifunctional diacids												
Hydroxysuccinic, hC_4	BDL[a]	0.89	0.34	0.16	1.28	0.74	0.15	1.15	0.61	0.21	0.71	0.43
Ketomalonic, kC_3	0.02	0.94	0.18	0.02	0.14	0.08	0.03	0.29	0.13	0.10	1.33	0.44
Ketopimelic, kC_7	0.001	1.52	0.47	0.21	1.19	0.65	0.16	0.46	0.28	0.10	0.44	0.22
Total diacids	0.001	80.95	4.00	0.02	81.00	4.12	0.00	75.62	4.00	0.00	70.97	3.83
Ketoacids												
Glyoxylic, ωC_2	2.65	6.95	4.62	1.43	4.24	3.11	2.37	8.18	4.81	4.28	10.00	7.05
3-Oxopropanoic, ωC_3	0.001	0.28	0.05	0.01	0.32	0.12	0.01	0.05	0.02	0.01	0.09	0.05
4-Oxobutanoic, ωC_4	0.001	0.44	0.10	0.02	0.13	0.05	BDL[a]	0.93	0.13	0.01	0.22	0.05
9-Oxononanoic, ωC_9	BDL[a]	1.24	0.26	BDL[a]	0.92	0.24	0.25	0.66	0.37	BDL[a]	0.74	0.24
Pyruvic acid, Pyr	0.13	1.03	0.60	0.24	0.78	0.47	0.24	1.39	0.57	0.33	1.40	0.74
Total ketoacids	0.00	6.95	1.13	0.01	4.24	0.80	0.01	8.18	1.18	0.01	10.00	1.63
α-Dicarbonyls												
Glyoxal, Gly	0.09	2.71	0.55	0.09	0.46	0.24	0.15	1.07	0.44	0.37	4.08	1.24
Methylglyoxal, MeGly	0.35	5.21	1.86	0.52	1.45	0.92	1.19	2.78	1.70	0.72	5.63	2.64
Total α-dicarbonyls	0.09	5.21	1.20	0.09	1.45	0.58	0.15	2.78	1.07	0.37	5.63	1.94

[a]Spring, March to May; summer, June to August; autumn, September to November; winter, December to February; n, number of samples; BDL, below detection limit.

Packard, HP6890) equipped with a split/splitless injector, fused silica capillary column (HP-5, 25 m × 0.2 mm id × 0.5 μm film thickness) and flame ionization detector. The oven temperature was held at 50°C for 2 min, ramped at 30°C/min to 120°C, then at 6°C/min to 310°C, and held for 10 min. Peak identification was carried out by comparison of the GC retention times with those of authentic standards (derivatives of C_2–C_{11} diacids, glyoxylic acid, 4-oxobutanoic acid, pyruvic acid, glyoxal and methylglyoxal). Identification of esters and acetals was also confirmed by mass spectral analysis using a GC/mass spectrometry system (Thermoquest, Trace MS) with similar GC column conditions. The quantification of the compounds was performed in comparison to the GC response factors with those of authentic standards. The GC peak areas were calculated with Shimadzu C-R7A Plus integrator.

[13] We spiked free diacids on precombusted quartz fiber filters in order to test the recovery. They were extracted and analyzed like the real samples. The recoveries ranged between 80% and 85% for oxalic acid and more than 90% for malonic, glutaric, succinic, and adipic acids. *Kawamura and Yasui* [2005] reported that the recoveries were 88%, 72%, and 47% for glyoxylic acid, pyruvic acid, and methylglyoxal, respectively, following the same analytical procedure in our laboratory. Repeated analyses of the filter sample showed that the analytical error of this method was less than 10% for major species reported in this study. Field blanks showed small peaks of oxalic, succinic, adipic, and phthalic acids and methylglyoxal. However, their levels were very low (0.1%–3%) compared to those of the real samples. The reported concentrations for the samples are corrected for the field blanks, but not for recoveries.

[14] The concentrations of OC and EC were measured using an OC/EC analyzer (Sunset Laboratory Inc., Portland, OR). The WSOC was measured with a carbon analyzer (Shimadzu, TOC-5000), whereas water-soluble inorganic ions were measured using a Metrohm 761 ion chromatography system (Metrohm, Herisau, Switzerland). The detailed analytical methods for the measurements of OC, EC,

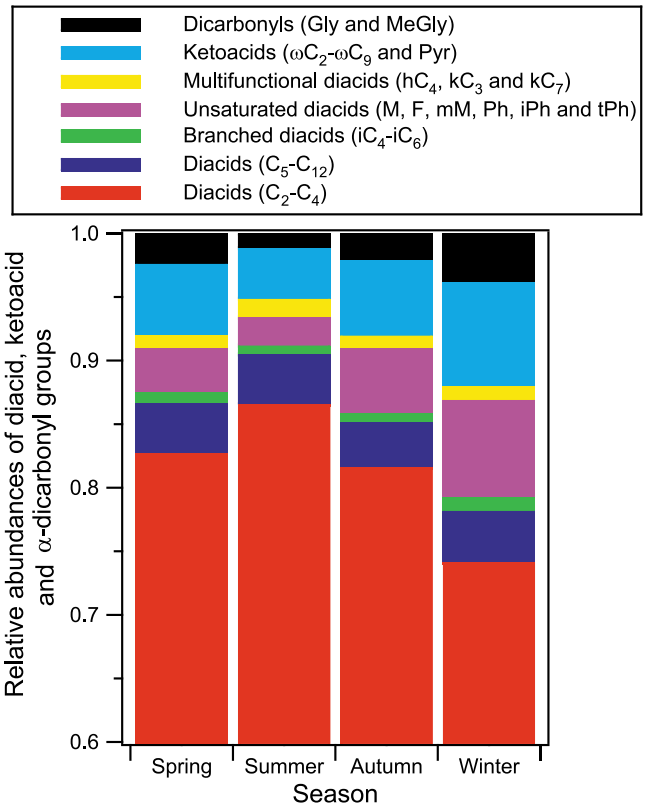

Figure 3. Seasonal difference in the relative abundances of diacids, ketoacids, and α-dicarbonyls in total diacids and related compounds. The *y* axis is scaled from 60% because straight chain diacids (C_2–C_4) in each season account for >60% and hence the relative abundances of other organics can be visualized.

WSOC, and water-soluble inorganic ions are described by *Kundu et al.* [2010b].

3. Results and Discussion

3.1. Molecular Composition of Diacids, Ketoacids, and α-Dicarbonyls

[15] Straight and branched chain aliphatic diacids, diacids with additional functional groups, unsaturated aliphatic diacids, aromatic diacids, ketoacids, and α-dicarbonyls were detected in this study. Table 1 presents their concentration ranges and average concentrations for four seasons together with abbreviations of the compound names. Figure 2 shows seasonally averaged molecular distributions of diacids and related compounds. Although large variations were observed among seasons, oxalic acid (C_2) was found to be the most abundant species followed by malonic acid (C_3) in all seasons. Concentrations (20–1290 ng m^{-3}, average 560 ng m^{-3}) of oxalic acid (C_2) and its relative abundances (64%–81%, average 71%) to total diacids and related compounds showed a maximum in summer and a minimum in winter. Table 2 shows relative abundances of diacids and related compounds in the total organic species detected. The relative abundances of oxalic acid (C_2) in summer are higher than those in other seasons (Table 2), pointing out an enhanced photochemical production of oxalic acid (C_2) in summer [*Kawamura and Ikushima*, 1993]. The dominant presence of oxalic acid (C_2) has been reported for many aerosol samples from urban [*Kawamura and Kaplan*, 1987; *Kawamura and Ikushima*, 1993; *Ho et al.*, 2007; *Miyazaki et al.*, 2007] and remote marine sites [*Kawamura and Sakaguchi*, 1999; *Kerminen et al.*, 2000; *Mochida et al.*, 2003a, 2003b].

[16] The third most abundant species is succinic acid (C_4) followed by glyoxylic acid (ωC_2), glutaric acid (C_5), methylglyoxal (MeGly), phthalic acid (Ph), and adipic acid (C_6) in warmer seasons (spring and summer; Figure 2).

Table 3. Comparison Between the Concentrations of Diacids and Related Compounds at the Gosan Site and Its Surrounding Locations

Location	Type	Period	Size	Reference	Total Diacids[a] Range (ng m^{-3})	Total Diacids[a] Average (ng m^{-3})	Total Ketoacids[a] Range (ng m^{-3})	Total Ketoacids[a] Average (ng m^{-3})	Total α-Dicarbonyls[a] Range (ng m^{-3})	Total α-Dicarbonyls[a] Average (ng m^{-3})
Gosan, Jeju Island, South Korea	Remote/marine	Apr 2001 to Mar 2002	TSP	*Kawamura et al.* [2004]	130–2070	660	2–172	53	0.1–84	12
East China Sea	Open ocean	15 Mar to 19 Apr 2001	TSP	*Mochida et al.* [2003b]	410–1500	850	—	—	—	—
Japan Sea	Open ocean	16 Mar to 19 Apr 2001	TSP	*Mochida et al.* [2003b]	480–2100	1200	—	—	—	—
Chichi-jima, Japan	Remote/marine	Apr 1990 to Nov 1993	TSP	*Mochida et al.* [2003a]	6–550	139	—	—	—	—
Tokyo	Urban	Apr 1988 to Feb 1989	TSP	*Kawamura and Ikushima* [1993]	90–1370	480	—	—	—	—
Tokyo	Urban	2–3 Jun 1989 21–22 Jul 1989 20–21 Nov 1989	TSP	*Kawamura and Yasui* [2005]	164–1804	506	22–285	96.7	8–116	37
Chinese megacities	Urban	13–14 Jan 2003 Jun and Jul 2003	$PM_{2.5}$	*Ho et al.* [2007]	319–1940	904	5–118	45	BDL[b]–64	12
This study	Remote/marine	Apr 2003 to Apr 2004	TSP		142–1875	636	8–170	41	2–108	15

[a]Total diacids, ketoacids, and dicarbonyls include the chemical species listed in Table 1. See also cited references.
[b]BDL, below detection limit.

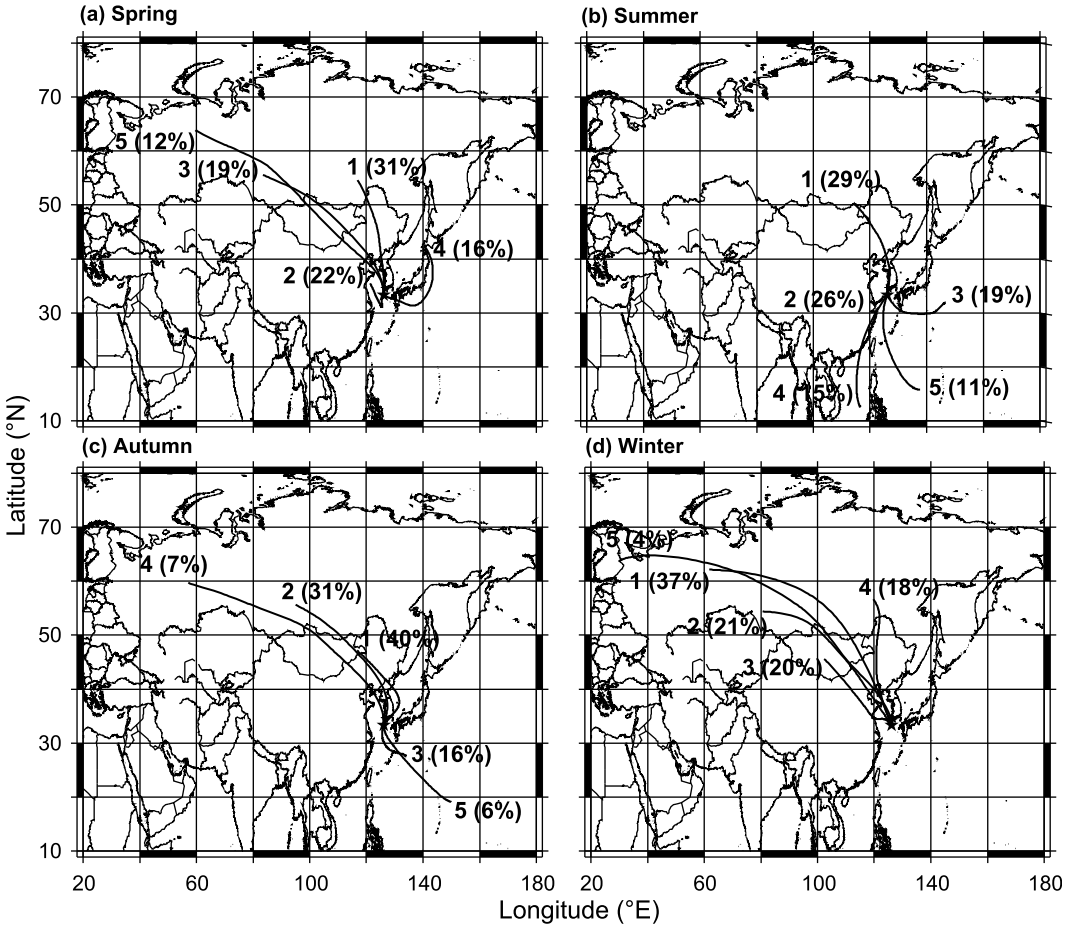

Figure 4. Mean horizontal plots of air mass backward trajectories for the main trajectory clusters in (a) spring, (b) summer, (c) autumn, and (d) winter. Backward trajectories for 5 days at 500 m above ground level were drawn with the NOAA HYSPLIT model. The trajectories in each season were grouped into five clusters as suggested by the model. The numbers 1 to 5 indicate the name of mean clusters. Clusters are arbitrarily named according to descending order of the origin of air masses. The numbers in parentheses indicate the percentage of total air mass transport from the origins. The star indicates the location of sampling site.

Either succinic acid (C_4) or glyoxylic acid (ωC_2) is the third most abundant species in colder seasons (autumn and winter) followed by phthalic acid (Ph), methylglyoxal (MeGly), glutaric acid (C_5), and adipic acid (C_6) (Figure 2). Azelaic acid (C_9) was the most abundant in the range of C_7–C_{12} diacids in all seasons. The highest relative abundances for straight chain (C_2–C_{12}), and multifunctional diacids were found in summer, whereas the highest relative abundances for branched and unsaturated diacids, ketoacids, and dicarbonyls were observed in winter (Figure 3).

Table 4. Contributions of Diacids, Ketoacids, and α-Dicarbonyls to Carbonaceous Fractions (Organic Carbon and Water-Soluble Organic Carbon) of Aerosols at Gosan, Jeju Island, South Korea

Abundance in Bulk Carbon	Spring		Summer		Autumn		Winter	
	Range (%)	Average (%)	Range (%)	Average (%)	Range (%)	Average (%)	Range (%)	Average (%)
Organic carbon								
Total diacids	2–8.8	5.3	3.4–14.8	8.4	4.4–17.1	7.6	2.8–7.7	5.2
Total ketoacids	0.2–0.8	0.4	0.2–0.7	0.4	0.3–1.2	0.6	0.2–0.8	0.5
Total α-dicarbonyls	0.04–0.5	0.2	0.06–0.3	0.2	0.13–0.5	0.3	0.2–0.7	0.3
Water-soluble organic carbon								
Total diacids	4.2–14.0	9.6	6.8–25.2	15.3	7.7–26.4	14.6	4.8–12.7	8.5
Total ketoacids	0.3–1.2	0.7	0.4–1.1	0.7	0.6–2.1	1.0	0.4–1.2	0.8
Total α-dicarbonyls	0.08–0.9	0.4	0.1–0.5	0.3	0.3–1.1	0.5	0.3–1.0	0.5

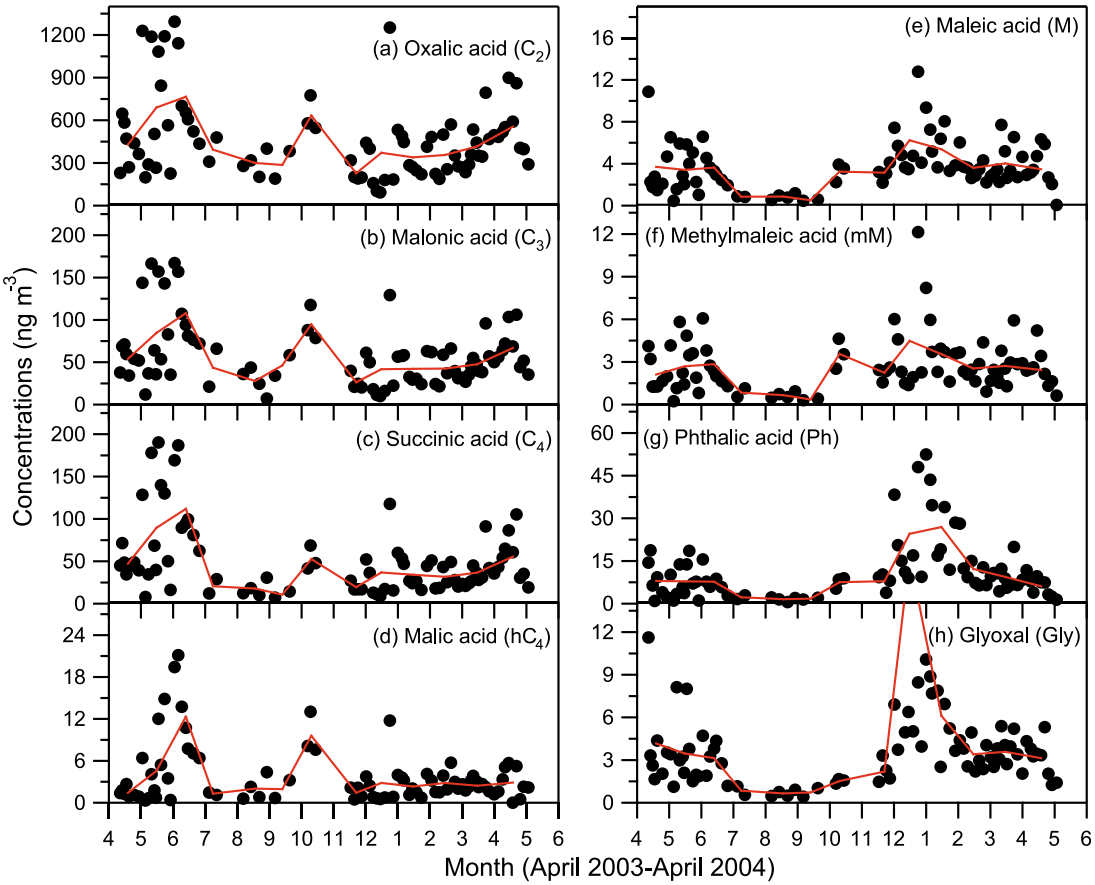

Figure 5. Seasonal variations of (a) oxalic acid (C_2), (b) malonic acid (C_3), (c) succinic acid (C_4), (d) malic acid (hC_4), (e) maleic acid (M), (f) methylmaleic acid (mM), (g) phthalic acid (Ph), and (h) glyoxal (Gly). The red lines indicate monthly average data points.

[17] The average concentrations of total diacids are 735 ng m^{-3} in spring, 784 ng m^{-3} in summer, 525 ng m^{-3} in autumn, and 500 ng m^{-3} in winter (Table 1). The concentrations of total diacids at the Gosan site and its surrounding areas are compared in Table 3. Gosan data of this study is similar to those reported at Gosan for aerosol samples collected between April 2001 and March 2002 [*Kawamura et al.*, 2004]. Similar concentrations were reported over the East China Sea for aerosols collected by a ship during ACE-Asia campaign, whereas much higher concentrations were reported over the Japan Sea [*Mochida et al.*, 2003b]. Total diacid concentrations in aerosols over Chichi-jima Island in the western North Pacific, ~2000 km away from East Asia, are several times lower than those observed at our Gosan site, suggesting that the Gosan site is strongly influenced by the continental outflow from China, Korea, and Japan due to its vicinity. Total diacid concentrations at our site are higher than those in urban Tokyo, but similar to those reported in 14 Chinese megacities [*Ho et al.*, 2007]. This comparison demonstrates that the outflows from China to Gosan are an important transport pathway.

[18] Air mass back trajectories are given in Figure 4. It is worthy to note that the highest average concentration of total diacids was observed in summer (Table 1), although 45% of air masses are transported from the oceans (Figure 4b). *Ho et al.* [2007] reported that during winter total diacids in central and southern China were higher than those in northern China, whereas during summer total diacids were higher in northern and central China than in southern China. Figure 4b shows that 55% of air masses in summer are transported over northern and central China. This air mass transport pattern along with the higher concentrations of total diacids over northern and central China in summer [*Ho et al.*, 2007] may explain the maximum average concentration of total diacids at Gosan in summer.

[19] Average total ketoacid concentrations are 46 ng m^{-3} in spring, 36 ng m^{-3} in summer, 34 ng m^{-3} in autumn, and 47 ng m^{-3} in winter. Total α-dicarbonyls concentrations are, on average, 18 ng m^{-3} in spring, 9 ng m^{-3} in summer, 11 ng m^{-3} in autumn, and 23 ng m^{-3} in winter. These concentrations are compared with those at the surrounding locations of the Gosan site (Table 3). The values are similar to those reported at our sampling site for aerosol samples collected between April 2001 and March 2002 [*Kawamura et al.*, 2004]. Concentrations of ketoacids and α-dicarbonyls reported in 14 Chinese megacities [*Ho et al.*, 2007] are similar to our results at the Gosan site, further suggesting an important outflow and chemical evolution of organics in the gas and aerosol phases during a long-range transport (average 1–2 days) from China to the Gosan site.

[20] The secondary organic carbon (SOC) can provide information about the photochemical aging of organic aerosols. The SOC was estimated using the EC tracer method [*Lim and Turpin*, 2002] and the representative ratio

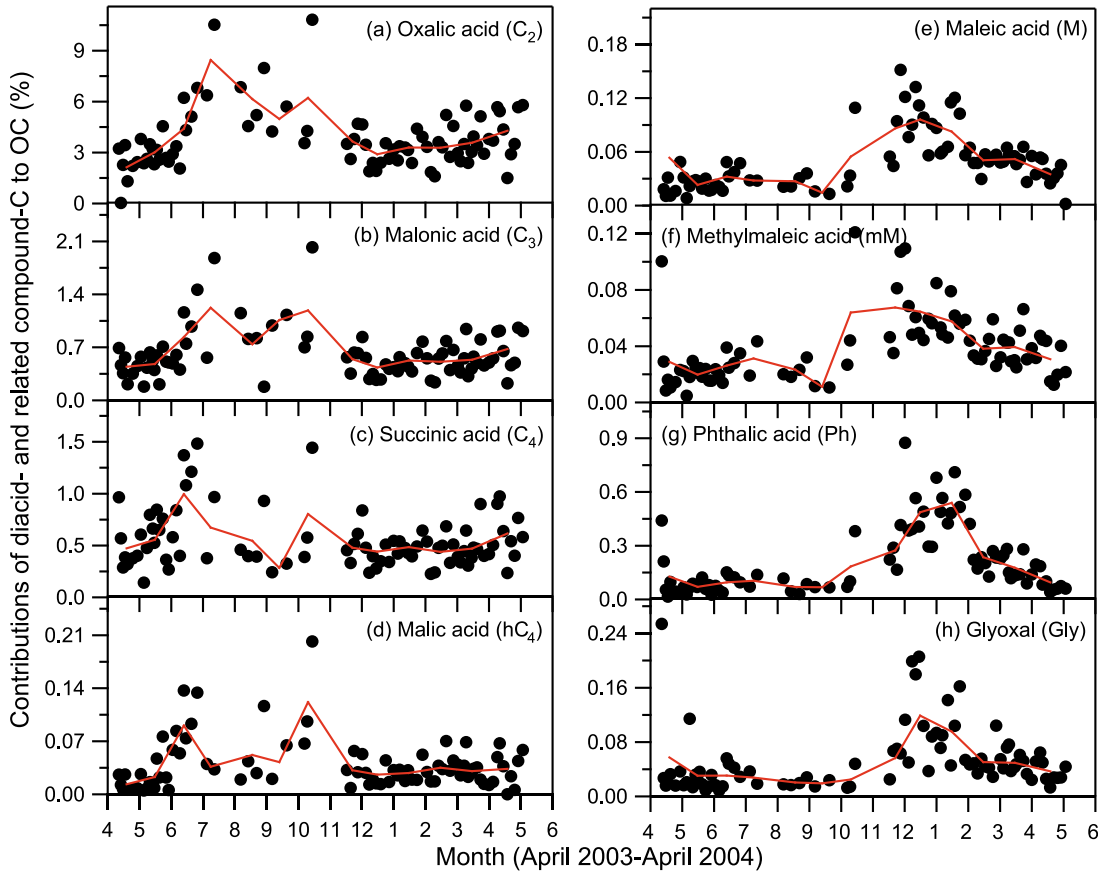

Figure 6. Seasonal variations in the carbon component of (a) oxalic acid (C_2), (b) malonic acid (C_3), (c) succinic acid (C_4), (d) malic acid (hC_4), (e) maleic acid (M), (f) methylmaleic acid (mM), (g) phthalic acid (Ph), and (h) glyoxal (Gly) to organic carbon. The red lines indicate monthly average data points.

$(OC/EC)_{primary}$ = 1.99, which was derived from OC and EC data of aerosol samples collected from northern China [*Ho et al.*, 2007]. It is reasonable to use this value because major fraction of air masses at the Gosan site are transported from northern China (Figure 4) and the direct application of the EC tracer method should be erroneous under conditions of extensive chemical processes in the Gosan aerosols [*Strader et al.*, 1999]. We found that the carbon content of total diacids correlate well with the SOC (r^2 = 0.60, p < 0.0001, n = 84). Additionally, the contributions of diacids, ketoacids, and α-dicarbonyls to OC and WSOC are several times higher than those reported in 14 Chinese megacities [*Ho et al.*, 2007] (Table 4). These results suggest an important secondary production of diacids and related compounds due to the oxidation of volatile and semivolatile organic precursors and a photochemical aging of organic aerosols during a long-range transport from East Asia.

3.2. Seasonal Variations of Diacids, Ketoacids, and α-Dicarbonyls

[21] Individual species of diacids and related compounds showed two different seasonal trends. The first group of compounds, including straight chain and multifunctional diacids (such as oxalic (C_2), malonic (C_3), succinic (C_4), and malic (hC_4) acids), showed maximum concentrations in late spring to early summer (Figures 5a–5d). In contrast, the second group of compounds, including unsaturated diacids (such as maleic (M), methylmaleic (mM), and phthalic (Ph) acids) and α-dicarbonyls (such as glyoxal (Gly)), showed maxima in winter (Figures 5e–5h). The different seasonal variations between the first and second groups suggest a difference in the sources or atmospheric processing. If the physical parameters such as lower mixing heights, surface inversion layers, and infrequent precipitations were the causes for the maximum concentrations, both the first and second groups showed a same trend. Thus, the different seasonal trends should be caused by a difference in the emission of their precursors or photochemical processing.

[22] The organic precursors that produce the compounds showing maximum concentrations in winter are mainly aromatics in nature although glyoxal (Gly), to some extent, can be produced due to the oxidation of some nonaromatic organics such as ethene, ethyne, and isoprene [*Warneck*, 2003; *Ervens et al.*, 2004; *Ieda et al.*, 2006]. The temperature ranges between −14°C and 5°C during winter in northern China [*Ho et al.*, 2007], from which almost all of the air masses are transported over our sampling site (Figure 4d). Coals/biomasses, in which combustion efficiency is very low, are commonly used in China for heating and cooking [*Wang et al.*, 2006]. Total residential energy consumption in Beijing, located in northern China, in colder seasons (autumn and winter) is 5.4 tons of coal equivalent in 2006,

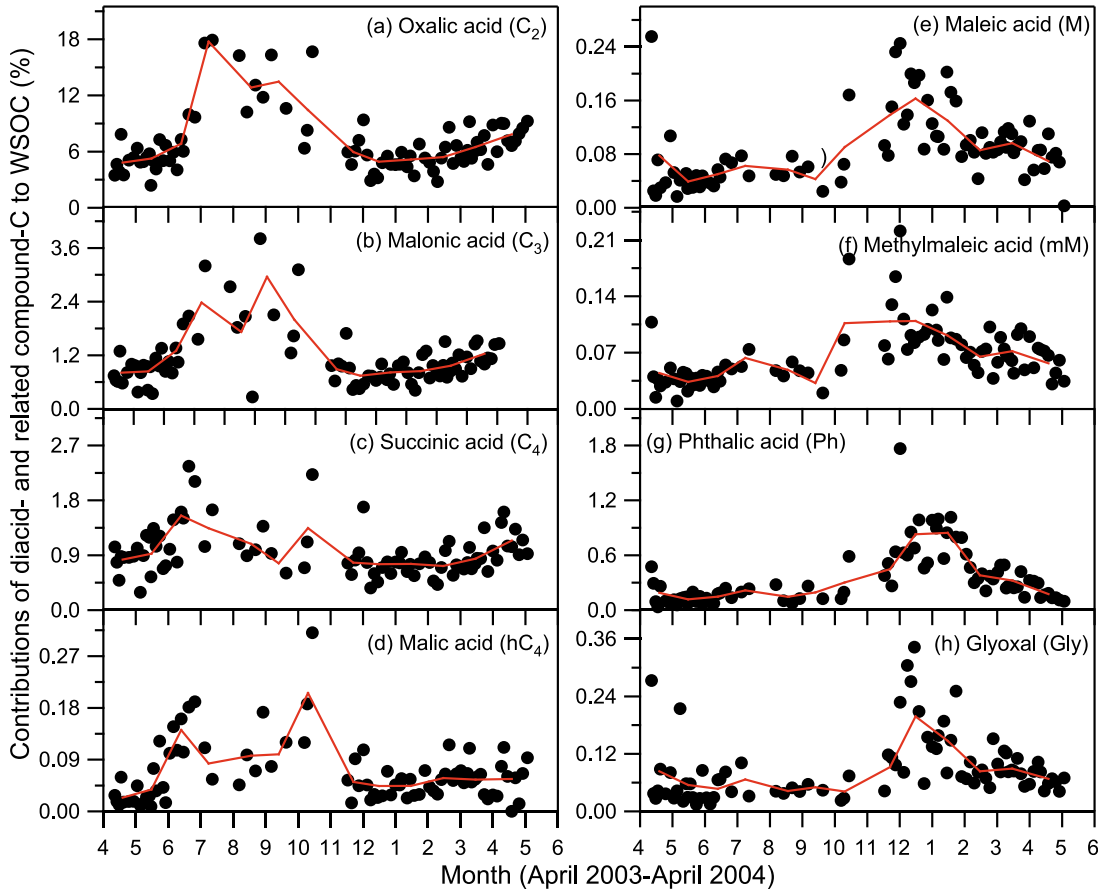

Figure 7. Seasonal variations in the carbon component of (a) oxalic acid (C_2), (b) malonic acid (C_3), (c) succinic acid (C_4), (d) malic acid (hC_4), (e) maleic acid (M), (f) methylmaleic acid (mM), (g) phthalic acid (Ph), and (h) glyoxal (Gly) to water-soluble organic carbon. The red lines indicate monthly average data points.

which is 54% higher than that in warmer seasons (spring and summer; http://www.bjstats.gov.cn). Coal/biomass combustion emits huge amounts of aromatics (e.g., the emission of polycyclic aromatic hydrocarbons in Chinese megacities is more than seven times higher in winter than in summer) [*Wang et al.*, 2006].

[23] Carbon contents of individual diacids and related compounds were normalized by OC and WSOC to examine the seasonal variations. Figures 6 and 7 present seasonal variations of individual compounds normalized by OC and WSOC, respectively. Higher values were found in summer for straight chain and multifunctional diacids (Figures 6a–6d and 7a–7d), being consistent with an enhanced secondary production due to higher oxidant concentrations and warmer temperature. In contrast, higher values were observed in winter for unsaturated acids and α-dicarbonyls (Figures 6e–6h and 7e–7h), suggesting an enhanced emission potentially from coal/biomass combustion. Higher contributions of total diacids to OC were observed in summer, whereas those of total ketoacids and α-dicarbonyls showed higher values in autumn and winter (Table 4). Similar seasonal variations were observed for the contributions of total diacids, ketoacids, and α-dicarbonyls to WSOC (Table 4).

3.3. Seasonal Variations in the Concentration Ratios of Diacids and Related Compounds

[24] Figure 8 shows the seasonal variations of $C_2/\omega C_2$, C_2/Pyr, C_2/Gly, C_3/C_4, F/M, and hC_4/C_4 ratios. These organic species (except oxalic acid (C_2)) have been proposed to be associated in atmospheric chain reactions to produce oxalic acid [*Kawamura et al.*, 1996]. $C_2/\omega C_2$, C_2/Pyr, and C_2/Gly ratios have shown higher values in summer and lower values in winter (Figures 8a–8c). This trend is a possible indication of photochemical production of oxalic acid (C_2) from glyoxylic (ωC_2) and pyruvic (Pyr) acids and glyoxal (Gly). *Carlton et al.* [2006] demonstrated that photochemical oxidation of pyruvic acid (Pyr) yields oxalic (C_2) and glyoxylic (ωC_2) acids in the aerosol phase and acetic and formic acids in the gas phase. Oxalic acid (C_2) is also produced from oxidation of glyoxal via formation of glyoxylic acid as intermediate in cloud waters [*Warneck*, 2003].

[25] Lower C_3/C_4 ratios (ranging from 0.25 to 0.44 with an average of 0.35 [*Kawamura and Kaplan*, 1987]) were observed in aerosols from automobile emission. This is in contrast to those reported in atmospheric aerosols from Tokyo (0.56–2.9, average 1.6 [*Kawamura and Ikushima*, 1993]) and Chinese megacities (0.6–1.1, average 0.74 [*Ho et al.*, 2007]). Thus, C_3/C_4 ratios may effectively be used

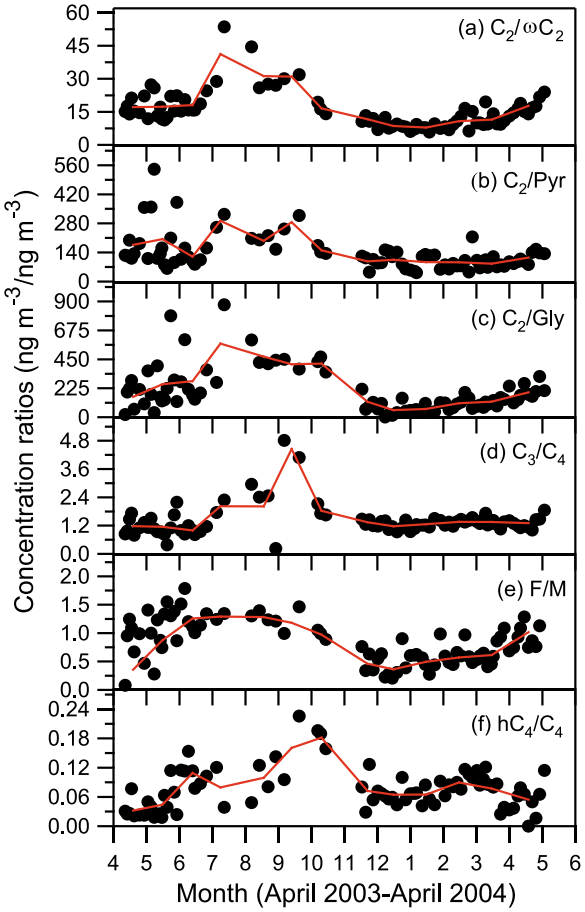

Figure 8. Seasonal variations in the ratios of (a) $C_2/\omega C_2$, (b) C_2/Pyr, (c) C_2/Gly, (d) C_3/C_4, (e) F/M, and (f) hC_4/C_4. The red lines indicate monthly average data points.

to distinguish the relative importance of their primary and secondary sources [*Kawamura and Ikushima*, 1993]. It has been proposed that succinic acid (C_4) can be degraded to malonic acid (C_3) due to the abstraction of its hydrogen by OH radicals and subsequent decarboxylation reactions [*Kawamura and Ikushima*, 1993]. Figure 8d shows higher C_3/C_4 ratios in summer. This result may suggest that a significant fraction of malonic acid (C_3) is secondarily produced in the atmosphere by photochemical degradation of succinic acid (C_4). Since the Gosan site is heavily influenced by the air mass transported from East Asia, it is interesting to compare the C_3/C_4 ratios at the Gosan site with those from different cities in East Asia (Figure 9a). The C_3/C_4 ratios in Chinese cities ranged between 0.35 and 1.69 (average 0.84) in summer, and 0.13 and 1.06 (average 0.60) in winter [*Ho et al.*, 2007]. The mean values at Gosan were observed as 1.2 in spring, 2.6 in summer, 1.3 in autumn, and 1.3 in winter. These values are about two to three times higher than those reported in Chinese megacities. Furthermore, summer average at Gosan is 2.7 times higher than that in urban Tokyo [*Kawamura and Yasui*, 2005]. Therefore, it appears that malonic acid (C_3) is photochemically produced during long-range transport of air masses from East Asia to Gosan.

[26] In order to further strengthen this logic, the C_3/C_4 ratios at Gosan are compared with those at Chichi-jima Island in the western Pacific, Japan, located 1000 to 3000 km away from East Asian countries, but significantly influenced by the air mass flow from East Asia. The C_3/C_4 ratios at Chichi-jima (spring, 2; summer, 3.8; autumn, 1.6; 1.2, winter [*Mochida et al.*, 2003a]) in all the seasons (except winter) are 1.3–1.7 times higher than those at Gosan. This suggests that the production of C_3 from C_4 is enhanced during a long-range transport to the Pacific. Interestingly, the C_3/C_4 ratios in aerosols of both Chichi-jima and Gosan have shown maxima in summer, indicating an enhanced photochemical production in warmer weather. Although very high values of C_3/C_4 ratios (3–5) were observed in aerosols collected from a background site in South Africa [*Limbeck et al.*, 2001], lower C_3/C_4 ratios (0.31–1.4) have been found in downtown and west Los Angeles [*Kawamura and Kaplan*, 1987] and Philadelphia [*Ray and Mcdow*, 2005].

[27] The laboratory studies have shown the formation of maleic anhydride from the oxidation of aromatic hydrocarbons such as benzene and toluene [*Bandow et al.*, 1985]. Maleic acid (M) can be isomerized to fumaric acid (F) in the presence of sunlight. This isomerization reaction should be enhanced during summer. Figure 8e shows the seasonal changes in F/M ratio from April 2003 to April 2004. The F/M ratios are higher during summer and lower during winter. This trend is probably related with an enhanced isomerization reaction in summer under intensified solar radiation. *Kawamura and Ikushima* [1993] also reported the similar seasonal variations in Tokyo aerosols. Figure 9b depicts the comparison of F/M ratios at Gosan along with those reported for aerosols over Chinese megacities, other East Asian cities, and Chichi-jima in the western Pacific. The F/M ratios in summer and winter are higher at Gosan than in East Asian cities, which is probably due to an enhanced isomerization of maleic acid (M) to fumaric acid (F) during long-range transport from East Asia. Higher F/M ratios are seen at Chichi-jima, indicating more isomerization of maleic acid (M) to fumaric acid (F) in the remote marine atmosphere during a further transport from East Asia.

[28] The seasonal variations of hC_4/C_4 ratios are shown in Figure 8f. *Kawamura and Ikushima* [1993] hypothesized, based on the field observation, that malic acid (hC_4) can be photochemically generated from succinic acid (C_4) via hydroxylation reaction. The hC_4/C_4 ratios have shown higher values in summer, supporting this hypothesis. The average hC_4/C_4 ratio in summer was found to be 1.4–2 times higher than in other seasons, being consistent with the observation in urban Tokyo [*Kawamura and Ikushima*, 1993].

[29] Both adipic (C_6) and phthalic (Ph) acids or their precursors (e.g., cyclohexene and naphthalene) are primarily emitted from the anthropogenic sources [*Kawamura and Kaplan*, 1987; *Schauer et al.*, 1999, 2001, 2002]. In contrast, azelaic acid (C_9) is produced due to the oxidation of unsaturated fatty acids emitted from the biogenic sources [*Kawamura and Gagosian*, 1987; *Rogge et al.*, 1991]. Thus, these ratios (C_6/C_9 and Ph/C_9) provide their source strength from the anthropogenic and biogenic emissions. The higher the values of these ratios, the stronger the emissions from the anthropogenic sources. C_6/C_9 ratios in Figure 10a show the lower values in midsummer. This can be interpreted by significant influence of the oceanic air masses that contain biogenic unsaturated fatty acids such as oleic acid (a precursor of C_9 diacid [*Kawamura and Gagosian*, 1987]) in

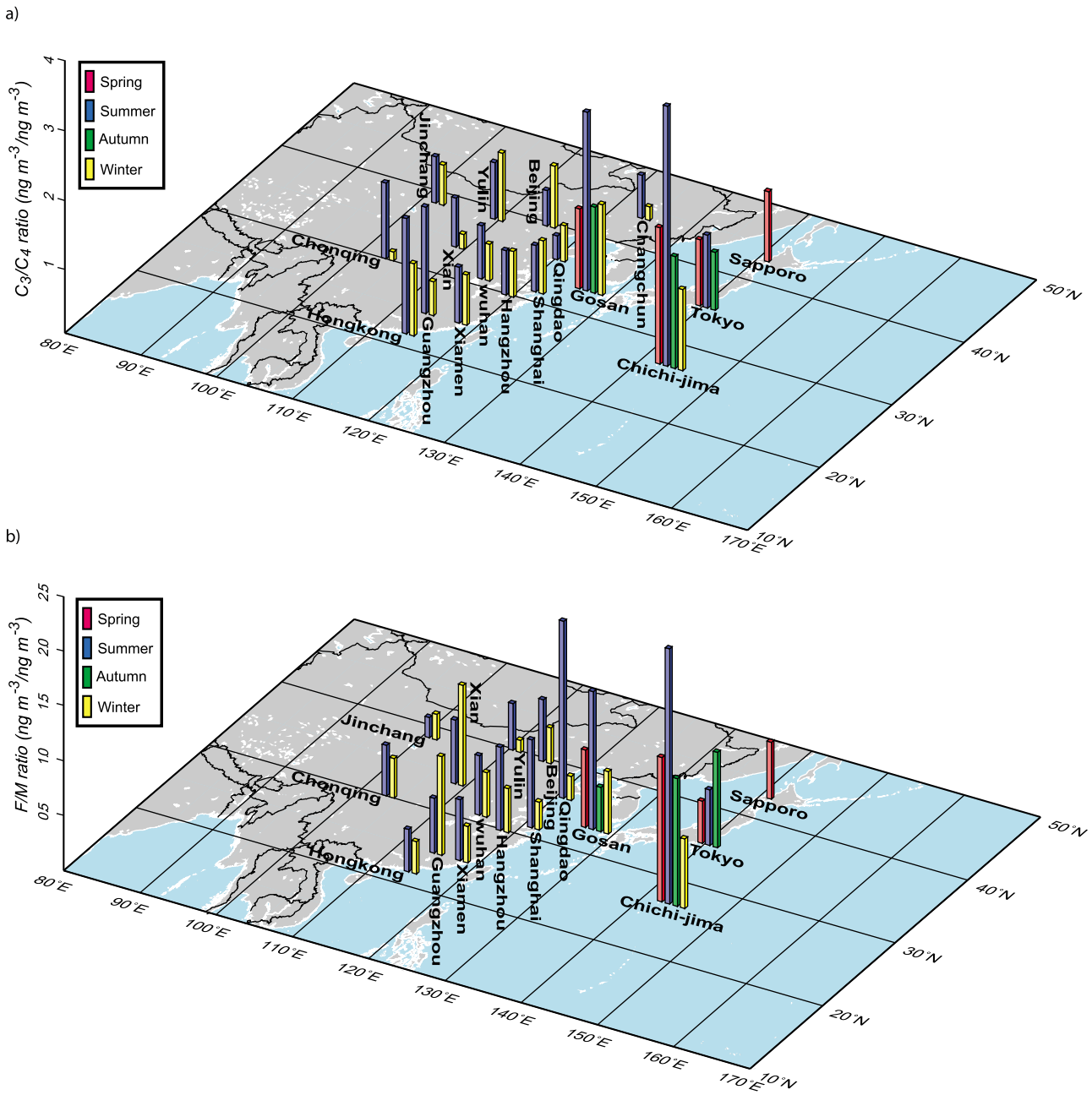

Figure 9. Depiction of (a) C_3/C_4 and (b) F/M ratios at Gosan, East Asian cities, and Chichi-jima Island in the western Pacific Ocean. The ratios in Chinese cities in summer and winter are compiled from *Ho et al.* [2007], those in Tokyo and Sapporo in Japan are derived from *Kawamura and Yasui* [2005] and S. Kundu and K. Kawamura (unpublished, 2007), and those at Chichi-jima Island are calculated from *Mochida et al.* [2003a].

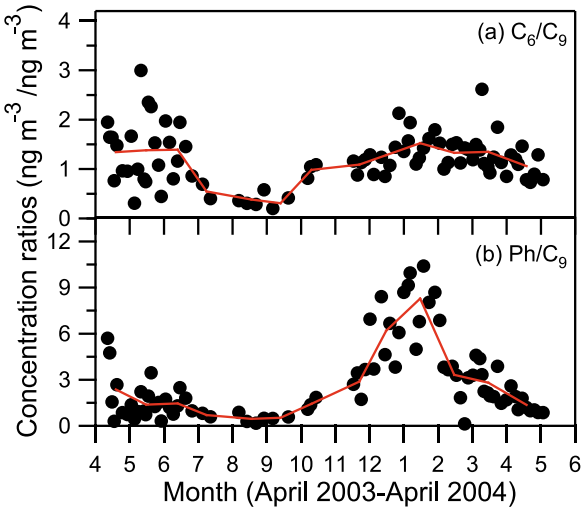

Figure 10. Seasonal variations in the ratios of (a) C_6/C_9 and (b) Ph/C_9. The red lines indicate monthly average data points.

Gosan aerosols during summer. Seasonal variations in Ph/C_9 ratios are shown in Figure 10b. They show a similar trend with C_6/C_9 ratios, but with an intensive contrast between winter and summer. The higher values in winter are caused by an enhanced transport of pollutants from East Asia, particularly in China (Figure 4d).

3.4. Sources of Diacids, Ketoacids, and α-Dicarbonyls

[30] Oxalic acid (C_2) can be produced from other diacids and related compounds determined in this study due to their oxidation [*Kawamura and Sakaguchi*, 1999; *Matsunaga et al.*, 1999; *Warneck*, 2003; *Lim et al.*, 2005; *Carlton et al.*, 2006; *Kundu et al.*, 2010a]. Relative abundance of C_2 (%) in diacids and related compounds can therefore be regarded as a proxy for photochemical aging of organic aerosols. *Kawamura and Yasui* [2005] reported that concentrations of diacids and related compounds show inverse correlations with relative abundance of C_2 (%) in total diacids for urban Tokyo aerosols in summer. In this study, lower concentrations of diacids and related compounds in summer samples are associated with higher relative abundances of C_2 (%) in total diacids and related compounds (Figure 11). These results potentially suggest that diacids and related compounds can be broken down to oxalic acid (C_2). Diacids and related compounds can be formed from other organics in gas and aerosol phases in the early stage of photochemical processing. On the basis of the absence of similar correlations for the samples of other seasons, it can be concluded that secondary production and degradation of organic aerosols are more intensified in summer due to the stronger solar radiation, higher concentrations of oxidants, and higher ambient temperature.

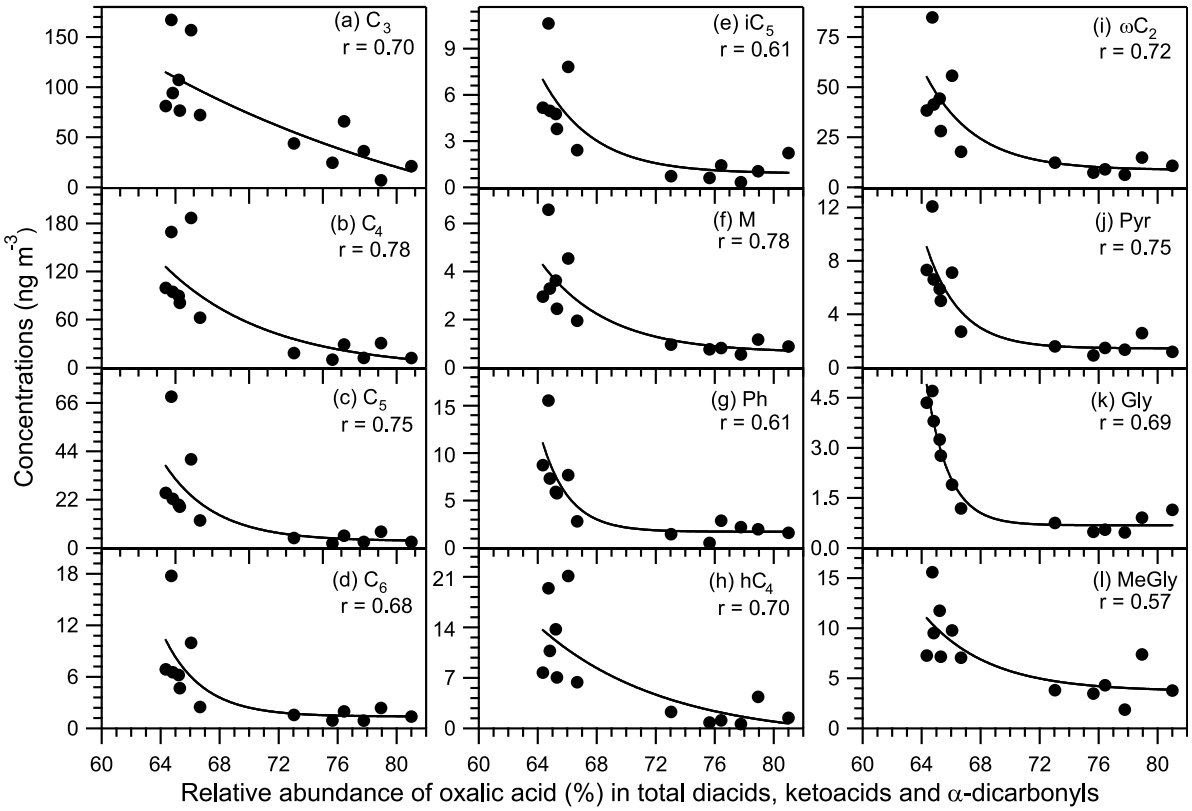

Figure 11. Summertime relations of relative abundances (%) of oxalic acid (C_2) in detected molecular organics with concentrations of (a) malonic acid (C_3), (b) succinic acid (C_4), (c) glutaric acid (C_5), (d) adipic acid (C_6), (e) methylsuccinic acid (iC_5), (f) maleic acid (M), (g) phthalic acid (Ph), (h) malic acid (hC_4), (i) glyoxylic acid (ωC_2), (j) pyruvic acid (Pyr), (k) glyoxal (Gly), and (l) methylglyoxal (MeGly).

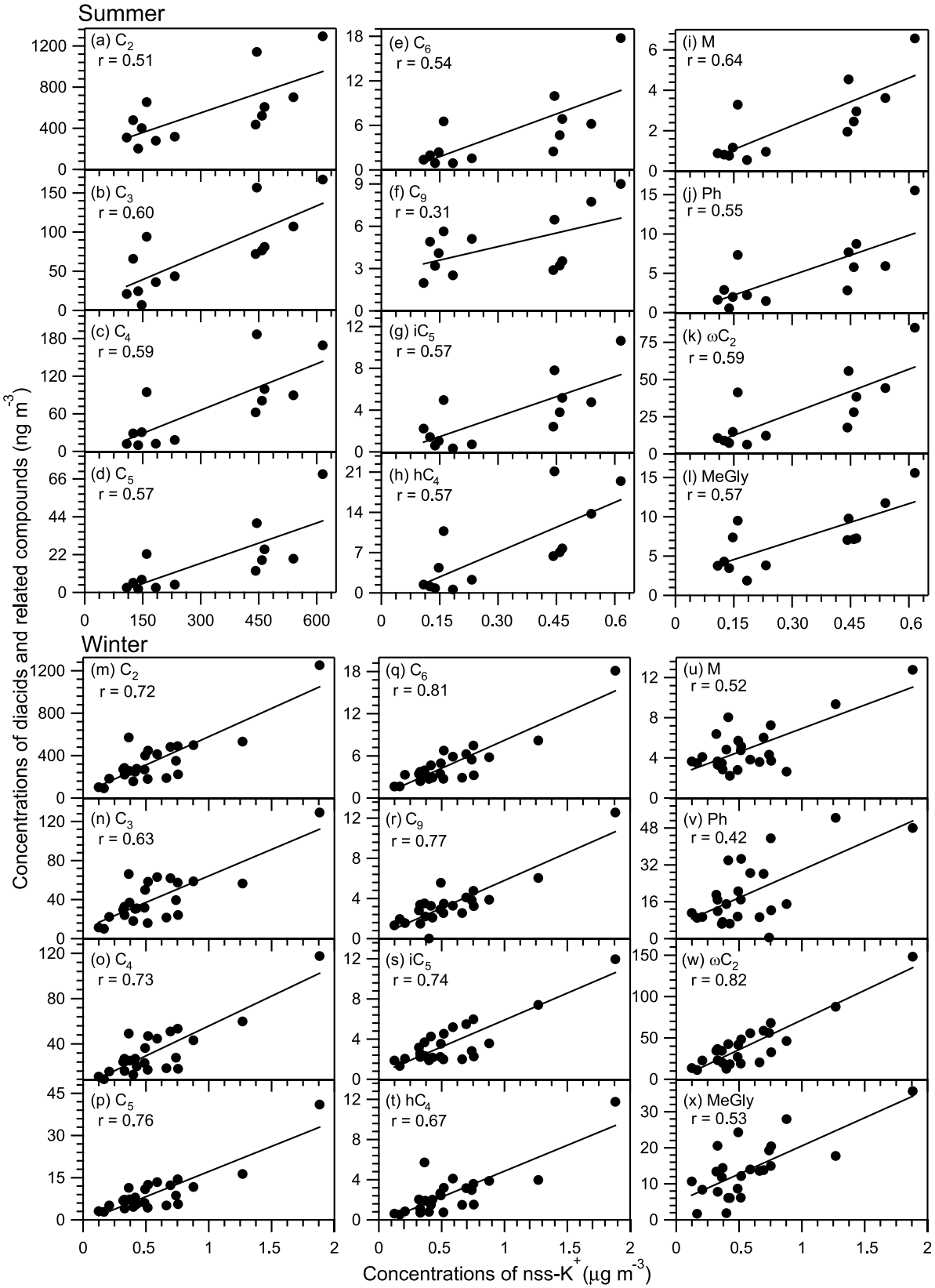

Figure 12. Summer- and wintertime relations between non-sea-salt K^+ and (a, m) oxalic acid (C_2), (b, n) malonic acid (C_3), (c, o) succinic acid (C_4), (d, p) glutaric acid (C_5), (e, q) adipic acid (C_6), (f, r) azelaic acid (C_9), (g, s) isosuccinic acid (iC_5), (h, t) malic acid (hC_4), (i, u) maleic acid (M), (j, v) phthalic acid (Ph), (k, w) glyoxylic acid (ωC_2), and (l, x) methylglyoxal (MeGly). Non-sea-salt K^+ is calculated as total K^+ minus $Na^+ \times 0.021$.

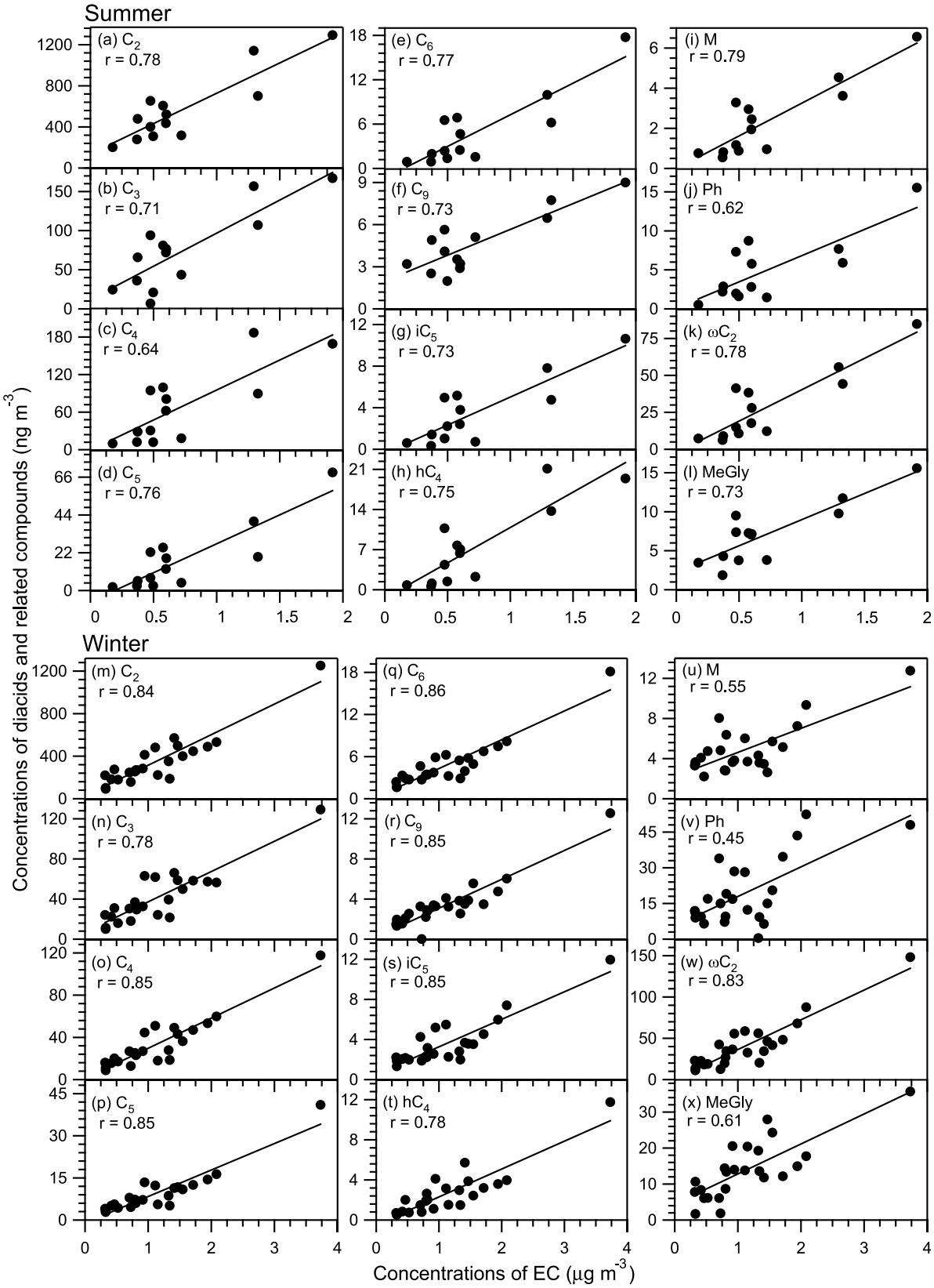

Figure 13. Summer- and wintertime relations between elemental carbon and (a, m) oxalic acid (C_2), (b, n) malonic acid (C_3), (c, o) succinic acid (C_4), (d, p) glutaric acid (C_5), (e, q) adipic acid (C_6), (f, r) azelaic acid (C_9), (g, s) isosuccinic acid (iC_5), (h, t) malic acid (hC_4), (i, u) maleic acid (M), (j, v) phthalic acid (Ph), (k, w) glyoxylic acid (ωC_2), and (l, x) methylglyoxal (MeGly).

[31] It has been demonstrated that biomass burning is an important source of diacids and related compounds [*Decesari et al.*, 2006; *Falkovich et al.*, 2005; *Kundu et al.*, 2010a]. In order to evaluate the impacts of biomass burning and combustion sources at Gosan, we draw scatterplots of biomass burning tracer (non-sea-salt K^+) and combustion tracer (EC) with diacids and related compounds in Figures 12 and 13, respectively. Although fair to good positive correlations were observed for diacids and related compounds with K^+ and EC in summer and winter, no statistically significant correlations were observed in spring and autumn. These results suggest an enhanced contribution of the combustion sources for diacids and related compounds and their precursors in summer and winter. The better correlations in winter suggest that biomass and fossil fuel combustion significantly contributes to the water-soluble organic species in Gosan aerosols. The weaker correlations in summer may suggest an importance of enhanced oceanic contribution and photochemical processing.

[32] Similar good correlations were also observed between secondary aerosol tracers (SO_4^{2-} and NO_3^-) and diacids and related compounds only in summer (r^2 = 0.20–0.79, n = 13) and winter (r^2 = 0.38–0.83, n = 24; data are not shown). This again demonstrates that both emission and secondary production are important processes in Gosan aerosols. More tight relations between secondary tracers as well as combustion tracers and diacids and related compounds were observed in winter than in summer. This result can be interpreted by the presence of more specific sources for diacids and related compounds as well as their precursors in winter. As shown in Figure 4d, almost all air masses in winter are transported from northern China, where combustion of fossil fuel/biofuel is very common in cold winter (see http://www.bjstats.gov.cn). This again supports the idea that northern China is an important source region for winter aerosols at Gosan.

4. Conclusions

[33] Diacids and related compounds (ketoacids and α-dicarbonyls) have been determined in atmospheric aerosol samples collected from April 2003 to April 2004 over Gosan in Jeju Island, Korea. The characteristic seasonal variations of diacids and related compounds were found at the Gosan site, which are associated with their different sources and photochemical processing. A year-round data set showed that oxalic acid (C_2) is the dominant species followed by malonic acid (C_3) in all seasons. This study demonstrates an enhanced photochemical formation and degradation of dicarboxylic acids and related compounds in summer. It also shows photochemical aging of organic aerosols during long-range transport from the East Asian continent to Gosan. Comparison of concentrations at the Gosan site with available data set in East Asian cities suggests that atmospheric transport of diacids and related compounds as well as their precursors from Chinese cities to Gosan is the most important source. These findings are consistent with seasonal variations of diacids and related compounds, whose concentrations maximized in winter and summer and correlated positively with combustion tracers (K^+ and EC) and secondary tracers (SO_4^{2-} and NO_3^-). We also found that the concentrations of these organics and combustion/secondary tracers are most tightly correlated in winter samples, demonstrating that Asian outflows from northeast China most likely affect the air quality of Gosan in Jeju Island and the surrounding ocean in the western North Pacific.

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References

Arimoto, R., R. A. Duce, J. M. Prospero, D. L. Savoie, R. W. Talbot, J. E. Dibb, B. G. Heikes, B. J. Ray, N. F. Lewis, and U. Tomza (1997), Comparisons of trace constituents from ground stations and the DC-8 aircraft during PEM-West B, *J. Geophys. Res.*, *102*, 28,539–28,550.

Baboukas, E. D., M. Kanakidou, and N. Mihalopoulos (2000), Carboxylic acids in gas and particulate phase above the Atlantic Ocean, *J. Geophys Res.*, *105*, 14,459–14,471.

Bandow, H., N. Washida, and H. Akimoto (1985), Ring cleavage reactions of aromatic hydrocarbons studied by FT-IR spectroscopy: I. Photooxidation of toluene and benzene in the NO_x-air system, *Bull. Chem. Soc. Jpn.*, *58*, 2531–2540.

Bunce, N. J., L. Liu, and J. Zhu (1997), Reaction of naphthalene and its derivatives with hydroxyl radicals in the gas phase, *Environ. Sci. Technol.*, *31*, 2252–2259.

Carlton, A. G., B. J. Turpin, K. E. Altieri, S. Seitzinger, A. Reff, H.-J. Lim, and B. Erven (2006), Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, *Atmos. Environ.*, *41*, 7588–7602.

Carmichael, G. R., Y. Zhang, L.-L. Chen, S.-M. Hong, and H. Ueda (1996), Seasonal variation on aerosol composition at Cheju Island, Korea, *Atmos. Environ.*, *30*, 2407–2416.

Carmichael, G. R., M. S. Hong, H. Ueda, L. L. Chen, K. Murano, J. K. Park, H. Lee, Y. Kim, C. Kang, and S. Shim (1997), Aerosol composition at Cheju Island, Korea, *J. Geophys. Res.*, *102*, 6047–6061.

Chen, L.-L., et al. (1997), Influence of continental outflows on the aerosol composition at Cheju Island, South Korea, *J. Geophys. Res.*, *102*, 28,551–28,574.

Cruz, C. N., and S. N. Pandis (1997), A study of the ability of secondary organic aerosol to act as cloud condensation nuclei, *Atmos. Environ.*, *31*, 2205–2214.

Decesari, S., et al. (2006), Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds, *Atmos. Chem. Phys.*, *6*, 375–402.

Ervens, B., G. Feingold, G. J. Frost, and S. M. Kreidenweis (2004), A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, *J. Geophys. Res.*, *109*, D15205, doi:10.1029/2003JD004387.

Falkovich, A. H., E. R. Graber, G. Schkolnik, Y. Rudich, W. Maenhaut, and P. Artaxo (2005), Low molecular weight organic acids in aerosol particles from Rondônia, Brazil, during the biomass-burning, transition and wet periods, *Atmos. Chem. Phys.*, *5*, 781–797.

Fisseha, R., J. Dommen, M. Sax, D. Paulsen, M. Kalberer, R. Maurer, F. Höfler, E. Weingartner, and U. Baltensparger (2004), Identification of organic acids in secondary organic aerosol and the corresponding gas phase from Chamber experiments, *Anal. Chem.*, *76*, 6535–6560.

Folkers, M., T. F. Mentel, and A. Wahner (2003), Influence of an organic coating on the reactivity of aqueous aerosols probed by heterogeneous hydrolysis of N_2O_5, *Geophys. Res. Lett.*, *30*(12), 1644, doi:10.1029/2003GL017168.

Fraser, M. P., Z. W. Yue, R. J. Tropp, S. D. Kohl, and J. C. Chow (2002), Molecular composition of organic fine particulate matter in Houston, TX, *Atmos. Environ.*, *36*, 5751–5758.

Gao, S., D. A. Hegg, G. Frick, P. F. Caffrey, L. Pasternack, C. Cantrell, W. Sullivan, J. Ambrusko, T. Albrechcinski, and T. W. Kirchstetter (2001), Experimental and modeling studies of secondary organic aerosol formation and some applications to the marine boundary layer, *J. Geophys. Res.*, *106*(D21), 27,619–27,634.

Gao, S., D. A. Hegg, P. V. Hobbs, T. W. Kirchstetter, B. I. Magi, and M. Sadilek (2003), Water-soluble organic components in aerosols associ-

ated with savanna fires in southern Africa: Identification, evaluation, and distribution, *J. Geophys. Res.*, *108*(D13), 8491, doi:10.1029/2002JD002324.

Hallquist, M., et al. (2009), The formation, properties and impact of secondary organic aerosol: Current and emerging issues, *Atmos. Chem. Phys.*, *9*, 5155–5236.

Hatakeyama, S., T. Tanonaka, J. Weng, H. Bandow, H. Takagi, and H. Akimoto (1985), Ozone-cyclohexene reaction in air: Quantitative analyses of particulate products and the reaction mechanism, *Environ. Sci. Technol.*, *19*, 935–942.

Ho, K. F., J. J. Cao, S. C. Lee, K. Kawamura, R. J. Zhang, J. C. Chow, and J. G. Watson (2007), Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in urban atmosphere of China, *J. Geophys. Res.*, *112*, D22S27, doi:10.1029/2006JD008011.

Hoell, J. M., D. D. Davis, S. C. Liu, R. Newell, M. Shipham, H. Akimoto, R. J. McNeal, R. J. Bendura, and J. W. Drewry (1996), Pacific Exploratory Mission-West A (PEM-West A): September–October 1991, *J. Geophys. Res.*, *101*, 1641–1653.

Hoell, J. M., D. D. Davis, S. C. Liu, R. E. Newell, H. Akimoto, R. J. McNeal, and R. J. Bendura (1997), The Pacific Exploratory Mission-West Phase B: February–March, 1994, *J. Geophys. Res.*, *102*, 28,223–28,239.

Huebert, B. J., T. Bates, P. B. Russel, G. Y. Shi, Y. J. Kim, K. Kawamura, G. Carmichael, and T. Nakajima (2003), An overview of ACE-Asia: Strategies for quantifying the relationships between Asian aerosols and their climate impacts, *J. Geophys. Res.*, *108*(D23), 8633, doi:10.1029/2003JD003550.

Ieda, T., Y. Kitamori, M. Mochida, R. Hirata, T. Hirano, K. Inukai, Y. Fujinuma, and K. Kawamura (2006), Diurnal variations and vertical gradients of biogenic volatile and semi-volatile organic compounds at the Tomakomai larch forest station in Japan, *Tellus, Ser. B*, *59*, 177–186.

Jang, M., and S. R. McDow (1997), Products of benz[a]anthracene photodegradation in the presence of known organic constituents of atmospheric aerosols, *Environ. Sci. Technol.*, *31*, 1046–1053.

Kalberer, M., J. Yu, D. R. Cocker, R. C. Flagan, and J. H. Seinfeld (2000), Aerosol formation in the cyclohexene-ozone system, *Environ. Sci. Technol.*, *34*, 4894–4901.

Kawamura, K. (1993), Identification of C_2-C_{10} ω-oxocarboxylic acids, pyruvic acid, and C_2-C_3 α-dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC-MS, *Anal. Chem.*, *65*, 3505–3511.

Kawamura, K., and R. B. Gagosian (1987), Implications of ω-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids, *Nature*, *325*, 330–332.

Kawamura, K., and K. Ikushima (1993), Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, *27*, 2227–2235.

Kawamura, K., and I. R. Kaplan (1987), Motor exhaust emission as a primary source of dicarboxylic acids in Los Angeles ambient air, *Environ. Sci. Technol.*, *21*, 105–110.

Kawamura, K., and F. Sakaguchi (1999), Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropic, *J. Geophys. Res.*, *104*, 3501–3509.

Kawamura, K., and K. Usukura (1993), Distribution of low molecular weight dicarboxylic acids in the North Pacific aerosol samples, *J. Oceanogr.*, *49*, 271–283.

Kawamura, K., and O. Yasui (2005), Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, *39*, 1945–1960.

Kawamura, K., H. Kasukabe, O. Yasui, and L. A. Barrie (1995), Production of dicarboxylic acids in the arctic atmosphere at polar sunrise, *Geophys. Res. Lett.*, *22*, 1253–1256.

Kawamura, K., H. Kasukabe, and L. A. Barrie (1996), Source and reaction pathways of dicarboxylic acids, ketoacids, and dicarbonyls in artic aerosols at polar sunrise, *Atmos. Environ.*, *30*, 1709–1722.

Kawamura, K., N. Umemoto, M. Mochida, T. Bertram, S. Howell, and B. J. Huebert (2003), Water-soluble dicarboxylic acids in the tropospheric aerosols collected over east Asia and western North Pacific by ACE-Asia C-130 aircraft, *J. Geophys. Res.*, *108*(D23), 8639, doi:10.1029/2002JD003256.

Kawamura, K., M. Kobayashi, N. Tsubonuma, M. Mochida, T. Watanabe, and M. Lee (2004), Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in *Geochemical Investigation in Earth and Space Science; A Tribute to Issac R. Kaplan*, *The Geochemical Society Special Publication Series*, vol. 9, edited by R. J. Hill, pp. 243–265, Elsevier, Amsterdam, Netherlands.

Kerminen, V.-M., K. Teinila, R. Hillamo, and T. Makela (1999), Size segregated chemistry of particulate dicarboxylic acids in the Artic atmosphere, *Atmos. Environ.*, *33*, 2089–2100.

Kerminen, V.-M., C. Ojanen, T. Pakkanen, R. Hillamo, M. Aurela, and J. Merilainen (2000), Low-molecular weight dicarboxylic acids in an urban and rural atmosphere, *J. Aerosol. Sci.*, *31*, 349–362.

Khwaja, H. A. (1995), Atmospheric concentrations of carboxylic acids and related compounds at a semiurban site, *Atmos. Environ.*, *29*, 127–139.

Kim, J. Y., Y. S. Ghim, C. H. Song, S.-C. Yoon, and J. S. Han (2007), Seasonal characteristics of air masses arriving at Gosan, Korea, using fine particle measurements between November 2001 and August 2003, *J. Geophys. Res.*, *112*, D07202, doi:10.1029/2005JD006946.

Kim, K.-H., M. Lee, G. Lee, Y. P. Kim, Y.-H. Youn, J.-M. Oh (2002), Observations of aerosol-bound ionic composition at Cheju Island Korea, *Chemosphere*, *48*, 317–327.

Kim, Y. P., S.-G. Shim, and K. C. Moon (1998), Monitoring of air pollutants at Kosan, Cheju Island, Korea, during March–April 1994, *J. Appl. Meteorol.*, *37*, 1117–1126.

Kundu, S., K. Kawamura, T. W. Andreae, A. Hoffer, and M. O. Andreae (2010a), Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in biomass burning aerosols: Implications for photochemical production and degradation in smoke layers, *Atmos. Chem. Phys.*, *10*, 2209–2225.

Kundu, S., K. Kawamura, T. W. Andreae, A. Hoffer, and M. O. Andreae (2010b), Diurnal variation in the water-soluble inorganic ions, organic carbon and isotopic compositions of total carbon and nitrogen in biomass burning aerosols from the LBA-SMOCC campaign in Rondônia, Brazil, *J. Aerosol Sci.*, *41*, 118–133.

Lee, M., M. Song, K. J. Moon, J. S. Han, G. Lee, and K.-R. Kim (2007), Origins and chemical characteristics of fine aerosols during the northeastern Asia regional experiment (Atmospheric Brown Cloud-East Asia Regional Experiment 2005), *J. Geophys. Res.*, *112*, D22S29, doi:10.1029/2006JD008210.

Legrand, M., S. Preunkert, T. Oliveira, C. A. Pio, S. Hammer, A. Gelencsér, A. Kasper-Giebl, and P. Laj (2007), Origin of C_2–C_5 dicarboxylic acids in the European atmosphere inferred from year-around aerosol study conducted at a west-east transect, *J. Geophys. Res.*, *112*, D23S07, doi:10.1029/2006JD008019.

Li, S. M., and J. W. Winchester (1993), Water-soluble organic constituents in Arctic aerosols and snow pack, *Geophys. Res. Lett.*, *20*, 45–48.

Lim, H. J., and B. J. Turpin (2002), Origins of primary and secondary organic aerosol in Atlanta: Results of time-resolved measurements during the Atlanta Supersite experiment, *Environ. Sci. Technol.*, *36*, 4489–4496.

Lim, H.-J., A. G. Carlton, and B. J. Turpin (2005), Isoprene forms secondary organic aerosol through cloud processing: Model simulations, *Environ. Sci. Technol.*, *39*, 4441–4446, doi:10.1021/es048039h.

Limbeck, A., H. Pauxbaum, L. Otter, and M. C. Scholes (2001), Semivolatile behaviour of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA), *Atmos. Environ.*, *35*, 1853–1862.

Matsunaga, S., K. Kawamura, T. Nakatsuka, and N. Ohkouchi (1999), Preliminary study on laboratory photochemical formation of low molecular weight dicarboxylic acids from unsaturated fatty acid (oleic acid), *Res. Org. Geochem.*, *14*, 19–25.

Mayol-Bracero, O. L., P. Guyon, B. Graham, G. Roberts, M. O. Andreae, S. Decesari, M. C. Facchini, S. Fuzzi, and P. Artaxo (2002), Water soluble organic compounds in biomass burning aerosols over Amazonia 2: Apportionment of the chemical composition and importance of the polyacidic fraction, *J. Geophys. Res.*, *107*(D20), 8091, doi:10.1029/2001JD000522.

Mészáros, E., T. Barcza, A. Gelencsér, J. Hlavay, G. Y. Kiss, Z. Krivácsy, A. Molnár, and K. Ployák (1997), Size distributions of inorganic and organic species in the atmospheric aerosol in Hungary, *J. Aerosol. Sci.*, *28*, 1163–1175.

Miyazaki, Y., Y. Kondo, S. Han, M. Koike, D. Kodama, Y. Komazaki, H. Tanimoto, and H. Matsueda (2007), Chemical characteristics of water-soluble organic carbon in the Asian outflow, *J. Geophys. Res.*, *112*, D22S30, doi:10.1029/2007JD009116.

Miyazaki, Y., S. G. Aggarwal, K. Singh, P. K. Gupta, and K. Kawamura (2009), Dicarboxylic acids and water-soluble organic carbon in aerosols in New Delhi, India, in winter: Characteristics and formation processes, *J. Geophys. Res.*, *114*, D19206, doi:10.1029/2009JD011790.

Mochida, M., A. Kawabata, K. Kawamura, H. Hatsushika, and K. Yamazaki (2003a), Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific, *J. Geophys. Res.*, *108*(D6), 4193, doi:10.1029/2002JD002355.

Mochida, M., K. Kawamura, N. Umemoto, M. Kobayashi, S. Matsunaga, H.-J. Lim, B. J. Turpin, T. S. Bates, and B. R. T. Simoneit (2003b), Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: Continental outflow of organic aerosols

during the ACE-Asia campaign, *J. Geophys. Res.*, *108*(D23), 8638, doi:10.1029/2002JD003249.

Park, M. H., Y. P. Kim, C.-H. Kang, and S.-G. Shim (2004), Aerosol composition change between 1992 and 2002 at Gosan, Korea, *J. Geophys. Res.*, *109*, D19S13, doi:10.1029/2003JD004110.

Pradeep Kumar, P., K. Broekhuizen, and J. P. D. Abbatt (2003), Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species, *Atmos. Chem. Phys. Disc.*, *3*, 949–982.

Ray, J., and S. R. Mcdow (2005), Dicarboxylic acid concentration trends and sampling artifacts, *Atmos. Environ.*, *39*, 7906–7919.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1991), Sources of fine organic aerosol, 1, Charbroilers and meat cooking operations, *Environ. Sci. Technol.*, *25*, 1112–1125.

Satsumabayashi, H., H. Kurita, Y. Yokouchi, and H. Ueda (1990), Photochemical formation of particulate dicarboxylic acids under long range transport in central Japan, *Atmos. Environ., Part A*, *24*, 1443–1450.

Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit (1999), Measurement of emissions from air pollution sources, 1, C_1 through C_{29} organic compounds from meat charboiling, *Environ. Sci. Technol.*, *33*, 1566–1577.

Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit (2001), Measurement of emissions from air pollution sources. 3. C_1–C_{29} organic compounds from fireplace combustion of wood, *Environ. Sci. Technol.*, *35*, 1716–1728.

Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit (2002), Measurement of emissions from air pollution sources. 5. C_1–C_{32} organic compounds from gasoline-powered motor vehicles, *Environ. Sci. Technol.*, *36*, 1169–1180.

Stephanou, E. G., and N. Stratigakis (1993), Oxocarboxylic and α,ω-dicarboxylic acids: Photooxidation products of biogenic unsaturated fatty acids present in urban aerosols, *Environ. Sci. Technol.*, *27*, 1403–1407.

Stockwell, W. R., F. Kirchner, M. Kuhn, and S. Seefeld (1997), A new mechanism for regional atmospheric chemistry modeling, *J. Geophys. Res.*, *102*, 25,847–25,879.

Strader, R., F. Lurmann, and S. N. Pandis (1999), Evaluation of secondary organic aerosol formation in winter, *Atmos. Environ.*, *33*, 4849–4863.

Topping, D., H. Coe, G. McFiggans, R. Burgess, J. Allan, M. R. Alfarra, K. Bower, T. W. Choularton, S. Decesari, and M. C. Facchini (2004), Aerosol chemical characteristics from sampling conducted on the island of Jeju, Korea, during ACE Asia, *Atmos. Environ.*, *38*, 2111–2123.

Wang, G., K. Kawamura, and M. Lee (2009), Comparison of organic compositions in dust storm and normal aerosol samples collected at Gosan, Jeju Island, during spring, *Atmos. Environ.*, *43*, 219–227.

Wang, H., K. Kawamura, and K. Yamazaki (2006), Water-soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmosphere over the Southern Ocean and Western North Pacific, *J. Atmos. Chem*, *53*, 43–61.

Warneck, P. (2003), In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.*, *37*, 2423–2427.

Yamasoe, M. A., P. Artaxo, A. H. Miguel, and A. G. Allen (2000), Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: Water-soluble species and trace elements, *Atmos. Environ.*, *34*, 1641–1653.

Yang, H., J. Xu, W. Wu, C. H. Wan, and J. Z. Yu (2004), Chemical characterization of water-soluble organic aerosols at Jeju Island collected during ACE-Asia, *Environ. Chem.*, *1*, 13–17, doi:10.1071/EN04006.

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