Organic and inorganic aerosol compositions in Ulaanbaatar, Mongolia, during the cold winter of 2007 to 2008: Dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls

Jinsang Jung,[1,2] Batmunkh Tsatsral,[2] Young J. Kim,[2] and Kimitaka Kawamura[1]

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[1] To investigate the distributions and sources of water-soluble organic acids in the Mongolian atmosphere, aerosol samples ($PM_{2.5}$, n = 34) were collected at an urban site (47.92°N, 106.90°E, ~1300 m above sea level) in Ulaanbaatar, the capital of Mongolia, during the cold winter. The samples were analyzed for water-soluble dicarboxylic acids (C_2–C_{12}) and related compounds (ketocarboxylic acids and α-dicarbonyls), as well as organic carbon (OC), elemental carbon, water-soluble OC, and inorganic ions. Distributions of dicarboxylic acids and related compounds were characterized by a predominance of terephthalic acid (tPh; 130 ± 51 ng m^{-3}, 19% of total detected organic acids) followed by oxalic (107 ± 28 ng m^{-3}, 15%), succinic (63 ± 20 ng m^{-3}, 9%), glyoxylic (55 ± 18 ng m^{-3}, 8%), and phthalic (54 ± 27 ng m^{-3}, 8%) acids. Predominance of terephthalic acid, which has not been reported previously in atmospheric aerosols, was mainly due to uncontrolled burning of plastic bottles and bags in home stoves for heating and waste incineration during the cold winter. This study demonstrated that most of the air pollutants were directly emitted from local sources such as heat and power plants, home stoves, and automobiles. Development of an inversion layer (<700 m above ground level) over the basin of Ulaanbaatar accelerated the accumulation of pollutants, causing severe haze episodes during the winter season.

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1. Introduction

[2] Organic aerosols are a major fraction of tropospheric aerosols, accounting for up to 70% of the fine aerosol mass [*Jacobson et al.*, 2000; *Kanakidou et al.*, 2005]. Organic aerosols contribute to the radiative balance on the Earth by scattering sunlight. Organic aerosols play a key role in cloud nucleation. In regions that are affected by anthropogenic pollutants, organic aerosols may play an important role in determining the climate effect of clouds as sulfate aerosols [*Novakov and Penner*, 1993]. Model simulation results indicate that organic aerosol can enhance the cloud droplet concentration and is therefore an important component of the aerosol-cloud-climate feedback system [*O'Dowd et al.*, 2004]. The cloud condensation nuclei activity of aerosol particles can significantly be perturbed by particulate water-soluble organic aerosols [*Saxena et al.*, 1995; *Facchini et al.*, 1999]. Their chemical composition is known to lower the surface tension or to alter the bulk hygroscopicity of aerosol particles [*Raymond and Pandis*, 2002; *Abdul-Razzak and Ghan*, 2004; *Lance et al.*, 2004; *Shilling et al.*, 2007].

[3] Dicarboxylic acids and related compounds (ketocarboxylic acids and α-dicarbonyls) are well recognized as ubiquitous components of atmospheric aerosols from urban [*Kawamura and Ikushima*, 1993; *Ho et al.*, 2007; *Aggarwal and Kawamura*, 2008; *Miyazaki et al.*, 2009], rural/suburban [*Khwaja*, 1995; *Limbeck et al.*, 2001; *Legrand et al.*, 2007], coastal and remote marine [*Kawamura and Sakaguchi*, 1999; *Mochida et al.*, 2003; *Sempéré and Kawamura*, 2003; *Kawamura et al.*, 2004; *Wang et al.*, 2006a; *Legrand et al.*, 2007], Arctic [*Kawamura et al.*, 1996a; *Kerminen et al.*, 1999; *Narukawa et al.*, 2003], and Antarctic regions [*Kawamura et al.*, 1996b]. However, almost no study has been conducted concerning organic acids near an Asian dust source region. Organic acids may interact with Asian dusts that contain alkaline and trace metals by forming organo-metal complexes [e.g., *Deguillaume et al.*, 2005]. For example, oxalic acid is important ligand for ion, dissolving iron (III) hydroxide in aerosol liquid phase. Dicarboxylic acids and related compounds are directly emitted from primary sources and also formed by secondary processes in the atmosphere [*Grosjean et al.*, 1978; *Hatakeyama et al.*, 1987; *Kawamura and Ikushima*, 1993; *Kawamura et al.*, 1996a; *Limbeck and Puxbaum*, 1999; *Sempéré and*

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan.
[2]Advanced Environmental Monitoring Research Center, Gwangju Institute of Science and Technology, Gwangju, South Korea.

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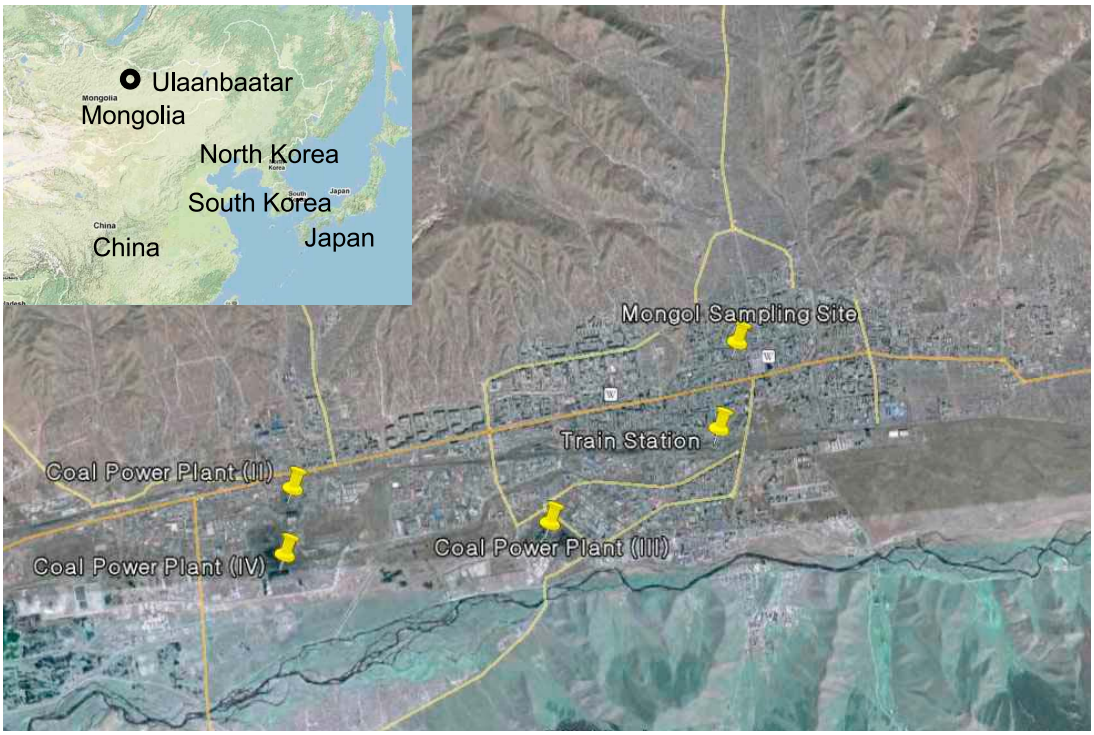

Figure 1. Image map of the sampling site (47.92°N, 106.90°E) in Ulaanbaatar, Mongolia (Google Earth imagery (© Google Inc., used with permission)). The map in top left corner shows a location of Ulaanbaatar, Mongolia, over East Asia. Three heat and power plants are located 4.5 to 8.5 km southwest of the sampling site. The main vehicle road and train station are located at 0.5 and 1.5 km south of the sampling site, respectively.

Kawamura, 2003; *Crahan et al.*, 2004; *Yu et al.*, 2005; *Sorooshian et al.*, 2006, 2007a; *Volkamer et al.*, 2006]. Many studies were conducted to identify primary emissions of dicarboxylic acids and related compounds from auto exhaust [*Kawamura and Kaplan*, 1987; *Wang et al.*, 2006b; *Ho et al.*, 2006; *Huang and Yu*, 2007], biomass burning [*Narukawa et al.*, 1999; *Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002; *Gao et al.*, 2003; *Decesari et al.*, 2006; *Falkovich et al.*, 2005; *Kundu et al.*, 2010], and cooking activities [*Rogge et al.*, 1991; *Robinson et al.*, 2006]. However, studies have rarely been conducted to examine the organic acids emitted from lignite coal burning.

[4] Ulaanbaatar is the capital of Mongolia (population: 1.0 million), located in a valley surrounded by high mountains ranging from 1,652 to 1,949 m above sea level. It is the coldest capital in the world during the winter from October to March, requiring a lot of fuel consumption for space heating [data available from http://www.rrcap.unep.org/pub/soe/mongoliasoe.cfm; *Asian Development Bank*, 2006]. It was roughly estimated that three combined heat and power plants, 250 small- and medium-sized heat-only boilers, and 70,000 traditional gers (traditional tent dwelling) and wooden house stoves consume annually 5, 0.4, and 0.2–0.35 million tons of lignite coal, respectively. In winter, each ger or wooden house stove consumes on average 5 tons of lignite coal and 4.7 m^3 of wood [*World Bank*, 2004]. Approximately 80,000 vehicles are used in Ulaanbaatar, most of which are secondhand after more than 10 years of use. Around 80% of them do not meet emission standards [*Guttikunda*, 2007]. Waste incineration in home stoves generally occurs without emission control. Severe haze episodes are frequently reported in Ulaanbaatar during the winter under the conditions of atmospheric inversion and low wind speed [*Japan Environmental Council*, 2005]. However, sources, formation mechanisms, and chemical composition of the haze aerosols in Ulaanbaatar are poorly understood.

[5] In this study, we conducted the first measurements of dicarboxylic acids and related compounds, organic carbon (OC)/elemental carbon (EC), water-soluble OC (WSOC), and inorganic ions in the atmospheric aerosols collected in Ulaanbaatar, Mongolia, during a cold winter. Here we report on unique characteristics of molecular distributions of dicarboxylic acids and related compounds. Sources and formation processes of atmospheric aerosols will be discussed with detailed aerosol chemical composition and air mass backward trajectories.

2. Measurement and Method

2.1. Aerosol Sampling

[6] $PM_{2.5}$ aerosol sampling for collection of 24 h samples was carried out every day starting at 1100 local time (LT) from 29 November 2007 to 6 January 2008 at an urban site in Ulaanbaatar, Mongolia (Figure 1). The aerosol sampler was installed on the rooftop of the National Agency for Meteorology, Hydrology and Environmental Monitoring (NAMHEM) building (47.92°N, 106.90°E, ~10 m height), which is located in the northern part of Ulaanbaatar (~1300 m above sea level). The $PM_{2.5}$ sampler consisted of a Teflon-coated aluminum cyclone impactor (URG-2000-30EH) with

a cut size of 2.5 μm and a 47 mm Teflon filter pack (URG-2000-30F). The flow rate was maintained at 16.7 L min^{-1} using a mass flow controller. For the aerosol sampling, two types of filters were used: quartz filters (Whatman, 47 mm) for the analysis of carbonaceous components and Teflon filters (Gelman, 2 μm, 47 mm) for inorganic ions. The sample was not denuded in this study. Recent studies demonstrated that dicarboxylic acids are observed predominantly in particles [*Baboukas et al.*, 2000; *Mochida et al.*, 2003]. Although some gas phase organics could be in part adsorbed on the quartz filter, we assume that positive artifacts should be minimal and not seriously affect the results. Quartz filters were prebaked at 850°C for 3 h before sampling and stored in a freezer at −20°C before and after sampling. For organic analysis, half of each quartz filter was wrapped in prebaked aluminum foil and transported to the laboratory in Sapporo. Quartz filter discs were transferred into prebaked glass vials (480°C, overnight) with a Teflon-lined screw cap and stored at −20°C until analysis. A total of 34 quartz and Teflon filters were used in this study. The concentration reported in this study is ambient concentration.

2.2. Chemical Analyses

[7] Samples were analyzed for dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls using a method reported previously [*Kawamura and Ikushima*, 1993; *Kawamura*, 1993]. Briefly, an aliquot (0.4 cm^2) of quartz filter was extracted with ultra pure organic-free Milli-Q water (10 mL, three times) under ultrasonication (5 min, three times). The extracts were concentrated to almost dryness using a rotary evaporator and then derivatized with 14% borontrifluoride (BF_3)/*n*-butanol at 100°C for 1 h to derive the carboxyl groups to butyl esters and the aldehyde groups to dibutoxy acetals. The esters and acetals were extracted with *n*-hexane, and then determined using a capillary gas chromatograph (GC) (Hewlett-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 a flame ionization detector. Peak identification was performed by comparing the GC retention times with those of authentic standards. Identification of esters and acetals was also confirmed by mass spectra of the sample using a GC-mass spectrometry (Thermo, Trace MS) system.

[8] Recoveries of authentic standards spiked to a precombusted quartz fiber filter were 85% for oxalic acid and more than 90% for malonic, succinic, glutaric, and adipic acids. The detection limits of the major organic acids (C_2, C_4, C_9, Ph, tPh, ωC_2), which are defined as three times the standard deviation (3σ) of field blanks, are determined to be 0.5–2 ng m^{-3}. The analytical errors of major species were less than 5% based on the triplicate analyses of different sections of the same filter sample collected in Sapporo using a high-volume air sampler. The field and lab blanks showed small peaks of oxalic, phthalic, terephthalic, and glyoxylic acids and methylglyoxal. The levels of field blanks were generally less than 10% of the actual samples, except for glyoxylic acid (less than 20%). Concentrations of all the species reported here are corrected for the field blanks but not for recoveries.

[9] OC and EC were determined using a Sunset Laboratory carbon (OC/EC) analyzer using the thermal-optical transmittance protocol for pyrolysis correction [*Birch and Cary*, 1996; *Jeong et al.*, 2004; *Kim et al.*, 2006; *Jung et al.*, 2009b]. A 2.0 cm^2 punch of the quartz filter was placed in a quartz boat inside the thermal desorption chamber of the analyzer, and then stepwise heating was applied. External calibration was performed before the analysis using a known amount of sucrose. The detection limits of OC and EC, which are defined as 3σ of field blanks, were 0.26 and 0.01 μgC m^{-3}, respectively. The analytical errors of OC and EC were less than 5% and 3%, respectively, based on the triplicate analyses of filter sample.

[10] To measure WSOC, an aliquot (0.4 cm^2) of quartz filter was extracted with organic-free Milli-Q water (7 mL) under ultrasonication (5 min, three times). The water extracts were then passed through a syringe filter (Millex-GV, 0.45 μm, Millipore), and WSOC was quantified using a total organic carbon (TOC) analyzer (Shimadzu, TOC–V_{SCH}) equipped with a catalytic oxidation column/nondispersive infrared detector. The sample was measured twice and the average was used in this study. External calibration was performed before sample analyses using potassium hydrogen phthalate. The detection limit of WSOC, which is defined as 3σ of field blanks, was 0.23 μgC m^{-3}. The analytical error of WSOC was less than 6%.

[11] To measure water-soluble inorganic ions, an aliquot (6.6 cm^2) of Teflon filter was extracted in the same manner as for WSOC and then analyzed by ion chromatography (Dionex, DX–120). The anions, chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}), were detected by an IONPAC AS4A–SC column using 3.5 mM sodium carbonate/1.0 mM sodium bicarbonate (flow rate: 1.2 mL m^{-1}; sample loop volume: 50 μL; time eluted: 15 min). The cations, sodium (Na^+), ammonium (NH_4^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), were detected by an IONPAC CS12 column using 20 mM methanesulfonic acid as an eluent (flow rate: 1.0 mL m^{-1}; sample loop volume: 50 μL; time eluted: 20 min). The detection limits of major inorganic ions, which are defined as 3σ of field blanks, were 0.01, 0.11, and 0.03 μg m^{-3} for NO_3^-, SO_4^{2-}, and NH_4^+, respectively.

2.3. Meteorological Data and Air Mass Backward Trajectories

[12] Meteorological parameters (wind speed, wind direction, and ambient temperature) were obtained from an automatic weather station located at 8 km west of the sampling site, which was operated by the NAMHEM of Mongolia. Ambient temperature during the entire sampling period varied from −30.3°C to −4.4°C with an average of −17.5 ± 5.0°C. Cold weather in Ulaanbaatar during winter can be attributed to its high latitude of 47.92°N and elevated geographical location of ~1300 m above sea level. Wind speed varied from 0.0 to 5.7 m s^{-1} with an average of 1.5 ± 1.0 m s^{-1}. The prevailing surface wind direction was northeasterly or northwesterly in the nighttime (1900 to 0900 LT) and westerly (1000 to 1800 LT) with higher wind speeds of 1.9 ± 1.0 m s^{-1} in the daytime. Since Ulaanbaatar is surrounded by high mountains (except the western part of the city), relatively strong westerly winds in the daytime transport pollutants emitted from heat and power plants to the sampling site (Figure 1). Thus, 24 h aerosol collection can capture aerosols from many emission sources (lignite coal burning, burning of plastic bottles and bags, auto exhaust, etc.). Consequently, the data in this study is representative in this region not largely

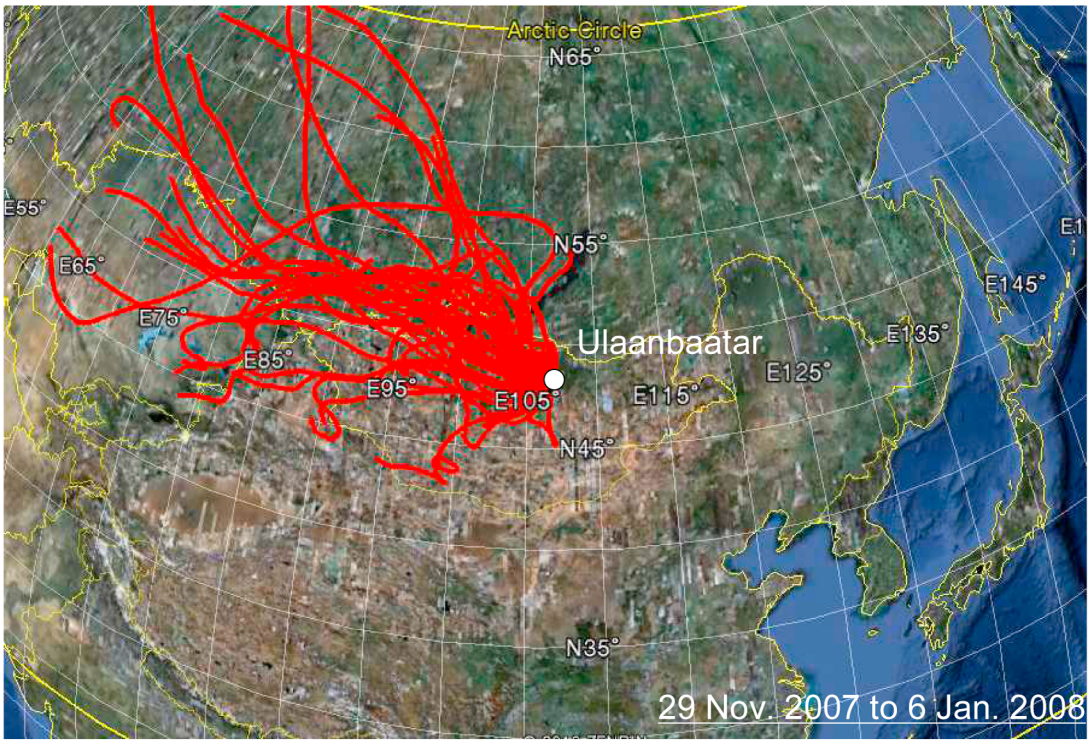

Figure 2. Four day backward trajectories arriving at 500 m above the sampling site during the entire sampling period.

affected by some specific sources in the vicinity of the sampling site.

[13] Vertical profiles of ambient temperature from ~300 m to ~1000 m over the sampling site was obtained from the Global Data Assimilation System sounding product from National Oceanic and Atmospheric Administration (NOAA)'s Air Resources Laboratory (ARL) (available at http://www.ready.noaa.gov/ready.html). Sulfur dioxide (SO_2) data were obtained by the NAMHEM of Mongolia at 1.5 km west of the sampling site. During the sampling period, two precipitation events occurred on 27 and 28 December 2007 with daily rainfall of 1.4 and 1.8 mm, respectively.

[14] Air mass backward trajectories were computed at 500 m above the sampling site with the Hybrid Single-Particle Lagrangian Trajectory (HYSPLIT) NOAA/ARL model [*Draxler and Rolph*, 2010; *Rolph*, 2010]. Up to 20% errors of the traveled distance are typical for those trajectories computed from analyzed wind field [*Stohl*, 1998]. Thus, calculated air mass pathways indicate the general airflow pattern rather than the exact pathway of an air mass. All backward trajectories were calculated starting at 0000 UT (0800 LT) and extending 96 h back with a 1 h time interval. Air masses during the entire sampling period mainly originated from northwest of Mongolia (Figure 2).

3. Results and Discussion

3.1. Molecular Distributions of Dicarboxylic Acids, Ketocarboxylic Acids, and α-Dicarbonyls in $PM_{2.5}$ Aerosols

[15] A homologous series of α,ω-dicarboxylic acids (C_2–C_{12}) and ketocarboxylic acids (ωC_2–ωC_4, ωC_9, and pyruvic acids), aromatic (phthalic, isophthalic, and terephthalic acids) dicarboxylic acids, and α-dicarbonyls (glyoxal and methylglyoxal) were detected in the $PM_{2.5}$ samples. We also detected unsaturated aliphatic acids (maleic, fumaric, and methylmaleic acids) and multifunctional dicarboxylic acids (malic, ketomalonic, and 4-ketopimelic acids). Table 1 summarizes average concentrations of these compounds in the $PM_{2.5}$ aerosols as well as OC, EC, WSOC, and inorganic ions during the sampling period. Bar graphs of dicarboxylic acids and related compounds are shown in Figure 3. Hereafter, dicarboxylic acids and ketocarboxylic acids are denoted as diacids and ketoacids, respectively.

[16] Concentrations of total diacids ranged from 146 to 779 ng m^{-3} with an average of 536 ± 156 ng m^{-3}. In general, terephthalic acid (tPh) was found as the most abundant diacid species. Relative abundances of tPh in total diacids ranged from 9 to 32% (average 23%), followed by oxalic (C_2) (11–48%, average 21%), succinic (C_4) (9–15%, average 12%) and phthalic (Ph) acids (2–20%, average 10%). The high relative abundances of C_4 and Ph in total diacids were also reported in urban aerosols in Sapporo [*Aggarwal and Kawamura*, 2008] and 14 Chinese megacities [*Ho et al.*, 2007] and primary auto exhaust from near a roadside and tunnel in Hong Kong [*Ho et al.*, 2006; *Wang et al.*, 2006b]. High abundance of C_2 followed by C_4 was also observed from biomass burning aerosols [*Kundu et al.*, 2010]. C_3 was reported as one of major diacids in urban and remote marine aerosols (Table 2). However, C_3 in Ulaanbaatar samples was a minor constituent (10th out of 23 identified diacids). Negligible amounts of the multifunctional diacids (malic, ketomalonic, and 4-ketopimelic acids) were observed. Concentration ranges of total ketoacids and dicarbonyls were

Table 1. Concentrations of Dicarboxylic Acids (Diacids), Ketocarboxylic Acids (Ketoacids), and α-Dicarbonyls as well as OC, EC, WSOC, and Inorganic Ions in the $PM_{2.5}$ Samples Collected at Ulaanbaatar, Mongolia, From 29 November 2007 to 6 January 2008[a]

		Concentration				
	Chemical Formula	Minimum	Maximum	Average	SD[b]	Median
Saturated *n*-dicarboxylic acids[c]						
Oxalic, C_2	HOOC-COOH	35	166	107	28	106
Malonic, C_3	HOOC-CH_2-COOH	5	22	13	4	13
Succinic, C_4	HOOC-$(CH_2)_2$-COOH	17	89	63	20	67
Glutaric, C_5	HOOC-$(CH_2)_3$-COOH	2	62	26	14	24
Adipic, C_6	HOOC-$(CH_2)_4$-COOH	0	25	11	6	11
Pimelic, C_7	HOOC-$(CH_2)_5$-COOH	2	28	13	6	13
Suberic, C_8	HOOC-$(CH_2)_6$-COOH	0	7	4	1	5
Azelaic, C_9	HOOC-$(CH_2)_7$-COOH	11	67	42	12	44
Sebacic, C_{10}	HOOC-$(CH_2)_8$-COOH	1	10	5	2	5
Undecanedioic, C_{11}	HOOC-$(CH_2)_9$-COOH	1	7	4	2	4
Dodecanedioic, C_{12}	HOOC-$(CH_2)_{10}$-COOH	0	1	0	1	0
Branched dicarboxylic acids[c]						
Methylmalonic, iC_4	HOOC-$CH(CH_3)$-COOH	0	4	1	1	1
Methylsuccinic, iC_5	HOOC-$CH(CH_3)$-CH_2-COOH	9	39	25	9	27
Methylglutaric, iC_6	HOOC-$CH(CH_3)$-$(CH_2)_2$-COOH	1	5	3	1	3
Unsaturated dicarboxylic acids[c]						
Maleic, M	HOOC-CH = CH-COOH (cis)	0	4	2	1	2
Fumaric, F	HOOC-CH = CH-COOH (trans)	0	3	1	1	1
Methylmaleic, mM	HOOC-$C(CH_3)$ = CH-COOH (cis)	6	18	12	4	13
Phthalic, Ph	HOOC-(C_6H_4)-COOH (ortho)	3	125	54	27	54
Isophthalic, iPh	HOOC-(C_6H_4)-COOH (meta)	0	38	18	8	18
Terephthalic, tPh	HOOC-(C_6H_4)-COOH (para)	19	233	130	51	129
Multifunctional dicarboxylic acids[c]						
Malic, hC_4	HOOC-CH(OH)-CH_2-COOH	0	8	1	2	0
Ketomalonic, kC_3	HOOC-C(O)-COOH	0	5	1	1	0
4-Ketopimelic, kC_7	HOOC-$(CH_2)_2$-C(O)-$(CH_2)_2$-COOH	0	0	0	0	0
Total dicarboxylic acids[c]		146	779	536	156	579
Ketocarboxylic acids[c]						
Pyruvic, Pyr	CH_3-C(O)-COOH	10	65	24	10	23
Glyoxylic, ωC_2	OHC-COOH	22	102	55	18	54
3-Oxopropanoic, ωC_3	OHC-CH_2-COOH	2	8	5	2	5
4-Oxobutanoic, ωC_4	OHC-$(CH_2)_2$-COOH	11	58	33	14	33
9-Oxononanoic, ωC_9	OHC-$(CH_2)_7$-COOH	1	20	9	4	9
Subtotal		57	187	126	39	128
α-dicarbonyls[c]						
Glyoxal, Gly	OHC-CHO	4	20	14	4	15
Methylglyoxal, mGly	CH_3-C(O)-CHO	1	35	20	9	22
Subtotal		10	54	35	12	36
Total (all detected species)[c]		225	187	126	39	128
EC[d]		1.4	9.9	6.7	2.2	6.7
OC[d]		5.8	52.8	31.8	11.8	33.4
WSOC[d]		0.0	37.2	17.2	8.5	18.5
OC/EC ratio		3.0	6.0	4.7	0.8	4.9
Inorganic ions[e]						
Cl^-		0.3	3.4	2.0	0.8	2.0
NO_3^-		1.4	10.5	4.9	2.0	4.9
PO_4^{3-}		0.0	5.7	3.1	1.6	3.3
SO_4^{2-}		2.8	20.0	10.3	3.7	10.3
Na^+		0.9	3.0	2.1	0.5	2.1
NH_4^+		1.1	10.2	5.8	2.2	6.2
K^+		0.1	0.3	0.2	0.1	0.2
Ca^{2+}		0.2	1.8	1.0	0.4	0.9
Mg^{2+}		0.0	0.2	0.1	0.0	0.1

[a]OC, organic carbon; EC, elemental carbon; WSOC, water-soluble organic carbon.
[b]SD, standard deviation.
[c]Concentrations are in ng m^{-3}.
[d]Values are in μgC m^{-3}.
[e]Values are in μg m^{-3}.

57–187 ng m^{-3} (average 126 ± 39 ng m^{-3}) and 10–54 ng m^{-3} (average 35 ± 12 ng m^{-3}), respectively. Glyoxylic acid (ωC_2) was the most abundant ketoacid species, comprising 27–58% (average 44%) of total ketoacids, followed by 4-oxobutanoic acid (ωC_4; 16–35%, average 26%) and pyruvic acid (Pyr; 11–38%, average 19%). Methylglyoxal was observed to be more abundant than glyoxal.

[17] The predominance of tPh has never been reported in atmospheric aerosols. Most previous studies of atmospheric aerosols have reported the predominance of C_2 in biomass burning [*Kundu et al.*, 2010], urban [*Kawamura and Ikushima*, 1993; *Ho et al.*, 2006, 2007; *Wang et al.*, 2006b; *Aggarwal and Kawamura*, 2008; *Miyazaki et al.*, 2009; *Pavuluri et al.*, 2010], and remote marine aerosols

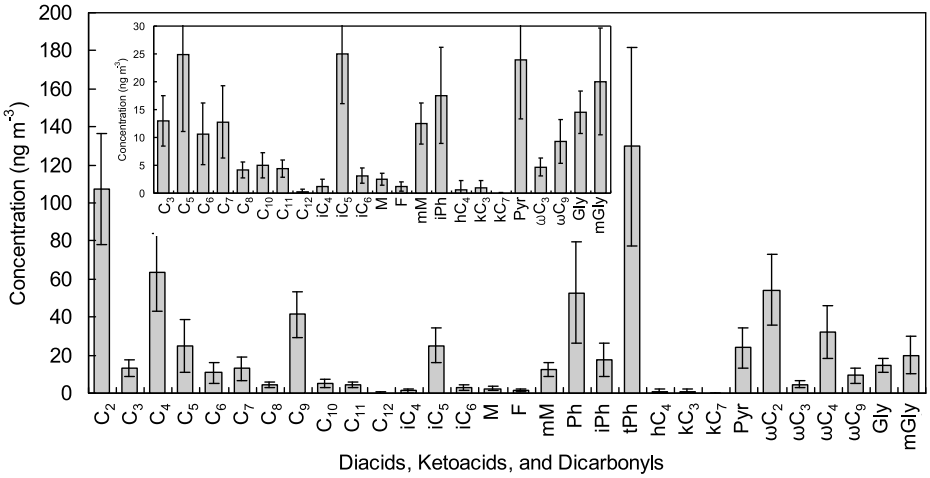

Figure 3. Average molecular distributions of dicarboxylic acids (diacids), ketocarboxylic acids (ketoacids), and α-dicarbonyls in the $PM_{2.5}$ samples collected at Ulaanbaatar, Mongolia, during the entire sampling period. To highlight the minor species (average <30 ng m^{-3}), their molecular distributions are also shown with an enhanced *y* axis scale. See Table 1 for abbreviations.

[*Kawamura and Sakaguchi*, 1999; *Mochida et al.*, 2003; *Sempéré and Kawamura*, 2003] as well as in Arctic aerosols [*Kawamura et al.*, 1996a]. The one exception was an Antarctic summer aerosol sample, which showed predominance of C_4 [*Kawamura et al.*, 1996b], followed by C_2 and Ph. Since tPh is a major chemical component of polyester (polyethylene terephthalate) fiber and plastic bottles, the burning of plastic bottles and shopping bags emits a significant amount of tPh [*Simoneit et al.*, 2005]. Home stoves for space heating and cooking are one of the major emission sources in Ulaanbaatar during the cold winter. Most people generally consume lignite coal or wood for their home stoves. However, some poor people burn plastic wastes in their home stoves [*Guttikunda*, 2007]. Waste incinerators containing a lot of plastics were frequently found to occur in open space without emission control [*Kawamura and Pavuluri*, 2010]. Hence, the predominance of tPh can be explained by the burning of plastic products.

[18] During photochemical production of diacids, the contribution of diacid carbon (diacid-C) to aerosol total carbon (TC) increases in the urban atmosphere [*Kawamura and Yasui*, 2005]. The contribution of total diacid-C to TC (and also to OC) in the Ulaanbaatar aerosols varied from 0.2% to 0.9% (0.5% to 1.5%) with an average of 0.6% ± 0.2% (0.8% ± 0.2%). The average diacid-C/TC ratio is slightly lower than those obtained at Asian megacities in Tokyo (0.95%) [*Kawamura and Ikushima*, 1993] and Sapporo, Japan (1.8%) [*Aggarwal and Kawamura*, 2008]. However, they are several times lower than those obtained at remote marine sites in the western Pacific (3.2%) [*Sempéré and Kawamura*, 2003] and in the tropical to western North Pacific (8.5%), where photochemical processing is significant [*Kawamura and Sakaguchi*, 1999] (Table 2). The lower diacid-C/TC ratios compared to those from other Asian cities and the remote marine sites can be explained by not only less photochemical aging but also the enhanced emission of hydrophobic carbonaceous aerosols from combustion sources. The diacid-C/OC ratios are also slightly lower than those obtained at Asian megacities in New Delhi, India (1.0%) [*Miyazaki et al.*, 2009], and in Sapporo, Japan (4.8%) [*Aggarwal and Kawamura*, 2008]. Interestingly, they are about two times higher than that from auto exhaust (summer: 0.41%; winter: 0.51%) [*Wang et al.*, 2006b], but about two times lower than that from biomass burning (daytime: 1.7%; nighttime: 1.4%) [*Kundu et al.*, 2010], indicating that the Ulaanbaatar aerosols are influenced by both fossil fuel combustion and biomass burning.

3.2. Major Inorganic Ions and Particulate Carbonaceous Components in the $PM_{2.5}$ Aerosols

[19] SO_4^{2-} was the most abundant inorganic ion, whose concentrations ranged from 2.8 to 20.0 $\mu g\ m^{-3}$ with an average of 10.3 ± 3.7 $\mu g\ m^{-3}$. It accounts for 34.0% ± 3.9% of the total inorganic ion mass. The second most abundant species was NH_4^+ (range: 1.1–10.2 $\mu g\ m^{-3}$; average: 5.8 ± 2.2 $\mu g\ m^{-3}$; relative abundance: 18.8% ± 2.5%), followed by NO_3^- (range: 1.4–10.5 $\mu g\ m^{-3}$; average: 4.9 ± 2.0 $\mu g\ m^{-3}$; relative abundance: 16.0% ± 3.8%). Diurnal variations of meteorological parameters are shown in Figure 4 together with the concentrations of all inorganic ions. Wind direction and wind speed showed clear diurnal variations with relatively strong westerly winds in the afternoon. When a strong wind came from northwest of Ulaanbaatar, lower concentrations of inorganic ions were observed. When wind speed was low, higher concentrations of inorganic ions were generally observed.

[20] Observation results showed that the molar ratio of NH_4^+ to ($2 \times SO_4^{2-} + NO_3^-$) is close to 1 with an average of 1.09 ± 0.19. It can be concluded that there was sufficient ammonia (NH_3) in the air to neutralize all sulfuric acid (H_2SO_4) and nitric acid (HNO_3). Thus, the dominant chemical forms of the SO_4^{2-} and NO_3^- aerosols were ammonium sulfate $(NH_4)_2SO_4$ and ammonium nitrate NH_4NO_3, respectively. Since $PM_{2.5}$ aerosols were collected in this study, relatively low concentrations of Ca^{2+} were obtained with an average of 1.0 ± 0.4 $\mu g\ m^{-3}$ due to their dominance in coarse mode [*Guo et al.*, 2010]. Thus, this study did not consider Ca^{2+} for the neutralization of SO_4^{2-} and NO_3^-. Relatively high concentrations of PO_4^{3-} were observed with a range of 0.0

Table 2. Comparison of Characteristics of Diacids in Atmospheric Aerosols in This Study With Those Obtained From Previous Studies

Location	Sampling Period	Aerosol Type	Mean Diacid Concentration (Range) (ng/m^3)	Major Species	Diacid-C/OC (Diacid-C/TC)[a] (%)	WSOC/OC (WSOC/TC) (%)	Reference
Ulaanbaatar, Mongolia	Nov 2007 to Jan 2008	$PM_{2.5}$	536.0 (146.1–779.1)	tPh>C_2>C_4>Ph	0.8 (0.6)	53.2 (43.8)	This study
Sapporo, Japan	May to Jul 2005	TSP	406 (106–787)	C_2>C_3>C_4>Ph	4.8 (1.8)	44 (39)	*Aggarwal and Kawamura* [2008]
Chinese cities	Jun to Jul 2003	$PM_{2.5}$	892 (211–2162)	C_2>Ph>C_4>C_3	2.3 (1.4[b])	48 (37)	*Ho et al.* [2007]
Chinese cities	Jan 2003	$PM_{2.5}$	904 (319–1940)	C_2>C_4>Ph>C_3	1.3 (1.0[b])	41 (32)	*Ho et al.* [2007]
New Delhi, India	Sep 2006 to Apr 2007 (day)	TSP	1777 (835–2835)	C_2>C_4>C_3>C_9	1.0[b]	37	*Miyazaki et al.* [2009]
	Sep 2006 to Apr 2007 (night)	TSP	2875 (979–6030)	C_2>C_4>C_3>C_9	1.2[b]	25	
Tokyo, Japan	Apr 1988 to Feb 1989	TSP	480 (90–1360)	C_2>C_3>C_4>C_9	(0.95)		*Kawamura and Ikushima* [1993]
Chennai, India	Jan to Feb, May 2007	PM_{10}	612 (176–1436)	C_2>C_3>C_4>tPh	(1.58)		*Pavuluri et al.* [2010]
Gasoline vehicle		TSP		C_2>mM>C_4>M			*Kawamura and Kaplan* [1987]
Diesel vehicle		TSP		C_2>mM>M>C_4			*Kawamura and Kaplan* [1987]
Roadside, Hong Kong	Jan, Jun, Nov 2003	$PM_{2.5}$	692 (224–1381)	C_2>Ph>C_3>C_4	1.12–2.47		*Ho et al.* [2006]
Tunnel, Hong Kong	Aug 2003	$PM_{2.5}$	454 (260–677)	C_2>Ph>iPh>tPh	0.41		*Wang et al.* [2006b]
Tunnel, Hong Kong	Feb 2004	$PM_{2.5}$	771 (114–812)	C_2>Ph>iPh>tPh	0.51		*Wang et al.* [2006b]
Biomass burning	Sep 2002 (day)	$PM_{2.5}$	1849 (1039–3480)	C_2>C_4>C_3>C_6	1.7		*Kundu et al.* [2010]
Biomass burning	Sep 2002 (night)	$PM_{2.5}$	2500 (1773–3193)	C_2>C_4>C_3>C_5	1.4		*Kundu et al.* [2010]
Chichi-jima island, Japan	Jan to Mar 1991 to 1993	TSP	230 (120–400)	C_2>C_3>C_4>Ph			*Mochida et al.* [2003]
Chichi-jima island, Japan	Jul to Sep 1991 to 1993	TSP	54 (7–170)	C_2>C_3>C_4>Ph			*Mochida et al.* [2003]
Tropical to western North Pacific	Sep to Dec 1990	TSP	62 (100–248)	C_2>C_3>C_4>C_6	(8.8)		*Kawamura and Sakaguchi* [1999]
Western Pacific	Aug to Oct 1992	TSP	7.3 (7–605)	C_2>C_3>C_4>C_9	(3.2)	(40)	*Sempéré and Kawamura* [2003]
Arctic	Jul 1987 to Jun 1988	TSP	25 (4.3–97)	C_2>C_4>C_3>Ph			*Kawamura et al.* [1996a]
Antarctic	Feb to Dec 1991	$PM_{0.7}$	30 (6–89)	C_4>C_2>Ph>C_9	(1.35)		*Kawamura et al.* [1996b]

[a]Diacid-C, total diacid carbon.
[b]Calculated from average values in the references.

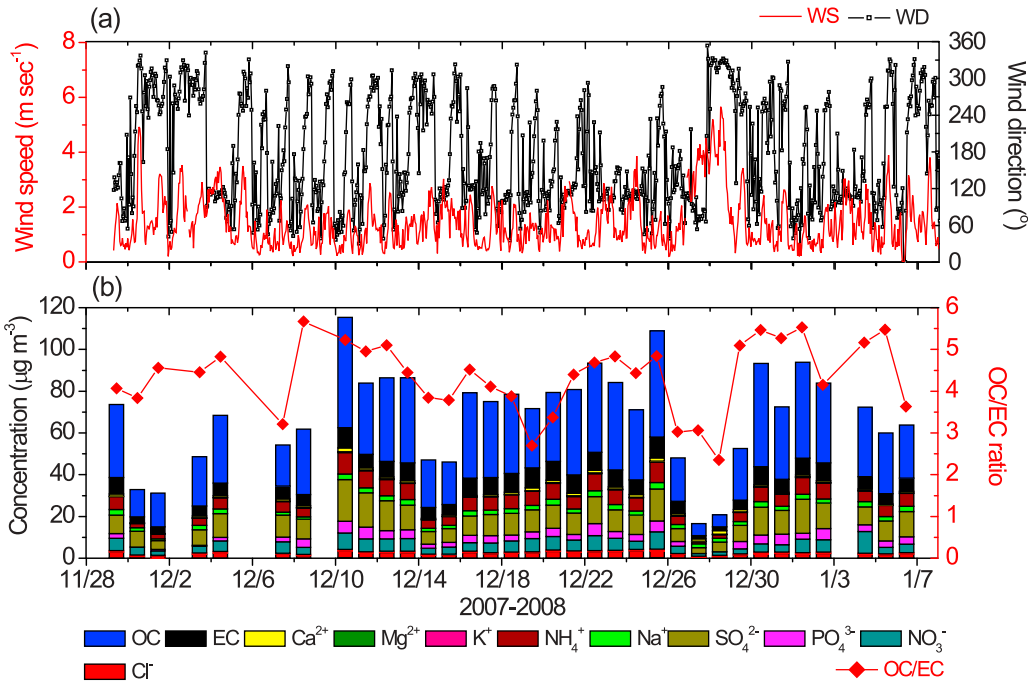

Figure 4. Diurnal variations of (a) wind speed and wind direction and (b) particulate chemical composition and the organic carbon/elemental carbon (OC/EC) ratio during the entire sampling period.

to 5.7 μg m^{-3} and an average of 3.1 ± 1.6 μg m^{-3}. Negligible amounts of PO_4^{3-} were reported in previously studied urban aerosols in Asia and the United States except for urban sites in Bangladesh where the concentrations ranged from 0.08 to 0.16 μg m^{-3} [*Salam et al.*, 2003, and references therein]. Higher concentrations of PO_4^{3-} in Ulaanbaatar could be attributed to fertilizer-rich soil or to the presence of phosphate-containing minerals in the soil [*Ilyin and Ratnikova*, 1981].

[21] Concentrations of OC and EC ranged from 5.8 to 52.8 μgC m^{-3} (average 31.8 ± 11.8 μgC m^{-3}) and 1.4 to 9.9 μgC m^{-3} (average 6.7 ± 2.2 μgC m^{-3}), respectively. OC/EC ratios were calculated to be 2.97–5.99 with an average of 4.75 ± 0.81. A strong correlation (R^2 = 0.78) between OC and EC, as seen in Figure 5a, indicates similar sources of particulate OC and EC. The OC level in Ulaanbaatar is much higher than those obtained at megacities in China and Korea while the EC level is comparable to those from China but slightly higher than those obtained in Korea [*Ye et al.*, 2003; *Kim et al.*, 2007; *Jung et al.*, 2009a, 2009b]. Average SO_4^{2-}/TC ratio in Ulaanbaatar is measured to be ~0.3 μg m^{-3}/μgC m^{-3}, which is much lower than those from other Asian urban sites in Seoul, Korea (~0.5 μg m^{-3}/μgC m^{-3}) [*Kim et al.*, 2007], Sapporo, Japan (~0.6 μg m^{-3}/μgC m^{-3}) [*Aggarwal and Kawamura*, 2009], and Beijing (~1.2 μg m^{-3}/μgC m^{-3}) and Guangzhou (~1.4 μg m^{-3}/μgC m^{-3}), China [*Jung et al.*, 2009a, 2009b], indicating that emissions from lignite coal burning did not significantly contribute to $PM_{2.5}$ pollutants in Ulaanbaatar during the winter.

[22] WSOC concentrations ranged from 0.0 to 37.2 μgC m^{-3} (average 17.2 ± 8.5 μgC m^{-3}) while WSOC/OC ratios ranged from 0.0% to 86.9% (average 53.2% ± 20.3%). The WSOC/OC ratio in this study is slightly higher than those measured at Sapporo, Japan (44%) [*Aggarwal and Kawamura*, 2008], Christchurch, New Zealand (48%) [*Wang et al.*, 2005], and 14 Chinese cities (summer: 48%; winter: 40%) [*Ho et al.*, 2007]. It was much higher than those reported at Gosan, Korea (30%), during the ABC campaign [*Miyazaki et al.*, 2007] and in New Delhi, India (25%), during the nighttime [*Miyazaki et al.*, 2009]. A high WSOC/OC ratio (45%–75%) was reported in biomass burning aerosols over Amazonia [*Mayol-Bracero et al.*, 2002]. Since smoldering combustion of biomass produces high amounts of WSOC [*Andreae et al.*, 1996; *Novakov and Corrigan*, 1996], a higher WSOC/OC ratio in Ulaanbaatar suggests that significant fractions of organic aerosols were derived from smoldering combustion of wood under the extremely cold conditions.

[23] The OC/EC ratios (4.7 ± 0.8) in Ulaanbaatar were much higher than those obtained in Beijing (1.9) [*Jung et al.*, 2009b], Guangzhou (2.0) [*Jung et al.*, 2009a], Shanghai (2.3) [*Ye et al.*, 2003], China, and Seoul, Korea (1.8) [*Kim et al.*, 2007]. OC/EC ratios of automobile emissions in California from diesel and gasoline engines are known to be 0.5 ± 0.4 and 0.9 ± 0.4, respectively [*Kirchstetter et al.*, 2004]. A similar OC/EC ratio (0.53) was measured in a tunnel in Austria [*Laschober et al.*, 2004]. However, OC/EC ratios from biomass burning give higher values of 5 to 8 [*Andreae and Merlet*, 2001]. From those studies, it can be estimated that the OC level in Ulaanbaatar was highly enhanced by emission from biomass burning. To further investigate the effects of biomass burning on OC, K^+ can be used as a tracer of wood burning [*Andreae*, 1983]. A moderate correlation coefficient (R^2 = 0.54) obtained from OC versus K^+ concentrations (see Figure 5b) supports that the OC in Ulaanbaatar was influenced by the biomass burning emissions during the sampling period.

[24] OC/EC ratios are site specific. The accumulation of pollutants under stagnant conditions may enhance the formation of secondary organic aerosols, resulting in high OC/EC

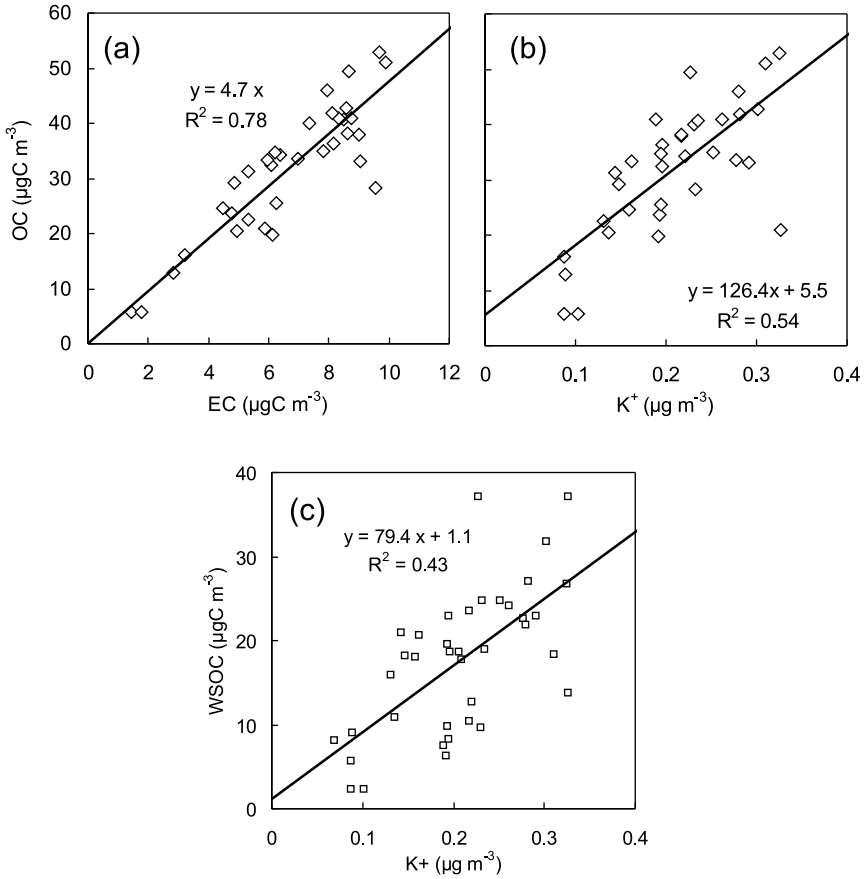

Figure 5. Scatterplots of (a) particulate OC versus EC, (b) OC versus K^+, and (c) WSOC versus K^+. The regression line for OC versus EC was forced through zero.

ratios and WSOC concentrations. To explore the causes of high water-soluble fractions and OC/EC ratios during the sampling period, we compared WSOC with K^+ and EC. Moderate correlations were observed between WSOC and K^+ ($R^2 = 0.43$; Figure 5c) and WSOC and EC ($R^2 = 0.44$). Daily average concentrations of WSOC, K^+, and EC could vary simultaneously according to the emission strength of sources, resulting in good correlation with each other. Thus, we further compared WSOC concentrations and OC/EC ratios. A poor correlation ($R^2 = 0.11$) was observed between WSOC concentrations and OC/EC ratios. The moderate correlations between WSOC and K^+ and the poor correlation between WSOC and OC/EC ratios implied that high WSOC concentrations and high OC/EC ratios in this study were attributed not only to secondary production of WSOC under the stagnant condition but also the enhanced primary emission of WSOC from biomass burning, especially from wood burning in home stoves.

3.3. Haze Episode by Local Emission Versus Long-Range Transport

[25] Meteorological conditions play a key role in the formation of heavy pollution episodes by the accumulation of local pollutants or transport of pollutants from nearby source regions [*Heald et al.*, 2006; *Fu et al.*, 2008; *Jung et al.*, 2009b]. The inversion height is defined as such where air temperature increases with altitude [*Liu et al.*, 2007]. This stable atmospheric condition prevents aerosols from diffusing into higher levels of the atmosphere, resulting in higher aerosol loadings near the ground surface [*Taubman et al.*, 2004; *Liu et al.*, 2007; *Fu et al.*, 2008]. Ulaanbaatar is a basin surrounded by high mountains, capturing air pollutants within the city. Cold air blowing into the basin and the radiative cooling on the ground helps development of an inversion layer over Ulaanbaatar in winter [*Japan Environmental Council*, 2005].

[26] Vertical profiles of average ambient temperature at the sampling site in Ulaanbaatar are shown in Figure 6. The vertical profile was integrated to the surface level using surface ambient temperature data obtained from a nearby measurement station. A strong temperature inversion was observed below 700–800 m above the ground level in the morning and also in the evening throughout the sampling period, which implied frequent formation of an inversion layer over Ulaanbaatar. Low wind speeds of 1.5 ± 1.0 m s^{-1} accelerated the accumulation of air pollutants below the inversion layer, resulting in severe haze episodes during the sampling period. The prevailing surface wind in the daytime (1000 to 1800 LT) was westerly or northwesterly with relatively higher wind speeds of 1.9 ± 1.0 m s^{-1}. Since most of the heat and power plants are located southwest or west of the city center (Figure 1), relatively strong westerly winds in the daytime transport pollutants emitted from the heat and power plants downtown. Thus, the sampling site was highly

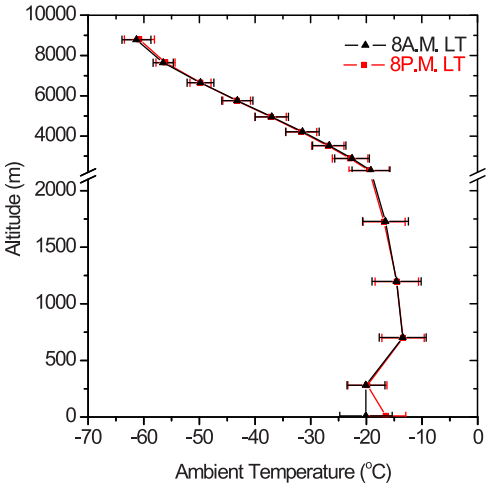

Figure 6. Vertical profiles of average ambient temperature over the sampling site during the entire sampling period. Black and red lines represent the profiles obtained at 0800 and 2000 LT, respectively.

influenced not only by emissions of home stoves and auto vehicles but also by emissions from heat and power plants.

[27] Since Mongolia is located north of China and south of Russia, long-range transported pollutants from these countries are possible sources of air pollution in Ulaanbaatar. From satellite remote sensing, it was previously observed that smoke plumes from forest fires in Siberia were frequently transported to Mongolia and eastern China [*Lee et al.*, 2005]. To detect the fire activities using satellite remote sensing, the NASA/GSFC Moderate Resolution Imaging Spectroradiometer Rapid Response fire map was used in this study [*Giglio et al.*, 2003; *Davies et al.*, 2004]. However, no significant fire activities were observed in the forest region of Siberia during the entire sampling period (not shown). Four day air mass backward trajectories arriving at 500 m altitude over the sampling site clearly showed that most of the air masses originated from northwest of Mongolia (Figure 2), which coincide with the prevailing westerly or northwesterly surface wind in the daytime. From the fire map and air mass backward trajectories, it was concluded that long-range transport of fire plume and anthropogenic pollutants from Russia and China were rarely encountered over the sampling site. Therefore, most of the pollutants in Ulaanbaatar were of local origin during the sampling period. From similar diurnal patterns of wind speed and wind direction and the HYSPLIT backward trajectories during the entire sampling period as well as 24 h sample collection, it is difficult to categorize the atmospheric conditions according to air mass origin and meteorological patterns. Thus, we did not categorize the pollution episode.

3.4. Primary Versus Secondary Production of Dicarboxylic Acids and Related Compounds

[28] C_2 is known to be formed by hydroxyl radical (OH·) oxidation of various precursors including longer-chain diacids and glyoxylic acid (ωC_2) [*Kawamura and Ikushima*, 1993; *Ervens et al.*, 2004; *Lim et al.*, 2005; *Carlton et al.*, 2006], as well as from primary emissions from auto exhaust [*Kawamura and Kaplan*, 1987; *Wang et al.*, 2006b; *Ho et al.*, 2006] and biomass burning [*Narukawa et al.*, 1999; *Graham et al.*, 2002; *Gao et al.*, 2003; *Kundu et al.*, 2010]. It was proposed that malic acid (hC_4) can be formed by hydration of maleic acid (M) and/or hydroxylation of C_4, and is further oxidized to C_2 and C_3. C_3 may be further oxidized to C_2 through intermediate compounds such as hydroxymalonic acid or ketomalonic acid (kC_3) [*Kawamura and Ikushima*, 1993]. A good correlation between C_2 and precursor compounds, such as ωC_2, C_3, and C_4 as well as kC_3 and hC_4, would imply secondary production of C_2 through photochemical degradation of the precursor compounds [*Ervens et al.*, 2004; *Legrand et al.*, 2007]. However, no significant relations were obtained between C_2 and its precursor compounds, such as ωC_2 ($R^2 = 0.15$), kC_3 (0.26), and hC_4 (−0.17), indicating that most of the C_2 was directly emitted from combustion sources (Table 3).

[29] Pyruvic acid (Pyr) has also been reported to act as a precursor of C_2 via ωC_2 in aqueous phase reaction [*Lim et al.*, 2005; *Carlton et al.*, 2006] and shown to originate from aromatic hydrocarbons and isoprene [*Talbot et al.*, 1995]. However, poor correlation between Pyr and ωC_2 (0.31) was observed. Good or moderate correlations between C_2 and C_3 ($R^2 = 0.79$) and C_2 and C_4 ($R^2 = 0.51$) indicate that these three compounds were emitted from similar sources, probably from fossil fuel combustion. This is supported by the low abundance of C_3 in the molecular distribution of diacids; C_3 diacid is less stable in the high-temperature combustion process due to the presence of more reactive hydrogen atoms on the α-carbon that is activated by adjacent two carboxyl groups [*Kawamura and Kaplan*, 1987]. This is in contrast to the photochemically aged aerosols in which C_3 is abundant [*Kawamura and Ikushima*, 1993; *Kawamura and Sakaguchi*, 1999]. Very low concentrations of kC_3 (1 ± 1 ng m^{-3}) and hC_4 (1 ± 2 ng m^{-3}) also indicate insignificant photochemical oxidation processing.

[30] Moderately good correlation was observed between total diacids and the SO_4^{2-} concentrations ($R^2 = 0.49$; Figure 7a). This moderately good correlation could be attributed to not only the increased formation of secondary organic aerosols via oxidation of gaseous volatile organic compounds but also the increased emissions from sources as discussed in section 3.2. Positive correlations of C_2/C_4 and C_3/C_4 mass ratios with oxidants and/or secondary aerosols would suggest that C_2 and C_3 are likely produced by the photochemical degradation of C_4 and longer-chain diacids [*Kawamura and Ikushima*, 1993]. As shown in Figures 7b and 7c, C_2/C_4 and C_3/C_4 ratios as well as the total diacid

Table 3. Correlation Coefficients (R^2) Among Selected Diacids and Related Compounds[a]

Components	C_2	C_3	C_4	tPh	hC_4	kC_3	Pyr	ωC_2
C_2	1							
C_3	**0.79**	1						
C_4	**0.51**	0.73	1					
tPh	0.41	**0.70**	**0.87**	1				
hC_4	**−0.17**	0.01	0.08	0.08	1			
kC_3	**0.26**	0.35	0.38	0.20	0.01	1		
Pyr	0.31	0.52	0.64	0.63	−0.05	0.12	1	
ωC_2	**0.15**	0.59	0.47	0.58	0.14	0.08	**0.31**	1

[a]Boldface indicates values discussed in text.

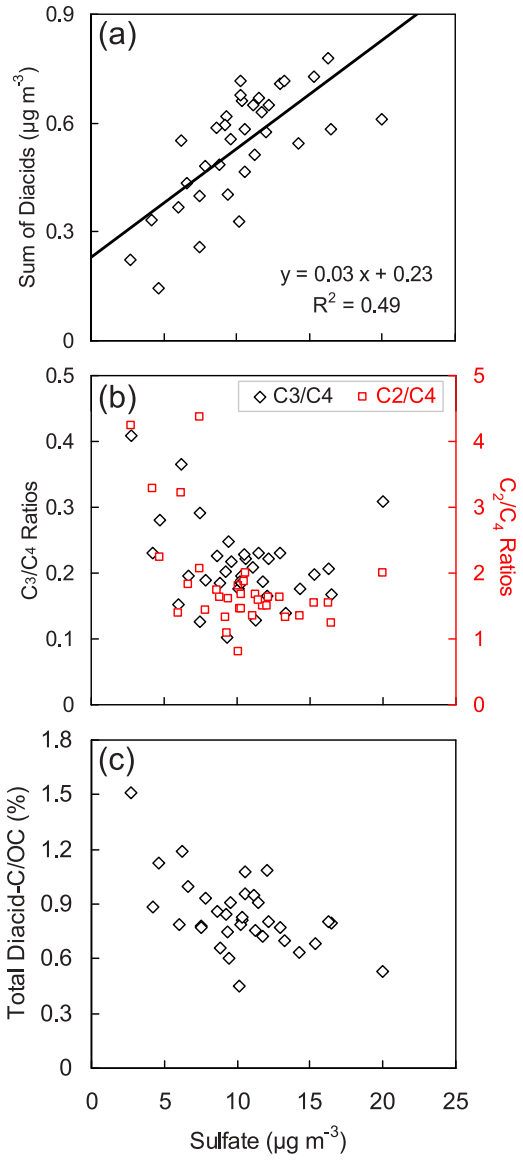

Figure 7. Scatterplots of (a) total diacids, (b) C_3/C_4 and C_2/C_4 ratios, and (c) the total diacid carbon mass to total OC mass ratio (total diacid-C/OC) versus sulfate concentrations.

carbon to OC mass (total diacid-C/OC) ratio were compared with the SO_4^{2-} concentrations. Average C_2/C_4 and C_3/C_4 ratios were calculated to be 1.84 ± 0.79 and 0.21 ± 0.06, respectively, while total diacid-C/OC was 0.84% ± 0.20%. No increasing or decreasing trends of C_2/C_4, C_3/C_4, and total diacid-C/OC ratios as a function of SO_4^{2-} concentration were found, except for few higher points at lower SO_4^{2-} concentrations, again suggesting that secondary production of C_2 and C_3 through photochemical oxidation of C_4 and longer-chain diacids was not important during the cold winter.

[31] There are several studies regarding the production of C_2, C_3, and C_4 from the phochemical degradation of longer-chain diacids [*Kawamura and Ikushima*, 1993; *Ervens et al.*, 2004; *Carlton et al.*, 2006; *Legrand et al.*, 2007]. C_2/C_4 and C_3/C_4 ratios were used in many previous studies to evaluate photochemical aging and tracking the possible sources of diacids [*Ho et al.*, 2007; *Legrand et al.*, 2007; *Sorooshian et al.*, 2007b; *Aggarwal and Kawamura*, 2008; *Kundu et al.*, 2010]. *Aggarwal and Kawamura* [2008] compared C_3/C_4 ratios from urban source regions in East Asia and from downwind remote sites. They clearly observed increases of C_3/C_4 ratios from the source regions to the downwind remote sites. Mass concentration ratios among diacids (C_2/C_4, C_3/C_4, C_6/C_9, and Ph/C_9) in the Ulaanbaatar samples were compared with those reported previously in different atmospheric aerosols (Figures 8a and 8b). The C_2/C_4 and C_3/C_4 ratios of our samples are lower than those from previously studied urban aerosols in Asian countries [*Kawamura and Ikushima*, 1993; *Ho et al.*, 2007; *Aggarwal and Kawamura*, 2008; *Miyazaki et al.*, 2009; *Pavuluri et al.*, 2010], freshly emitted aerosols from sources such as auto exhaust and biomass burning [*Kawamura and Kaplan*, 1987; *Ho et al.*, 2006; *Wang et al.*, 2006b; *Kundu et al.*, 2010], and aged aerosols from remote regions [*Kawamura et al.*, 1996a, 1996b; *Kawamura and Sakaguchi*, 1999; *Mochida et al.*, 2003; *Sempéré and Kawamura*, 2003]. The one exception from low altitudinal (<500 m) aerosol samples in the urban atmosphere (Houston, TX) showed a much lower C_3/C_4 ratio (~0.05) [*Sorooshian et al.*, 2007b].

[32] Because C_2 and C_3 are less abundant in the Ulaanbaatar aerosols, they are unlikely produced through photochemical degradation of C_4 and longer-chain diacids. Lower C_2/C_4 and C_3/C_4 ratios could be explained by the introduction of more fresh aerosols rather than aged aerosols. Interestingly, the C_2/C_4 and C_3/C_4 ratios are still much lower than those from auto exhaust and biomass burning. A good correlation between K^+ and OC as well as high OC/EC ratios suggests that OC was mainly emitted from biomass burning as discussed in section 3.2. However, much lower C_2/C_4 and C_3/C_4 ratios than those from biomass burning in Brazil [*Kundu et al.*, 2010] suggests that diacids and related compounds in the Ulaanbaatar aerosols were likely emitted not only from biomass burning but also from incomplete combustion of fossil fuels. Higher C_2/C_4 and C_3/C_4 ratios from biomass burning in Brazil than those from this study were also attributed to photochemical production of C_2 and C_3 from C_4 within biomass burning plume [*Kundu et al.*, 2010].

[33] Adipic (C_6) and phthalic (Ph) acids may be produced by the oxidation of anthropogenic cyclohexene [*Grosjean et al.*, 1978; *Hatakeyama et al.*, 1987] and aromatic hydrocarbons such as naphthalene [*Kawamura and Ikushima*, 1993], respectively. In contrast, azelaic acid (C_9) is mainly produced by the oxidation of biogenic unsaturated fatty acids containing a double bond at the C-9 position [*Kawamura and Gagosian*, 1987]. Consequently, C_6/C_9 and Ph/C_9 ratios can be used as tracers to evaluate the source strength of anthropogenic versus biogenic precursors to the diacids [*Kawamura and Yasui*, 2005]. A C_6/C_9 mass ratio of 0.28 in this study was much lower than those obtained at urban areas in Japan and China [*Kawamura and Ikushima*, 1993; *Ho et al.*, 2007; *Aggarwal and Kawamura*, 2008], but comparable to those obtained at urban areas in India (0.34 in Chennai [*Pavuluri et al.*, 2010] and 0.41 in daytime (0.44 in nighttime) in New Delhi [*Miyazaki et al.*, 2009]).

[34] *Kawamura and Kaplan* [1987] reported that diesel fuel vehicular exhaust showed a higher Ph/C_6 ratio (6.58) than that from gasoline fuel vehicle (2.05). A Ph/C_6 ratio of 4.69 obtained in this study is higher than those from the

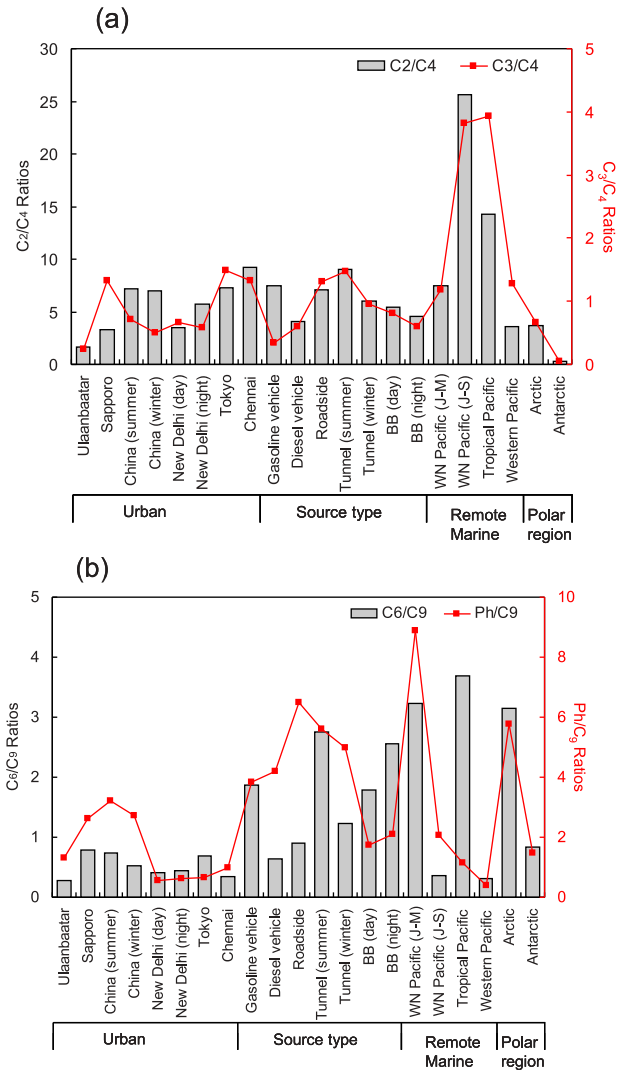

Figure 8. Comparison of mass ratios of (a) C_2/C_4 and C_3/C_4 and (b) C_6/C_9 and Ph/C_9 in this study with those obtained from previous studies of atmospheric aerosols. Site name or source type represents the reference from which the data are taken: Ulaanbaatar, present study; Sapporo, *Aggarwal and Kawamura* [2008]; China (summer), summer samples of *Ho et al.* [2007]; China (winter), winter samples of *Ho et al.* [2007]; New Delhi (day), daytime samples of *Miyazaki et al.* [2009]; New Delhi (night), nighttime samples of *Miyazaki et al.* [2009]; Tokyo, *Kawamura and Ikushima* [1993]; Chennai, *Pavuluri et al.* [2010]; gasoline vehicle and diesel vehicle, *Kawamura and Kaplan* [1987]; roadside, *Ho et al.* [2006]; tunnel (summer), summer samples of *Wang et al.* [2006b]; tunnel (winter), winter samples of *Wang et al.* [2006b]; BB (day), daytime biomass burning samples of *Kundu et al.* [2010]; BB (night), nighttime biomass burning samples in *Kundu et al.* [2010]; WN Pacific (J-M), samples collected in the western North Pacific from January to March 1991 to 1993 from *Mochida et al.* [2003]; WN Pacific (J-S), samples collected in the western North Pacific from July to September 1991 to 1993 from *Mochida et al.* [2003]; Tropical Pacific, *Kawamura and Sakaguchi* [1999]; Western Pacific, *Sempéré and Kawamura* [2003]; Arctic, *Kawamura et al.* [1996a]; Antarctic, *Kawamura et al.* [1996b].

urban areas in India (1.38 in New Delhi, 2.92 in Chennai), where similar Ph/C_9 and C_6/C_9 ratios were obtained [*Miyazaki et al.*, 2009; *Pavuluri et al.*, 2010]. This result can be partially explained by enhanced emissions from diesel fuel vehicles, which are very common in Ulaanbaatar [*World Bank*, 2004; *Guttikunda*, 2007]. They reported that most heavy-duty trucks and passenger cars are diesel fuel vehicles of more than 10 years old. A Ph/C_9 ratio of 1.30 in this study is comparable to those obtained at urban areas in India, but lower than those in urban areas in China and Japan (Figure 8b). Both the C_6/C_9 and Ph/C_9 ratios in our samples were much lower than those from auto exhausts and biomass burning [*Kawamura and Kaplan*, 1987; *Ho et al.*, 2006; *Wang et al.*, 2006b; *Kundu et al.*, 2010], indicating higher production of C_9 through an oxidation of biogenic unsaturated fatty acids possibly from domestic cooking [*Rogge et al.*, 1991].

[35] Systematically similar correlations of diacids and related compounds were observed against four tracers (i.e., SO_2, K^+, EC, and OC; Table 4). This can be attributed to dominant emissions from home stoves and heat and power plants mainly for space heating during winter. Among the major diacids and related compounds in Ulaanbaatar, C_4, iC_5, tPh, and mGly showed relatively good correlation with all four tracers, indicating that these compounds are in part emitted from wood burning and lignite coal burning as well as waste incineration. In addition to the major compounds, minor compounds (C_3, C_7, C_8, C_{10}, iC_6, mM, iPh, and Gly) also showed relatively good correlation with all four tracers, indicating that these compounds are also in part directly emitted from the sources.

[36] However, M, ωC_2, ωC_3, and ωC_4 showed better correlation with SO_2 than with the other tracers. This suggests that they are in part directly emitted from lignite coal burning. Because C_6, Ph, and C_9 may be produced via the oxidation of anthropogenic hydrocarbons and biogenic unsaturated fatty acids, poor correlations of these compounds were observed against all four tracers. Since intermediate compounds such as hC_4 and kC_3 are of secondary origin, poor correlations between multifunctional diacids (hC_4 and kC_3) and the four tracers are reasonably obtained. PO_4^{3-} showed good correlation with C_4, iC_4, iC_6, and tPh with $R^2 > 0.7$. The correlations of PO_4^{3-} with diacids and related compounds are similar to those of carbonaceous aerosols with K^+. Thus, it is estimated that PO_4^{3-} might be produced from similar emission mechanisms of biomass burning and waste incinerator.

[37] Generally, diacids and related compounds showed better correlation with SO_2 than SO_4^{2-}, indicating secondary production is less significant during the cold winter. It was reported that SO_4^{2-} fraction dramatically increased with pollution level at urban sites in China [*Jung et al.*, 2009a, 2009b]. A correlation between C_2 and SO_4^{2-} and its linear regression slope have been used to investigate production processes of C_2 mainly via aqueous phase reactions [*Yu et al.*, 2005]. A strong correlation between C_2 and SO_4^{2-} was observed at urban cities in East Asia ($R^2 > 0.69$) [*Yu et al.*, 2005] and in New Delhi, India ($R^2 > 0.65$) [*Miyazaki et al.*, 2009], suggesting that aqueous phase reactions in cloud/fog are an important pathway for the formation of secondary organic aerosols. However, poor correlation between C_2 and SO_4^{2-} ($R^2 = 0.35$) was observed in this study, suggesting insignificant photochemical production of C_2 via aqueous phase reactions

Table 4. Correlation Coefficients (R^2) for the Concentrations of Diacids, Ketoacids, and α-Dicarbonyls Against SO_2, K^+, EC, OC, PO_4^{3-}, and SO_4^{2-}[a]

Compound, Abbreviation	SO_2	K^+	EC	OC	PO_4^{3-}	SO_4^{2-}
Saturated n-Dicarboxylic Acids						
Oxalic, C_2	0.69	0.56	0.39	0.35	0.27	0.36
Malonic, C_3	0.80	0.77	0.63	0.61	0.68	0.64
Succinic, C_4	0.67	0.76	0.83	0.85	0.77	0.77
Glutaric, C_5	0.30	0.27	0.42	0.52	0.34	0.35
Adipic, C_6	0.45	0.33	0.48	0.58	0.45	0.39
Pimelic, C_7	0.60	0.60	0.69	0.72	0.61	0.59
Suberic, C_8	0.64	0.70	0.79	0.79	0.61	0.61
Azelaic, C_9	0.61	0.44	0.43	0.41	0.39	0.19
Sebacic, C_{10}	0.74	0.68	0.62	0.60	0.55	0.37
Undecanedioic, C_{11}	0.58	0.49	0.42	0.41	0.25	0.24
Branched Dicarboxylic Acids						
Methylmalonic, iC_4	0.34	0.38	0.31	0.36	0.39	0.42
Methylsuccinic, iC_5	0.67	0.68	0.81	0.85	0.79	0.76
Methylglutaric, iC_6	0.68	0.69	0.77	0.85	0.80	0.73
Unsaturated Dicarbxylic Acids						
Maleic, M	0.76	0.56	0.55	0.45	0.48	0.44
Fumaric, F	0.54	0.51	0.41	0.45	0.38	0.46
Methylmaleic, mM	0.79	0.77	0.78	0.74	0.69	0.73
Phthalic, Ph	0.32	0.36	0.53	0.60	0.45	0.51
Isophthalic, iPh	0.68	0.73	0.79	0.78	0.69	0.73
Terephthalic, tPh	0.72	0.79	0.83	0.82	0.71	0.63
Multifunctional Dicrboxylic Acids						
Malic, hC_4	0.05	0.16	0.15	0.14	0.01	0.11
Ketomalonic, kC_3	0.16	0.20	0.28	0.20	0.30	0.30
4-Ketopimelic, kC_7	0.12	0.30	0.24	0.32	0.25	0.43
Ketocarboxylic Acids						
Pyruvic, Pyr	0.63	0.60	0.62	0.60	0.51	0.43
Glyoxylic, ωC_2	0.71	0.56	0.42	0.35	0.48	0.30
3-Oxopropanoic, ωC_3	0.83	0.74	0.61	0.56	0.58	0.55
4-Oxobutanoic, ωC_4	0.73	0.58	0.56	0.60	0.65	0.58
9-Oxononanoic, ωC_9	0.61	0.62	0.73	0.79	0.61	0.74
α-Dicarbonyls						
Glyoxal, Gly	0.63	0.69	0.66	0.67	0.63	0.66
Methylglyoxal, mGly	0.68	0.66	0.70	0.72	0.63	0.64

[a]SO_2, sulfur dioxide; K^+, potassium; OC, organic carbon; EC, elemental carbon; PO_4^{3-}, phosphate; SO_4^{2-}, sulfate.

under cold and dry atmospheric condition during the winter in Ulaanbaatar.

4. Summary and Conclusion

[38] This study reports, for the first time, the molecular distributions of dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls as well as OC, EC, WSOC, and inorganic ions in the aerosols from Ulaanbaatar, Mongolia, during the cold winter of 2007 to 2008. Distributions of dicarboxylic acids and related compounds were characterized by a predominance of tPh, followed by oxalic (C_2), succinic (C_4), glyoxylic (ωC_2), and phthalic (Ph) acids. Predominance of tPh, which has not been reported previously in atmospheric aerosols, was mainly due to uncontrolled combustion of plastic bottles and bags in home stoves for space heating and waste incineration during the cold winter. On the basis of a weak correlation of C_2 with its precursor compounds and negligible amount of intermediate compounds, such as malic (hC_4) and ketomalonic (kC_3) acids, it was concluded that secondary production of diacids through photochemical processing was not important during the winter in Ulaanbaatar. Correlation analysis of diacids and related compounds against combustion and biomass burning tracers (SO_2, K^+, EC, and OC) suggested that C_4, iC_5, tPh, and mGly are mostly emitted from wood and lignite coal burning as well as waste incineration. However, M, ωC_2, and ωC_4 are in part emitted from lignite coal burning and/or produced by the oxidation of gaseous precursor compounds emitted directly from lignite coal burning. Haze episodes in Ulaanbaatar were enhanced by the formation of an inversion layer and low wind speeds during the winter, which accelerated the accumulation of pollutants emitted from local sources such as heat and power plants, home stoves, and automobiles. Since Ulaanbaatar is located at a high altitude of ~1300 m above sea level, the high concentrations of anthropogenic pollutants in this city can be transported to the upper troposphere in the same manner as Asian dust during the spring. This study suggests that the pollutants emitted from Ulaanbaatar may affect the regional air quality and thus contribute to the aerosol's effects relevant to climate change.

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References

Abdul-Razzak, H., and S. J. Ghan (2004), Parameterization of the influence of organic surfactants on aerosol activation, *J. Geophys. Res.*, *109*, D03205, doi:10.1029/2003JD004043.

Aggarwal, S. G., and K. Kawamura (2008), Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for photochemical aging during long-range atmospheric transport, *J. Geophys. Res.*, *113*, D14301, doi:10.1029/2007JD009365.

Aggarwal, S. G., and K. Kawamura (2009), Carbonaceous and inorganic composition in long-range transported aerosols over northern Japan: Implication for aging of water-soluble organic fraction, *Atmos. Environ.*, *43*, 2532–2540.

Andreae, M. O. (1983), Soot carbon and excess fine potassium: Long-range transport of combustion-derived aerosols, *Science*, *220*, 1148–1151.

Andreae, M. O., and P. Merlet (2001), Emission of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles*, *15*(4), 955–966.

Andreae, M. O., E. Atlas, H. Cachier, W. R. Cofer III, G. W. Harris, G. Helas, R. Koppmann, J.-P. Lacaux, and D. E. Ward (1996), Trace gas and aerosol emissions from savanna fires, in *Biomass Burning and Global Change*, edited by J. S. Levine, pp. 278–295, MIT Press, Cambridge, Mass.

Asian Development Bank and the Clean Air Initiative for Asian Cities Center (2006), *Country Synthesis Report on Urban Air Quality Management: Mongolia*, 20 pp., Asian Dev. Bank, Philippines.

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.

Birch, M. E., and R. A. Cary (1996), Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, *Aerosol Sci. Technol.*, *25*, 221–241.

Carlton, A. G., B. J. Turpin, H.-J. Lim, K. E. Altieri, and S. Seitzinger (2006), Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, *Geophys. Res. Lett.*, *33*, L06822, doi:10.1029/2005GL025374.

Crahan, K. K., D. Hegg, D. S. Covert, and H. Jonsson (2004), An exploration of aqueous oxalic acid production in the coastal marine atmosphere, *Atmos. Environ.*, *38*, 3757–3764.

Davies, D., S. Kumar, and J. Descloitres (2004), Global fire monitoring using MODIS near-real-time satellite data, *GIM Int.*, *18*(4), 41–43.

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

Deguillaume, L., M. Leriche, K. Desboeufs, G. Mailhot, C. George, and N. Chaumerliac (2005), Transition metals in atmospheric liquid phases: Sources, reactivity, and sensitive parameters, *Chem. Rev.*, *105*, 3388–3431.

Draxler, R. R., and G. D. Rolph (2010), HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT.php), NOAA Air Resour. Lab., Silver Spring, Md.

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.

Facchini, M. C., M. Mircea, S. Fuzzi, and R. J. Charlson (1999), Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, *401*, 257–259.

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.

Fu, Q., G. Zhuang, J. Wang, C. Xu, K. Huang, J. Li, B. Hou, T. Lu, and D. G. Streets (2008), Mechanism of formation of the heaviest pollution episode ever recorded in the Yangtze River Delta, China, *Atmos. Environ.*, *42*, 2023–2036.

Gao, S., D. A. Hegg, P. V. Hobbs, T. W. Kirchstetter, B. I. Magi, and M. Sadilek (2003), Water-soluble organic components in aerosols associated with savanna fires in southern Africa: Identification, evolution, and distribution, *J. Geophys. Res.*, *108*(D13), 8491, doi:10.1029/2002JD002324.

Giglio, L., J. Descloitres, C. O. Justice, and Y. J. Kaufman (2003), An enhanced contextual fire detection algorithm for MODIS, *Remote Sens. Environ.*, *87*, 273–282.

Graham, B., O. L. Mayol-Bracero, P. Guyon, G. C. Roberts, S. Decesari, M. C. Facchini, P. Artaxo, W. Maenhaut, P. Koll, and M. O. Andreae (2002), Water-soluble organic compounds in biomass burning aerosols over Amazonia 1. Characterization by NMR and GC-MS, *J. Geophys. Res.*, *107*(D20), 8047, doi:10.1029/2001JD000336.

Grosjean, D., K. V. Cauwenberghe, J. P. Schmid, P. E. Kelly, and J. N. Pitts Jr. (1978), Identification of C3–C10 aliphatic dicarboxylic acids in airborne particulate matter, *Environ. Sci. Technol.*, *12*, 313–317, doi:10.1021/es60139a005.

Guo, S., M. Hu, Z. B. Wang, J. Slanina, and Y. L. Zhao (2010), Size-resolved aerosol water-soluble ionic compositions in the summer of Beijing: Implication of regional secondary formation, *Atmos. Chem. Phys.*, *10*, 947–959.

Guttikunda, S. (2007), Urban air pollution analysis for Ulaanbaatar, report, World Bank Consult., Washington, D. C.

Hatakeyama, S., M. Ohno, J. Weng, H. Takagi, and H. Akimoto (1987), Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air, *Environ. Sci. Technol.*, *21*, 52–57.

Heald, C. L., D. J. Jacob, R. J. Park, B. Alexander, T. D. Fairlie, R. M. Yantosca, and D. A. Chu (2006), Transpacific transport of Asian anthropogenic aerosols and its impact on surface air quality in the United States, *J. Geophys. Res.*, *111*, D14310, doi:10.1029/2005JD006847.

Ho, K. F., S. C. Lee, J. J. Cao, K. Kawamura, T. Watanabe, Y. Cheng, and J. C. Chow (2006), Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong, *Atmos. Environ.*, *40*, 3030–3040.

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

Huang, X.-F., and J. Z. Yu (2007), Is vehicle exhaust a significant primary source of oxalic acid in ambient aerosols?, *Geophys. Res. Lett.*, *34*, L02808, doi:10.1029/2006GL028457.

Ilyin, A. V., and G. I. Ratnikova (1981), Primary, bedded, structureless phosphorite of the Khubsugul Basin, Mongolia, *J. Sediment. Res.*, *51*(4), 1215–1222.

Jacobson, M. C., H.-C. Hansson, K. J. Noone, and R. J. Charlson (2000), Organic atmospheric aerosols: Review and state of the science, *Rev. Geophys.*, *38*(2), 267–294.

Japan Environmental Council (2005), *The State of the Environment in Asia 2005/2006*, 389 pp., Springer, Hicom, Japan.

Jeong, C.-H., P. K. Hopke, E. Kim, and D.-W. Lee (2004), The comparison between thermal-optical transmittance elemental carbon and Aethalometer black carbon measured at multiple monitoring sites, *Atmos. Environ.*, *38*, 5193–5204.

Jung, J., H. Lee, Y. J. Kim, X. Liu, Y. Zhang, J. Gu, and S. Fan (2009a), Aerosol chemistry and the effect of aerosol water content on visibility impairment and radiative forcing in Guangzhou during the 2006 Pearl River Delta campaign, *J. Environ. Manage.*, *90*, 3231–3244.

Jung, J., H. Lee, Y. J. Kim, X. Liu, Y. Zhang, M. Hu, and N. Sugimoto (2009b), Optical properties of atmospheric aerosols obtained by in situ and remote measurements during 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006), *J. Geophys. Res.*, *114*, D00G02, doi:10.1029/2008JD010337.

Kanakidou, M., et al. (2005), Organic aerosol and global climate modelling: A review, *Atmos. Chem. Phys.*, *5*, 1053–1123.

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 photooxidation 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 C. M. Pavuluri (2010), New directions: Need for better understanding of plastic waste burning as inferred from high abundance of terephthalic acid in South Asian aerosols, *Atmos. Environ.*, *44*, 5320–5321.

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

Kawamura, K., R. Sempéré, Y. Imai, Y. Fujii, and M. Hayashi (1996b), Water soluble dicarboxylic acids and related compounds in Antarctic aerosols, *J. Geophys. Res.*, *101*, 18,721–18,728.

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*, edited by R. J. Hill et al., *Spec. Publ. Geochem. Soc.*, *9*, 243–265.

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

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

Kim, H.-S., J.-B. Huh, P. K. Hopke, T. M. Holsen, and S.-M. Yi (2007), Characteristics of the major chemical constituents of $PM_{2.5}$ and smog events in Seoul, Korea in 2003 and 2004, *Atmos. Environ.*, *41*, 6762–6770.

Kim, Y. J., M. J. Kim, K. H. Lee, and S. S. Park (2006), Investigation of carbon pollution episodes using semi-continuous instrument in Incheon, Korea, *Atmos. Environ.*, *40*(22), 4064–4075.

Kirchstetter, T. W., A. Strawa, G. Hallar, R. Harley, G. Kendall, J. Hesson, E. Stevenson, and A. Miguel (2004), Characterization of particle and gas phase pollutant emissions from heavy- and light-duty vehicles in a California roadway tunnel, *Eos Trans. AGU*, *85*(47), Fall Meet. Suppl., Abstract A11A-0021.

Kundu, S., K. Kawamura, T. W. Andreae, A. Hoffer, and M. O. Andreae (2010), 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.

Lance, S., A. Nenes, and T. A. Rissman (2004), Chemical and dynamical effects on cloud droplet number: Implications for estimates of the aerosol indirect effect, *J. Geophys. Res.*, *109*, D22208, doi:10.1029/2004JD004596.

Laschober, C., A. Limbeck, J. Rendl, and H. Puxbaum (2004), Particulate emissions from on-road vehicles in the Kaisermühlen-tunnel (Vienna, Austria), *Atmos. Environ.*, *38*, 2187–2195.

Lee, K. H., J. E. Kim, Y. J. Kim, J. Kim, and W. Hoyningen-Huene (2005), Impact of the smoke aerosol from Russian forest fires on the atmospheric environment over Korea during May 2003, *Atmos. Environ.*, *39*, 85–99.

Legrand, M., S. Preunkert, T. Oliveira, C. A. Pio, S. Hammer, A. Gelencér, A. Kasper-Giebl, and P. Laj (2007), Origin of C2–C5 dicarboxylic acids in the European atmosphere inferred from year-round aerosol study conducted at a west–east transect, *J. Geophys. Res.*, *112*, D23S07, doi:10.1029/2006JD008019.

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.

Limbeck, A., and H. Puxbaum (1999), Organic acids in continental background aerosol, *Atmos. Environ.*, *33*, 1847–1852.

Limbeck, A., H. Puxbaum, L. Otter, and M. C. Scholes (2001), Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA), *Atmos. Environ.*, *35*(10), 1853–1862.

Liu, J., X. Xia, P. Wang, Z. Li, Y. Zheng, M. Cribb, and H. Chen (2007), Significant aerosol direct radiative effects during a pollution episode in northern China, *Geophys. Res. Lett.*, *34*, L23808, doi:10.1029/2007GL030953.

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.

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 (2003), 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.

Narukawa, M., K. Kawamura, N. Takeuchi, and T. Nakajima (1999), Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, *26*(20), 3101–3104.

Narukawa, M., K. Kawamura, K. G. Anlauf, and L. A. Barrie (2003), Fine and coarse modes of dicarboxylic acids in the Arctic aerosols collected during the Polar Sunrise Experiment 1997, *J. Geophys. Res.*, *108*(D18), 4575, doi:10.1029/2003JD003646.

Novakov, T., and C. E. Corrigan (1996), Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Geophys. Res. Lett.*, *23*, 2141–2144.

Novakov, T., and J. E. Penner (1993), Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature*, *365*, 823–826.

O'Dowd, C. D., M. C. Facchini, F. C. Cavalli, D. Ceburnis, M. Mircea, S. Decesari, S. Fuzzi, Y. J. Yoon, and J. P. Putaud (2004), Biogenically drived organic contribution to marine aerosol, *Nature*, *431*, 676–679.

Pavuluri, C. M., K. Kawamura, and T. Swaminathan (2010), Water-soluble organic carbon, dicarboxylic acids, ketoacids, and α-dicarbonyls in the tropical Indian aerosols, *J. Geophys. Res.*, *115*, D11302, doi:10.1029/2009JD012661.

Raymond, T. M., and S. N. Pandis (2002), Cloud activation of single-component organic aerosol particles, *J. Geophys. Res.*, *107*(D24), 4787, doi:10.1029/2002JD002159.

Robinson, A. L., R. Subramanian, N. M. Donahue, A. Bernadop-Bricker, and W. Rogge (2006), Source apportionment of molecular markers and organic aerosol: 3. Food cooking emissions, *Environ. Sci. Technol.*, *40*, 7820–7827.

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.

Rolph, G. D. (2010), Real-time Environmental Applications and Display system (READY) Website (http://ready.arl.noaa.gov), NOAA Air Resour. Lab., Silver Spring, Md.

Salam, A., H. Bauer, K. Kassin, S. M. Ullah, and H. Puxbaum (2003), Aerosol chemical characteristics of a mega-city in Southeast Asia (Dhaka–Bangladesh), *Atmos. Environ.*, *37*, 2517–2528.

Saxena, P., L. Hildemann, P. McMurry, and J. Seinfeld (1995), Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, *100*(D9), 18,755–18,770.

Sempéré, R., and K. Kawamura (2003), Trans-hemispheric contribution of C_2–C_{10} α, ω-dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions, *Global Biogeochem. Cycles*, *17*(2), 1069, doi:10.1029/2002GB001980.

Shilling, J. E., S. M. King, M. Mochida, D. R. Worsnop, and S. T. Martin (2007), Mass spectral evidence that small changes in composition caused by oxidative aging processes alter aerosol CCN properties, *J. Phys. Chem. A*, *111*, 3358–3368.

Simoneit, B. R. T., P. M. Medeiros, and B. M. Didyk (2005), Combustion products of plastics for refuse burning in the atmosphere, *Environ. Sci. Technol.*, *39*, 6961–6970.

Sorooshian, A., et al. (2006), Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004, *J. Geophys. Res.*, *111*, D23S45, doi:10.1029/2005JD006880.

Sorooshian, A., M. L. Lu, F. J. Brechtel, H. Jonsson, G. Feingold, R. C. Flagan, and J. H. Seinfeld (2007a), On the source of organic acid aerosol layers above clouds, *Environ. Sci. Technol.*, *41*, 4647–4654.

Sorooshian, A., N. L. Ng, A. W. H. Chan, G. Feingold, R. C. Flagan, and J. H. Seinfeld (2007b), Particulate organic acids and overall water-soluble aerosol composition measurements from the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), *J. Geophys. Res.*, *112*, D13201, doi:10.1029/2007JD008537.

Stohl, A. (1998), Computation, accuracy and applications of trajectories: A review and bibliography, *Atmos. Environ.*, *32*, 947–966.

Talbot, R. W., B. W. Mosher, B. G. Heikes, D. J. Jacob, J. W. Munger, B. C. Daube, W. C. Keene, J. R. Maben, and R. S. Artz (1995), Carboxylic acids in the rural continental atmosphere over the eastern United States during the Shenandoah Cloud and Photochemistry Experiment, *J. Geophys. Res.*, *100*(D5), 9335–9343.

Taubman, B. F., L. T. Marufu, B. L. Vant-Hull, C. A. Piety, B. G. Doddridge, R. R. Dickerson, and Z. Li (2004), Smoke over haze: Aircraft observations of chemical and optical properties and the effects on heating rates and stability, *J. Geophys. Res.*, *109*, D02206, doi:10.1029/2003JD003898.

Volkamer, R., J. L. Jimenez, F. S. Martini, K. Dzepina, Q. Zhang, D. Salcedo, L. T. Molina, D. R. Worsnop, and M. J. Molina (2006), Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, *Geophys. Res. Lett.*, *33*, L17811, doi:10.1029/2006GL026899.

Wang, H., K. Kawamura, and D. Shooter (2005), Carbonaceous and ionic components in wintertime atmospheric aerosols from two New Zealand cities: Implications for solid fuel combustion, *Atmos. Environ.*, *39*, 5865–5875.

Wang, H., K. Kawamura, and K. Yamazaki (2006a), Water soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and western Pacific Ocean, *J. Atmos. Chem.*, *53*, 43–61.

Wang, H., K. Kawamura, K. F. Ho, and S. C. Lee (2006b), Low molecular weight dicarboxylic acids, ketoacids and dicarbonyls in the fine particles from a roadway tunnel: significant secondary production from the precursors in vehicular emissions, *Environ. Sci. Technol.*, *40*, 6255–6260.

World Bank (2004), *Mongolia Environment Monitor 2004: Challenges of Urban Development*, 33 pp., Washington, D. C.

Ye, B., X. Ji, H. Yang, X. Yao, C. K. Chan, S. H. Cadle, T. Chan, and P. A. Mulawa (2003), Concentration and chemical composition of $PM_{2.5}$ in Shanghai for a 1-year period, *Atmos. Environ.*, *37*, 499–510.

Yu, J. Z., S. F. Huang, J. H. Xu, and M. Hu (2005), When aerosol sulfate goes up, so does oxalate: Implication for the formation mechanisms of oxalate, *Environ. Sci. Technol.*, *39*, 128–133.

J. Jung and K. Kawamura, Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan. (kawamura@lowtem.hokudai.ac.jp)

Y. J. Kim and B. Tsatsral, Advanced Environmental Monitoring Research Center, Gwangju Institute of Science and Technology, Gwangju 500-712, South Korea.