

Chemical Characterization of Water-Soluble Organic Acids in Size-Segregated Particles at a Suburban Site in Saitama, Japan

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ABSTRACT

Saturated *n*-dicarboxylic acids (C₂-C₇, C₉), unsaturated dicarboxylic acids (maleic, fumaric, phthalic acid), ketocarboxylic acids (pyruvic, glyoxylic acid), and dicarbonyls (glyoxal, methylglyoxal) were determined in size-segregated samples with a high-volume Andersen air sampler at a suburban site in Saitama, Japan, May 12-17 and July 24-27, 2007 and January 22-31, 2008. The seasonal average concentrations of these detected organic acids were 670 ng/m³, accounting for about 4.4-5.7% (C/C) of water-soluble organic carbon (WSOC) and 2.3-3.6% (C/C) of organic carbon (OC). The most abundant species of dicarboxylic acids was oxalic acid, followed by malonic, phthalic, or succinic acids. Glyoxylic acid and methylglyoxal were most abundant ketocarboxylic acid and dicarbonyl, respectively. Seasonal differences, size-segregated concentrations, and the correlations of these acids with ambient temperatures, oxidants, elemental carbon (EC), OC, WSOC, and ionic components were also discussed in terms of their corresponding sources and possible secondary formation pathways. The results suggested that photochemical reactions contributed more to the formation of particulate organic acids in Saitama suburban areas than did direct emissions from anthropogenic and natural sources. However, direct emissions of vehicles were also important sources of several organic acids in particles, such as phthalic and adipic acids, especially in winter.

Key words: Dicarboxylic acids, Ketocarboxylic acids, Size distribution, Suburban aerosols, Secondary formation

1. INTRODUCTION

Water-soluble organic compounds have been identi-

fied on the basis of their solubility, condensability, and atmospheric occurrence (Saxena and Hildemann, 1996). They include organic anions, dicarboxylic acids, ketocarboxylic acids, dicarbonyls, carbohydrates, amino acids, aliphatic amines, urea, and some miscellaneous multifunctional compounds containing multiple hydroxyl, carboxyl, and carbonyl groups. Low-molecular-weight acidic compounds have been reported to account for 2-8% of water-soluble organic carbon (WSOC), though some researchers have reported this percentage to be as high as 15% (Falkovich, *et al.*, 2005; Graham *et al.*, 2002; Narukawa *et al.*, 1999). In particular, water-soluble dicarboxylic acids may affect the hygroscopic and cloud-nucleating properties of aerosols (Abbatt *et al.*, 2005; Peng *et al.*, 2001; Cruz and Pandis, 1998).

So far, most studies on dicarboxylic acids and their salts have focused on their chemical characterization in TSP or PM₁₀ with high-volume samplers (Li and Yu, 2005; Limbeck *et al.*, 2001; Rohrl and Lammel, 2001; Kawamura, 1993a). However, only limited size distribution data for dicarboxylic acids have been reported (Hsieh *et al.*, 2007; Yao *et al.*, 2002; Kerminen *et al.*, 2000, 1999). These size distribution results were determined by means of an ion chromatograph, including only low-molecular-weight dicarboxylic acids (C₂-C₆); there is less information on size-distributions of other dicarboxylic acids (such as phthalic acid and azelaic acid), ketocarboxylic acids and dicarbonyls. The presence of dicarboxylic acids in suspended particles may result from direct emissions (*e.g.*, automobile exhaust, fossil fuel combustion, biomass burning) or from photochemical oxidation of organic precursors of both anthropogenic and biogenic origin (Hsieh *et al.*, 2007; Kawamura and Yasuib, 2005; Kerminen *et al.*, 2000; Chebbi and Carlier, 1996). The formation pathways for particulate organic acids are largely unknown but may include condensation from the gas phase, liquid-phase production in aqueous aerosol particles or in cloud or fog droplets, and heterogeneous

reactions of precursor species at gas-particle interfaces (Kerminen *et al.*, 1999; Kawamura *et al.*, 1996). Therefore, a more detailed understanding of dicarboxylic acids in size-segregated particles, including their relationship with WSOC, organic carbon (OC), and elemental carbon (EC) in different environments, is still required.

In this study, normal saturated and unsaturated dicarboxylic acids, ketocarboxylic acids, and dicarbonyls were measured in size-segregated samples with a high-volume Andersen air sampler at a suburban site in Saitama, Japan. To better understand sources and formation pathways of organic acids, WSOC, OC, EC, and the main ionic components in the samples were also analyzed.

2. EXPERIMENTAL

2.1 Sampling

Atmospheric samples of suspended particulate matter (SPM) were collected at Saitama University, located in a suburban area of Saitama, about 30 km to the northwest of central Tokyo and about 4 km to the east of the business center of Saitama City, which has a population of more than one million (Jiang *et al.*, 2006). The sampling site was located on top of a 10-story office building at the University, and about 37 m above the ground level to avoid possible interference from local emission sources. Sampling was carried out during May 12-17, 2007 ($n=3$, 47.5 hours for each sample), July 24-27, 2007 ($n=4$, 23.5 hours for each sample) and January 22-31, 2008 ($n=5$, 47.5 hours for each sample).

The size-segregated samples were collected on quartz fiber filters (2500QAST, Pallflex; Shibata Scientific Technology Ltd., Tokyo, Japan) using a high-volume Andersen air sampler (AH-600F, Shibata Scientific Technology Ltd.) with standard four stage cascade impactors, which separated the particles into five size fractions (equivalent aerodynamic diameters: <1.1 , $1.1-2.0$, $2.0-3.3$, $3.3-7.0$, and >7.0 μm). After sampling, loaded filters were stored in a refrigerator at about -40°C before chemical analysis to prevent the evaporation of volatile components.

2.2 Analysis

Water-soluble dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in filter samples were analyzed by means of BF_3/n -butanol derivatization to their esters followed by gas chromatography/mass spectrometry (GC/MS) determination (Kawamura and Yasuib, 2005; Kawamura, 1993a). One-quarter of each filter was ultrasonically extracted with 15 mL of ultra-

pure water in an ice bath for 20 min, and this process was repeated more second times. The extracts were passed through a hydrophilic polytetrafluoroethylene filter (Advantec DISMIC-13HP) to remove filter debris and concentrated to *ca.* 0.5 mL in a rotary evaporator under vacuum at 48°C . After the extracts were further dried under a nitrogen stream, 14% BF_3/n -butanol (300 μL) was added to derivatize the carboxyl groups to butyl esters and the aldehyde groups to dibutoxy acetals at 100°C for 30 min. After adding 300 μL of acetonitrile and 10 mL of pure water, the derivatives were extracted with 10 mL of *n*-hexane, and then were washed with pure water (10 mL) two times. The *n*-hexane phase was concentrated under a nitrogen stream to *ca.* 50 μL . After adding the internal standard compound (tridecane), the derivatives were dissolved in 100 μL of *n*-hexane for GC/MS analysis.

Dibutyl esters and other derivatives were determined using a GC/MS (GCMS-QP 5050, Shimadzu Corporation, Kyoto, Japan) equipped with a split/splitless injector and a fused silica capillary column (DB-5; 30.0 m \times I.D. 0.32 mm \times 0.25 μm film thickness). The operating conditions were: inject temperature of 300°C ; column initial temperature of 50°C for 2 minutes, ramped to 120°C at $30^\circ\text{C min}^{-1}$ and then to 250°C at 8°C min^{-1} with a 5 min hold; helium carrier gas (flow rate, 50 mL/min; pressure, 80 kPa). The compounds were identified by comparison of GC retention times with mass chromatograms of authentic standards. Each chromatograph was calibrated with standard solutions prepared with target compound reagents to contain quantities to 100, 250, 500, 1,000, 2,500, 5,000, and 10,000 ng of each compound. Retention times, slopes, and *R*-squared values for calibration curves of target compounds, including saturated *n*-dicarboxylic acids (C_2 : oxalic, C_3 : malonic, C_4 : succinic, C_5 : glutaric, C_6 : adipic, C_7 : pimelic, and C_9 : azelaic acid), unsaturated dicarboxylic acids (M : maleic, F : fumaric, and Ph : phthalic acid), ketocarboxylic acids (Pyr : pyruvic and WC_2 : glyoxilic acid), and dicarbonyls (Gly : glyoxal and MeGly : methylglyoxal), are shown in Table 1.

OC and EC in filter samples were analyzed by means of a thermal/optical carbon analyzer (TOCA, DRI model 2001, Shibata Scientific Technology Ltd.), following The IMPROVE thermal/optical reflectance protocol (Chow and Watson, 2002). In the protocol, a 0.503-cm² punch aliquot of a sample quartz filter was heated at temperatures of 120°C (OC_1), 250°C (OC_2), 450°C (OC_3), and 550°C (OC_4) in a non-oxidizing helium atmosphere, and at 550°C (EC_1), 700°C (EC_2), and 800°C (EC_3) in an oxidizing atmosphere of 2% oxygen and 98% helium. The repeatability, determined from replicate analyses, was better than 5% for total carbon (TC) and 10% for OC and EC (Jiang *et al.*,

Table 1. Retention times, slopes and *R*-squared values (regression coefficients) for calibration curves of target compounds.

Retention time	Target compound	Type	Slope	R ² value
5.91	Methylglyoxal (MeGly)	Dicarbonyl	1.42	0.977
6.72	Oxalic (C ₂)	Saturated dicarboxylic acid	2.25	0.994
7.57	Malonic (C ₃)	Saturated dicarboxylic acid	1.77	0.998
8.76	Maleic (M)	Unsaturated dicarboxylic acid	1.95	0.998
9.04	Succinic (C ₄)	Saturated dicarboxylic acid	1.90	0.998
9.33	Fumaric (F)	Unsaturated dicarboxylic acid	1.75	0.997
9.47	Pyruvic (Pyr)	Ketocarboxylic acids	1.60	0.974
9.66	Glyoxylic (WC ₂)	Ketocarboxylic acids	3.24	0.971
10.32	Glutaric (C ₅)	Saturated dicarboxylic acid	1.77	0.998
11.69	Adipic acid (C ₆)	Saturated dicarboxylic acid	1.56	0.988
11.95	Glyoxal (Gly)	Dicarbonyl	4.26	0.991
12.95	Pimelic (C ₇)	Saturated dicarboxylic acid	1.08	0.994
14.19	Phthalic acid (Ph)	Unsaturated dicarboxylic acid	1.69	0.991
15.47	Azelaic (C ₉)	Saturated dicarboxylic acid	0.95	0.992

2006).

One-eighth of each filter was also extracted with 10 mL of ultrapure water in an ice bath for 20 min. The extract was used to analyze WSOC with a total organic carbon analyzer (TOC-VCHP, Shimadzu Corporation) and ionic components (anions: NO₃⁻, SO₄²⁻, and Cl⁻; cations: K⁺, Na⁺, NH₄⁺, and Ca²⁺) with an ion chromatography system (DX-100, DIOTEC Company of Tokyo, Tokyo, Japan). In addition, atmospheric pollutant and meteorological information (such as ambient temperature, relative humidity, and oxidants) was provided by the Atmospheric Environmental Regional Observation System of Japan, at a site located in the Saitama Institute of Public Health, which is about 500 m from the roadside site.

3. RESULTS AND DISCUSSION

3.1 Molecular Compositions of Water-soluble Organic Acids in Suspended Particulate Matter

All target compounds in the size-segregated SPM samples were detected, with obvious peaks being observed in the chromatograms. Table 2 shows the total average concentrations of dicarboxylic acids, ketocarboxylic acids, and dicarbonyls detected in the suburban samples during May 12-17 (spring) and July 24-27 (summer), 2007, and January 22-31 (winter), 2008. The results indicate that the most abundant species in the SPM for all suburban samples was oxalic acid (C₂), followed by malonic (C₃), phthalic (Ph) or succinic acid (C₄). Longer chain *n*-dicarboxylic acids were less abundant, except for azelaic acid (C₉), which was more abundant than glutaric (C₅), adipic (C₆), and pimelic acid (C₇).

Glyoxylic acid (WC₂) was an abundant species in

all target compounds, and its predominance in ketocarboxylic acids detected in urban atmospheres has been reported (Ho *et al.*, 2006; Kawamura and Yasuib, 2005). Glyoxal (Gly) and methylglyoxal (MeGly) were detected at abundant concentrations in SPM, and MeGly was the most abundant dicarbonyl observed in the particles, most likely because Gly is largely present in the gas phase (Ortiz *et al.*, 2006).

Most dicarboxylic acids were more abundant in summer than in other seasons, with the sum of these acids' concentrations increasing by 3.6 times in the summer relative to the other seasons (Table 2). Since mixing heights in summer are high, accumulation was not likely the reason for the higher observed concentrations of these acids during this season. Instead, their secondary formations are expected to be important in summer. In addition, a higher abundance of Ph in winter samples suggests that aromatic hydrocarbons are important precursors of Ph in Saitama.

3.2 Concentration Variations of Water-soluble Organic Acids in Size-segregated Particles

Size distribution data are useful for understanding the formation pathways of atmospheric species. As shown in Fig. 1, sulfate was present mostly in fine particles (< 1.1 μm). Previous studies of sulfate size distribution (Yao *et al.*, 2002; Blando and Turpin, 2000; Kerminen *et al.*, 1999) have reported a bimodal distribution of sulfate with mass mean diameters of about 0.2 ± 0.1 μm and 0.7 ± 0.3 μm. The smaller mode is generally ascribed to gas condensation, whereas the larger mode is ascribed to fog or cloud formation (Kerminen *et al.*, 1999). However, the size distribution of nitrate peaked in coarse particles (> 7 μm or 3.3-7 μm) during warm seasons (May and July), which is commonly ascribed to heterogeneous reactions, in-

Table 2. Concentrations of individual organic acids, OC, EC, WSOC, and ionic components in SPM.

Target compound	Spring		Summer		Winter	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
Water-soluble organic acids	Concentrations (ng/m ³)					
Oxalic (C ₂)	243	45	472	187	94	24
Malonic (C ₃)	59	20	166	49	15	5
Succinic (C ₄)	42	14	103	27	23	8
Glutaric (C ₅)	11.7	3.8	37.4	5.1	7.0	2.6
Adipic (C ₆)	7.3	2.5	18.0	6.9	7.9	2.7
Pimelic (C ₇)	3.3	2.5	4.7	2.4	2.8	2.1
Azelaic (C ₉)	16.3	9.5	35.6	12.3	23.9	16.1
Maleic (M)	4.2	2.1	10.4	3.3	6.2	2.4
Fumaric (F)	2.1	0.2	6.5	3.7	5.5	3.0
Phthalic (Ph)	38	1	149	64	505	15
Glyoxylic (WC ₂)	33.1	14.1	73.8	32.0	21.7	9.0
Pyruvic (Pyr)	23.0	7.9	55.0	19.0	18.4	5.2
Glyoxal (Gly)	5.9	1.8	14.1	5.0	6.3	2.2
Methylglyoxal (MeGly)	19.2	2.2	51.8	30.9	14.9	4.4
Total organic acids (OA)	508	121	1198	366	303	88
OC/EC/WSOC/ionic components	Concentrations (μg/m ³)					
Organic carbon (OC)	5.90	1.99	12.06	5.17	5.18	1.96
Pyrolytic OC (Py-OC)	1.93	0.37	3.53	1.62	1.08	0.48
Elemental carbon (EC)	0.90	0.10	1.44	0.36	1.24	0.55
Total carbon (TC)	6.79	1.94	13.50	5.53	6.42	2.47
Water-soluble OC (WSOC)	3.33	0.59	7.64	2.91	2.74	1.23
Chloride (Cl ⁻)	0.58	0.11	1.15	0.51	1.32	0.70
Nitrate (NO ₃ ⁻)	3.09	0.56	7.19	3.13	2.15	1.23
Sulfate (SO ₄ ²⁻)	5.09	0.81	12.00	4.52	2.15	0.82
Sodium (Na ⁺)	0.68	0.12	0.32	0.12	0.24	0.15
Ammonium (NH ₄ ⁺)	2.29	0.35	4.95	2.20	1.37	0.55
Calcium (Ca ²⁺)	0.51	0.27	1.46	0.66	0.36	0.13

cloud processes involving reactions with sea-salt aerosols, or both (Yao *et al.*, 2002). During warm seasons, nitrate in fine particles tends to transform into gaseous compounds due to the volatility of ammonium nitrate, which caused relatively lower concentration of nitrate in fine particles. During the cold period (January), nitrate in Saitama suburban samples had a similar size distribution as sulfate, and mainly existed in fine particles.

The size-segregated concentrations of TOC, WSOC and selected organic acids in suburban particles are also shown in Fig. 1. In spring and summer, WSOC and most organic acids had size distributions similar to those observed for sulfate, indicating that similar formation pathways had occurred. Using the size distribution of sulfate as a reference, most organic acids in fine particles (< 1.1 μm) are expected to be obvious distributions with Aitken mode and accumulation mode. In winter, water-soluble organic acids, especially adipic and phthalic acids, were more prevalent in > 1.1-μm particles than they were during warm periods. The following differences between summer and winter seasons can explain this observed difference in partitioning into > 1.1-μm particles: i) the lower tem-

perature during winter nights compared with summer nights; ii) changes in gas/particle repartitioning for semi-volatile species between warm and cold conditions (Jaffrezo *et al.*, 2005); and iii) different oxidation and formation pathways.

3.3 Correlations between Selected Organic Acids and Temperature, Oxidants, Sulfate, and Nitrate

The presence of water-soluble organic acids in SPM may result from direct emissions and secondary photochemical reactions. Strong correlations were observed among C₂, C₃, C₄, and WC₂ ($r > 0.92$ in Table 3, $n = 12$, $p < 0.001$), and this was consistent with atmospheric oxidation processes, which largely control the concentrations of these species in particles. Good correlation was also observed between Ph and C₆ ($r = 0.91$ in Table 3, $n = 12$, $p < 0.001$); these two dicarboxylic acids were well correlated with EC ($r > 0.53$ in Table 3, $n = 12$, $p < 0.07$), suggesting that the source of Ph and C₆ was related to incomplete combustion to a certain extent. Ph, an important aromatic acid, can be directly emitted from combustion sources and also can be generated by atmospheric degradation of aro-

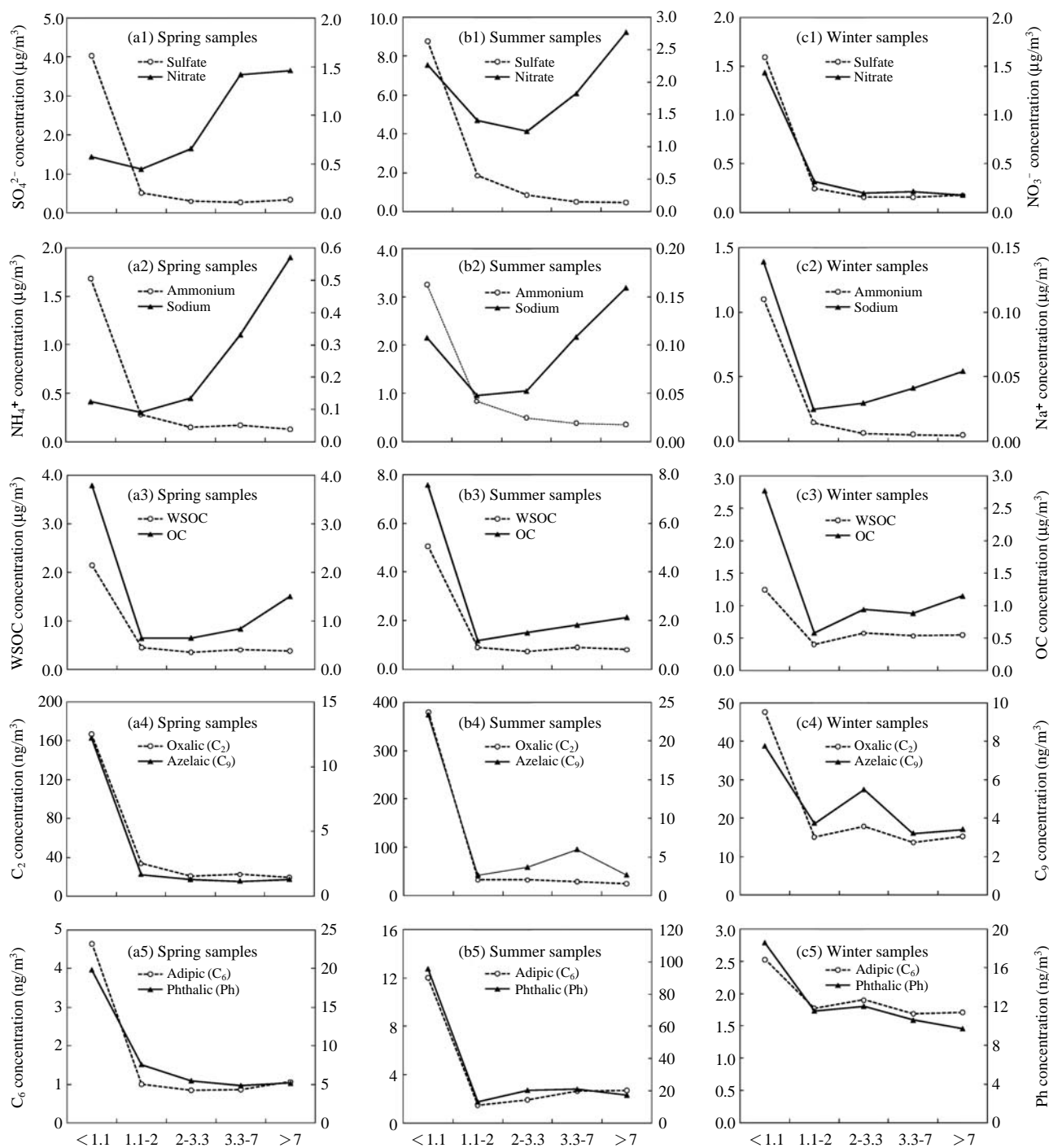


Fig. 1. Size-segregated concentrations of sulfate, nitrate, ammonium, sodium, WSOC, OC, and selected organic acids in suburban particles in spring (a), summer (b), and winter (c).

matic hydrocarbons such as naphthalene (Ho *et al.*, 2006; Kawamura and Ikushima, 1993b). Laboratory experiments have shown that C_6 is produced by photochemical oxidation of cyclic alkenes, which are present in the atmosphere as a result of atmospheric

emissions from internal combustion engines (Hatakeyama *et al.*, 1987).

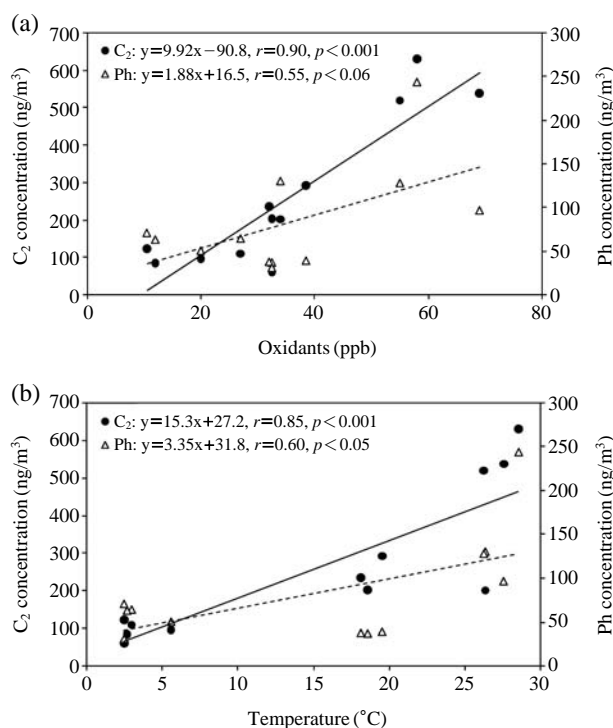
The different relationships between individual organic acids and ambient parameters and other pollutants may be associated with different sources and

Table 3. Correlation coefficients among selected organic acids, OA, OC₂, Py-OC, EC, WSOC, SO₄²⁻, and oxidants in SPM (*n*=12).

	C ₂	C ₃	C ₄	C ₆	Ph	WC ₂	OA	OC ₂	Py-OC	EC	WSOC	SO ₄ ²⁻	Oxidants
C ₂	1.00												
C ₃	0.95	1.00											
C ₄	0.95	0.96	1.00										
C ₆	0.83	0.75	0.87	1.00									
Ph	0.74	0.69	0.75	0.91	1.00								
WC ₂	0.92	0.93	0.95	0.85	0.64	1.00							
OA	0.98	0.95	0.98	0.90	0.83	0.93	1.00						
OC ₂	0.87	0.76	0.89	0.97	0.82	0.89	0.91	1.00					
Py-OC	0.89	0.85	0.93	0.82	0.58	0.98	0.90	0.90	1.00				
TEC	0.38	0.29	0.44	0.65	0.53	0.47	0.46	0.67	0.50	1.00			
WSOC	0.86	0.81	0.94	0.92	0.73	0.94	0.91	0.95	0.96	0.64	1.00		
SO ₄ ²⁻	0.97	0.94	0.96	0.81	0.70	0.96	0.96	0.86	0.94	0.40	0.91	1.00	
Oxidants	0.90	0.90	0.88	0.65	0.55	0.87	0.87	0.71	0.84	0.08	0.76	0.92	1.00

different production mechanisms. Good correlation was observed between OA and oxidants ($r=0.87$ in Table 3, $n=12$, $p<0.001$), especially in warm period (spring and summer) ($r=0.92$, $n=7$, $p<0.005$). The increase of the correlation was found to depend on carbon chain length and on the structure of the acid species, which is consistent with results reported in previous studies (Ho *et al.*, 2006; Kawamura and Yabuuchi, 2005). In particular, C₂ had the strongest correlation with oxidants ($r=0.90$, $n=12$, $p<0.001$; Fig. 2a), followed by C₃ ($r=0.90$, $n=12$, $p<0.001$) and C₄ ($r=0.88$, $n=12$, $p<0.005$). These correlations were related to secondary photochemical processes. However, Ph displayed a lower correlation with oxidants ($r=0.55$, $n=12$, $p<0.06$) than did the other organic acids, further suggesting that its origin was primary emissions from vehicles. In addition, similar relationship was observed between all of the studied acids and daily average temperature (Fig. 2b).

Furthermore, individual organic acids were more strongly correlated with sulfate than with nitrate in SPM. C₂ is the single most abundant organic acid identified in ambient aerosols. Yu *et al.* (2005) observed a strong correlation between C₂ and sulfate at different locations, and they argued that there exists a common dominant formation pathway of the two chemically distinct species. As shown in Fig. 3, C₂ correlated very strongly with sulfate ($r=0.97$, $n=12$, $p<0.001$) in Saitama aerosol. Sulfate is a major aerosol component whose formation pathways have been well investigated in the past few decades, and in-cloud processing is recognized as the major production pathway of sulfate (Yu *et al.*, 2005; Yao *et al.*, 2002). The present results also highlight the potential importance of in-cloud processing as a pathway leading to the formation of low-molecular-weight dicarboxylic acids.

**Fig. 2.** Correlations of C₂ and Ph concentrations in SPM with ambient oxidants (a) and temperature (b) in Saitama (*n*=12).

3.4 Relationship of Individual Organic Acids with OA, OC, EC, Py-OC, and WSOC

To further clarify the behaviour of carbonaceous compounds, Table 4 shows concentration ratios of OA (the total of all detected organic acids, $\mu\text{g-C}/\text{m}^3$), OC, and WSOC. Generally, the relative carbon abundances of OA in WSOC and in OC were 5.1% and 3.0%, respectively. Abundances of C₂ in OA, WSOC, and OC during the warm periods were higher than those during the cold periods, but Ph had relatively high abun-

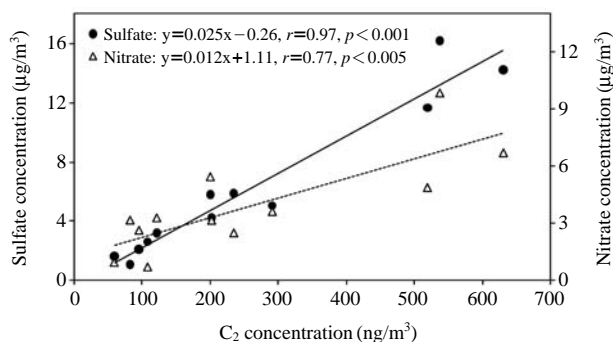


Fig. 3. Correlations of C_2 concentrations with sulfate and nitrate in SPM in Saitama ($n=12$).

Table 4. Concentration ratios of OA ($\mu\text{g-C}/\text{m}^3$), OC, Py-OC, WSOC, and EC in SPM.

Ratio	Spring	Summer	Winter	Average
OA/WSOC	0.053	0.057	0.044	0.051
OA/OC	0.030	0.036	0.023	0.030
Py-OC/WSOC	0.58	0.46	0.39	0.48
Py-OC/OC	0.33	0.29	0.21	0.28
WSOC/OC	0.56	0.63	0.53	0.58
OC/EC	6.57	8.39	4.17	6.38

dances in winter.

OC and EC concentrations in the filter samples were analyzed with the TOCA using a temperature program based on the IMPROVE method. The individual organic acids in SPM had good correlations with OC_2 ($r > 0.76$ in Table 3, $n=12$, $p < 0.005$), but weak correlations with OC_1 ($50\text{-}120^\circ\text{C}$) and OC_4 ($450\text{-}550^\circ\text{C}$). Therefore, the concentration distribution of OC_2 ($120\text{-}250^\circ\text{C}$) reflected well the distributions of organic acids. Furthermore, charring during sample-heating in the TOCA caused the laser adsorption of the sample to rise above the initial value. When the sample's laser adsorption returns to its initial value, an intersection with FID response gives the amount of pyrolytic organic carbon (Py-OC). Yu *et al.* (2002) have suggested that charring might be influenced by WSOC. In Saitama suburban samples, the correlation of Py-OC and WSOC was strong ($r=0.96$, $n=12$, $p < 0.001$; Fig. 4). Further, Py-OC in SPM had a strong correlation with OA ($r=0.90$), and also had good correlations with individual organic acids ($r=0.89$ for C_2 , 0.85 for C_3 , 0.93 for C_4 , 0.98 for WC_2 in Table 3; $n=12$, $p < 0.001$), indicating that these organic acids was closely related to the occurrence of OC charring.

3.5 The Ratios of C_3/C_4 , C_6/C_9 , and Ph/C_9

Table 5 shows the ratios of C_3/C_4 , C_6/C_9 , and Ph/C_9 in SPM, with literature data determined in different

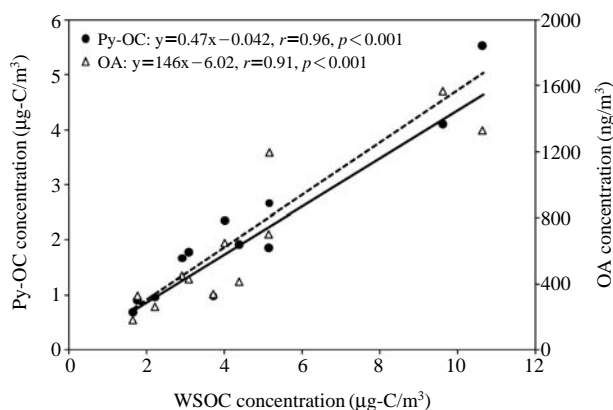


Fig. 4. Correlations of WSOC with Py-OC and OA in SPM in Saitama ($n=12$).

environments (Hsieh *et al.*, 2007; Ho *et al.*, 2006; Kawamura and Yasuib, 2005; Ray and McDow, 2005; Graham *et al.*, 2002; Wang *et al.*, 2002; Kawamura and Sakaguchi, 1999).

C_3 is derived from the incomplete combustion of fossil fuels or from secondary atmospheric production. Because C_3 is thermally less stable than C_4 , the degradation of C_3 in the combustion process is probably more significant than its production. The ratio of C_3/C_4 in particles can act as an informative indicator to distinguish secondary sources from primary vehicle exhaust in this regard: a C_3/C_4 ratio of > 3.0 indicates photochemical production of dicarboxylic acids, whereas a ratio of $0.3\text{-}0.5$ indicates a traffic-emissions origin of these dicarboxylic acids (Hsieh *et al.*, 2007; Ho *et al.*, 2006; Kawamura *et al.*, 1996). As shown in Table 5, the C_3/C_4 ratio in Saitama suburban samples during summer was 1.61 and much higher than the level of pure traffic emissions, and also higher than ratios observed at urban sites (0.92 in Philadelphia, Ray and McDow, 2005; 1.00 in Tokyo, Kawamura and Yasuib, 2005; 1.44 in Hong Kong, Ho *et al.*, 2006), indicating that C_3 was in part produced secondarily by photochemical reactions in the atmosphere. However, the C_3/C_4 ratio in winter was very low (0.66), reflecting the strong influence of vehicle exhaust.

Because C_6 and Ph are produced by the atmospheric oxidation of anthropogenic sources, whereas C_9 is produced from biogenic unsaturated fatty acids, C_6/C_9 and Ph/C_9 ratios may be used as a potential indicator of source strength of anthropogenic and biogenic precursors to organic acids in particles (Ho *et al.*, 2006; Kawamura and Ikushima, 1993b). C_6/C_9 and Ph/C_9 ratios in summer in the present study (0.50 and 1.08) were lower than ratios observed in Tokyo aerosols (1.49 and 2.36; Kawamura and Yasuib, 2005), suggesting that the relative contribution of biogenic to anthropogenic

Table 5. Average concentrations (ng/m³) and their ratios of selected dicarboxylic acids reported in the literature.

Site/type	Season	Size	Method	C ₂	C ₃	C ₄	C ₆	C ₉	Ph	C ₃ /C ₄	C ₆ /C ₉	Ph/C ₉	Remark
Philadelphia, USA/urban	Summer	PM ₁₀	GC-MS	/	14	15	2.0	1.0	4	0.92	2.00	3.50	Ray and McDow, 2005
Nanjing, China/urban	Winter and spring	PM _{2.5}	GC-MS/FID	660	89	113	37	144	/	0.78	0.25	/	Wang <i>et al.</i> , 2002
Hong Kong/urban road side	Winter	PM _{2.5}	GC-MS/FID	478	89	72	10.7	16.8	78	1.24	0.64	4.64	Ho <i>et al.</i> , 2006
	Summer	PM _{2.5}	GC-MS/FID	268	48	33	12.7	9.1	90	1.44	1.40	9.92	Ho <i>et al.</i> , 2006
Tainnan, Taiwan/suburban	Autumn and summer	PM _{2.5}	IC	449	21	30	/	/	/	0.70	/	/	Hsieh <i>et al.</i> , 2007
Robdinia, Brazil/pasture	Autumn	PM _{2.5}	GC-MS	619	115	95	6.5	11.3	24	1.21	0.58	2.12	Graham <i>et al.</i> , 2002
Robdinia, Brazil/forest	Autumn	PM _{2.5}	GC-MS	329	56	31	3.0	5.9	14	1.82	0.51	2.31	Graham <i>et al.</i> , 2002
Pacific Ocean/marine	Autumn and winter	TSP	GC-MS/FID	40	11	2.8	2.1	0.57	0.66	3.93	3.68	1.16	Kawamura and Sakaguchi, 1999
	Summer	TSP	GC-MS/FID	257	58	58	19.4	13.1	31	1.00	1.49	2.36	Kawamura and Yasuib, 2005
Tokyo, Japan/urban	Winter	TSP	GC-MS/FID	186	41	47	14.2	20.6	24	0.85	0.69	1.17	Kawamura and Yasuib, 2005
	Summer	SPM	GC-MS	472	166	103	18.0	35.6	149	1.61	0.50	1.08	This work
Saitama, Japan/suburban	Summer	SPM	GC-MS	472	166	103	18.0	35.6	149	1.61	0.50	1.08	This work
	Winter	SPM	GC-MS	94	15	23	7.9	23.9	56	0.66	0.33	2.33	This work

inputs in summer in suburban Saitama was much more significant than those in Tokyo, a metropolitan adjacent to Saitama.

4. CONCLUSIONS

Saturated dicarboxylic acids, unsaturated dicarboxylic acids, ketocarboxylic acids, and dicarbonyls were determined in size-segregated samples with a high-volume Andersen air sampler at a suburban site in Saitama, Japan, during May 12-17 and July 24-27, 2007 and January 22-31, 2008. The seasonal average concentrations of these detected organic acids were 670 ng/m³, accounting for about 4.4-5.7% (C/C) of WSOC and 2.3-3.6% (C/C) of OC, respectively. Oxalic acid (C₂) was the most abundant species in the SPM, followed by malonic (C₃), phthalic (Ph) or succinic acid (C₄). Longer chain *n*-dicarboxylic acids were less abundant, except for azelaic acid (C₉). Glyoxylic acid (WC₂) and methylglyoxal (MeGly) were the most abundant ketocarboxylic acid and dicarbonyl, respectively, in the particles.

The C₃/C₄ ratio, which is an informative indicator to distinguish secondary sources from primary vehicle exhaust, was 1.41-1.61 during warm seasons and much higher than the level of pure traffic emissions, indicating that these dicarboxylic acids were in part produced secondarily by photochemical reactions in the atmosphere. Strong correlations were also observed between C₂, C₃, C₄, and WC₂. These organic acids also had strong correlations with oxidants and sulfate. These results are consistent with atmospheric oxidation processes that largely control the concentrations of these acids in suburban particles. The results of seasonal observations further indicated that photochemical reactions contributed more to the particulate organic acids in Saitama suburban areas than did direct emissions from anthropogenic and natural sources.

However, Ph and C₆ concentrations were well correlated with EC in SPM, showing the intense effects of vehicle exhaust. Correspondingly, Ph showed smaller correlation coefficients with oxidants and sulfate than did other acids. These results suggested that Ph and C₆ in SPM can be directly emitted from anthropogenic sources, especially from vehicles.

In spring and summer, the concentration of individual organic acid in fine particles (< 1.1 μm) exceeded half of the concentration in SPM. WSOC and most organic acids concentrations had similar size distributions as did sulfate, with a main peak in fine particles, indicating similar formation pathways. In winter, water-soluble organic acids in particles (> 1.1 μm) accounted for a larger proportion of the total in SPM. These results can be explained in terms of the lower winter temperatures, which strongly affected the gas/particle repartitioning and oxidation pathways of semi-volatile species, and further influenced the size distributions of water-soluble organic acids.

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