Comparison of Water-Soluble Organic Components in Size-Segregated Particles between a Roadside and a Suburban Site in Saitama, Japan

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ABSTRACT

To clarify the characteristics of the water-soluble organic components in atmospheric aerosols, size-separated aerosol samples were simultaneously collected at a roadside site (R) and a suburban background site (S) in Saitama, Japan, during spring and summer 2007 and winter 2008. Chemical compositions, including water-soluble organic carbon (WSOC), organic carbon, inorganic ionic components, and individual water-soluble organic acids (saturated dicarboxylic acids, unsaturated dicarboxylic acids, ketocarboxylic acids, and dicarbonyls), were analyzed in size-separated samples. The seasonal variation of WSOC in Saitama aerosols was larger than the spatial difference between the two sites, with summer WSOC concentrations being 2.5-2.8 times those in the other seasons. Seasonal average concentrations of the detected organic acids in $PM_{7.0}$ were 542 ng/m^3 (R) and 670 ng/m^3 (S). Strong correlations were observed between C_2-C_5 n-dicarboxylic acids and ambient oxidants. The concentration ratios of individual n-dicarboxylic acids (C_2-C_5) to elemental carbon were significantly higher in suburban samples than in roadside samples, indicating that the contribution of secondary formation to these acids was larger in suburban samples. During the warm seasons, the concentrations of sulfate, ammonium, WSOC, and individual acids in fine particles were very high, whereas nitrate, chloride, sodium, and calcium concentrations were higher in coarse particles. Comparisons between the two sites showed that secondary formation contributed more to the total amount of particulate water-soluble organic acids in Saitama aerosols than direct emissions from anthropogenic and natural sources. However, vehicle exhaust was also an important source of dicarboxylic acids in Saitama aerosols, especially in the near-roadside environment.

Keywords: Water-soluble organic carbon; Dicarboxylic acids; Size distribution; Secondary formation.

INTRODUCTION

Water-soluble organic compounds potentially play an important role in aerosol–cloud interaction, and are contributors to cloud condensation nuclei (CCN). The ability of water-soluble organic particles to act as CCN has been explained on the basis of both the hygroscopic and surface-active properties of water-soluble organic compounds, which in turn depend on their chemical composition (Decesari *et al.*, 2005). Water-soluble organic compounds include dicarboxylic acids, ketocarboxylic acids, dicarbonyls, carbohydrates, amino acids, aliphatic amines, urea, and some miscellaneous multifunctional compounds containing multiple hydroxyl, carboxyl, and carbonyl groups (Saxena and Hildemann, 1996). It is commonly believed that the water-soluble organic carbon (WSOC) fraction is "low" for primary organic carbon (OC) and that it increases with aging of the aerosol, together with the general oxidation state of organic matter (Saxena and Hildemann, 1996; Decesari *et al.*, 2001; Jaffrezo *et al.*, 2005). As oxidized species, low-molecular-weight (LMW) dicarboxylic and ketocarboxylic acids are very important water-soluble organic fractions, and may affect aerosol's hygroscopic and cloud-nucleating properties (Cruz and Pandis, 1998; Peng *et al.*, 2001; Abbatt *et al.*, 2005).

Dicarboxylic acids in aerosols may derive 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 (Kerminen *et al.*, 2000; Kawamura and Yasui, 2005; Hsieh *et al.*, 2007). In most urban areas of Japan, suspended particulate matter (SPM, particle diameter < 10 μm) is a major atmospheric pollutant (Takahashi *et al.*, 2008). Direct vehicle emissions and secondary formation from related gaseous pollutants are the dominant sources of SPM. However, few investigations of dicarboxylic acids in aerosols at a roadside environment have been conducted (Ho *et al.*, 2006a; Wang *et al.*, 2006). Therefore, the whole understanding of water-soluble organic components in size-segregated particles, including the relationships among OC, elemental carbon (EC), WSOC, individual dicarboxylic acids, and ambient oxidants between roadside and background environments, is still required.

This study focused on water-soluble organic components of size-segregated particles collected by aerosol samplers at a roadside site and a suburban site in Saitama, Japan. Detailed chemical characterizations of water-soluble organic acids (mainly dicarboxylic acids) as well as OC, EC, and WSOC in size-segregated samples were measured to clarify the sources and formation pathways of these water-soluble organic components.

EXPERIMENTAL

Atmospheric samples were collected at Saitama University, which is in suburban Saitama, about 30 km northwest of central Tokyo and about 4 km east of the business center of Saitama City. Two sites were chosen for simultaneous sampling of size-segregated particles. One site is situated at about 1.5 m away from a main traffic artery (National Road 463) near the university, and about 1.2 m above ground level. Another site, as a suburban site, was on the top of a 10-story office building the university,

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about 300 m away from roadside site, and about 37 m above the ground level to avoid possible interference from campus emission sources. Sampling was carried out during 12-17 May 2007 ($n = 3$, 47.5 hours for each sample), 24-27 July 2007 ($n = 4$, 23.5 hours for each sample), and 22-31 January 2008 ($n = 5$, 47.5 hours for each sample). The size-segregated samples were collected on quartz fiber filters (AHQ-630 and 2500QAT-UP, Pallflex, Shibata Scientific Technology Ltd., Tokyo, Japan) in high-volume Andersen air samplers (AH-600F, Shibata Scientific Technology Ltd.) with the standard four-stage cascade impactor and a back-up filter, which separated 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). The sampler was operated at a flow rate of 566 L/min.

Detailed analysis methods for water-soluble organic acids, WSOC, OC, EC, and ionic components are described elsewhere (Bao and Sakamoto, 2009). In brief, water-soluble dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in filter samples were analyzed by BF_3/*n*-butanol derivatization to their esters followed by gas chromatography/mass spectrometry (GC/MS) (Kawamura and Yasui, 2005). One-quarter of each filter was ultrasonically extracted with 15 mL of ultrapure water in an ice bath for 20 min (three times). The extract was then dried and reacted with 14% BF_3/*n*-butanol (300 μL) at 100°C for 30 min. After extraction with *n*-hexane and drying with a nitrogen stream, dibutyl esters and other derivatives were determined with a GC/MS (GCMS-QP 5050, Shimadzu Corporation, Japan) equipped with a split/splitless injector and a fused silica capillary column (DB-5; 30.0 m × I.D. 0.32 mm × 0.25 μm film thickness). The target compounds were identified by comparison of GC retention times with mass chromatograms of authentic standards. The quantification was based on a calibration function for the complete procedure that has been determined with standard solutions containing quantities of 100, 250, 500, 1000, 2500, 5000, and 10000 ng of each compound. Retention times, slopes, and regression coefficients of the calibration curves of the target compounds, including saturated *n*-dicarboxylic acids, unsaturated dicarboxylic acids, ketocarboxylic acids, and dicarbonyls are shown in Table 1. The concentrations of target compounds reported in this paper have been corrected by those of the procedural blanks, but they are not corrected for the collection efficiency of the sampling system.

OC and EC in the filter samples were analyzed with a thermal/optical carbon analyzer (DRI model 2001, Shibata), following the IMPROVE thermal/optical reflectance protocol

(Chow and Watson, 2002; Jiang *et al.*, 2006). One-eighth of each filter was also extracted with 10 mL of ultrapure water in an ice bath for 20 min, and the extract was used to analyze WSOC with a total organic carbon analyzer (TOC-VCHP, Shimadzu) and inorganic ionic components with an ion chromatography system (DX-100, DIOTEC Company of Tokyo, Japan). In addition, concentration data of ambient 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.

RESULTS AND DISCUSSION

Concentration Differences of Carbonaceous Components between Roadside and Suburban PM₇.₀

Table 2 shows the average concentrations of OC, EC, total carbon (TC), WSOC, chloride, nitrate, sulfate, sodium, ammonium, and calcium in roadside (R) and suburban (S) $PM_{7.0}$ during 12-17 May (spring) and 24-27 July (summer) 2007 and 22-31 January (winter) 2008. The average seasonal concentrations of WSOC were 3.9 μg/m³ (R) and 4.6 μg/m³ (S), and accounted for about 57% (R) and 58% (S) of OC, and about 45% (R) and 49% (S) of TC. WSOC was more abundant in summer than in other seasons; summer concentrations were 2.5-2.8 times those of other seasons.

EC is emitted directly from combustion sources and undergoes little chemical transformation after emission. It is thus a good indicator of primary anthropogenic air pollutants (Ho *et al.*, 2006b). However, OC and WSOC are emitted from primary emission sources and can also be derived from chemical reactions of gaseous organic precursors in the atmosphere. In Saitama, diesel vehicle exhaust is probably the main source of EC. To clarify the contribution of vehicle exhaust, we calculated chemical composition ratios of suburban particles to roadside particles (S/R ratios) (Table 2). The EC S/R ratios in $PM_{7.0}$ of 0.72 (spring), 0.66 (summer), and 0.52 (winter) reflect the large contribution of vehicle exhaust to the roadside particles. However, WSOC concentrations in suburban particles were a little higher than those in roadside particles, suggesting important contributions of secondary generation and atmospheric transport to WSOC concentrations in particulate matter in suburban Saitama City.

Since EC is an indicator of primary emission, the ratio of OC to EC has been used to infer the origin of carbonaceous particles (Ho *et al.*, 2006b). We found that OC/EC ratios were higher in

Table 1. Retention times, slopes and, regression coefficients (r^2) of the calibration curves of the target compounds.

Retention time	Target compound	Type	Slope	r^2 value
5.91	Methylglyoxal (MeGly)	Dicarbonyl	1.42	0.977
6.72	Oxalic acid (C_2)	Saturated *n*-dicarboxylic acid	2.25	0.994
7.57	Malonic acid (C_3)	Saturated *n*-dicarboxylic acid	1.77	0.998
8.76	Maleic acid (M)	Unsaturated dicarboxylic acid	1.95	0.998
9.04	Succinic acid (C_4)	Saturated *n*-dicarboxylic acid	1.90	0.998
9.33	Fumaric acid (F)	Unsaturated dicarboxylic acid	1.75	0.997
9.47	Pyruvic acid (Pyr)	Ketocarboxylic acid	1.60	0.974
9.66	Glyoxylic acid (WC_2)	Ketocarboxylic acid	3.24	0.971
10.32	Glutaric acid (C_5)	Saturated *n*-dicarboxylic acid	1.77	0.998
11.69	Adipic acid (C_6)	Saturated *n*-dicarboxylic acid	1.56	0.988
11.95	Glyoxal (Gly)	Dicarbonyl	4.26	0.991
12.95	Pimelic acid (C_7)	Saturated *n*-dicarboxylic acid	1.08	0.994
14.19	Phthalic acid (Ph)	Unsaturated dicarboxylic acid	1.69	0.991
15.47	Azelaic acid (C_9)	Saturated *n*-dicarboxylic acid	0.95	0.992

Table 2. Average concentrations of carbonaceous and water-soluble inorganic components in $PM_{7.0}$ and their suburban/roadside ratios.

Component	Roadside sample			Suburban sample			Suburban/roadside ratio		
	Spring	Summer	Winter	Spring	Summer	Winter	Spring	Summer	Winter
	Concentration ($\mu g/m^3$)						Mass/mass		
OC	4.33	10.0	5.74	5.90	12.1	5.18	1.36	1.21	0.90
EC	1.24	2.19	2.36	0.90	1.44	1.24	0.72	0.66	0.52
TC	5.57	12.2	8.10	6.79	13.5	6.42	1.22	1.11	0.79
WSOC	2.87	6.22	2.52	3.33	7.64	2.74	1.16	1.23	1.09
Cl^-	0.36	0.63	0.95	0.58	1.15	1.32	1.61	1.83	1.38
NO_3^-	2.15	4.13	1.99	3.09	7.19	2.15	1.44	1.74	1.08
SO_4^{2-}	3.29	8.00	1.64	5.09	12.0	2.15	1.55	1.50	1.31
Na^+	0.37	0.23	0.16	0.68	0.32	0.24	1.82	1.36	1.50
NH_4^+	1.57	3.02	1.00	2.29	4.95	1.37	1.46	1.64	1.37
Ca^{2+}	0.34	1.42	0.38	0.51	1.46	0.36	1.49	1.03	0.94

summer (4.57-8.39) than in winter (2.43-4.17), owing to the relatively higher OC concentrations in summer. The average OC/EC ratios at the suburban site were about 1.8 times those at the roadside site because of the elevated EC concentrations at the roadside site. The average summer WSOC/EC ratios at the two sites were about 2.5 times the winter ratios, and the suburban ratios were about 1.9 times the roadside ratios. These results indicated the contribution of secondary formation is more important for suburban organic aerosols, especially in summer.

Suburban/Roadside Ratios of Individual Water-Soluble Organic Acids in $PM_{7.0}$ and Their Origins

All targeted water-soluble organic acids, including dicarboxylic acids, ketocarboxylic acids, and two dicarbonyls, in the size-segregated samples with obvious peaks in the chromatograms were inspected. Table 3 shows the total average concentrations of these individual organic acids in roadside (R) and suburban (S) samples during the three seasons. The most abundant species in $PM_{7.0}$ was oxalic acid (C_2), followed by malonic (C_3), phthalic (Ph), or succinic acids (C_4). Longer chain *n*-dicarboxylic acids were less abundant, except for azelaic acid (C_9). Glyoxylic acid (WC_2) was one of abundant species in all target compounds, and its predominance among the

ketocarboxylic acids in the urban atmosphere has been reported previously (Kawamura and Yasui, 2005; Ho *et al.*, 2006a). Glyoxal (Gly) and methylglyoxal (MeGly) were detected with obvious concentrations in $PM_{7.0}$, and MeGly was the most abundant dicarbonyl in these particles, probably because glyoxal is mainly present in the gas phase (Kawamura *et al.*, 1996).

Water-soluble organic acids in $PM_{7.0}$ can derive either from direct emissions or secondary photochemical reactions. Different S/R ratios of individual organic acids in $PM_{7.0}$ may be associated with different sources and different production mechanisms. C_2, as a final photochemical reaction product, was the most abundant dicarboxylic acid at the two sites, and its S/R ratio in $PM_{7.0}$ (1.10-1.94) was much higher than the S/R ratio of EC (0.52-0.72). The S/R ratios of C_3, C_4, C_5, and C_9 were also greater than 1.0 (Table 3). In particular, C_9 is known to be an oxidation product of biogenic unsaturated fatty acids containing a double bond predominantly at the C_9-position (Kawamura *et al.*, 1996; Ho *et al.*, 2006a). The air at the roadside site (about 1.2 m above ground level and near a main traffic artery) is relative fresh, whereas long-range transportation and secondary formation have important contributions to water-soluble components at the suburban site (about 300 meters away from the roadside site and about 37 m above the ground level). The saturated *n*-dicarboxylic

Table 3. Average concentrations of individual organic acids in $PM_{7.0}$ and their suburban/roadside ratios.

Target Compound	Roadside sample			Suburban sample			Suburban/roadside ratio		
	Spring	Summer	Winter	Spring	Summer	Winter	Spring	Summer	Winter
	Concentration (ng organic acid/m^3)						Mass/mass		
Oxalic (C_2)	125	428	86	243	472	94	1.94	1.10	1.10
Malonic (C_3)	32	122	13.0	59.3	166	15	1.87	1.37	1.19
Succinic (C_4)	249	74	23	42	103	23	1.75	1.39	1.03
Glutaric (C_5)	6.6	30.4	6.4	11.7	37.4	7.0	1.78	1.23	1.10
Adipic (C_6)	5.7	22.1	7.7	7.3	18.0	7.9	1.30	0.81	1.03
Pimelic (C_7)	2.0	5.1	2.3	3.3	4.7	2.8	1.66	0.92	1.23
Azelaic (C_9)	8.4	28.7	20.0	16.3	35.6	23.9	1.93	1.24	1.20
Maleic (M)	2.7	9.6	9.3	4.2	10.4	6.2	1.56	1.08	0.67
Fumaric (F)	1.5	5.5	5.5	2.1	6.5	5.5	1.42	1.18	1.00
Phthalic (Ph)	28	175	58	38	149	56	1.31	0.85	0.96
Glyoxylic (WC_2)	18.2	52.3	17.3	33.1	73.8	21.7	1.82	1.41	1.25
Pyruvic (Pyr)	14.9	55.3	15.8	23.0	55.0	18.4	1.54	1.00	1.16
Glyoxal (Gly)	3.0	13.8	6.9	5.9	14.1	6.3	2.00	1.02	0.92
Methylglyoxal (MeGly)	15.6	31.5	13.6	19.2	51.8	14.9	1.23	1.64	1.09
Total organic acids (OA)	288	1053	284	508	1198	303	1.77	1.14	1.07

acids (except for C_6) in suburban $PM_{7.0}$ were thus not emitted mainly in vehicle exhaust, but can be attributed mostly to secondary photochemical generation from anthropogenic and natural sources.

The S/R ratios of Ph and C_6 in $PM_{7.0}$ were much smaller than those of C_2-C_5 *n*-dicarboxylic acids (Table 3). In particular, Ph was one of most abundant dicarboxylic acids in both roadside and suburban particles. This aromatic acid can be directly emitted from combustion sources (Kawamura and Kaplan, 1987; Ho *et al.*, 2006a) and can also be generated by atmospheric degradation of aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993; Wang *et al.*, 2006). Laboratory experiments have also shown that C_6 can be 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; Kawamura *et al.*, 1996). The lower S/R ratios of Ph and C_6 in $PM_{7.0}$ may be explained by the fact that Ph and C_6 in roadside particles can be either directly emitted from vehicle exhaust or produced by the rapid oxidation of vehicle exhaust gases in ambient air.

To further specify the relative contribution of secondary formation to water-soluble organic acids, we examined their concentration ratios relative to EC in $PM_{7.0}$. The ratios of OC, WSOC, and organic acids (OA) to EC in summer samples at the suburban site were about 1.8, 2.2, and 3.0 times those in winter samples. As shown in Fig. 1, the ratios of individual *n*-dicarboxylic acids (C_2-C_5) to EC were clearly higher in suburban samples than in roadside samples, and they were also clearly higher in summer samples than in winter samples, further indicating a larger contribution of secondary formation to LMW *n*-dicarboxylic acids in suburban particles than in roadside particles, especially in summer.

Concentration Variations of Water-Soluble Organic Components in Size-Segregated Particles

Size distribution data are useful for understanding the formation pathways of atmospheric species. Table 4 shows the average concentrations of water-soluble carbonaceous and ionic components in fine particles (< 1.1 μm), together with their ratios to the total concentrations in $PM_{7.0}$ ($PM_{1.1}/PM_{7.0}$ ratio). Size

distributions of sulfate, nitrate, ammonium, sodium, WSOC, OC, C_2, and Ph in roadside particles are also presented in Fig. 2. In general, the size distributions of water-soluble components showed similar tendencies between the suburban and roadside sites. During the warm seasons (spring and summer), sulfate and ammonium were very high in fine particles at both sites, whereas sodium and chloride concentrations were higher in coarse particles; these results are consistent with those of a previous study of urban aerosols in Tokyo (Takahashi *et al.*, 2008). The likely main source of the chloride and sodium during the warm seasons is sea salt.

Previous studies of sulfate size distributions (Kerminen *et al.*, 1999; Blando and Turpin, 2000; Yao *et al.*, 2002) 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). In summer, sulfate and nitrate compete for the available ammonia, and ammonia is preferentially scavenged by sulfate, rather than by nitrate, to form ammonium sulfate (Kuhns *et al.*, 2003), which leads to a lower concentration of nitrate in fine particles (< 1.1 μm). Because it is semi-volatile, ammonium nitrate in fine particles also tends to transform into gaseous compounds in summer. However, the size distribution showed that nitrate peaked in coarse particles (> 7 μm or 3.3-7 μm) during the warm seasons in Fig. 2(a1-b1); this distribution is commonly ascribed to heterogeneous reactions, in-cloud processes involving reactions with sea-salt aerosols, or both (Yao *et al.*, 2002). During the cold season (January), the size distributions of nitrate and sulfate at both sites were similar; nitrate was present mainly in fine particles, possibly because low temperatures enhanced ammonium nitrate formation in fine particles.

The size-segregated concentrations of TOC, WSOC and selected organic acids in roadside particles are also shown in Fig. 2(a2-c3). In spring and summer, size distributions of WSOC and most organic acids were similar to those of sulfate, indicating that similar formation pathways had occurred. Using size distribution of sulfate as a reference, most organic acids in fine particles (< 1.1 μm) are expected to be obvious distributions with an accumulation mode or a droplet mode. In this study, $PM_{1.1}/PM_{7.0}$
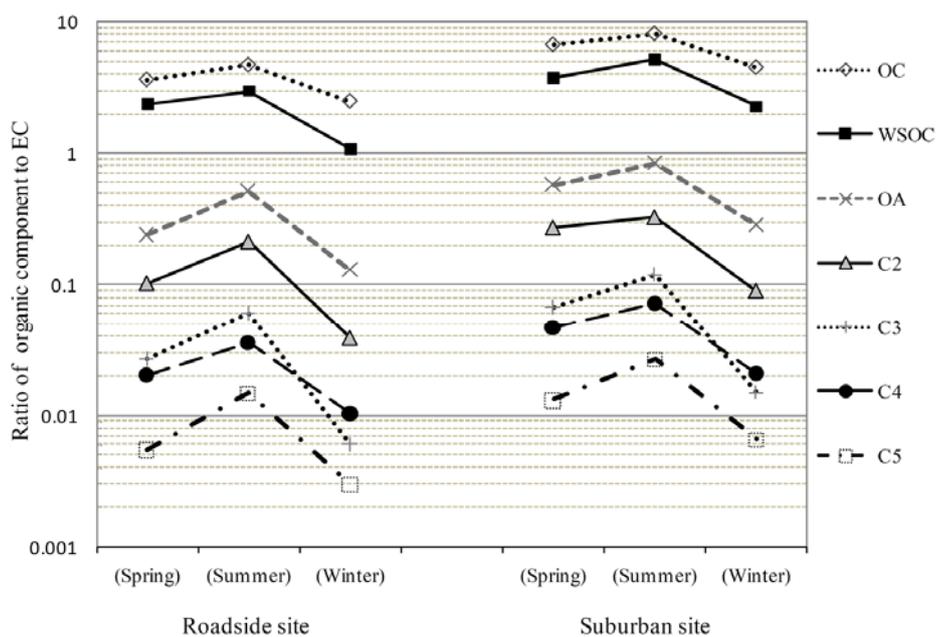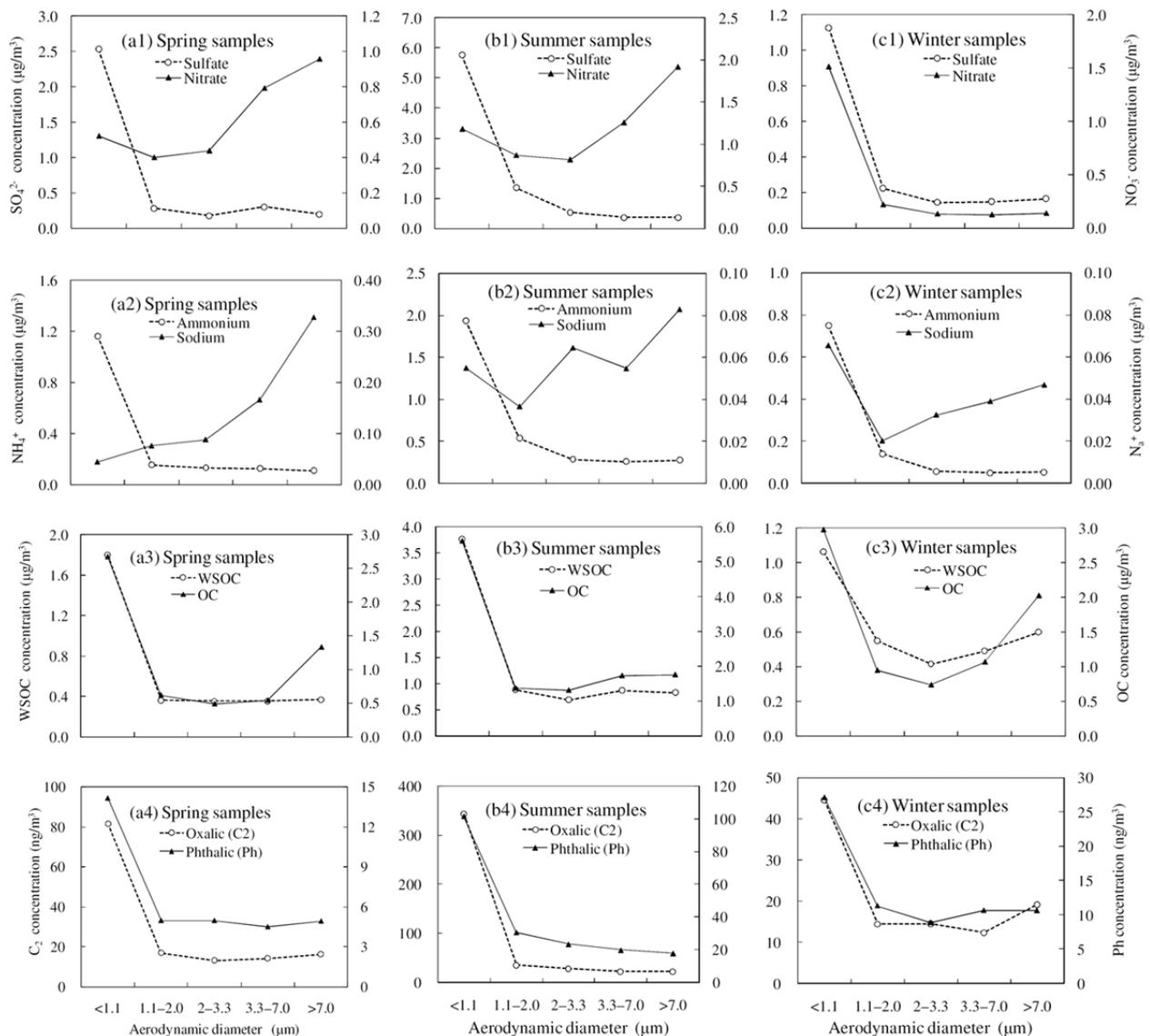

Fig. 1. Ratios of organic components to EC in roadside and suburban $PM_{7.0}$.

Table 4. Average concentrations of water-soluble organic and inorganic components in fine particles ($PM_{1.1}$) and their $PM_{1.1}/PM_{7.0}$ ratios.

Species	Roadside sample						Suburban sample					
	Spring		Summer		Winter		Spring		Summer		Winter	
	Average ($\mu g/m^3$)	Ratio[a] (%)	Average ($\mu g/m^3$)	Ratio (%)	Average ($\mu g/m^3$)	Ratio (%)	Average ($\mu g/m^3$)	Ratio (%)	Average ($\mu g/m^3$)	Ratio (%)	Average ($\mu g/m^3$)	Ratio (%)
OC	2.68	62	5.60	56	2.98	52	3.79	64	7.56	63	2.77	54
WSOC	1.80	63	3.77	61	1.06	42	2.14	64	5.07	66	1.24	45
OA	0.17	60	0.74	70	0.13	45	0.33	66	0.90	75	0.13	42
Oxalic (C_2)	0.082	65	0.343	80	0.044	52	0.167	69	0.379	80	0.048	50
Phthalic (Ph)	0.014	50	0.101	58	0.027	47	0.020	53	0.095	64	0.019	33
Chloride	0.05	13	0.18	29	0.70	73	0.11	18	0.48	42	1.02	77
Nitrate	0.52	24	1.18	29	1.51	76	0.57	19	2.26	34	1.43	66
Sulfate	2.53	77	5.76	72	1.13	69	4.03	79	8.76	73	1.59	74
Sodium	0.04	12	0.08	33	0.07	42	0.12	18	0.11	34	0.14	59
Ammonium	1.16	74	1.94	64	0.75	75	1.68	73	3.25	66	1.10	81
Calcium	0.13	37	0.42	29	0.09	25	0.17	34	0.53	36	0.05	15

[a] *Ratio = [concentration in $PM_{1.1}$] / [concentration in $PM_{7.0}$].*

Fig. 2. Size-segregated concentrations of sulfate, nitrate, ammonium, sodium, WSOC, OC, C_2, and Ph acids in roadside particles.

ratios of water-soluble organic components (WSOC, OA, and individual organic acids, such as C_6 and Ph) were significantly decreased in winter in comparison with the warm season ratios (Table 4). The following differences between warm and cold season may explain this observed difference in partitioning into particles > 1.1 μm: (i) lower nighttime temperature and higher nighttime relative humidity during winter than during summer; (ii) changes in gas/particle repartitioning of semi-volatile species between warm and cold conditions (Jaffrezo *et al.*, 2005); and (iii) different emission and oxidation rates of primary species between warm and cold seasons.

The Relationship between OC, WSOC, OA, Selected Organic Acids, and Oxidants

Several studies have reported a positive association between WSOC and ozone concentrations, suggesting a degree of dependency between the processes that lead to the formation of oxidized species in gas and particulate phases. However, this positive relationship does not hold under all environmental conditions, because the relationship between WSOC and ozone is also influenced by oxidation and removal processes (Sullivan *et al.*, 2004; Jaffrezo *et al.*, 2005). To clarify the secondary formation of water-soluble organic components in Saitama aerosols, we examined the relationships between OC, WSOC, and OA in $PM_{7.0}$ and ambient oxidants (mainly ozone) (Fig. 3). In general, we observed higher correlations at the suburban site than at the roadside site, which reflects the different relative contributions of primary emission and secondary formation at the two sites. The correlation between OC and oxidants at the roadside site was not strong ($r = 0.58$, Fig. 3(a)), but good correlations between WSOC and oxidants were found at both sites ($r = 0.73$ at roadside site and $r = 0.76$ at suburban site, Fig. 3b). A possible explanation for this difference is that secondary formation contributed in large part both to roadside and suburban WSOC in Saitama. OA showed a strong relationship with oxidants at the two sites ($r = 0.84$ at roadside site and $r = 0.87$ at suburban site, Fig. 3(c)), and most of the OA mass in Saitama aerosols can be regarded as a product of photochemical oxidation. Strong correlations between WSOC and OA were also observed at the two sites ($r = 0.91$ at roadside site and $r = 0.95$ at suburban site, $n = 12$, $p < 0.001$).

Furthermore, good correlation was observed between individual *n*-dicarboxylic acids (C_2-C_5) and oxidants, with no significant differences between the two sites. In particular, C_2 in suburban $PM_{7.0}$ showed the strongest correlation with oxidants ($r = 0.90$, $n = 12$, $p < 0.001$; Fig. 4(a)), followed by C_3 ($r = 0.90$, $n = 12$, $p < 0.001$), C_4 ($r = 0.88$, $n = 12$, $p < 0.001$), and C_5 ($r = 0.82$, $n = 12$, $p < 0.005$) (Fig. 4(b)). This sequence is consistent with atmospheric oxidation processes, which largely control the concentrations of these species in particles (Kawamura and Yasui, 2005; Ho *et al.*, 2006a). However, Ph and C_6 at the suburban site displayed lower correlations with oxidants ($r = 0.55$ for Ph and 0.65 for C_6, $n = 12$, $p < 0.07$) than did the other dicarboxylic acids, further suggesting that they originated as primary emissions from vehicles.

In addition, WSOC were strongly correlated with sulfate ($r = 0.91$, $n = 12$, $p < 0.001$) at suburban site. Furthermore, individual organic acids were also strongly correlated with sulfate in SPM. C_2 is the single most abundant organic acid identified in ambient aerosols, and correlated very strongly with sulfate ($r = 0.97$, $n = 12$, $p < 0.001$) in Saitama aerosol. Yu *et al.* (2005) observed a strong correlation between C_2 and sulfate at different locations, and they argued that there exists a common dominant formation pathway of the two chemically distinct species. 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 (Yao *et al.*, 2002; Yu *et al.*, 2005). The present results also highlight

the potential importance of in-cloud processing as a pathway leading to the formation of LMW dicarboxylic acids.

C_3/C_4 and C_6/C_9 ratios

Table 5 shows the C_3/C_4 and C_6/C_9 ratios in $PM_{2.0}$, $PM_{7.0}$, and total suspended particles (TSP) at the suburban and roadside sites, along with data from the literature for various other sites in different environments (Kawamura and Sakaguchi, 1999; Graham *et al.*, 2002; Wang *et al.*, 2002; Kawamura and Yasui, 2005; Ray and McDow, 2005; Ho *et al.*, 2006a).

C_3 can be derived from the incomplete combustion of fossil fuels or from secondary atmospheric production. Because C_3 is thermally less stable than C_4, more C_3 probably degrades during combustion process than is produced (Ho *et al.*, 2006a). Therefore, the C_3/C_4 ratio in particles is an informative indicator
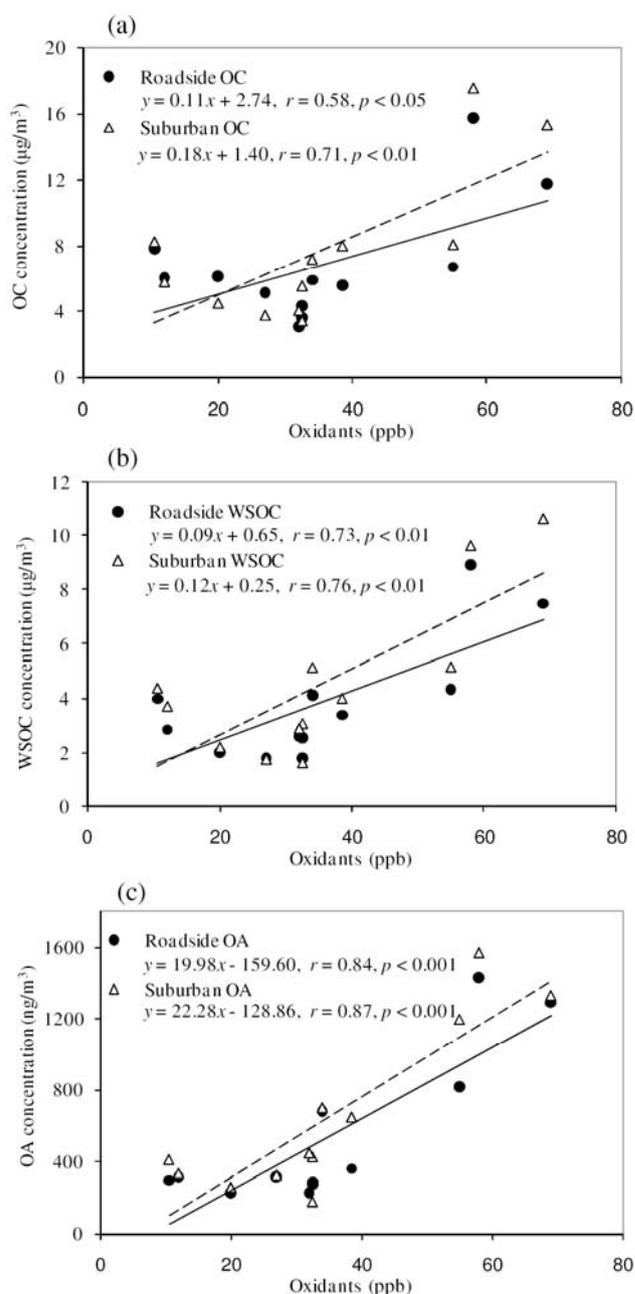

Fig. 3. Correlations of OC, WSOC, and OA in $PM_{7.0}$ with ambient oxidants in Saitama ($n = 12$).
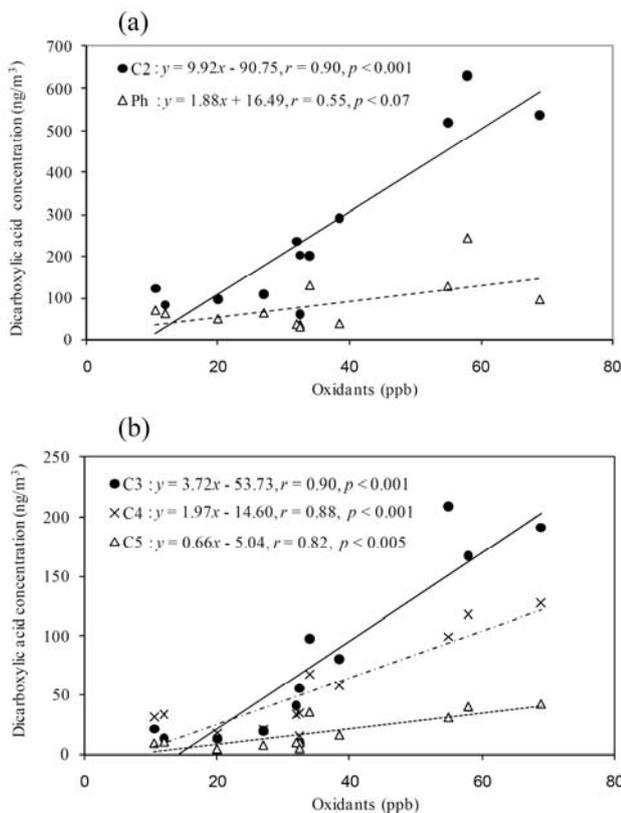
Fig. 4. Correlations of dicarboxylic acids in suburban $PM_{7.0}$ with ambient oxidants in Saitama ($n = 12$).

to distinguish secondary sources from primary vehicle exhaust: a C_3/C_4 ratio of > 3.0 indicates photochemical production of dicarboxylic acids, whereas one of 0.3-0.5 indicates a traffic-

emission origin of dicarboxylic acids (Kawamura *et al.*, 1996; Ho *et al.*, 2006a; Hsieh *et al.*, 2007). The seasonal variation of C_3/C_4 ratios in Saitama was larger than the spatial change in the ratios between the two sites (Table 5). At the roadside site, the C_3/C_4 ratio was 1.57-1.73 in summer, much higher than the level of pure traffic emissions, indicating the secondary production of some C_3 by photochemical reactions in the atmosphere. In contrast, in winter the C_3/C_4 ratio was very low at the roadside site (0.53-0.68), reflecting the strong influence of vehicle exhaust. The C_3/C_4 ratios (1.62 in $PM_{2.0}$, 1.61 in $PM_{7.0}$, and 1.56 in TSP) in summer at the Saitama suburban site were higher than those reported for other urban sites (0.78 in Nanjing $PM_{2.5}$, 0.92 in Philadelphia PM_{10}, 1.0 in Tokyo TSP), but lower than those reported for forest or marine sites (1.82 in Rondonia $PM_{2.5}$, 3.93 in Pacific Ocean TSP).

C_6 is produced by atmospheric oxidation of anthropogenic sources, and C_9 is produced from biogenic unsaturated fatty acids. Thus, the C_6/C_9 ratio is a potential indicator of the relative strength of anthropogenic and biogenic precursors to organic acids in particles (Kawamura and Ikushima, 1993; Ho *et al.*, 2006a; Wang *et al.*, 2006). The C_6/C_9 ratio was higher at the roadside site than at the suburban site, and it was also higher in summer than in winter. In the suburban TSP, the C_6/C_9 ratios (0.54 in summer and 0.41 in winter) were lower than the ratios in Tokyo TSP (1.49 in summer and 0.69 in winter; Kawamura and Yasui, 2005). In roadside $PM_{2.0}$, the C_6/C_9 ratios (0.70 in summer and 0.46 in winter) were also lower than those in Hong Kong roadside $PM_{2.5}$ (1.40 in summer and 0.64 in winter; Ho *et al.*, 2006a). These results suggest that in suburban Saitama, the relative contribution of anthropogenic sources in summer was much less than that at the urban sites of Tokyo and Hong Kong.

CONCLUSIONS

Size-separated aerosol samples were simultaneously collected at a roadside site and a suburban background site in Saitama, Japan, in three seasons from 2007 to 2008, and were subsequently analyzed for their chemical compositions, including

Table 5. Comparison of average concentrations (ng/m^3) of selected dicarboxylic acids and ratios reported in this study and in the literatures.

Site/type	Season	Size	Method	C_3	C_4	C_6	C_9	C_3/C_4	C_6/C_9	Source
Pacific Ocean/marine	Autumn & winter	TSP	GC-MS/FID	11	2.8	2.1	0.57	3.93	3.68	Kawamura and Sakaguchi, 1999
Rondonia, Brazil/pasture	Autumn	$PM_{2.5}$	GC-MS	115	95	6.5	11.3	1.21	0.58	Graham *et al.*, 2002
Rondonia, Brazil/forest	Autumn	$PM_{2.5}$	GC-MS	56	31	3.0	5.9	1.82	0.51	Graham *et al.*, 2002
Nanjing, China/urban	Winter & spring	$PM_{2.5}$	GC-MS/FID	89	113	37	144	0.78	0.25	Wang *et al.*, 2002
Philadelphia, USA/urban	Summer	PM_{10}	GC-MS	14	15	2.0	1.0	0.92	2.00	Ray and McDow, 2005
Tokyo, Japan/urban	Summer	TSP	GC-MS/FID	58	58	19.4	13.1	1.00	1.49	Kawamura and Yasui, 2005
	Winter	TSP	GC-MS/FID	41	47	14.2	20.6	0.85	0.69	Kawamura and Yasui, 2005
Saitama, Japan/suburban	Summer	$PM_{2.0}$	GC-MS	133	82	13.5	26.0	1.62	0.52	This study
	Summer	$PM_{7.0}$	GC-MS	166	103	18.0	35.6	1.61	0.50	This study
	Summer	TSP	GC-MS	185	118	20.7	38.3	1.56	0.54	This study
	Winter	$PM_{2.0}$	GC-MS	11	15	4.3	11.5	0.75	0.38	This study
	Winter	$PM_{7.0}$	GC-MS	15	23	7.9	23.9	0.66	0.33	This study
	Winter	TSP	GC-MS	17	28	9.6	23.6	0.63	0.41	This study
Hong Kong/urban roadside	Summer	$PM_{2.5}$	GC-MS/FID	48	33	12.7	9.1	1.44	1.40	Ho *et al.*, 2006a
	Winter	$PM_{2.5}$	GC-MS/FID	89	72	10.7	16.8	1.24	0.64	Ho *et al.*, 2006a
Saitama, Japan/roadside	Summer	$PM_{2.0}$	GC-MS	99	57	15.2	21.7	1.73	0.70	This study
	Summer	$PM_{7.0}$	GC-MS	122	74	22.1	28.7	1.64	0.77	This study
	Summer	TSP	GC-MS	134	85	25.6	31.0	1.57	0.82	This study
	Winter	$PM_{2.0}$	GC-MS	10	14	4.4	9.7	0.68	0.46	This study
	Winter	$PM_{7.0}$	GC-MS	13	23	7.7	20.0	0.57	0.38	This study
	Winter	TSP	GC-MS	15	29	9.9	18.9	0.53	0.52	This study

WSOC, OC, EC, inorganic ionic components, and individual water-soluble organic acids. Seasonal differences of these chemical compositions, spatial variation, and their relationships with ambient oxidants, were discussed in terms of secondary formation of water-soluble organic components in aerosols. In general, the seasonal variation of WSOC in Saitama aerosols was larger than spatial differences between the two measurement sites. Summer WSOC concentrations were 2.5-2.8 times those in the other seasons.

Oxalic acid (C_2), which is a final photochemical reaction product, was the most abundant dicarboxylic acid at the two sites. Longer chain *n*-dicarboxylic acids were less abundant, except for azelaic acid (C_9). The C_3/C_4 ratio, which is an informative indicator to distinguish secondary sources from primary traffic sources, was 1.33-1.68 in the warm seasons (spring and summer), much higher than the level of pure traffic emissions, indicating that these dicarboxylic acids were produced in part secondarily by photochemical reactions in the atmosphere. Strong correlations were also observed between C_2-C_5 *n*-dicarboxylic acids and ambient oxidants. These results are consistent with atmospheric oxidation processes, which largely control the concentrations of these species in suburban particles. However, the S/R ratio of EC in $PM_{7.0}$ was below 0.72, indicating intense effect of vehicle exhaust on the roadside particles. Correspondingly, the S/R ratios of C_6 and Ph were much smaller than those of C_2-C_5 acids. Ph, an aromatic acid, was one of most abundant dicarboxylic acids in roadside particles and showed a lower correlation with oxidants than C_2-C_5 acids. These results suggest that Ph and C_6 in the particles were directly emitted from automobiles.

During the warm seasons, sulfate, ammonium, WSOC, and individual *n*-dicarboxylic acids were very high in fine particles, whereas nitrate, chloride, sodium, and calcium concentrations were higher in coarse particles. The nitrate concentration peak was in coarse particles in summer and fine particles in winter, possibly because low temperatures enhance ammonium nitrate formation in fine particles. In winter, the detected organic acids in particles > 1.1 μm accounted for a larger proportion of the total in TSP. Lower temperatures and higher relative humidity at nighttime in winter may have strongly affected gas–particle repartitioning, further influencing the size distributions of water-soluble organic acids.

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