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COMPARATIVE DISTRIBUTIONS OF DICARBOXYLIC ACIDS AND RELATED POLAR COMPOUNDS IN SNOW, RAIN AND AEROSOLS FROM URBAN ATMOSPHERE

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Abstract—Nine wet precipitation (snow, sleet and rain) and four aerosol samples, collected from Tokyo, were studied for the molecular distributions of dicarboxylic acids and related polar compounds (ketoacids and dicarbonyls) by a capillary gas chromatography (GC) and GC–mass spectrometry. Wet samples were also analysed for dissolved organic carbon (DOC), whereas aerosol samples were studied for total carbon, total nitrogen and water soluble organic carbon. A homologous series of dicarboxylic acids (C_2–C_9) were detected in both wet precipitation (12–540 $\mu g\ \ell^{-1}$) and aerosol (1.1–3.0 $\mu g\ m^{-3}$) samples. Although oxalic acid (C_2) was generally the dominant diacid species followed by either malonic, succinic or phthalic acid in the samples studied, its relative abundance in total diacids was different between the wet precipitation (34 $\pm$8%) and aerosol (51 $\pm$ 5%) samples. These results suggest that oxalic acid is more enriched at near-ground level than upper levels of the troposphere. Time series of precipitation samples showed that diacid carbon concentration normalized by DOC decreased as a function of time during precipitation events. These results suggest that diacids, which exist as particles, are more efficiently scavenged from the atmosphere than other water soluble organic compounds.

Key word index: Diacids, ketoacids, dicarbonyls, snow, rain, aerosols, DOC, TOC, oxalic acid.

INTRODUCTION

Low molecular weight (LMW) dicarboxylic acids have been detected in aerosol samples from continental (Schuetzle *et al.*, 1975; Cronn *et al.*, 1977; Grosjean *et al.*, 1978; Yokouchi and Ambe, 1986; Kawamura and Kaplan, 1987; Satsumabayashi *et al.*, 1989, 1990) and remote marine (Kawamura and Gagosian, 1987; Kawamura and Usukura, 1993) atmosphere. Recent studies on molecular distribution of dicarboxylic acids generally showed the predominance of oxalic acid (C_2), followed by malonic acid (C_3) or succinic acid (C_4) in the aerosols (Kawamura and Ikushima, 1993). Their concentrations are generally higher in the summer. These dicarboxylic acids are derived from primary emissions from motor exhausts (Kawamura and Kaplan, 1987) and from secondary atmospheric reactions of anthropogenic hydrocarbons such as cyclic olefins (Grosjean *et al.*, 1978; Grosjean and Friedlander, 1980; Hatakeyama *et al.*, 1985) and biogenic unsaturated fatty acids (Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1987). Although direct precursors have not been clearly identified, photochemical oxidations of aromatic hydrocarbons such as benzene and toluene, as well as malonic, succinic and maleic acids, have been considered to result in oxalic acid (Kawamura and Ikushima, 1993).

Because dicarboxylic acids are very water soluble and mostly present as particles, they may be involved with a cloud condensation process and effectively removed from the atmosphere by in-cloud and below-cloud scavenging processes. Previous studies showed that diacids are abundantly present in rainwater samples (Norton *et al.*, 1983; Likens *et al.*,1983: Kawamura *et al.*, 1985). However, only few studies were conducted to clarify the diacid distributions on a molecular level in wet precipitations and there is no data available for urban snow, although snow and ice core samples from Greenland were studied for diacids (Kawamura and Yasui, 1991).

In the present study, we collected snow and rain samples in the urban atmosphere of Tokyo in time series and analysed for the molecular distributions of diacids and related polar compounds such as ketoacids and dicarbonyls. Wet precipitation samples were also analysed for total (TOC) and dissolved organic carbon (DOC). Aerosol samples collected at the same location, were studied for the diacids and related compounds, total carbon (TC) and nitrogen (TN), and water soluble organic carbon (WSOC). Here, we compare the distributions of dicarboxylic acids, ketocarboxylic acids and dicarbonyls between wet precipitations and aerosols and discuss the wet scavenging processes of polar organic compounds from the atmosphere.

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EXPERIMENTAL

Collection of snow, rain and aerosol samples

Nine precipitation samples were collected in winter and summer seasons of 1992 during one snow (18 March) and two rain events (rain I: 30 June, rain II: 1 August) at the rooftop of Tokyo Metropolitan University, Faculty of Science Building (*ca.* 40 m above the ground level). The University campus is located at *ca.* 30 km west of central Tokyo. Rainwater samples were collected in a pre-cleaned brown glass bottle using a stainless steel rain collector with a cross section of 2800 cm^2. Snow/sleet samples were collected by the same collector. After sampling, a bactericide ($HgCl_2$) was added to the melted snow and rainwater samples, which were stored in a brown glass bottle with a Teflon-lined cap at 4°C prior to analysis. Rainwater samples were protected from biodegradation with $HgCl_2$ during sample collection.

Aerosol samples were collected in the winter and summer of 1992 with a pre-combusted (500°C) Pallflex quartz fiber filter (20 × 25 cm) using a high-volume air sampler (Shibata HVC1000) at a rooftop of the Faculty of Science Building. Four aerosol samples were used in this study. Total aerosol mass was determined by weighing the filter before and after sample collection.

Determination of dicarboxylic acids and related compounds by GC and GC–MS

Dicarboxylic acids, ketoacids and dicarbonyls were measured by the method elaborated for liquid samples (Kawamura and Yasui, 1991). Wet samples (100–150 ml) were concentrated by a rotary evaporator under a vacuum and dried in a nitrogen stream. The dried samples were then reacted with 14% borontrifluoride in *n*-butanol (0.3 ml) to derive carboxyl and aldehyde groups to the butyl esters and dibutoxy acetals, respectively. The derivatives of dicarboxylic acids, ketoacids and dicarbonyls were extracted with *n*-hexane (5 ml) in the presence of an organic free pure water (3 ml) and acetonitrile (0.3 ml), and the extracts were washed with the pure water (3 ml × 2). The derivatives were concentrated to 50 μl and determined by a Hewlett Packard (HP 5890) gas chromatograph (GC) equipped with a split/splitless injector, a HP-5 fused silica capillary column (0.32 mm i.d. × 25 m × 0.52 μm), and an FID detector. Identification of the derivatives were performed by a comparison of GC retention times and mass spectra with those of authentic standards. Identification of the compounds were confirmed by a GC–mass spectrometer system (Finnigan-MAT ITS-40).

Recoveries of diacids in the analytical procedure were 70% (oxalic), 77% (malonic), 86% (succinic) and 90% (adipic). Procedural blanks showed small peaks of oxalic, pyruvic and phthalic acid derivatives in the GC chromatogram; however, they presented less than 1, 2 and 4% of actual samples, respectively. Analytical errors in the determination of diacids were within 5.5% for dicarboxylic acids, 15% for ketoacids, 8% for glyoxal and 26% for methylglyoxal based on duplicate analysis of the rain I sample. The concentrations of the acids presented here are corrected for the procedural blanks. Although glyoxylic acid has been suggested to be partly oxidized to oxalic acid, possible overestimation is less than 3% of oxalic acid concentrations (Kawamura *et al.*, 1985), which is within the analytical error of this procedure.

Aerosol samples were analysed for diacids by the method of Kawamura and Ikushima (1993). A part of the aerosol filter sample was cut into pieces and extracted with pure water (organic free) under a sonication to separate water soluble dicarboxylic acids and related polar compounds. The organic free water was prepared by boiling Milli Q water with $KMnO_4$ to oxidize organic impurities followed by subsequent distillation. The water extracts were concentrated, derivatized and analysed by the methods described above.

Measurement of DOC and TOC in rain and snow samples

Wet precipitation samples were filtered through a pre-heated (500°C) Pallflex quartz fiber filter for the measurement of DOC: according to the manufacturer 99.99% of the dioctylphthalate particles (0.3 μm) are retained on the filter under atmospheric conditions. An aliquot of unfiltered and filtered samples (4 ml) were taken in the 7 ml pre-heated (450°C) glass screw vials with a Teflon-lined cap. After acidification with 1.2 M HCl solution (50 μl), the samples were bubbled with pure nitrogen gas for 3 min to purge inorganic carbon. The water sample (20–50 μl) was injected to a Shimadzu TOC-500 carbon analyser with a combustion column packed with a platinum-coated alumina (Kawamura *et al.*, 1992). Injections were repeated five times for each sample. Two data sets having the highest and lowest values were discarded, whereas the remaining three values were averaged and used for TOC and DOC values in this study. The analytical precision of the procedure was within 2%. Particulate organic carbon (POC) was calculated by the difference between TOC and DOC values. The data presented here are corrected for the system blanks.

Measurements of TC, TN and WSOC in aerosol samples

A part of the filter sample (*ca.* 5 cm^2) was cut off and subjected to a CHN corder (Yanagimoto MT-3) for the determination of TC and TN. Analytical errors for TC and TN based on duplicate analyses were 10 and 9%, respectively. WSOC in the aerosol samples was also measured by the following method. A part of the aerosol filter samples (*ca.* 20 cm^2) was cut in pieces and extracted with a pure water (20 ml) for 5 min under ultrasonication. The water extracts were then filtered on Pallflex quartz fiber filter to remove particles and filter debris. An aliquot (4 ml) of filtrates was taken in the 7 ml pre-combusted (450°C) glass screw vials with a Teflon-lined cap and acidified with 1.2 M HCl. After purging the dissolved inorganic carbon with N_2, the samples were analysed for WSOC by the method described above for DOC measurement. Analytical precision of the WSOC measurement was 2% based on duplicate analysis of the filter sample (24–25 February).

RESULTS AND DISCUSSION

TC, TN and WSOC in aerosol samples

Table 1 gives concentrations of aerosol mass, TC and total nitrogen TN, and WSOC in the aerosol samples. The concentration range of TC was 11–64 $\mu g\,m^{-3}$ (av. 32 $\mu g\,m^{-3}$), which comprised 5.7–19% of total aerosol mass. These results are similar to the studies on carbonaceous fraction in total aerosol mass in the urban atmosphere: 17% in Beijing (Sekine *et al.*, 1992), 20% in Seoul (Hashimoto *et al.*, 1991), 30% in southern California (Appel *et al.*, 1983). Interestingly, summer samples showed 4–6 times higher TC concentrations than the winter samples. Relative abundance of TC in aerosol mass was also higher in the summer samples (17–19%) than the winter samples (6–7%). These results seem to suggest that more particulate organic matter is produced in the summer probably by the photochemical gas-to-particle conversion (Warneck, 1988; Turpin and Huntzicker, 1991).

Concentrations of TN were 2–18 $\mu g\,m^{-3}$ in the aerosol samples, which are 3–5 times lower than the TC contents. However, they still comprise a significant

Table 1. Total carbon (TC) and nitrogen (TN) contents and water soluble organic carbon (WSOC) in the urban aerosol samples collected from Tokyo, 1992

Sampling date Sampling time	24–25 February 20:10–17:45	25–26 February 18:00–17:55	22–23 July 22:25–4:40	23 July 4:40–18:20
Aerosol mass ($\mu g\ m^{-3}$)	166	186	389	216
TC ($\mu gC\ m^{-3}$)	11.3	10.6	64.0	42.0
TC/aerosol (%)	6.8	5.7	17.1	19.4
TN ($\mu gN\ m^{-3}$)	2.0	3.1	17.9	10.9
TN/aerosol (%)	1.2	1.7	4.6	5.0
C/N ratio	5.6	3.4	3.7	3.9
WSOC ($\mu gC\ m^{-3}$)	3.2	3.4	21.3	23.2
WSOC/aerosol mass (%)	1.9	1.8	5.5	10.7
WSOC/TC (%)	28	32	32	55

portion of total aerosol mass (1.2–5.0% of total aerosols). The C/N weight ratios ranged from 3.4 to 5.6 with an average of 4.2. The summer samples showed higher TN contents (*ca.* 3–8 times) than winter samples. The relative abundance of TN in total aerosol mass also showed higher values in the summer samples (4.6–5.0%) than winter samples (1.2–1.7%), suggesting that enhanced photochemical oxidations of NO_x result in an increased concentration of particulate nitrate in the atmosphere. Although there is no reported data on TN, Satsumabayashi *et al.* (1990) indicated that NO_3^- and NH_4^+ comprised 10 and 11% of total aerosol mass in Takasaki, being consistent with the present results.

WSOC showed a concentration range of 3.2–23 $\mu g\ m^{-3}$, which comprised from 1.8 to 10.7% of total aerosol mass. Interestingly, WSOC contents are *ca.* 7 times higher in summer than winter samples (see Table 1). The relative abundance of WSOC in aerosols is also higher in summer (5.5–10.7%) than winter samples (1.8–1.9%), suggesting that WSOC including diacids and other water soluble organic compounds, are produced more in the summer than the winter season. Although WSOC fraction may contain water-insoluble carbon such as black carbon in fine particle size ($>0.3\ \mu m$) which may partly pass through the Pallflex quartz fiber filter during filtration, we feel that a possible overestimation of WSOC is not significant. The WSOC was found as a significant fraction of total aerosol carbon: WSOC accounted for 28–55% of total aerosol carbon. Interestingly, WSOC/TC ratios were higher in the aerosol samples collected during day time than those collected at night time (see Table 1). This result suggests that water-soluble organic compounds in the urban aerosols are enriched during day time probably due to an enhanced photochemical production of polar compounds such as dicarboxylic acids.

During wet precipitation process, aerosol particles are scavenged from the atmosphere and their WSOC fraction should dissolve in water droplets, as well as gaseous organic compounds, and contribute to dissolved organic carbon in the wet precipitation samples. By contrast, water insoluble organic fraction of aerosol particles would contribute to POC in the wet precipitation samples.

TOC, DOC and POC in snow and rain samples

Table 2 gives TOC, DOC, and POC contents in the wet precipitation samples. TOC range in snow/sleet samples was 23–27 $mgC\ \ell^{-1}$(av. 25 $mgC\ \ell^{-1}$) whereas that of rain samples was 1.2–15.4 $mgC\ \ell^{-1}$ (av. 4.9 $mgC\ \ell^{-1}$). Higher TOC values in the snow/sleet samples may be caused by a better efficiency in scavenging organic compounds from the atmosphere by snow flakes than rain droplets. Because snow flakes have more surface area than rain drops in terms of a unit of weight, they may effectively adsorb and scavenge other water soluble organic compounds such as aldehydes, volatile fatty acids and ketones. The TOC values in rainwaters are similar to those reported for Los Angeles rainwaters (5–10 $mgC\ \ell^{-1}$, Liljestrand and Morgan, 1980; Kawamura and Kaplan, 1991). As seen in Table 2, organic carbon in the precipitation was found mostly in the dissolved form (71–99%, av. 90%). Our results seemed to be in good agreement with the previous results of Likens *et al.* (1983), who reported the organic matter lower than 1000 Da were dominant and gave DOC/TOC ratios higher than 0.7 in New Hampshire rains. Because combustion-derived fine carbon particles such as black carbon are present abundantly in urban atmosphere (Appel *et al.*, 1983; Goldberg, 1985; Turpin and Huntzicker, 1991), they may be present in the precipitation samples in colloidal size, suggesting that black carbon may represent a certain fraction of DOC.

In the rain event II (1 August), the second rain showed higher TOC and DOC values than the first rain (Table 2). This is probably caused by more efficient scavenging of organic materials due to much lower precipitation rate in the second rain. By contrast, during rain event I (30 June) in which precipitation rates were rather stable (see Table 2), both DOC and TOC concentrations decreased as a function of time, suggesting that organic compounds were scavenged from the atmosphere during an early stage of wet precipitation. However, a fractionation seemed

Table 2. Total organic carbon (TOC) and dissolved organic carbon (DOC) in the wet precipitation samples collected from Tokyo in 1992 and precipitation data

Samples	Snow/Sleet (8 March)			Rain I (30 June)				Rain II (1 August)	
Precipitation event	1st(Snow)	2nd(Snow +Sleet)	3rd(Sleet)	1st	2nd	3rd	4th	1st	2nd
Time	09:00–10:30	10:30–11:30	11:30–12:30	11:55–12:45	14:20–15:00	19:00–19:35	22:40–23:15	19:00–19:40	19:40–21:45
Precipitation (mm)	NDET	0.88	0.90	1.7	1.6	1.8	NDET	3.3	0.31
Precipitation rate (mm h^{-1})	NDET	0.88	0.90	2.1	2.3	3.0	NDET	4.9	0.15
TOC (mgC ℓ^{-1})	23.1	NDET	26.7	2.9	1.8	1.2	1.5	6.8	15.4
DOC (mgC ℓ^{-1})	19.7	NDET	22.6	2.1	1.4	1.0	1.3	6.7	14.8
POC (mgC ℓ^{-1})	3.4	NDET	4.1	0.85	0.38	0.15	0.17	0.04	0.59
DOC/TOC(%)	85	—	85	71	79	87	89	99	96

POC: particulate organic carbon, NDET: not determined.

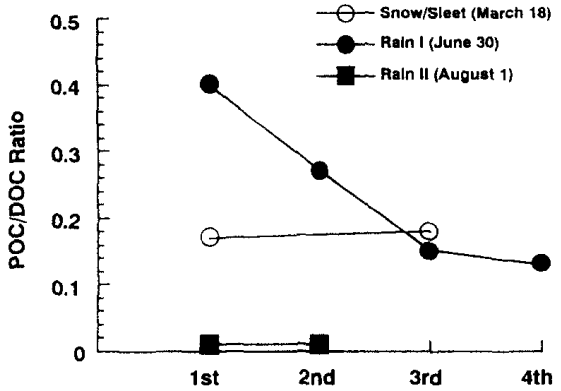

Fig. 1. Changes in the particulate organic carbon (POC)/dissolved organic carbon (DOC) ratios in the rain and snow samples during precipitation events.

to occur during wet precipitation between water soluble and water insoluble organic matter in the air. As shown in Fig. 1, POC/DOC ratios decreased as a function of time from 0.43 to 0.15 during rain event I. Generally, POC originates only from water-insoluble fraction of aerosol particles whereas DOC originates from both water-soluble fraction of aerosols and gaseous organic components in the atmosphere. It is unlikely that the water-insoluble fraction of the aerosols is more effectively scavenged than the water-soluble fraction of the aerosols. Thus, the present results (Fig.1) suggest that aerosol particles are more efficiently scavenged from the air than gaseous organic compounds.

Distribution of dicarboxylic acids, ketoacids and dicarbonyls in snow and rain samples

Figure 2 shows a reconstructed ion chromatogram of derivatives of dicarboxylic acids, ketocarboxylic acids and dicarbonyls isolated from the snow sample. A homologous series of straight-chain saturated (C_2–C_9) dicarboxylic acids were identified in the snow/sleet and rainwater samples together with branched-chain (*iso*) saturated (C_4, C_5), aliphatic unsaturated (maleic: *cis* C_4, fumaric: *trans* C_4, methylmaleic: *cis* C_5, aromatic (phthalic: C_8), oxo (oxomalonic, C_3) and hydroxy (malic: C_4) diacids. As seen in Fig. 2, the diacid distribution is generally characterized by a predominance of oxalic acid, followed by either succinic (C_4), azelaic (C_9) or phthalic (C_8) acid. Unsaturated diacids showed a predominance of *cis*-configuration (maleic acid) over *trans*-configuration (fumaric acid). In addition to diacids, ketocarboxylic acids and dicarbonyls were also detected in the samples. The ketocarboxylic acids detected in the wet precipitations include pyruvic acid (C_3) and a homologous series of ω-oxocarboxylic acids (C_2–C_6, C_9). The dicarbonyl group includes glyoxal (C_2) and methylglyoxal (C_3). Among these three compound classes, the diacid group was the most abundant.

Table 3 gives concentrations of individual diacids as well as ketoacids and dicarbonyls in wet precipitation

Table 3. Concentrations of dicarboxylic acids and related polar compounds in the wet precipitation samples collected from Tokyo, 1992

Samples (Date)	Snow/Sleet (18 March)			Rain I (30 June)				Rain II (1 August)	
	1st	2nd	3rd	1st	2nd	3rd	4th	1st	2nd
Time	9:00–10:30	10:30–11:30	11:30–12:30	11:55–12:45	14:20–15:00	19:00–19:35	22:40–23:15	19:00–19:40	19:40–21:45
Diacids ($\mu g\,\ell^{-1}$)									
Oxalic, C_2	13.4	8.91	7.34	41.2	13.6	4.09	6.37	125	205
Malonic, C_3	2.46	2.21	2.02	14.5	4.09	0.78	0.92	51.4	76.5
Methylmalonic, iC_4	0.30	0.35	0.18	1.22	0.33	0.30	0.19	3.62	4.28
Oxomalonic, C_3	0.30	0.48	0.15	0.53	0.23	1.01	0.08	3.30	3.91
Maleic, uC_4	1.61	2.52	2.15	4.87	3.87	0.86	0.46	46.2	48.4
Succinic, C_4	5.60	4.13	3.45	21.0	4.79	1.75	1.28	65.6	95.5
Methylsuccinic, iC_5	0.93	0.62	0.54	3.29	0.82	0.49	0.25	6.55	10.5
Fumaric, uC_4	0.56	0.22	0.44	1.99	0.70	0.27	0.36	3.82	4.64
Methylmaleic, iuC_5	0.82	1.50	1.06	2.62	1.55	0.51	0.40	27.2	25.8
Malic, hC_4	1.00	1.17	0.49	ND	0.28	ND	ND	6.76	6.74
Glutaric, C_5	1.60	1.49	0.63	5.15	1.55	0.55	0.29	10.5	16.4
Methylglutaric, iC_6	0.36	0.18	ND	0.95	0.35	0.20	0.09	1.49	2.66
Adipic, C_6	3.07	2.65	0.94	5.02	1.17	0.18	0.42	5.17	7.78
Pimelic, C_7	0.64	0.74	0.15	1.02	0.20	0.00	0.07	2.43	0.48
Suberic, C_8	1.15	0.76	ND	2.41	0.19	0.11	0.21	ND	1.91
Phthalic, C_8	4.07	4.07	2.25	4.07	8.10	0.78	0.38	30.7	24.6
Azelaic, C_9	4.56	11.5	0.85	4.71	0.62	0.36	0.58	2.11	3.04
Sub total	42.4	43.5	22.6	115	42.4	12.2	12.4	393	538
Total diacid-C ($\mu g\,C\,\ell^{-1}$)	17.3	19.3	8.69	42.7	16.9	4.53	4.33	145	191
Diacid-C/DOC (%)	0.088	—	0.038	2.03	1.20	0.45	0.33	2.17	1.29
Ketoacids ($\mu g\,\ell^{-1}$)									
Pyruvic, C_3	1.34	3.26	0.79	2.22	3.13	1.38	0.95	16.3	12.5
Glyoxylic, C_2	5.27	4.38	3.86	5.75	4.04	0.57	0.20	62.2	51.0
3-Oxopropanoic, C_3	0.27	0.40	0.39	4.21	1.52	0.62	0.40	15.3	7.85
4-Oxobutanoic, C_4	1.85	1.77	0.93	5.21	2.10	0.74	0.26	12.9	17.0
5-Oxopentanoic, C_5	0.48	0.65	0.12	0.73	0.58	0.20	0.09	2.03	2.34
6-Oxohexanoic, C_6	0.82	1.25	0.31	0.81	0.26	0.09	0.07	1.93	1.14
9-Oxononanonic, C_9	1.35	1.48	0.36	0.45	0.30	0.13	ND	1.42	1.68
Sub total	11.4	13.2	6.77	19.4	11.9	3.73	1.97	112	93.5
Total ketoacid-C ($\mu gC\,\ell^{-1}$)	4.74	5.64	2.57	7.37	4.58	1.48	0.76	39.7	34.5
Ketoacid-C/DOC (%)	0.024	—	0.011	0.35	0.33	0.14	0.058	0.59	0.23
Dicarbonyls ($\mu g\,\ell^{-1}$)									
Glyoxal, C_2	2.62	4.53	3.56	4.43	5.31	1.27	0.05	48.4	53.2
Methylglyoxal, C_3	1.82	1.39	1.60	3.12	3.82	1.24	0.51	11.7	35.6
Sub total	4.44	5.92	5.16	7.55	9.13	2.51	0.57	60.1	88.8
Total dicarbonyl-C ($\mu gC\,\ell^{-1}$)	1.99	2.57	2.27	3.39	4.11	1.15	0.28	25.9	39.8
Dicarbonyl-C/DOC (%)	0.010	—	0.010	0.16	0.29	0.11	0.022	0.39	0.27

i: iso, u: unsaturated, h: hydroxy, DOC: dissolved organic carbon.
ND: Not Detected. For snow/sleet samples: 1st: snow, 2nd: snow/sleet, 3rd: sleet

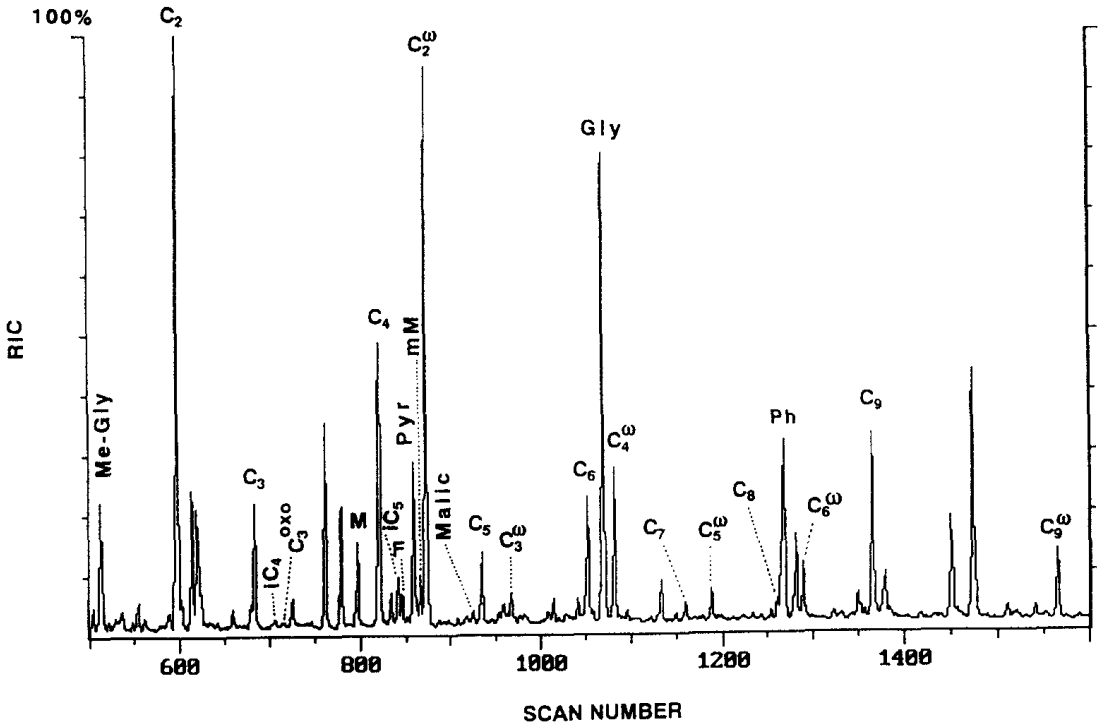

Fig. 2. A reconstructed total ion chromatogram (RIC) of the derivatives of dicarboxylic acids, ketocarboxylic acids and dicarbonyls isolated from the snow sample (the first snow, 18 March 1992) collected in Tokyo. For abbreviation, see Table 3. C_n means dicarboxylic acid with *n* carbon numbers. iC_n indicates branched-chain (*iso*) diacid. M, F and mM are maleic, fumaric and methylmaleic acids, respectively. $C_n\omega$ indicates ω-oxocarboxylic acid with *n* carbon numbers. Malic, Gly, Me-Gly, Ph and Pyr mean malic acid, glyoxal, methylglyoxal, phthalic acid and pyruvic acid, respectively.

samples. Concentration ranges of the total dicarboxylic acids (C_2–C_9) were 23–43 $\mu g\,\ell^{-1}$ in the snow/sleet samples and 12–538 $\mu g\,\ell^{-1}$ in the rain samples. On the other hand, ketoacids were less abundant than diacids: their concentration ranges were 6.8–114 $\mu g\,\ell^{-1}$ in the snow/sleet samples and 2.0–112 $\mu g\,\ell^{-1}$ in the rainwater samples. Concentrations of dicarbonyls were much lower than diacids and ketoacids: their concentration ranges were 4.4–5.9 $\mu g\,\ell^{-1}$ in the snow/sleet samples and 0.6–89 $\mu g\,\ell^{-1}$ in the rainwater samples. The August rain samples (rain II, 1 August) showed higher concentrations of these compound classes compared to other precipitation samples. This is probably because the diacids were more accumulated in the atmosphere under the condition of intensive solar radiation which continued for several days before the precipitation event and were apparently more concentrated in the rainwaters due to the low precipitation rate during the rain event (Table 2).

Oxalic acid (C_2) was found to be the most abundant diacid species in the wet precipitation samples studied, except for one snow/sleet sample which showed a predominance of azelaic acid (C_9). This feature has been obtained in the aerosol samples from central Tokyo (Kawamura and Ikushima, 1993). However, relative abundance of oxalic acid in the total diacids largely fluctuate among the precipitation samples: the C_2 diacid comprised only 21–32% of the total diacids (av. $28 \pm 5.4\%$) in the snow/sleet samples whereas that in the rain samples comprised from 32 to 52% of the total diacids (av. $37 \pm 7\%$). Similar low values for C_2 diacid have been reported in Greenland snow and ice samples (Kawamura and Yasui, 1991). The second most abundant species was succinic acid (C_4) followed by azelaic (C_9), phthalic or malonic acid (C_3) in the wet precipitation samples. The C_4 diacid comprised 9.5–15.2% (av. $13 \pm 2\%$) in the snow/sleet samples whereas it comprised 10.4–18.3% (av. $15 \pm 3\%$) in the rain samples. The C_9 diacid comprised 0.5–26% (av. $6.1 \pm 8.2\%$), whereas phthalic acid comprised 3–19% (av. $8.1 \pm 4.9\%$) of the total diacids in the wet precipitation samples. The C_3 diacid accounted for 6–9% ($7 \pm 2\%$) in snow/sleet samples whereas it accounted for 6–14% (av. $11 \pm 3\%$) in the rainwaters.

Among ketocarboxylic acids, pyruvic or glyoxylic acid generally were the dominant species. It is of interest to note that glyoxylic acid (C_2) is always the most abundant ω-oxocarboxylic acid in both snow and rain samples, followed by C_4 or C_3 species. The higher ω-oxoacids are less abundant. Their molecular distributions seem to be consistent with those of dicarboxylic acids, suggesting that these ketoacids are one of the precursors of dicarboxylic acids. It is also interesting to note that glyoxal is as abundant as

Table 4. Cencentrations of dicarboxylic acids and related polar compounds in the aerosol samples from Tokyo 1992

Date Time	24–25 Feb. 20:10–17:45	25–26 Feb. 18:00–17:55	22–23 July 22:25–4:40	23 July 4:40–18:20
Diacids (ng m^{-3})				
Oxalic, C_2	521	650	1352	1680
Malonic, C_3	105	129	322	453
Methylmalonic, iC_4	8.8	22	22	42
Oxomalonic, C_3	30	32	24	46
Maleic, uC_4	29	33	26	21
Succinic, C_4	139	142	279	251
Methylsuccinic, iC_5	24	30	12	18
Fumaric, uC_4	12	20	44	10
Methylmaleic, iuC_5	ND	ND	ND	ND
Malic, hC_4	17	47	73	63
Glutaric, C_5	39	48	81	88
Methylglutaric, iC_6	10	24	ND	5.3
Adipic, C_6	35	54	31	79
Pimelic, C_7	6.1	11.0	ND	38
Suberic, C_8	0.79	6.8	ND	12
Phthalic, C_8	130	85	135	157
Azelaic, C_9	41	46	43	48
Sub total	1150	1379	2443	3012
Total diacid-C (ng m^{-3})	422	492	817	1001
Diacids/aerosol mass (%)	0.69	0.74	0.63	1.39
Diacid-C/TC (%)	3.70	4.60	1.28	2.40
Diacid-C/WSOC (%)	13.2	14.5	3.8	4.3
Ketoacids (ng m^{-3})				
Pyruvic, C_3	45	41	27	89
Glyoxylic, C_2	120	161	174	238
3-Oxopropanoic, C_3	17	18	31	28
4-Oxobutanoic, C_4	55	28	45	70
5-Oxopentanoic, C_5	8.9	9.3	17	29
6-Oxohexanoic, C_6	7.9	5.0	9.5	16
9-Oxononanoic, C_9	12	7.6	22	8.8
Sub total	265	270	326	479
Total ketoacid-C (ngC m^{-3})	104	99	125	180
Ketoacids/aerosol mass (%)	0.16	0.15	0.084	0.22
Ketoacid-C/TC (%)	0.92	0.93	0.19	0.46
Ketoacid-C/WSOC (%)	3.2	2.9	0.58	0.78
Dicarbonyls (ng m^{-3})				
Glyoxal, C_2	45	38	43	46
Methylglyoxal, C_3	24	67	40	39
Sub total	69	105	83	90
Total dicarbonyl-C (ngC m^{-3})	31	49	38	39
Dicarbonyls/aerosol mass (%)	0.042	0.056	0.021	0.042
Dicarbonly-C/TC (%)	0.27	0.47	0.059	0.092
Dicarbonly-C/WSOC (%)	0.96	1.5	0.18	0.17

TC: total carbon in aerosols, WSOC: water soluble organic carbon in aerosols.

glyoxylic acid in the wet precipitation samples. Glyoxal and methylglyoxal have been reported in the marine air (Zhou and Mopper, 1990), rain and fog samples (Steinberg and Kaplan, 1984; Munger *et al.*, 1990) and snow and ice samples from Greenland (Kawamura and Yasui, 1991). They are produced by the photochemical oxidation of aromatic hydrocarbons such as benzene and toluene (Bandow *et al.*, 1985). These dicarbonyls may be intermediates in the photochemical oxidation reactions of aromatic hydrocarbons to oxalic acid (Norton *et al.*, 1983).

Distribution of dicarboxylic acids, ketoacids and dicarbonyls in aerosol samples

The dicarboxylic acids (C_2–C_9), ketoacids (C_2–C_6, C_9) and dicarbonyls (C_2–C_3) were also detected in aerosol samples. Molecular distributions of these compounds are roughly similar to those of wet precipitations. The concentration ranges of total diacids, ketoacids and dicarbonyls were 1150–3010, 265–479 and 69–105 ng m^{-3}, respectively. They accounted for 0.6–1.4% (av. 0.9%), 0.08–0.2% (av. 0.15%) and 0.04–0.21% (av. 0.09%) of total aerosol mass,

respectively. Interestingly, dicarboxylic acids comprise a significant fraction of aerosol TC and WSOC; 1.3–4.6%(av. 3.0%) of TC and 3.8–15% (av. 9%) of WSOC. These results suggest that diacids can be important contributor to DOC in wet precipitations. On the other hand, ketoacids accounted for less significant fraction of TC and WSOC: 0.2–0.9% (av. 0.6%) of aerosol TC and for 0.6–3.2% (av. 1.7%) of WSOC. By contrast, dicarbonyls accounted for only 0.1–0.5% of aerosol TC and 0.2–1.5% of WSOC. These water soluble compounds should partly contribute to the DOC in the wet precipitation samples.

The diacid molecular distributions in the present aerosol samples are similar to those reported in the central Tokyo by Kawamura and Ikushima (1993). As seen in Table 4, oxalic acid (C_2) was found to be the most abundant (51%) followed by malonic (C_3) or succinic (C_4) acid. The C_3 and C_4 diacids represents 12 and 11% of the total diacids, respectively. These three species accounted for 70% (av.) of total diacids detected. Phthalic acid was the forth most abundant followed by glutaric (C_5), azelaic and/or adipic as well as malic acid (hydroxy dicarboxylic acid). Interestingly, the relative abundance of shorter chain diacids (C_2, C_3) are lower in the winter than the summer samples. Thus, succinic acid is the second most abundant diacid (av. 11%) in February aerosols followed by malonic (av. 9%) whereas the opposite situation was observed for the samples collected in July. Azelaic acid represented 4% (av.) of the winter aerosols and 2% (av.) of those of summer time. This seems to indicate that strong solar radiations and subsequent oxidation reactions of precursors produce preferentially oxalic and malonic acid, being consistent without previous results (Kawamura and Ikushima, 1993).

Comparative distribution of dicarboxylic acids in wet precipitations and aerosols

The distributions of diacids in ambient aerosols and wet precipitation samples are not directly comparable; however, their molecular distribution and relative abundance in DOC (for the rains and snows), or in TC (for aerosols) may give us an insight on physicochemical processes or vertical distribution of polar organic compounds in the air column. Although oxalic acid was generally the predominant diacid in snow, rain and aerosol samples, its relative abundance in the total diacids showed a diversity; 28% (snow), 37% (rain) and 51% (aerosols), as stated above. As shown in Fig. 3, oxalic acid accounted for 34% of total diacids in the wet precipitation samples whereas this acid comprised 51% in the aerosol samples. The shorter chain aliphatic diacids (C_2 and C_3) are depleted in rain and snow samples: they represented 43 and 62% of total diacids in the wet precipitation and aerosol samples, respectively. The difference in the diacid distribution between the two sample types may suggest that (1) oxalic and malonic acids are depleted by selective degradation in the rain droplets or in the storage bottles, or (2) oxalic acid is enriched in the atmosphere near ground level and relatively depleted in upper levels of the troposphere.

Biological degradation of the oxalic acid after wet deposition is unlikely, because rainwater samples were protected from biological activity during sample collection and sample storage by mercuric chloride added to the samples. This consideration is also supported by the fact that C_2 diacid is also relatively depleted in snow/sleet samples (Table 3), in which biodegradation is very unlikely during the snow fall. Chemical (non-biological) degradation of oxalic acid cannot be excluded; however, it is not easy to explain the selective degradation of oxalic acid in the falling rain drops and during storage: samples were stored in the brown glass bottles in darkness. We feel that post-depositional depletion of oxalic and malonic acids during precipitation or sample storage is not the case. Thus, the latter case is more likely.

The aerosol samples were collected near the ground surface, whereas the rain droplets and snow flakes scavenge the dicarboxylic acids from the air column including upper levels of the troposphere (probably few hundred meters to few kilometers above the ground). Thus, the difference in the molecular distributions of diacids between wet precipitation and aerosol samples may reflect the difference in the diacid distributions in the ground level and upper levels of the

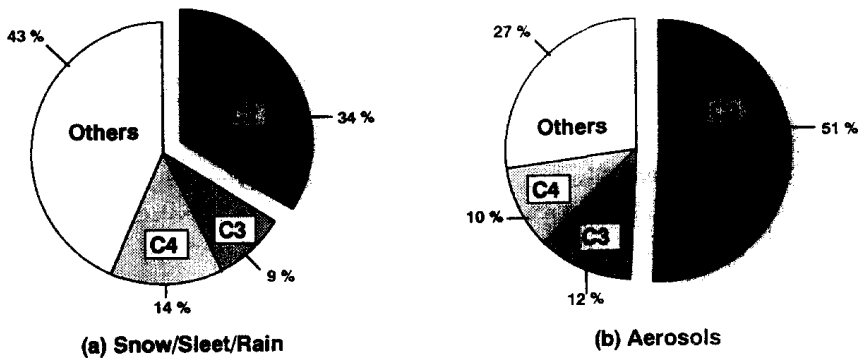

Fig. 3. Pie diagrams of the averaged relative abundance (%) of oxalic (C_2), malonic (C_3), succinic (C_4) and other dicarboxylic acids in (a) snow/sleet and rain samples ($n=9$), and (b) aerosol samples ($n=4$) collected in the Tokyo area.

troposphere. Although there is no comparison study on diacid distributions between the lower and upper troposphere, it is likely that oxalic acids are more extensively produced near the ground levels than the upper levels of the troposphere. Our previous observations of diacids near the ground surface of Tokyo atmosphere indicated that concentrations of dicarboxylic acids largely increased in the summer season with oxalic acid being predominant (C_2: 52% of total diacids for annual average, Kawamura and Ikushima, 1993). Major photochemical precursors of the oxalic acid have been considered as aromatic hydrocarbons such as benzene and toluene emitted from anthropogenic sources (Kawamura and Ikushima, 1993). Because these aromatic hydrocarbons are photochemically reactive, they may be mostly oxidized near the ground level and are unlikely transported high enough to the upper troposphere.

Although LMW diacids are mostly present as aerosol particles in the atmosphere (Kawamura and Kaplan, 1987), they could be partly present in the gaseous phase, in which case oxalic acid should be enriched compared to higher diacids. If this is the case, wet precipitation samples should show higher relative abundance of oxalic acid than aerosol samples because rain droplets and snow flakes scavenge, in addition to aerosols, gaseous diacids. However, such a result was not obtained in this study (see Fig. 3). Hence, our results indicate that the molecular distributions of dicarboxylic acids are not vertically homogeneous in the air column of the troposphere (from the ground to upper levels). A possible depletion of oxalic acid in the upper troposphere may also be caused by preferential degradation of oxalic acid, which is probably exposed to stronger solar radiation.

Relative abundance of polar compounds in DOC and wet scavenging process

The concentrations of major diacids and ketoacids generally decreased as a function of time during the precipitation event, except for the rain event II (1 August) whose precipitation rates largely changed during the rainfall (see Tables 2 and 3). These results suggest that diacids and ketoacids in the atmosphere are scavenged in an early stage of wet precipitation event. During the wet scavenging processes of these polar compounds, there seems no clear trend which suggests a systematical molecular discrimination. On the other hand, concentrations of dicarbonyls did not show a clear decreasing trend with time (Table 3), although their concentrations seemed to decrease with time in the rain event I. Interestingly, concentrations of diacids clearly decreased during the precipitation events as a function of time when diacid-carbon contents are normalized by DOC.

The C_2–C_9 diacid-carbon contents are also presented in Table 3. Total diacid-C range was 8.7–17 $\mu g\,C\,\ell^{-1}$ in the snow/sleet samples whereas that was 4–191 $\mu g\,C\,\ell^{-1}$ in the rain samples. Their relative abundance in DOC was 0.04–0.09% in the snow/sleet samples. By contrast, the relative abundance of diacid-C in DOC in the rainwater samples (0.33–2.1%) was much higher than those of the snow/sleet samples. The lower values in the snow/sleet samples are probably caused by the higher DOC values in the snow/sleet samples: snow flakes may more efficiently adsorb and scavenge non-polar to polar volatile organic compounds as well as particulate organic compounds than rain droplets do, as pointed out before. Figure 4 plots the relative abundance (%) of diacid-C, ketoacid-C and dicarbonyl-C contents in DOC of the precipitation samples as a function of time. The diacid-C/DOC decreased with time in all the precipitation events: for example, during rain event I, diacid-C/DOC decreased from the first rain (2%) to the fourth rain (0.3%). These results indicate that diacids which mostly exist as particles (Kawamura and Kaplan, 1987) are removed from the atmosphere during wet precipitation more efficiently than other water soluble organic compounds including volatile fatty acids and aldehydes.

Ketoacid-C/DOC ratios also showed a decreasing trend with time during precipitation events (Fig. 4). These results suggest that ketoacids are also preferentially scavenged from the air in a manner similar to diacids. By contrast, dicarbonyl-C/DOC ratios show a trend different from diacids and ketoacids. Their ratios remained rather constant in the snow/sleet event and largely increased in the second rain of rain event I (see Fig. 4). These results may suggest that wet scavenging process of glyoxal and methylglyoxal is different from diacids: the dicarbonyls may be significantly present in gaseous phase and their wet scavenging rate is less than that of diacids which are mostly present in particulate form. This is consistent with the results that glyoxal/oxalic acid ratios were greater in the wet precipitation samples (0.11–0.49, av. 0.33, except for rain I, fourth sample, Table 3) than the aerosol samples (0.03–0.09, av. 0.05, Table 4).

Aerosol particles are removed from the atmosphere by collisional capture during below-cloud (washout) scavenging (Warneck, 1988). By contrast, water-soluble gas components are scavenged by sorption in cloud and rain droplets, which is controlled by thermodynamic equilibrium between gas and liquid phases. Thus, particulate organic matter may be more efficiently scavenged than gaseous organic components. Aerosol particles which contain LMW diacids at a concentration level of few percent, should participate in the cloud condensation nuclei (CCN) processes because the diacids are very water soluble thus likely to interact with water vapor. Therefore, the diacids in the atmosphere probably act as CCN and are involved in the in-cloud (rainout) scavenging processes in the upper troposphere. We propose that dicarboxylic acids are active CCN species and participate in an early stage of wet precipitation processes. These processes can partly explain why dicarboxylic acid carbon contents normalized by DOC are higher in the early stage of wet precipitation (Fig. 4).

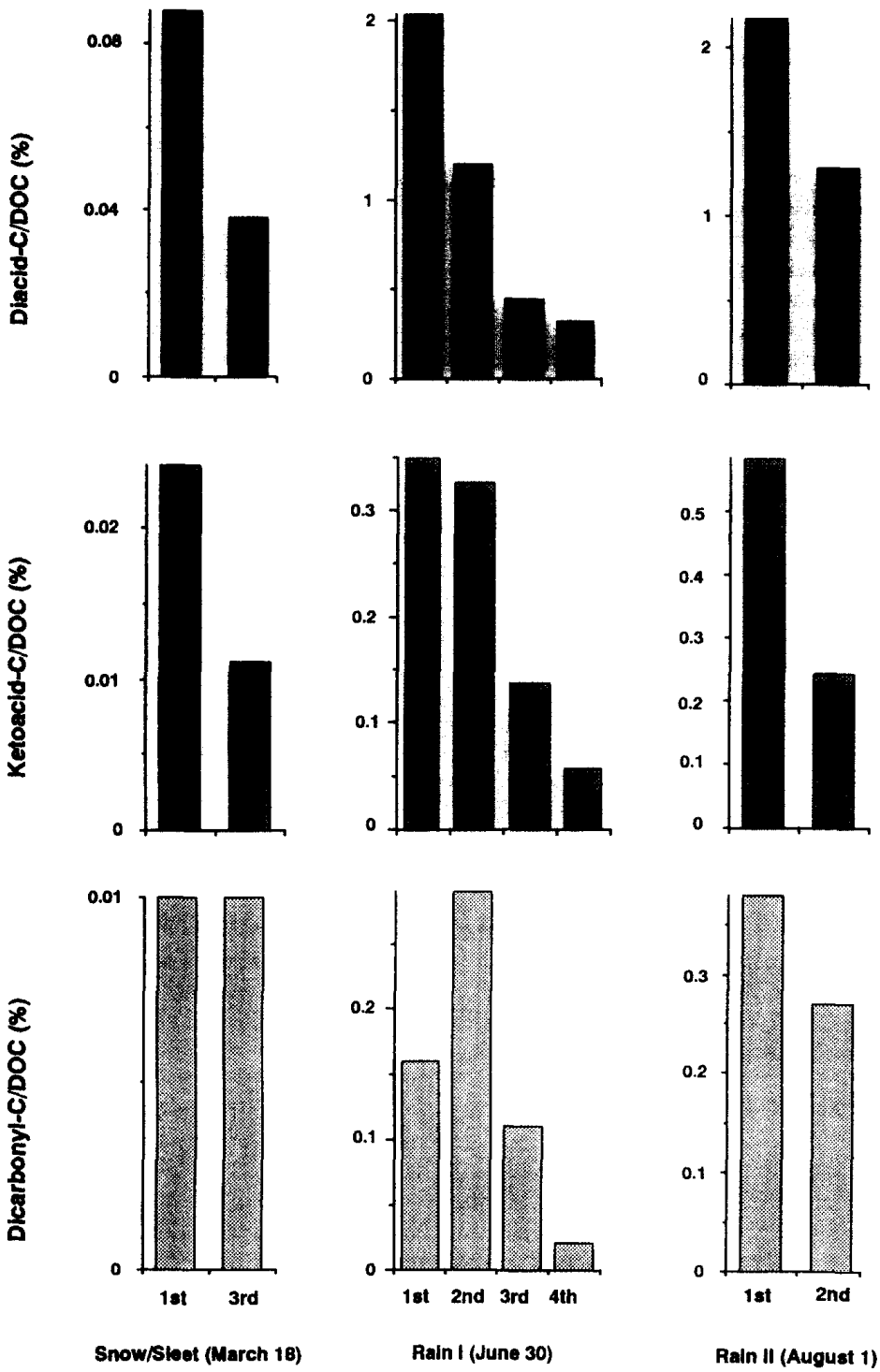

Fig. 4. Changes in relative abundance (%) of dicarboxylic acids, ketoacids and dicarbonyls in dissolved organic carbon (DOC) in snow/sleet and rain samples as a function of time during wet precipitation events.

SUMMARY AND CONCLUSION

Low molecular weight (C_2–C_9) dicarboxylic acids and related compounds have been detected in the snow/sleet and rain samples as well as aerosols collected from the urban atmosphere of Tokyo. Both wet precipitation and aerosol samples showed the predominance of oxalic acid (C_2); however, the diacid molecular distributions showed that, although they remained the most abundant, short chain diacids (C_2, C_3) are depleted in wet precipitations. This trend seems to indicate that dicarboxylic acid composition of the ground level aerosols is different from those of upper levels of the troposphere. The C_2 and C_3 diacids in the upper tropospheric aerosols may be relatively depleted, probably due to preferential photochemical degradation of these species.

Time series of rainwater samples showed that the diacid concentrations decreased as a function of time, suggesting that dicarboxylic acids are significantly

removed from the atmosphere by wet precipitation processes. Moreover, the relative abundance of dicarboxylic acid-carbon in dissolved organic carbon in wet precipitation samples decreased with time during rain events, suggesting that diacids are more effectively scavenged from the air by raindrops than other water-soluble organic compound classes such as aldehydes, ketones and volatile fatty acids. However, during wet precipitation events, systematic molecular fractionation was not observed in the distribution of diacids. This is consistent with that the diacids are present as particles in the atmosphere. Because of their water solubility and their significant concentration in the atmosphere, dicarboxylic acids may be important compound class which participate in in-cloud scavenging processes as CCN.

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