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## LOW MOLECULAR WEIGHT DICARBOXYLIC ACIDS AND RELATED POLAR COMPOUNDS IN THE REMOTE MARINE RAIN SAMPLES COLLECTED FROM WESTERN PACIFIC

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**Abstract**—During the western Pacific Ocean cruise of R/V Hakuho-Maru (20°N-40°S), fourteen rainwater samples were collected. They were studied by a capillary gas chromatography (GC) and GC-mass spectrometry (GC/MS) for the molecular distributions of C<sub>2</sub>–C<sub>10</sub>  $\alpha$ ,  $\omega$ -dicarboxylic acids and related polar compounds, i.e. ketoacids (C<sub>2</sub>–C<sub>9</sub>) and  $\alpha$ -dicarbonyls (C<sub>2</sub>–C<sub>3</sub>). Samples were also analysed for dissolved (DOC) and total organic carbon (TOC). Total diacid concentration range was 36–959  $\mu\text{g l}^{-1}$  and accounted for 3% (av.) of TOC (1.2–2.5  $\text{mgC l}^{-1}$ ), which is much higher than the previous numbers found in Tokyo rain samples (av. 1%). This indicates that low molecular weight dicarboxylic acids are an important class of organic compounds in the marine rains. All the samples showed that the smallest diacid (oxalic acid) which comprised 50% of the total diacids was the most abundant followed by malonic (C<sub>3</sub>) or succinic acid (C<sub>4</sub>). The shorter chain diacids (C<sub>2</sub>–C<sub>4</sub>) accounted for 63–90% (av. 80%) of total diacids and their relative abundances increase from the Northern to the Southern Hemisphere. These results suggest that shorter chain diacids are in part produced in the marine atmosphere by photochemical oxidation of organic matter through the intermediates such as ketoacids and dicarbonyls. The major portion of diacids and their precursors is probably derived from the Asian and Australian continents by a long-range transport.

### Texte

**Key word index:**  $\alpha$ ,  $\omega$ -dicarboxylic acids, ketoacids,  $\alpha$ -dicarbonyls, TOC, rainwaters, western Pacific.

### INTRODUCTION

Low molecular weight (LMW)  $\alpha$ ,  $\omega$ -dicarboxylic acids present in the atmosphere mainly originate from non-biological processes including incomplete combustion (Kawamura and Kaplan, 1987), ozonolysis and photooxidation of cyclic olefines and other organic compounds in the gaseous (Shuetzle *et al.*, 1975; Grosjean *et al.*, 1978; Grosjean and Friedlander, 1980; Norton *et al.*, 1983; Bandow *et al.*, 1985; Hatakayama *et al.*, 1985) and particulate phase (Kawamura and Gagosian, 1987; Stephanou, 1992; Stephanou and Stratigakis, 1993; Kawamura and Ikushima, 1993). In this manner, they have been reported as major organic compounds in urban (Cronn *et al.*, 1977; Kawamura and Kaplan, 1987; Sempéré and Kawamura, 1994), remote marine (Stephanou, 1992; Li and Winchester, 1993; Kawamura and Usukura, 1993) or polar aerosol samples (Kawamura *et al.*, 1992; 1996).

These water soluble compounds have been found at significant concentrations in wet precipitations from various locations (Lunde *et al.*, 1977; Norton *et al.*, 1983; Likens *et al.*, 1983; Kawamura and Kaplan, 1983; Kawamura *et al.*, 1985). However, to our knowledge, only few rainwater analyses were conducted by the use of BF<sub>3</sub>/*n*-butanol derivatization technique followed by gas chromatography (GC) determination which provides the molecular distributions of a homologous series of diacids (C<sub>2</sub>–C<sub>10</sub>) (Sempéré and Kawamura, 1994). At this time and among other techniques this method allows better recoveries especially for shorter chain diacids and permits the detection of  $\omega$ -oxocarboxylic acids (C<sub>2</sub>–C<sub>10</sub>), pyruvic acid and  $\alpha$ -dicarbonyls (C<sub>2</sub>–C<sub>3</sub>) as well (Kawamura and Usukura, 1993; Kawamura, 1993). These results indicated that among these water soluble compounds, shorter chain diacids, particularly oxalic acid, are the most abundant in the urban (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994; Khawaja, 1995) and marine aerosols (Kawamura and Usukura, 1993).

Determination of specific compounds in wet precipitations such as dicarboxylic acids can contribute

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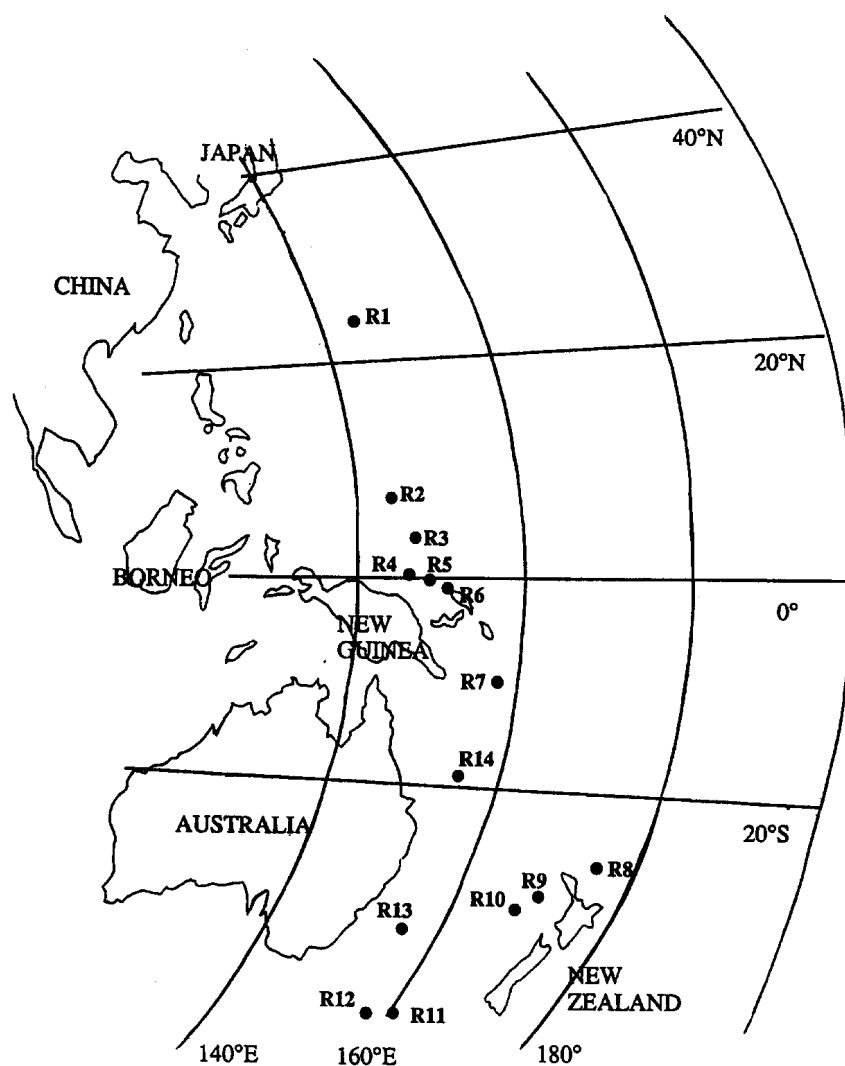


Fig. 1. Cruise track of R/V. Hakuho Maru: KH-92 started 16 September 1992 at Tokyo, Japan, and ended 26 October 1992 at Cairns, Australia. The circles indicate the sampling area for rainwater collection during the cruise.

to a better understanding of the transport of organic matter in the marine troposphere as well as to the heterogeneous oxidative processes such as oxidation/reduction of iron in the atmosphere (Zuo and Hoigné, 1992, 1994; Hoigné *et al.*, 1994). Moreover, LMW diacid emission and production represent a potential source of cloud condensation nuclei (Sempéré and Kawamura, 1994). However, only a few studies have been conducted on LMW diacids in remote marine atmosphere and there are no available data on the composition of  $C_2$ – $C_{10}$   $\alpha$ ,  $\omega$ -dicarboxylic acids and related polar compounds in rains for such environments. In this paper we report the detailed distribution of the LMW dicarboxylic acids, ketoacids and dicarbonyls in the marine rainwater samples collected from western Pacific Ocean. We discuss the sources of these compounds and formation mechanisms.

## EXPERIMENTAL

### Collection of rain samples

Fourteen rainwater samples (R1–R14) were collected at the upper deck of R/V Hakuho Maru (c. 14 m above the sea surface) during the KH92-4 cruise: August–October 1992. The cruise track is shown in Fig. 1. Rainwater samples were collected in a pre-cleaned brown glass bottle using a stainless steel rain collector with a cross-section of 2800 cm<sup>2</sup> and protected from biodegradation with HgCl<sub>2</sub> during sample collection. Sample storage was done at 4°C in darkness. The collected rainwater volumes and duration of rain ranged from 0.08 to 3.8 l and from 1 to 25.8 h, respectively. Table 1 presents sample informations.

### Determination of dicarboxylic acids and related compounds by GC and GC/MS

Rain 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 (BF<sub>3</sub>) in *n*-butanol (0.3 ml) to derive carboxyl and

Table 1. Total and dissolved organic carbon (TOC and DOC) in the wet precipitation samples collected from western Pacific atmosphere in 1992 and precipitation data

Sample ID	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14
Sampling date	Sept. 19	Sept. 21-22	Sept. 22	Sept. 22-23	Sept. 23	Sept. 23	Sep. 30-Oct.1	Oct. 6	Oct. 14	Oct. 15	Oct. 17	Oct. 17-18	Oct. 20-21	Oct. 25
Time	11:00-07:00	11:00-07:00	20:00-21:00	21:00-07:00	10:00-12:00	13:00-15:00	20:00-01:00	Oct. 6	05:00-10:00	06:10-08:50	10:50-14:25	15:50-13:00	04:40-06:30	11:00-11:30
Collection time (h)		20	1	10	2	2	5		5	2.66	3.58	20.8	25.8	1.50
Volume collected (ℓ)	0.08		3.8	1.0	1.0	0.30	0.50	0.10	0.15	0.30	0.70	2.8	1.8	0.20
Rainfall intensity (mm h <sup>-1</sup> )		0.09	13.6	0.36	1.80	0.55	0.36		0.10	0.41	0.69	0.05	0.25	0.47
TOC (mgC ℓ <sup>-1</sup> )	ND	ND	1.31	ND	ND	ND	ND	ND	ND	ND	ND	2.53	1.23	1.65
DOC (mgC ℓ <sup>-1</sup> )	ND	ND	1.20	ND	ND	ND	ND	ND	ND	ND	ND	2.38	1.14	1.43
POC (mgC ℓ <sup>-1</sup> )	ND	ND	0.11	ND	ND	ND	ND	ND	ND	ND	ND	0.15	0.09	0.22
DOC/TOC (%)			92									94	93	87
TOC flux (mgC m <sup>-2</sup> h <sup>-1</sup> )			17.8									1.22	0.31	0.79

POC: particulate organic carbon.  
ND: Not determined.

aldehyde groups to the butyl esters and dibutoxyacetals, respectively. The derivatives 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 with 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 was performed by a comparison of GC retention times with those of authentic standards. Identification of diacids and ketoacids was confirmed by a GC/MS (Finnigan-MAT ITS-40).

Recoveries of oxalic acid were 70% whereas those of malonic, succinic and adipic acids were 77, 86 and 90%, respectively. Procedural blanks run with organic free pure water showed only small peaks of oxalic, pyruvic and phthalic acid derivatives in the GC chromatograms; they presented less than 4% of the actual samples. Analytical errors in the determination of diacids were within 5% for dicarboxylic acids, 15% for ketoacids, 7% for glyoxal and 26% for methylglyoxal based on duplicates analysis of the rain sample R1. The concentrations of the acids presented here are corrected for the procedural blanks. The organic free water was prepared by boiling Milli Q water with KMnO<sub>4</sub> to oxidise organic impurities followed by subsequent distillation.

#### Measurement of DOC and TOC in rain samples

Wet precipitation samples were gently filtered with an all-glass filter holder through a pre-heated (500°C) Pallflex quartz fibre filter. An aliquot of unfiltered and filtered samples were taken in the pre-heated (450°C) glass screw vials (10 ml) with a Teflon lined cap. After acidification (pH < 2) with 1.2M HCl solution (50 μl), the samples were bubbled with pure nitrogen gas for 5 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 quartz wool impregnated with platinum. Injections were repeated five times for each sample. The data sets having the highest and lowest values were discarded, whereas the remaining three values were averaged and used for TOC and DOC calculation. The analytical precision of the procedure was within 2%. Particulate organic carbon (POC) was calculated by the difference between TOC and DOC values. The carbon blank of the water used for the standard solutions was estimated to be 120 μg by injections of different amount of pure water (10–50 μl) and subtracted for the standards. Unfortunately, we lost some samples for TOC measurements and are able to present only four remote marine (R3, R12 and R13 and R14) rainwater samples (Table 1).

## RESULTS AND DISCUSSION

### TOC, DOC and POC in rain samples

Table 1 gives results of total and dissolved organic carbon contents in the rain samples as well as precipitation data. TOC concentrations were found to be 1.2–2.5 mgC ℓ<sup>-1</sup> (*n* = 4; av. 1.6 ± 0.6). By contrast, previous results from Tokyo rains (Sempéré and Kawamura, 1994) showed higher TOC values ranging from 1.2 to 15.4 mgC ℓ<sup>-1</sup>. Rain organic matter collected from remote sites probably originated from the continent-derived dusts and gases through long-range atmospheric transport (Simoneit, 1977; Duce and Duursma, 1977; Atlas and Giam, 1981; Gagosian *et al.*, 1981, 1987; Kawamura and Gagosian, 1987) but

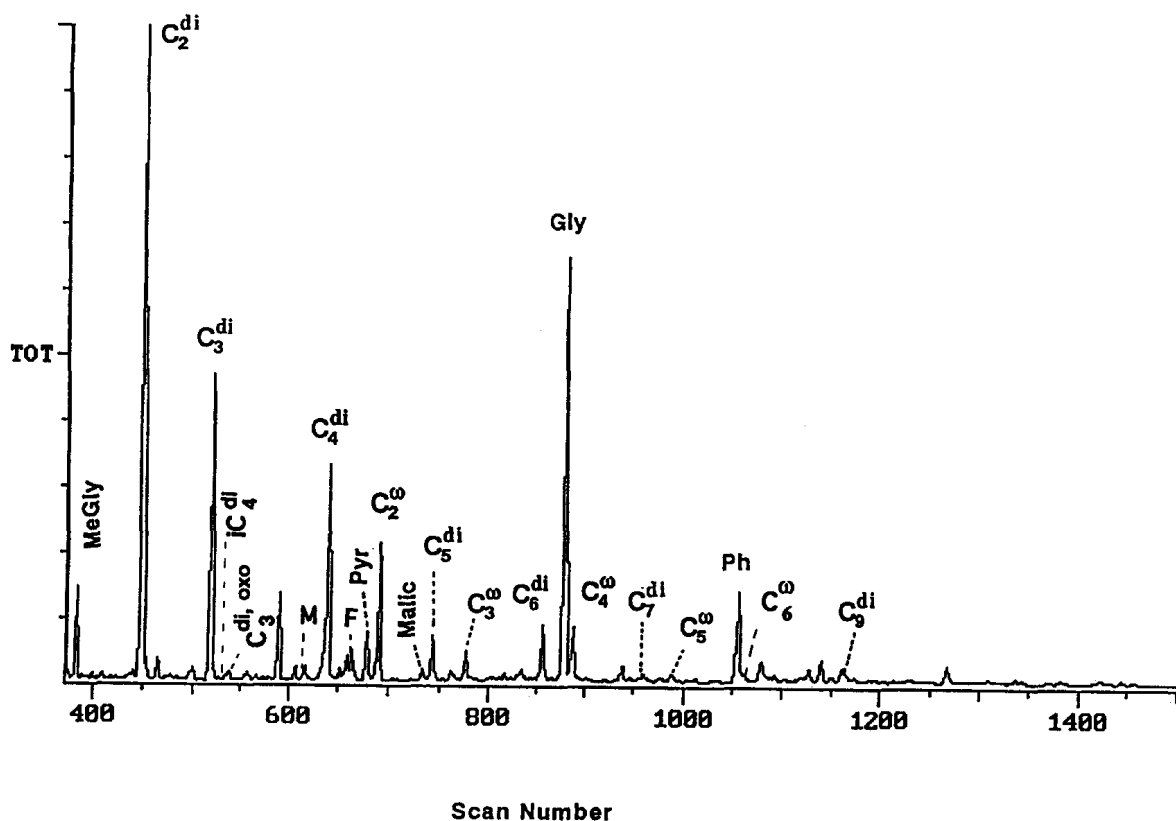


Fig. 2. A reconstructed total ion chromatogram (RIC) of the derivatives of dicarboxylic acids, ketocarboxylic acids and dicarbonyls isolated from the marine rain sample collected from the South Pacific (R13), October 1992. For abbreviation see Table 2.  $C_n$  means dicarboxylic acid with  $n$  carbon numbers.  $iC_n$  indicates branched chain (iso) diacid. M and F are abbreviations of unsaturated diacids: maleic and fumaric acids, respectively.  $C_n\omega$  indicates  $\omega$ -oxocarboxylic acid with  $n$  carbon numbers. Me-Gly, Pyr, Malic, Gly, Ph mean methylglyoxal, pyruvic, malic, glyoxylic and phthalic acids, respectively.

also from the ocean itself by direct sea-air gas exchange (Liss, 1973; Ratte *et al.*, 1993) as well as by sea-salt spray and bubble bursting mechanisms (Woodcock, 1953; Barger and Garret, 1970; Marty *et al.*, 1979).

Organic carbon in the precipitation was found mostly in the dissolved form (av. DOC % in TOC =  $92 \pm 3$ , see Table 1) being similar to the number (70–99%) reported for continental rains (urban and rural) (Liljestrand and Morgan, 1980; Likens *et al.*, 1983; Kawamura and Kaplan, 1991; Sempéré and Kawamura, 1994). However, the 'dissolved' phase was here operationally defined as those passing through the quartz fibre filter (effective retention =  $0.5 \mu\text{m}$ ) thus, besides gaseous and truly dissolved organic compounds, rain DOC may comprise a continuum of small particles in colloidal size range as well. As seen in Table 1, TOC values are generally higher when rainfall intensity is low, indicating that weaker rains scavenge organic materials more efficiently per unit of precipitation volume. Based on our limited numbers of TOC measurements, organic carbon flux was calculated to range from  $0.31 \text{ mgC m}^{-2} \text{ h}^{-1}$  (duration of 25.8 h) to  $17.8 \text{ mgC m}^{-2} \text{ h}^{-1}$  (duration of 1 h). For Enewetak Atoll rain samples (western North Pacific) which showed similar DOC values,

Zafiriou *et al.* (1985) estimated the wet plus dry deposition flux of  $0.63 \text{ gC m}^{-2} \text{ yr}^{-1}$ , being in the same order of magnitude as the flux of organic carbon to the deep sea in the north central Pacific Ocean (Smith, 1987). These results suggest that rainwaters may provide locally and temporally significant amount of organic carbon to the surface seawater in the Pacific Ocean.

#### Identification and origin of dicarboxylic acids, ketoacids and dicarbonyls in rain samples

Figure 2 shows a reconstructed total ion chromatogram of derivatives of dicarboxylic acids, ketoacids and dicarbonyls isolated from the rain sample R13. A homologous series of straight-chain saturated ( $C_2$ – $C_{10}$ ) dicarboxylic acids were identified in all the samples together with branched-chain (iso) saturated (methylmalonic:  $C_4$ , methylsuccinic:  $C_5$ ), aliphatic unsaturated (maleic: cis  $C_4$ ; fumaric: trans  $C_4$ ), aromatic (phthalic:  $C_8$ ), oxo (oxomalonic:  $C_3$ ; 4-oxopimelic:  $C_7$ ) and hydroxy (malic:  $C_4$ ) diacids. The distribution of normal saturated diacids is generally characterised by a predominance of oxalic acid followed by either malonic ( $C_3$ ) or succinic ( $C_4$ ) acid. The diacids with more carbon numbers are less abundant (Fig. 2). Interestingly, similar chain-length distribution has

been reported in urban rain and snow/sleet samples (Sempéré and Kawamura, 1994). Dicarboxylic acids have been considered to be mainly produced by secondary photochemical reactions occurring on anthropogenic and natural organic compounds (Grosjean *et al.*, 1978; Grosjean and Friedlander, 1980; Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1990) as well as direct emission from incomplete oxidation of fossil fuels during combustion processes (Kawamura and Kaplan, 1987). In the marine atmosphere, C<sub>6</sub>–C<sub>11</sub> diacids with a predominance of C<sub>9</sub> are produced by the photooxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987).

In addition to diacids, low molecular weight ketoacids and dicarbonyls were also detected in the rain samples. The ketoacids detected include pyruvic acid (C<sub>3</sub>) and a homologous series of ω-oxocarboxylic acids (C<sub>2</sub>–C<sub>9</sub>). The group of dicarbonyls includes glyoxal (C<sub>2</sub>) and methylglyoxal (C<sub>3</sub>). Dicarbonyls may be intermediates in the photochemical oxidation reactions of aromatic hydrocarbons to oxalic acid (Norton *et al.*, 1983). Diacids are *c.* 9 times more abundant than ketoacids which are considered as some of their precursors. On the other hand, a previous study reported a lower diacid/ketoacid ratio for snow/sleet (3) and rain (5) samples collected in Tokyo area (Sempéré and Kawamura, 1994). Some ketoacids (e.g. ω-oxoacids) are probably intermediate products in the photochemical oxidations of organic compounds such as unsaturated fatty acids which also produce dicarboxylic acids (Kawamura and Gagosian, 1987). Therefore, it is likely that stronger photochemical oxidative processes are responsible for higher diacid/ketoacid ratios found in the marine rainwaters than in the continental rains.

#### *Concentration levels of diacids, ketoacids and dicarbonyls in the western Pacific rainwaters*

Table 2 gives concentrations of individual diacid as well as ketoacid and dicarbonyl in wet precipitation samples. Concentration range of total dicarboxylic acids (C<sub>2</sub>–C<sub>10</sub>) was 35.9–959 μg ℓ<sup>-1</sup> (av. 237 μg ℓ<sup>-1</sup>) which is similar to those reported for the urban rains (12.2–538 μg ℓ<sup>-1</sup>, av. 186 μg ℓ<sup>-1</sup>; Sempéré and Kawamura, 1994). Significantly high concentrations (93.2–626 μg ℓ<sup>-1</sup>) were obtained for rain samples collected in the western South Pacific (R6–R13; Fig. 3) and close to the equator (R5; 148 μg ℓ<sup>-1</sup>). The highest concentration (959 μg ℓ<sup>-1</sup>) was obtained for the sample (R1) collected in the North Pacific. This area is known to receive high input of windblown dust from the deserts in China (Duce *et al.*, 1990). However, the diacids accounted for 1–5% (av. 3%) of DOC in the remote marine rainwaters being *c.* 3 times higher than those (0.3–2%; av. 1%) reported in the urban rains (Sempéré and Kawamura, 1994). These results are consistent with our aerosol studies (Sempéré and Kawamura, in press) and suggest that dicarboxylic acids detected in the western Pacific atmosphere are significantly produced in the marine atmosphere

probably by the photochemical oxidation of various organic compounds including hydrocarbons, aldehydes and carboxylic acids. Based on precipitation data, a flux of the diacids was calculated to range from 4.51 to 487 μg m<sup>-2</sup> h<sup>-1</sup>, (av. 122 μg m<sup>-2</sup> h<sup>-1</sup>).

Ketoacid concentration range is 3.51–106 μg ℓ<sup>-1</sup> (av. 29.4 μg ℓ<sup>-1</sup>) being in the same order of magnitude as those reported in continental rain samples from Tokyo (3.73–93.5 μg ℓ<sup>-1</sup>; av. 40.4 μg ℓ<sup>-1</sup>). The highest value was observed in the South Pacific sample (R10: 106 μg ℓ<sup>-1</sup>). This feature was mainly due to the high content of pyruvic acid (87.2 μg ℓ<sup>-1</sup>) whereas ω-oxoacids showed a concentration maximum in the R11 sample (32.1 μg ℓ<sup>-1</sup>). Total ketoacids accounted for 0.2–0.6% (av. 0.4%) of DOC which is higher than the value found for Tokyo rainwater samples (0.06–0.6%; av. 0.3%; Sempéré and Kawamura, 1994), being consistent with the case of diacid considerations. Flux of ketoacids was calculated to range from 0.59 to 82.2 μg m<sup>-2</sup> h<sup>-1</sup> (av. 21.3 μg m<sup>-2</sup> h<sup>-1</sup>).

Concentrations of dicarbonyls were lower than diacids as well (Table 2; Fig. 3): their concentration range is 0.69–37.8 μg ℓ<sup>-1</sup> (av. 11.8 μg ℓ<sup>-1</sup>) being in the same order of magnitude with that reported for the Tokyo rain samples (0.57–88.8 μg ℓ<sup>-1</sup>; av. 28.1 μg ℓ<sup>-1</sup>). They accounted for 0.1–0.7% (av. 0.4%) of DOC which is twice the value reported for the Tokyo rains (Sempéré and Kawamura, 1994). Higher dicarbonyl concentrations were observed in the samples collected in the higher latitudes of the Southern Hemisphere (e.g. R11–R13 : 16.3–37.8 μg ℓ<sup>-1</sup>). Glyoxal was more abundant than methylglyoxal in the South Pacific and vice versa in the North Pacific. Based on the concentration and precipitation data, a flux of the dicarbonyls was calculated to range from 0.20 to 42.2 μg m<sup>-2</sup> h<sup>-1</sup> (av. 10.6 μg m<sup>-2</sup> h<sup>-1</sup>).

#### *Molecular distribution of dicarboxylic acids, ketoacids and dicarbonyls in the western Pacific atmosphere*

The molecular distributions of dicarboxylic acids in the western Pacific rainwaters were characterised by a predominance of shorter chain diacids. Oxalic acid (C<sub>2</sub>) was the most abundant species comprising 39–64% (av. 50%) of the total diacids detected (Table 3, Fig. 4a). Preferential photochemical production of oxalic acid has been observed in the urban atmosphere where its concentration is well correlated with oxidant concentrations (Kawamura and Ikushima, 1993). Oxalic acid produced by the oxidation of many precursors containing carbon number > C<sub>2</sub> is an end product of the photochemical oxidation reactions and can be accumulated in the atmosphere (Kawamura and Ikushima, 1993). The predominance of oxalic acid has been observed in the urban rain and snow samples and ice/snow samples from Greenland. However, the relative abundance of oxalic acid in the total diacids (av. 50%) in the remote marine rainwaters is much higher than those in urban rain (37%), snow/sleet (28%) samples (Sempéré and Kawamura, 1994) and Greenland ice/snow samples (28%) (Kawamura

Table 2. Concentrations of dicarboxylic acids and related polar compounds in the rainwater samples collected from western Pacific atmosphere in 1992

Samples ID	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	Av.
Date	Sep.19	Sep.21-22	Sep.22	Sep.22-23	Sep.23	Sep.23	Sep.30-Oct.1	Oct.6	Oct.14	Oct.15	Oct.17	Oct.17-18	Oct.20-21	Oct.25	
<b>Diacids (<math>\mu\text{g}\ell^{-1}</math>)</b>															
Oxalic, C <sub>2</sub>	461	27.5	18.7	26.9	59.6	13	57.9	44.7	398	48.0	119	131	74.9	84.0	123
Malonic, C <sub>3</sub>	109	1.96	2.47	2.47	21.3	25.9	16.8	13.7	71.5	8.25	49.6	44.8	25.3	19.3	30.1
Methylmalonic, iC <sub>4</sub>	2.18	0.00	0.14	0.17	0.97	0.99	0.41	0.27	1.58	0.33	2.92	2.34	0.90	0.96	1.01
Oxomalonic, C <sub>3</sub>	5.32	0.35	0.00	0.00	0.59	0.96	0.29	0.32	3.29	0.68	1.17	0.84	0.51	1.12	1.14
Maleic, uC <sub>4</sub>	7.50	0.29	0.22	0.65	6.34	1.61	1.38	1.97	4.45	1.11	3.75	3.20	1.22	0.92	2.17
Succinic, C <sub>4</sub>	88.2	5.74	4.26	6.34	20.1	24.8	11.5	13.0	57.7	13.2	53.0	40.7	19.9	22.6	27.8
Methylsuccinic, iC <sub>5</sub>	5.72	0.15	0.24	0.33	0.82	0.99	0.46	0.49	1.89	1.60	4.92	4.07	1.50	1.90	1.87
Fumaric, uC <sub>4</sub>	13.5	0.62	0.38	0.60	1.68	2.85	0.57	0.74	5.35	1.71	1.96	1.48	3.06	1.78	2.66
Malic, hC <sub>4</sub>	1.09	0.23	0.35	0.00	0.57	1.91	0.51	0.32	0.45	3.14	0.26	0.18	0.05	0.04	0.66
Glutaric, C <sub>5</sub>	15.2	2.04	1.19	1.32	3.97	5.22	2.45	2.35	12.5	5.49	9.56	6.19	3.47	3.87	5.45
Adipic, C <sub>6</sub>	10.4	2.97	3.03	1.75	3.93	7.85	3.93	2.82	9.78	10.8	3.36	2.34	5.67	2.93	5.20
Pimelic, C <sub>7</sub>	11.9	1.04	0.65	0.56	1.78	2.43	1.21	0.74	6.74	1.95	1.10	0.70	0.89	0.82	2.36
Suberic, C <sub>8</sub>	10.8	1.42	1.19	0.94	2.08	3.75	2.23	1.52	5.60	6.59	1.02	0.86	0.98	0.95	2.91
Phthalic, C <sub>8</sub>	197	3.69	0.40	2.99	19.7	19.6	7.42	7.16	38.8	10.4	6.07	3.74	15.1	6.37	24.5
4-Oxopimelic, C <sub>7</sub>	8.18	0.47	0.21	0.30	0.77	1.87	0.57	0.39	3.18	0.23	3.71	2.28	1.14	0.85	1.80
Azelaic, C <sub>9</sub>	9.65	1.78	2.32	1.76	3.05	4.95	3.92	2.28	4.70	9.38	1.27	1.36	2.09	2.34	3.68
Sebacic, C <sub>10</sub>	1.60	0.26	0.15	0.23	0.42	0.77	0.59	0.37	1.47	1.30	0.10	0.10	0.32	0.30	0.58
Subtotal	959	50.5	35.9	47.4	148	219	112	93.2	626	124	262	246	157	151	237
Total diacid-C ( $\mu\text{gC}\ell^{-1}$ )	359	18.2	12.9	16.7	55.5	77.9	39.5	33.2	206	49.1	89.8	81.0	55.9	50.8	83.8
Diacid flux ( $\mu\text{g m}^{-2}\text{h}^{-1}$ )	NM	4.51	487	16.9	264	117	40.0	NM	67.1	50.0	183	118	39.1	71.9	122
<b>Ketoacids (<math>\mu\text{g}\ell^{-1}</math>)</b>															
Pyruvic, C <sub>3</sub>	8.27	2.41	2.19	0.64	10.2	15.4	3.60	5.30	3.26	87.2	11.8	10.0	3.39	0.97	11.9
Glyoxylic, C <sub>2</sub>	49.9	2.15	1.91	1.13	11.6	14.9	8.47	7.50	17.8	9.92	21.4	12.7	6.71	4.62	12.2
3-Oxopropanoic, C <sub>3</sub>	2.51	0.44	0.60	1.16	0.97	0.89	0.55	0.54	0.59	0.51	0.94	3.96	0.76	0.45	1.07
4-Oxobutanoic, C <sub>4</sub>	5.25	1.29	0.94	0.47	2.68	3.61	1.07	0.63	2.63	3.24	7.97	7.28	3.87	1.74	3.08
5-Oxopentanoic, C <sub>5</sub>	0.21	0.28	0.19	0.09	0.04	0.77	0.28	0.21	1.43	1.18	0.91	0.83	0.61	0.37	0.56
6-Oxohexanoic, C <sub>6</sub>	0.00	0.09	0.14	0.02	0.22	0.68	0.04	0.07	0.16	2.61	0.87	0.67	0.19	0.03	0.43
9-Oxononanoic, C <sub>9</sub>	0.51	0.00	0.09	0.00	0.06	0.11	0.03	0.00	0.07	1.03	0.02	0.14	0.03	0.05	0.16
Subtotal	66.7	6.65	6.05	3.51	25.76	36.3	14.0	14.2	26.0	106	43.9	35.6	15.6	8.22	29.4
Total ketoacid-C ( $\mu\text{gC}\ell^{-1}$ )	23.5	2.66	2.43	1.38	9.77	14.0	5.13	5.26	9.46	43.3	16.8	14.2	6.14	3.13	11.3
Ketoacid flux ( $\mu\text{g m}^{-2}\text{h}^{-1}$ )	NM	0.59	82.2	1.35	46.0	19.5	5.01	NM	2.77	42.6	30.6	17.1	3.87	3.91	21.3
<b>Dicarbonyls (<math>\mu\text{g}\ell^{-1}</math>)</b>															
Methylglyoxal, C <sub>3</sub>	8.95	1.26	1.98	0.48	3.77	6.98	1.62	3.21	5.46	0.11	8.72	16.0	5.21	4.09	4.93
Glyoxal, C <sub>2</sub>	7.94	0.97	1.13	0.21	11.5	7.82	2.16	3.67	8.09	0.95	18.8	21.8	11.1	4.81	6.87
Subtotal	16.9	2.24	3.11	0.69	15.3	14.8	3.78	6.88	13.6	1.06	27.5	37.8	16.3	8.91	11.8
Total dicarbonyl-C ( $\mu\text{gC}\ell^{-1}$ )	7.76	1.03	1.46	0.33	6.66	6.73	1.70	3.12	6.08	0.45	12.1	17.0	7.18	4.04	5.31
Dicarbonyl flux ( $\mu\text{g m}^{-2}\text{h}^{-1}$ )	NM	0.20	42.2	0.25	27.3	7.93	1.35	NM	1.45	0.43	19.2	18.2	4.05	4.24	10.6

i: iso; u: unsaturated; h: hydroxy; NM: not measured.

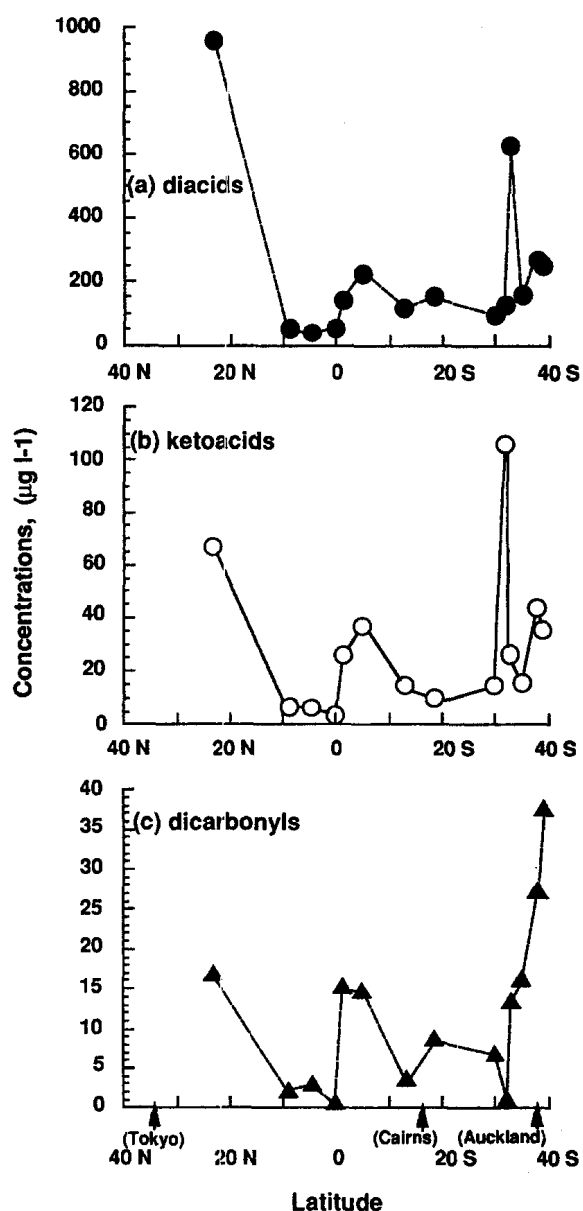


Fig. 3. Latitudinal distribution of the dicarboxylic acid (a), ketoacid (b) and dicarbonyl (c) concentrations in the western Pacific rainwater samples, September–October 1992.

and Yasui, 1991). These results suggest that photochemical reactions to produce oxalic acid is more significant in the marine atmosphere than continental air.

Interestingly, oxalic acid has been found in eastern Pacific Ocean waters by the use of HPLC (Steinberg and Bada, 1984). Unfortunately, these authors did not collect surface waters but reported oxalic acid concentrations of  $c. 10 \mu\text{g l}^{-1}$  at 75 m depth. They considered that oxalic acid is a product and substrate of marine bacteria. However, concentrations of oxalic acid in the western Pacific rainwaters were found to be 2–40 times higher than those reported in seawater, suggesting that sea-to-air transport of oxalic acid is not an important process.

Table 3. Relative abundance (%) of dicarboxylic acids and related polar compounds in the rainwater samples ( $n = 14$ ) collected from western Pacific atmosphere in 1992

Classes of compounds	Range	Average
<b>Diacids (%)</b>		
Oxalic, C <sub>2</sub>	39–64	50 ± 6
Malonic, C <sub>3</sub>	3.9–19	12 ± 5
Methylmalonic, iC <sub>4</sub>	0.0–1.1	0.5 ± 0.3
Oxomalonic, C <sub>3</sub>	0.0–0.7	0.4 ± 0.2
Maleic, uC <sub>4</sub>	0.6–4.3	1.2 ± 10
Succinic, C <sub>4</sub>	9.2–20	13 ± 3
Methylsuccinic, iC <sub>5</sub>	0.3–1.9	0.8 ± 0.5
Fumaric, uC <sub>4</sub>	0.5–2.0	1.1 ± 0.4
Malic, hC <sub>4</sub>	0.0–2.5	0.5 ± 0.6
Glutaric, C <sub>5</sub>	1.6–4.0	2.8 ± 1
Adipic, C <sub>6</sub>	1.0–8.7	3.6 ± 2
Pimelic, C <sub>7</sub>	0.3–2.0	1.1 ± 1
Suberic, C <sub>8</sub>	0.4–3.3	1.7 ± 1
Phthalic, C <sub>8</sub>	1.1–21	7.4 ± 5
4-Oxopimelic, C <sub>7</sub>	0.2–1.4	0.7 ± 0.3
Azelaic, C <sub>9</sub>	0.5–7.6	2.7 ± 2
Sebacic, C <sub>10</sub>	0.04–1.1	0.4 ± 0.2
Total	100	
<b>Ketoacids (%)</b>		
Pyruvic, C <sub>3</sub>	12–83	31 ± 18
Glyoxylic, C <sub>2</sub>	9.4–75	45 ± 16
3-Oxopropanoic, C <sub>3</sub>	0.5–33	6.7 ± 8
4-Oxobutanoic, C <sub>4</sub>	3.1–25	13 ± 7
5-Oxopentanoic, C <sub>5</sub>	0.2–4.5	2.5 ± 2
6-Oxohexanoic, C <sub>6</sub>	0.0–2.5	1.2 ± 1
9-Oxononanoic, C <sub>9</sub>	0.0–1.5	0.4 ± 0.4
Total	100	
<b>Dicarbonyls (%)</b>		
Methylglyoxal, C <sub>3</sub>	10–69	43 ± 15
Glyoxal, C <sub>2</sub>	31–90	57 ± 15
Total	100	

i: iso. u:unsaturated. h: hydroxy.

The second most abundant species was either succinic (C<sub>4</sub>), malonic (C<sub>3</sub>) or phthalic acid (C<sub>8</sub>) followed by glutaric (C<sub>5</sub>), adipic (C<sub>6</sub>) and azelaic (C<sub>9</sub>) acids (Fig. 4). The C<sub>4</sub> diacid comprised 9–20% (av. 13%) whereas malonic acid comprised 4–19% (av. 12%) of the total diacids (Table 3). Shorter chain diacids (C<sub>2</sub>–C<sub>4</sub>) accounted for  $c. 80\%$  of the total diacids and their relative abundances increase from the Northern to the Southern Hemisphere (Fig. 5). These results suggest that during long-range transport, photochemical oxidation of organic matter produced preferentially short chain diacids (C<sub>2</sub>–C<sub>4</sub>). Actually, in the marine atmosphere, volatile fatty acids with carbon numbers  $> C_4$  as well as mid-chain 4-oxo ketocarboxylic acids which are both present in the marine atmosphere (Kawamura and Gagosian, 1988; 1990) may serve as precursor compounds of succinic acid. Conversely, hydroxylation of succinic acid produces malic acid which is further decomposed to malonic acid (Kawamura and Ikushima, 1993). Some of these species may further be oxidised to result in oxalic acid in the remote marine atmosphere.

Phthalic (C<sub>8</sub>), glutaric (C<sub>5</sub>) and azelaic acids (C<sub>9</sub>) accounted for 1–21% (av. 7%), 2–4% (av. 3%) and



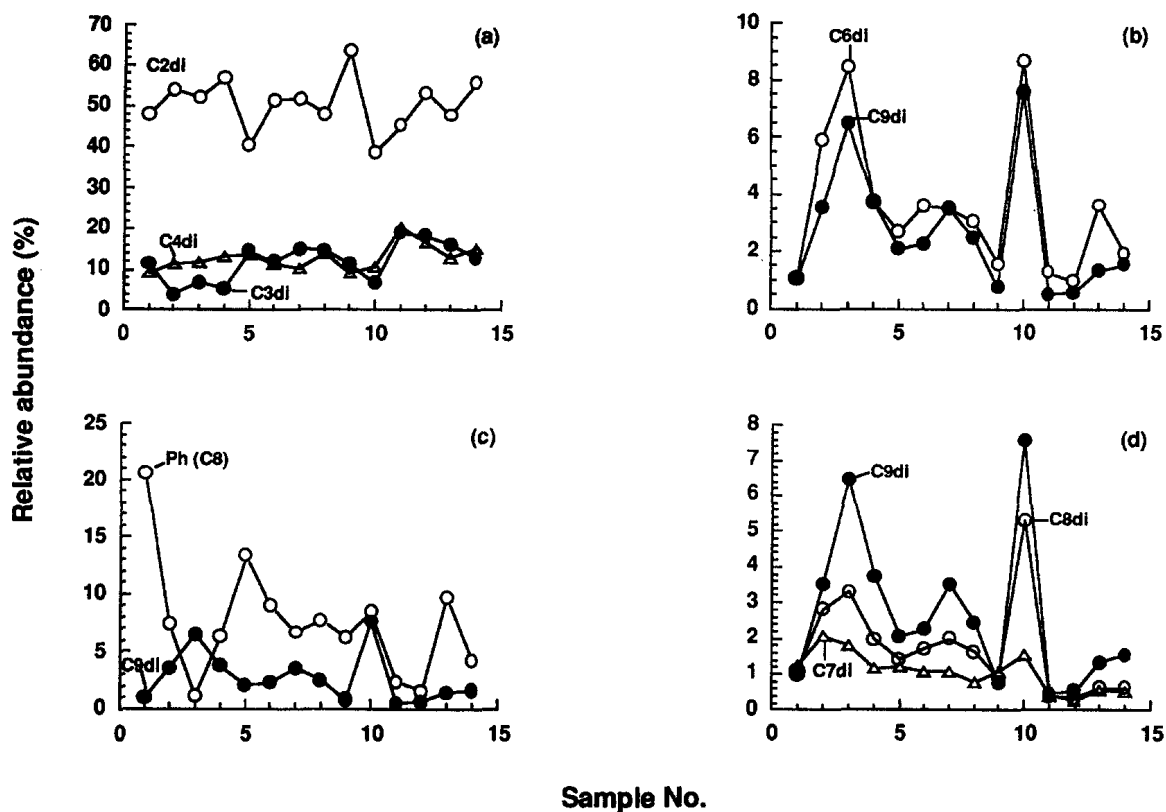


Fig. 4. Relative abundance of individual dicarboxylic acids in the western Pacific rainwater samples, September–October 1992: (a) oxalic acid ( $C_2$ ), malonic ( $C_3$ ) and succinic acids ( $C_4$ ); (b) adipic ( $C_6$ ) and azelaic acids ( $C_9$ ); (c) phthalic ( $C_8$ ) and azelaic acids; (d) pimelic acid ( $C_7$ ), suberic ( $C_8$ ) and azelaic acids.

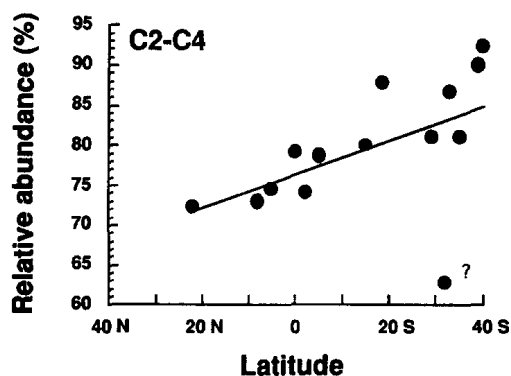


Fig. 5. Latitudinal changes in the relative abundance (%) of cumulated  $C_2$ – $C_4$  dicarboxylic acids including oxalic, malonic, methylmalonic, oxomalonic, maleic and succinic acids in the total diacids ( $C_2$ – $C_{10}$ ) in the western Pacific rainwater samples, September–October 1992.

0.5–8% (av. 3%) of the total diacid, respectively. Interestingly, phthalic acid was the second most abundant in the R1 sample (21%) whereas it represents less than 10% in the other marine rains (Table 3; Fig. 4c). Ester forms of this compound are used as plasticisers. Phthalic acid has been reported in high concentrations in Los Angeles (Kawamura *et al.*, 1985; Simoneit and Mazurek, 1989) and Tokyo aerosol

samples (Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994) as well as in Tokyo precipitation samples (Sempéré and Kawamura, 1994). This aromatic acid is potentially derived by the atmospheric oxidation of polynuclear aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993). Our results suggest that an anthropogenic source is more significant in western North Pacific (R1) well known to receive dust particles from China and other Asian countries (Duce *et al.*, 1990). However, marine sources producing phthalic acid cannot be precluded because phthalic acid was abundantly detected in the remote marine rainwaters.

The  $C_9$  diacid has been considered as a unique photochemical oxidation product of biogenic unsaturated fatty acids which contain a double bond predominantly at  $C_9$  position (Kawamura and Kaplan, 1983; Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1987). Relative abundance of azelaic acid in the total diacids ranged from *c.* 0.5% (R11) to *c.* 8% (R10). Interestingly, relative abundance of  $C_9$  diacid showed a negative correlation with that of phthalic acid in the samples (R1–R7) collected in the Northern Hemisphere and equatorial Pacific (Fig. 4c). On the other hand, glutaric ( $C_5$ ) and adipic ( $C_6$ ) acids have been reported as ozone oxidation products of cyclohexene (Grosjean *et al.*, 1978; Hatakeyama *et al.*,

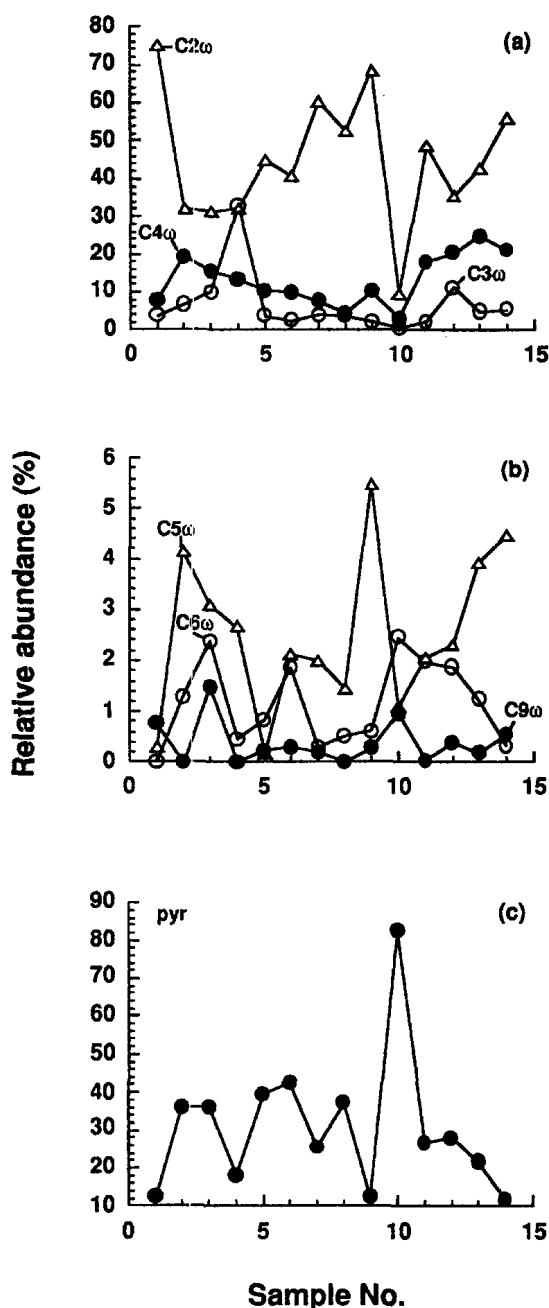


Fig. 6. Relative abundance of individual  $\omega$ -oxoacids and pyruvic acid in the western Pacific rainwater samples, September–October 1992: (a) glyoxylic (C<sub>2</sub>), 3-oxopropanoic, and 4-oxobutanoic acids; (b) 5-oxopentanoic, 6-oxohexanoic and 9-oxononanoic acids; (c) pyruvic acid (C<sub>8</sub>).

1985) and considered as a potential tracer of continental aerosol (Kawamura and Usukura, 1993). However, the C<sub>6</sub> diacid comprised only 1% of the total diacid in the R1 sample, which was collected in the mid-latitude of western North Pacific (Fig. 1). The relative abundance of C<sub>6</sub> diacid rather showed a parallel distribution with that of C<sub>9</sub> diacid (Fig. 4b), suggesting that adipic acid may be of natural origin in the remote rainwater. It is likely that the former considerations based on laboratory simulation (Hatakeyama *et al.*, 1985) and urban aerosol studies (Kawamura and Ikushima,

1993) are not valid for wet precipitation in the remote marine atmosphere.

Pyruvic or glyoxylic acid was the dominant ketoacid, the longer chain  $\omega$ -oxoacids being less abundant (Fig. 6). However, the chain length distributions of  $\omega$ -oxoacids seems to be consistent with those of  $\alpha$ , $\omega$ -dicarboxylic acid. The parallel distributions suggest that these LMW  $\omega$ -oxoacids are one of the precursors of LMW  $\alpha$ , $\omega$ -dicarboxylic acids. It is of interest to note that pyruvic acid (C<sub>3</sub>) is either the second or first dominant ketoacid species, being in good agreement with previous urban studies (Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994) suggesting a different source for pyruvic and  $\omega$ -oxoacids. Moreover, the lifetime of pyruvic acid is rather short (few hours) suggesting that the occurrence in rain samples of this species is mainly due to an *in situ* production rather than long-range transport. Interestingly, glyoxylic and pyruvic acids have been detected in eastern Pacific seawaters (Steinberg and Bada, 1984). The authors found pyruvic and glyoxylic acid concentrations at 75 m depth (no samples in the surface waters) to be 20 and 5  $\mu\text{g l}^{-1}$ , respectively. These values are also in the same order of magnitude as those reported for marine rainwater samples (Table 2). These ketoacids are probably more abundant in the surface waters due to stronger biological activities (Bada *et al.*, 1982) and may in part contribute to the ketoacids in the marine atmosphere.

$\omega$ -Oxononanoic acid (C<sub>9</sub>), a unique photooxidation product of biogenic unsaturated fatty acids whose double bond exists predominantly at the C<sub>9</sub> position (Kawamura and Gagosian, 1987) was also detected in some rain samples as only minor species. A similar trend was also observed in the relative abundance of C<sub>9</sub> diacid (Fig. 4b). Interestingly, this compound was found to be more abundant in the remote aerosol samples collected over the ocean in the same area (Sempéré and Kawamura, *in press*). The difference in the molecular distribution of C<sub>9</sub>  $\omega$ -oxoacid between aerosol and rain may suggest that the  $\omega$ -oxoacid is further oxidised to corresponding diacid and related compounds in the upper levels of the troposphere and/or in the rain droplets.

#### *Cis/trans configuration of unsaturated dicarboxylic acids in urban atmosphere*

Two aliphatic unsaturated diacids were detected in the marine rain samples: maleic (*cis* configuration) and fumaric acid (*trans* configuration). Interestingly, the *cis/trans* ratio showed a diversity ranging from 0.5 to 3.8 (av. 1.3). The M/F ratio is probably controlled by the production of maleic acid from the photochemical oxidation of benzene (Bandow *et al.*, 1985) and the subsequent isomerisation to fumaric acid (Kawamura and Ikushima, 1993). Alternatively, maleic acid may be produced from marine derived aromatics including phenolic materials, which have been reported to originate from macro algae and

enrich in the microlayers of seawater (Carlson, 1982). It is of interest to note that M/F ratios are lower than those (av. 5.8) from Tokyo rain samples (Sempéré and Kawamura, 1994). It is likely that the maleic acid production is enhanced in the urban atmosphere, whereas in remote areas the cis-trans isomerisation may prevail in the control of maleic acid concentration.

#### CONCLUSIONS AND SUMMARY

Remote marine rainwater samples collected over the western North Pacific showed the presence of homologous series of dicarboxylic acids ( $C_2$ - $C_{10}$ ) as well as ketoacids ( $C_2$ - $C_9$ ) and dicarbonyls ( $C_2$ - $C_3$ ). In all the rain samples, oxalic ( $C_2$ ) acid was found as the most abundant diacid species followed by malonic ( $C_3$ ) or succinic ( $C_4$ ) acid. Longer chain diacids are generally less abundant.

The concentrations of total diacids were found as high as  $959 \mu\text{g } \ell^{-1}$ . The concentration level (av.  $237 \mu\text{g } \ell^{-1}$ ) was unexpectedly high compared to continental rainwater (e.g.  $12$ - $540 \mu\text{g } \ell^{-1}$  for Tokyo rains). High concentrations were interpreted by (1) long-range atmospheric transport of continental air mass containing diacids and related polar compounds, and (2) production of diacids in the marine atmosphere by photo-induced oxidation of  $> C_3$  organic precursors of both continental and marine origin. Ketoacids such as glyoxylic ( $C_2$ ) and pyruvic ( $C_3$ ) acids are likely intermediates to result in oxalic acid. Photochemical production and subsequent accumulation were supported by the higher relative abundance of oxalic acid (av. 50%) in the remote marine rainwater than that of continental rain/snow (28-33%) and Greenland snow/ice (28%) samples.

The dicarboxylic acids were found as the important chemical species of rainwater DOC (av.  $1.6 \text{ mgC } \ell^{-1}$ ), accounting for up to 5% (av. 3%) of DOC. These values are c. 3 times higher than that of continental rainwaters. This study suggested that, in the remote marine atmosphere, organic compounds originated from either long-range transport of continental sources or sea-to-air emission of marine organic matter are subjected to photochemical oxidations to produce oxalic acid and other polar compounds.

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