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Trans-hemispheric contribution of C_2–C_{10} α, ω-dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions

Richard Sempéré[1] and Kimitaka Kawamura
Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan

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[1] Marine aerosol samples were collected during a western Pacific cruise covering the latitude range between 35°N and 40°S (140°E–180°E). They were analyzed for total carbon (TC), total nitrogen (TN), water-soluble organic carbon (WSOC) along with the molecular distributions of C_2–C_{10} α, ω-dicarboxylic acids, and related polar compounds, mainly, ω-oxocarboxylic acids (C_2–C_9) and α-dicarbonyls (C_2–C_3). Oxalic acid (C_2) was the most abundant followed by malonic (C_3) and succinic (C_4) acids. The total diacid concentration range was 7–605 ng m^{-3} (av. 85 ng m^{-3}) and the diacid-carbon accounted for 2–15% (average 8%) of WSOC which comprised 29–55% (average 40%) of TC. Dry depositions of total diacids over the northern and southern Pacific Ocean were estimated to be 256–1907 μg m^{-2} yr^{-1} (average 735; n = 4) and 22–396 μg m^{-2} yr^{-1} (average 134; n = 14), respectively, whereas the air-to-sea flux of oxalic acid was 18–1351 μg m^{-2} yr^{-1} (average 466 μg m^{-2} yr^{-1}) and 7.5–275 μg m^{-2} yr^{-1} (average 75 μg m^{-2} yr^{-1}) in the Northern and Southern Hemispheres. We observed that the concentration ratios of diacid-C/WSOC, azelaic acid (C_9)/ω-oxononanoic acid, maleic acid (iC_4 *cis*)/fumaric (iC_4 *trans*) acid and succinic acid (C_4)/total diacids were correlated with air temperature. These findings showed that the intensity of photochemical oxidation reactions and thus the variation in sunlight intensity characterized here by air temperature, significantly control the molecular distribution of water-soluble organic compounds during the long-range transport of anthropogenic and/or biogenic higher molecular weight organic compounds. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); *KEYWORDS:* aerosols, atmospheric chemistry, water-soluble organic compounds, diacids, western Pacific

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1. Introduction

[2] Aerosol studies in remote areas have been focused on the non-sea-salt sulphates [*Charlson et al.*, 1987, 1992; *Ayers and Gras*, 1991; *Hegg et al.*, 1991a, 1991b], the mineral dust distribution [*Uematsu et al.*, 1985; *Prospero and Savoie*, 1989; *Li et al.*, 1996] and their contribution to the Earth's radiative balance [*Houghton et al.*, 1995; *Tegen et al.*, 1996; *Andreae and Crutzen*, 1997]. However, although biomass burning and its impact on climate have been partly studied [*Andreae*, 1996], most of organic aerosol studies in remote areas have been related to the long-range transport of lipids [*Gagosian et al.*, 1987; *Peltzer and Gagosian*, 1989; *Sicre et al.*, 1990] and to the associated photochemical oxidation reactions [*Kawamura and Gagosian*, 1987; *Stephanou*, 1992; *Kawamura and Usukura*, 1993; *Kawamura et al.*, 1996]. Water-soluble organics such as diacids in aerosols probably play a role in the light-scattering balance as well, since they participate in the formation of cloud and fog [*Saxena et al.*, 1995;

[1]Now at Laboratoire de Microbiologie Marine, Centre d'Océanologie de Marseille, Université de la Méditerranée, Marseille, France.

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Saxena and Hildemann, 1996] and may act as cloud condensation nuclei [*Novakov and Penner*, 1993; *Saxena and Hildemann*, 1996; *Novakov and Corrigan*, 1996; *Kerminen et al.*, 1999]. However, very little is known about the distribution of water-soluble organic compounds in the remote marine atmosphere which covers the Northern and Southern Hemispheres.

[3] Among water-soluble organic compounds, low molecular weight (LMW) α, ω-dicarboxylic acids and related compounds, i.e., ω-oxocarboxylic acids (C_2–C_9) and α-dicarbonyls (C_2–C_3), are likely to be the most abundant. These compounds are produced in abundance in polluted areas by the incomplete combustion of fossil fuels [*Kawamura and Kaplan*, 1987; *Kerminen et al.*, 2000], cooking meat [*Rogge et al.*, 1991; *Schauer et al.*, 1999], biomass burning [*Andreae et al.*, 1991; *Talbot et al.*, 1992; *Narukawa et al.*, 1999] and directly by biogenic emission [*Kawamura and Gagosian*, 1990], but also the ozonolysis and photooxidation of numerous organic compounds, significantly produces α, ω-dicarboxylic acids and their ketoacid and dicarbonyl homologues [*Schuetzle et al.*, 1975; *Grosjean et al.*, 1978; *Norton et al.*, 1983; *Bandow et al.*, 1985; *Hatakeyama et al.*, 1987; *Kawamura and Gagosian*, 1987; *Kawamura and Ikushima*, 1993]. Consequently, these compounds have been reported at significant concentrations even in remote marine atmospheres [*Stephanou*, 1992; *Kawamura and Usukura*, 1993; *Sempéré and Kawamura*, 1996; *Kawamura and Sakaguchi*, 1999], in the semi-urban atmosphere [*Khwaja*, 1995], in the rural atmosphere [*Limbeck et al.*, 2001] as well as in the polar atmosphere [*Kawamura et al.*, 1995; *Li and Winchester*, 1993; *Kawamura et al.*, 1995, 1996] and ice core samples [*Kawamura and Yasui*, 1991; *Legrand and De Angelis*, 1996; *Kawamura et al.*, 2001a].

[4] Dicarboxylic acids are polar and have low vapor pressure, and some could be associated with atmospheric aerosols and other condensed phases [*Kawamura and Kaplan*, 1987; *Grosjean*, 1989; *Baudet et al.*, 1990; *Saxena and Hildemann*, 1996; *Hara et al.*, 2002]. Thus we could expect that if they are significantly abundant, due to their continuous photochemical source in the atmosphere, aerosols enriched with diacids would act as cloud condensation nuclei. In addition, oxalate and other organic anions are important in the photoredox chemistry of iron in the aerosols in cloud droplets [*Zuo and Hoigné*, 1992] although previous aerosol studies conducted in the Arctic and Antarctic atmospheres indicate that photochemical oxidation reactions significantly alter the molecular distribution of diacids in atmospheric particles [*Kawamura et al.*, 1995, 1996; *Narukawa et al.*, 2002]. These results suggested that far from their main anthropogenic sources, the photochemical oxidation reactions control the molecular distribution of diacids, ketoacids, and dicarbonyls. To our knowledge, there is no available data on the concentration of water-soluble organics over the Pacific Ocean covering the latitude range between 35°N and 40°S (140°E–180°E). In this paper, we report the total concentration of water-soluble organic carbon (WSOC) as well as C_2–C_{10} α, ω-dicarboxylic acids and related polar compounds, i.e., ω- oxocarboxylic acids (C_2–C_9), α-dicarbonyls (C_2–C_3), pyruvic acid, and aromatic (phthalic) diacid. We also present an estimate of their standing mass over the Pacific Ocean together with their annual dry deposition rate. Molecular distribution of these organic compounds will be discussed in relation to the sources and production mechanisms of these compounds as well as their role in the remote marine atmosphere.

2. Experimental

[5] Aerosol samples were collected from the upper deck of the R/V *Hakuho Maru* (~14 m above the sea surface) using a precombusted (500°C) Pallflex quartz fiber filter (20 × 25 cm) using a high-volume air sampler (Shibata HVC 1000) during the cruise KH92-4: August–October 1992. The aerosol sampler was operated under the control of the wind sector (±45°) and wind speed (≥5 m s^{-1}) system to avoid contamination from the ships exhaust [*Kawamura and Usukura*, 1993]. Sampling time was about 24 hours. The cruise track is shown in Figure 1. Total aerosol mass was determined by weighing the filter before and after sample collection. Filters were stored in clean glass jars with Teflon-lined screw caps at −20°C prior to analysis. Blank filters were exposed to the air in the sample shelters for a few seconds and then recovered.

[6] Part of the filter sample was cut off and analyzed in a CHN corder (Yanagimoto, MT 3) for the determination of total carbon (TC) and total nitrogen (TN). These measurements include all inorganic and organic forms. Note that our recent observations indicate that carbonate comprised only a few percent of TC (K. Kawamura, unpublished data). The analytical error based on duplicate analyses was ~10%. WSOC determination is previously described [*Sempéré and Kawamura*, 1994]. Briefly, part of the filter was cut in pieces and extracted using pure water. The water extracts were analyzed for dissolved organic carbon using a Shimadzu TOC 500. Analytical precision of the WSOC measurement was 6% based on duplicate analysis.

[7] Dicarboxylic acids and related compounds were analyzed by the method of *Kawamura and Ikushima* [1993]. Briefly, an aliquot of the filters was extracted for low molecular weight dicarboxylic acids and other water-soluble organics with pure water. The water extracts were then concentrated by a rotary evaporator under vacuum and dried in a nitrogen air 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 dibutoxyacetals, respectively. The derivatives were determined using a Hewlett Packard (HP 5890) gas chromatograph (GC) equipped with a split/splitless injector, a fused silica capillary column (HP-5 0.32 mm in diameter × 25 m × 0.52 μm), and an FID detector. Identification of the derivatives was performed by the comparison of GC retention times and mass spectra with those of authentic standards. Identification of the compounds was confirmed by a GC-spectrometer system (Finnigan- MAT ITS-40 and ThermoQuest Trace MS). Recovery was 70% for oxalic acid and better than 90%

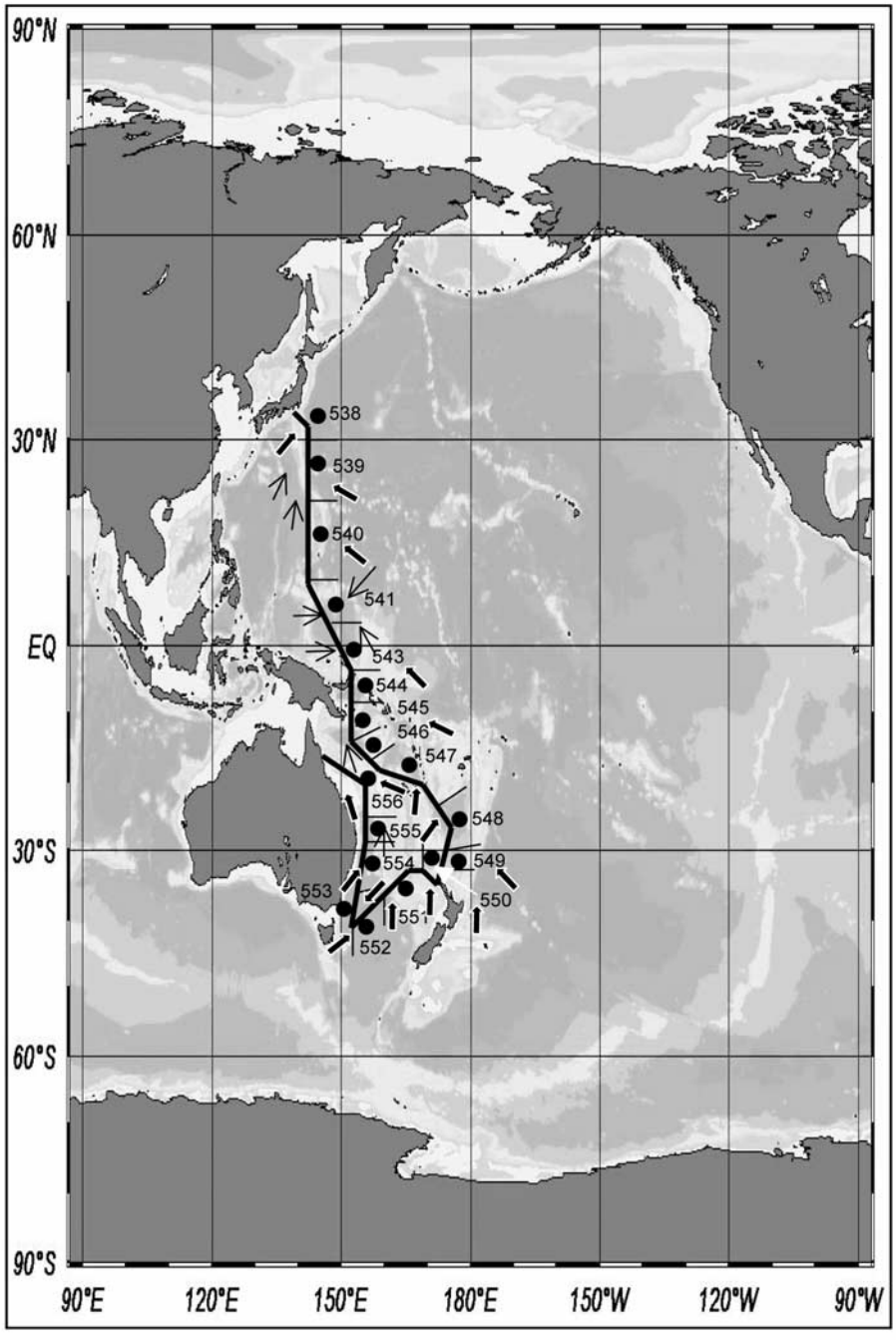

Figure 1. Cruise track of R/V *Hakuho Maru*: KH-92 started 16 September 1992 at Tokyo, Japan, and ended 26 October 1992 at Cairns, Australia. The aerosol samples were continuously collected during the cruise. The consecutive sampling areas are delimited by the sticks drawn on the cruise track, and the numbers in between correspond to the filter identification numbers. Arrows correspond to wind direction during the cruise; bold and regular arrows are related to wind speed higher and lower than 7 m s^{-1}, respectively.

for malonic, succinic and adipic acids. Procedural blanks only showed small peaks of oxalic, pyruvic, and phthalic acid derivatives in the GC chromatograms; however, they presented less than 4% of the actual samples. 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. The concentrations of the acids presented are

corrected for procedural blanks. All analyses were completed by 1993.

3. Results and Discussion

3.1. General Characteristics of the Aerosols

[8] The aerosol mass concentrations (Table 1, Figure 2a) ranged from 11 (5°N) to 68 μg m^{-3} (40°S near Australia). Such values are in the same order of magnitude of those previously reported for the Pacific atmosphere [*Kawamura and Usukura*, 1993; *Kawamura and Sakaguchi*, 1999] and other remote sites such as the tropical Indian Ocean (average 15 μg m^{-3} [*Krishnamurti et al.*, 1998]), and Atlantic Barbados (11 to 31 μg m^{-3} [*Li et al.*, 1996]). However, the values we report are 1 order of magnitude lower than the aerosol concentrations reported for the urban area of Tokyo [*Kawamura and Ikushima*, 1993; *Sempéré and Kawamura*, 1994].

[9] Concentrations of TC and TN (Table 1) for remote aerosol samples ranged from 190 to 5174 ng m^{-3} and from 16 to 1461 ng m^{-3} making up 0.7–18% and 0.09–5.2% of the aerosol mass, respectively (Figures 2b and 2c). C/N ratios showed diversity, ranging from 3. 3 (28°S) to 28 around the equator (5°N–5°S). WSOC showed a concentration range of 88 to 2324 ng m^{-3} and comprised 29–55% of TC (Table 1). Such high WSOC/TC ratios are close to the values reported for urban aerosols where observed TC values are 1–2 orders of magnitude higher [*Cadle and Groblicki*, 1982; *Mueller et al.*, 1982; *Sempéré and Kawamura*, 1994]. Similar WSOC/TC ratios have also been reported in relation to biomass burning [*Novakov and Corrigan*, 1996; *Narukawa et al.*, 2002]. Interestingly, our previous results indicate higher WSOC/TC ratios during the day compared to night and during summer compared to winter, suggesting photochemical production of these compounds [*Sempéré and Kawamura*, 1994]. Although dicarboxylic acids, ketoacids and dicarbonyls have been identified in the water soluble fraction of aerosols [*Sempéré and Kawamura*, 1994; *Narukawa et al.*, 1999], low molecular weight polyols, amino acids and other multifunctional groups may contribute to the water-soluble fraction [*Saxena and Hildemann*, 1996].

[10] This fraction of aerosols most likely contributes to the CCN ability of particles [*Saxena and Hildemann*, 1996]. The carbonaceous fraction of the aerosols (TC%) near the Japanese Islands (TC = 18%) was more than 5 times higher than to the rest of the samples, suggesting a significant atmospheric transport of continent-derived organic materials over the Pacific Ocean (Figure 2b). Such high TC%, as well as C/N ratios (3.5; Figure 2c) and WSOC/TC % ratios (45; Table 1) were found to be similar to the values reported for the Tokyo area [*Kawamura and Ikushima*, 1993; *Sempéré and Kawamura*, 1994] and other Asian urban areas [*Hashimoto et al.*, 1991; *Sekine et al.*, 1992] (only TC% reported by Sekine et al.). TC concentrations in remote Pacific aerosols were similar to those obtained from the remote Pacific Ocean (69–5270 ng m^{-3}) [*Kawamura and Sakaguchi*, 1999], in Chichi-Jima Island in the western North Pacific (400–1450 ng m^{-3}) [*Mochida et al.*, 2003a] and Antarctic aerosols (440–1020 ng m^{-3}) [*Kawamura et al.*,

Table 1. Total Carbon (TC), Total Nitrogen (TN) Contents and Water Soluble Organic Carbon (WSOC) in the Western Pacific Aerosols With Sampling Dates (in 1992) and Ambient Temperatures

	Northern Hemisphere											Southern Hemisphere						
	QFF 538 Sep 16–17	QFF 539 Sep 17	QFF 540 Sep 17–18	QFF 541 Sep 18–21	QFF 543 Sep 21–23	QFF 544 Sep 25–26	QFF 545 Sep 27–28	QFF 546 Sep 29–Oct 1	QFF 547 Oct 1–2	QFF 548 Oct 3–4	QFF 549 Oct 4–8	QFF 550 Oct 13–14	QFF 551 Oct 14–15	QFF 552 Oct 15–17	QFF 553 Oct 17–18	QFF 554 Oct 19–21	QFF 555 Oct 21–22	QFF 556 Oct 22–24
Latitude, °	35°–30°N	30°–20°N	20°–10°N	10°–5°N	5°N–5°S	5°–10°S	10°–15°S	15°–18°S	18°–25°S	25°–30°S	30°–33°S	33°–32°S	32°–38°S	38°–40°S	40°–35°S	35°–28°S	28°–24°S	24°S
Ambient air T, °C	26	25.8	25	27.5	27.5	27.5	28	26.2	25.5	21.8	19	16	16.5	14	13.8	14.5	19.5	24.5
Aerosol mass, μg m^{-3}	28	26	27	14	11	18	22	21	20	27	28	29	23	16	68	38	29	31
TC, ng m^{-3}	5174	1095	825	595	571	899	438	490	618	190	273	251	367	325	880	624	595	284
TN, ng m^{-3}	1461	176	76	109	24	32	133	80	224	23	36	31	64	16	246	35	46	40
C/N Ratio	3.5	6.2	10.9	5.5	23.9	28.5	3.3	6.1	2.8	8.1	7.7	8.1	5.7	19.8	3.6	17.6	12.8	7.2
WSOC, ng m^{-3}	2321	369	412	201	199	301	153	184	282	88	90	136	164	162	484	182	181	108
WSOC/TC, %	45	34	50	34	35	33	35	37	46	46	33	54	45	50	55	29	30	38

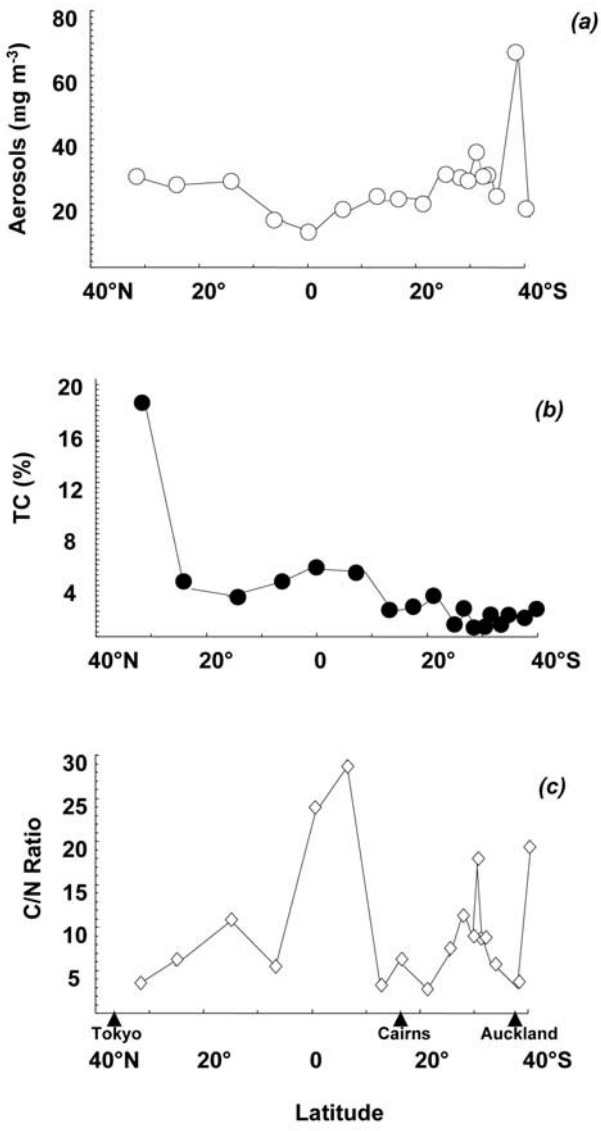

Figure 2. Latitudinal distribution of (a) total aerosol concentration, (b) total carbon (TC) content, and (c) C/N ratio of the western Pacific aerosol samples.

1996]. TN concentrations were close to values already reported for the Pacific Ocean (26–1440 ng m^{-3}) [*Kawamura and Sakaguchi*, 1999] and 1 order of magnitude lower than those of the urban area from the Tokyo atmosphere [*Kawamura and Ikushima*, 1993; *Sempéré and Kawamura*, 1994].

[11] Interestingly, our aerosol samples collected near the equator (5°N–10°S) showed low concentrations (11–18 μg m^{-3}) of aerosols, high C/N ratios (24–29) and moderately high TC% values (~5%), being in contrast with the values observed for the North and South subtropical area (20°S and 20°N) (Figure 2a). This suggests that at low latitudes, tropospheric aerosols are not only influenced by diffusive and wind transport from the two hemispheres but also by vertical mixing between the lower and upper troposphere, in line with the work of *Plumb and McConalong* [1988]. High C/N ratios (6–89), and relatively nitrogen depleted aerosols have been reported in Antarctic and Arctic aerosols [*Kawamura et al.*, 1995, 1996] whereas lower C/N ratios were found in the Tokyo area [*Sempéré and Kawamura*, 1994] where anthropogenically derived-NO_x is likely to lead to the formation of particulate nitrates. Since the organic content of the aerosol (TC%) was high near the equator, the low C/N ratios may be due to preferential destruction of nitrogenous compounds or to a mixing with nitrogen-poor air masses.

3.2. Concentration Levels and Relative Abundance of Water-Soluble Compounds

[12] The α, ω-Dicarboxylic acids (C_2–C_9), and aromatic acid (phthalic) as well as ω-oxocarboxylic (C_2–C_6; C_2–C_9) acids, α-ketoacid (pyruvic acid), and α-dicarbonyls were detected in the North and South Pacific aerosols. Their chemical structures are given in Figure 3. Dicarboxylic acids are the most abundant compound class (7.1–605 ng m^{-3}) followed by ketoacids (0.58–42 ng m^{-3}) and α-dicarbonyls (0.28–8.8 ng m^{-3}) (Table 2; Figures 4a–4c).

3.2.1. The α, ω-Dicarboxylic Acids

[13] Diacids accounted for 1.1–4.9% (average 3.2%) of TC and for 2.1–14.7% (average 8.2%) of WSOC (Figure 5). This indicates that diacids are a significant component of the water-soluble organic fraction of marine aerosols. Interestingly, lower ratios of diacids-C/TC and diacids- C/WSOC were observed in the Southern Hemisphere. Long chain diacids are generally less abundant whereas oxalic acid (C_2) was the most abundant (30–71%) followed by malonic acid (C_3: 12–27%) and succinic acid (C_4: 3–18%) (Figures 6a–6c). Interestingly, a similar molecular distribution was observed in some aerosol samples collected from the North Pacific [*Kawamura and Usukura*, 1993; *Kawamura and Sakaguchi*, 1999], from Tokyo [*Kawamura and Ikushima*, 1993; *Sempéré and Kawamura*, 1994] and in other urban areas [*Tran et al.*, 2000; *Neususs et al.*, 2000; *Yao et al.*, 2002]. Azelaic acid is the most abundant in the range of C_5–C_{10} diacid, being the third abundant diacid (QFF 545).

[14] Although they are less abundant than corresponding straight-chain dicarboxylic acids, branched chain saturated diacids including methylmalonic (iC_4) and methyl succinic (iC_5) were also detected in the Pacific aerosols. Two aliphatic unsaturated diacids were also detected in the marine aerosol samples: maleic (*cis* configuration) and fumaric (trans configuration). Note that the *cis*/*trans* ratio largely fluctuated, being normally greater than 1 near the Australian Continent and the Japanese Islands and lower in between (Figure 7). The latter case indicates that the *trans* configuration (fumaric acid (F)) was equal or more abundant than the *cis* configuration (maleic acid (M)) at low latitudes. Generally, *trans* configuration is more abundant in the marine atmosphere whereas the opposite was reported for the continental aerosols [*Kawamura and Sakaguchi*, 1999, and references therein], a point to be discussed later.In addition, we detected α, ω-dicarboxylic acids with an additional functional group, i.e., ketomalonic (kC_3),

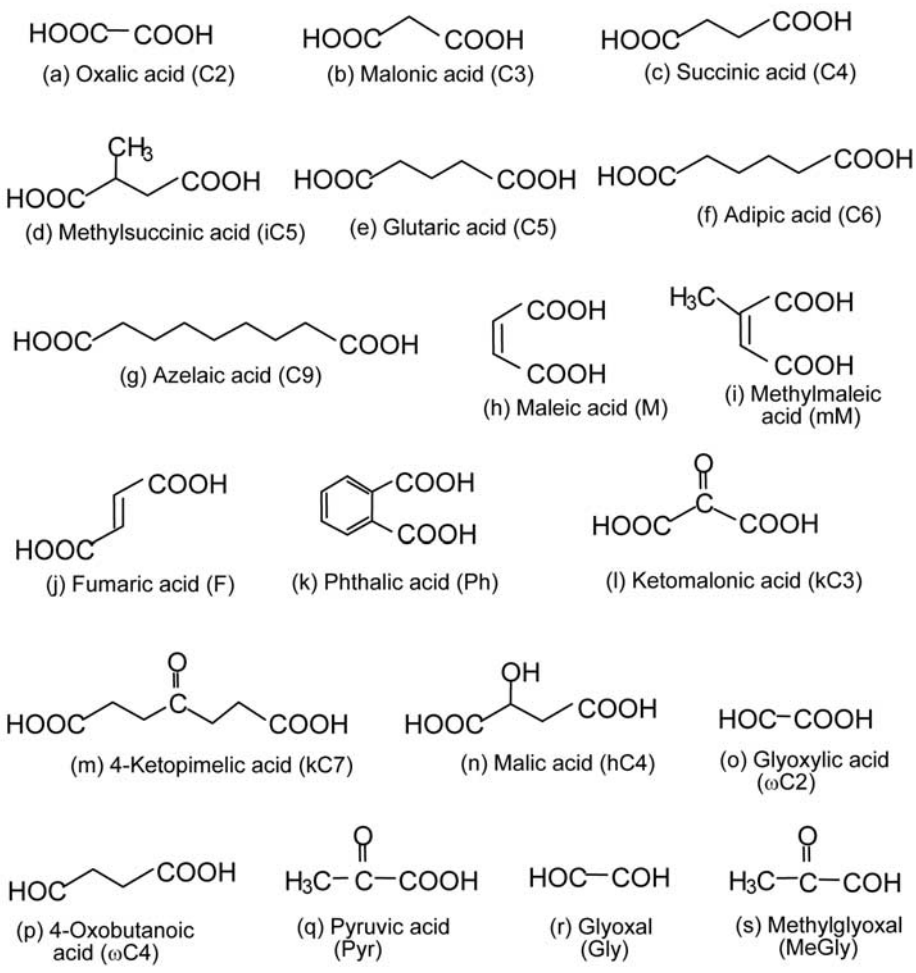

Figure 3. Chemical structures of dicarboxylic acids, ketoacids (only the most abundant) and dicarbonyls detected in the marine aerosols. For abbreviations, see Table 2. C_n means dicarboxylic acid; iC_n indicates branched chain (iso) diacid; M and F are abbreviations of unsaturated diacids: maleic and fumaric acids, respectively. $C_{n\omega}$ indicates ω-oxocarboxylic acid with n carbon numbers. Me-Gly, Pyr, Malic, Gly, and Ph mean methylglyoxal, pyruvic, malic, glyoxylic and phthalic acids, respectively.

4-oxopimelic [kC_7] and hydroxysuccinic acid (malic: hC_4). However, all these compounds are relatively minor species as they comprise less than 6% of the total diacids.

3.2.2. Ketoacids and Dicarbonyls

[15] Total concentrations of ketoacids ranged from 0.58 to 42 ng m^{-3} (average 5.4 ng m^{-3}) and the general distribution parallels those of α, ω-dicarboxylic acids although the concentrations are about 1 order of magnitude lower (Figures 4a–4c). The highest value was observed near Japan (QFF 538: 41.6 ng m^{-3}) followed by the South Pacific samples near Australia (QFF 553: 8.28 ng m^{-3}). Total ketoacids accounted for 0.09–0.37% (average 0.23%) of TC and for 0.16–1.1% (average 0.58%) of WSOC. Glyoxylic acid (ωC_2) was always the dominant or second (QFF 541) ketoacid followed by 9-oxononanoic, pyruvic or 4-oxobutanoic acids (Figure 8). Predominance of ωC_2 and ωC_4 were frequently reported for Antarctic aerosol samples [*Kawamura et al.*, 1996] and Greenland ice core samples [*Kawamura et al.*, 2001a]. Surprisingly, high relative abundance of 9-oxononanoic was observed in the northern tropical areas where we also found high relative abundance of C_9 diacid (QFF539-541). Except for this compound, ω-oxoacids having the longer chain length were less abundant (Figure 8).

[16] Concentrations of α-dicarbonyls ranged from 0.15 to 8.8 (average 1.1 ng m^{-3}). Their latitudinal distribution is similar to those of diacids and ketoacids, although concentrations were much lower. Total dicarbonyls accounted for 0.02–0.11% (average 0.50%) of TC and 0.07–0.22% (average 0.14%) of WSOC. Methylglyoxal was more abundant than glyoxal near the Japanese Islands (QFF 538) and in the southern tropical areas, whereas the opposite trend

Table 2. Concentration Ranges and Average Concentrations of Dicarboxylic Acids, Ketoacids and Dicarbonyls Collected From the Northern to the Southern Part of the Western Pacific Atmosphere (n = 18)

	Concentrations, ng m^{-3}		Relative Abundance, %	
	Range	Av. ± SD	Range	Av. ± SD
	Dicarboxylic Acids			
Oxalic, C_2	2.4–428.5	2.8 ± 13.7	34–71	51 ± 11
Malonic, C_3	1.0–78.6	1.0 ± 4.5	12–27	17 ± 4
Methylmalonic, iC_4	0.0–1.7	0.08 ± 0.15	0.2–20	0.8 ± 0.6
Oxomalonic, C_3	0.0–4.3	0.11 ± 0.24	0.0–2.3	1.0 ± 0.8
Maleic, uC_4	0.06–1.8	0.08 ± 0.17	0.2–1.7	0.8 ± 0.5
Succinic, C_4	1.0–33.4	0.78 ± 2.3	2.9–17.5	8.9 ± 4.0
Methylsuccinic, iC_5	0.0–2.5	0.09 ± 0.34	0.0–2.5	1.1 ± 0.6
Fumaric, uC_4	0.02–0.67	0.04 ± 0.12	0.1–1.3	0.5 ± 0.3
Malic, hC_4	0.0–0.18	0.0 ± 0.02	0.0–0.21	0.1 ± 0.2
Glutaric, C_5	0.49–7.6	0.28 ± 0.72	0.7–6.4	3.0 ± 1.9
Adipic, C_6	0.18–7.2	0.27 ± 0.55	0.3–4.9	2.0 ± 1.1
Pimelic, C_7	0.12–0.79	0.09 ± 0.13	0.0–1.3	0.5 ± 0.3
Suberic, C_8	0.20–3.7	0.29 ± 0.57	0.6–3.7	1.8 ± 0.9
Phthalic, C_8	0.40–20.3	0.34 ± 2.2	1.1–9.4	4.9 ± 2.6
4-Oxopimelic, C_7	0.0–6.1	0.09 ± 0.41	0.0–2.2	0.7 ± 0.6
Azelaic, C_9	0.42–8.7	0.87 ± 1.8	1.1–14	5.3 ± 3.1
Sebacic, C_{10}	0.0–0.57	0.08 ± 0.13	0.0–0.72	0.7 ± 0.9
Subtotal	7.1–604.6	7.3 ± 28.1	100	
% of TC	1.1–5.0	2.6 ± 3.2		
% of WSOC	2.1–14.7	6.8 ± 8.1		
	Ketoacids			
Pyruvic, C_3	0.13–8.2	0.09 ± 0.33	4.9–31	13 ± 7.5
Glyoxylic, C_2	0.34–24.6	0.39 ± 1.0	37–75	61 ± 12
3-Oxopropanoic, C_3	0.0–3.6	0.02 ± 0.14	1.1–14	5.1 ± 3.4
4-Oxobutanoic, C_4	0.0–3.7	0.05 ± 0.22	0.0–18	8.5 ± 4.8
5-Oxopentanoic, C_5	0.0–0.40	0.04 ± 0.07	0.0–7.6	2.8 ± 1.7
6-Oxohexanoic, C_6	0.0–0.42	0.0 ± 0.03	0.0–7.6	0.8 ± 2.0
9-Oxononanoic, C_9	0.02–1.8	0.06 ± 0.23	1.0–47	8.8 ± 13
Subtotal	0.58–41.6	0.65 ± 2.1	100	
% of TC	0.09–0.34	0.23 ± 0.23		
% of WSOC	0.16–1.1	0.60 ± 0.58		
	α-Dicarbonyls			
Methylglyoxal, C_3	0.0–5.0	0.07 ± 0.27	0.0–57	42 ± 14
Glyoxal, C_2	0.14–3.8	0.07 ± 0.23	43–100	58 ± 14
Subtotal	0.15–8.8	0.14 ± 0.50	100	
% of TC	0.03–0.12	0.05 ± 0.05		
% of WSOC	0.06–0.29	0.13 ± 0.14		

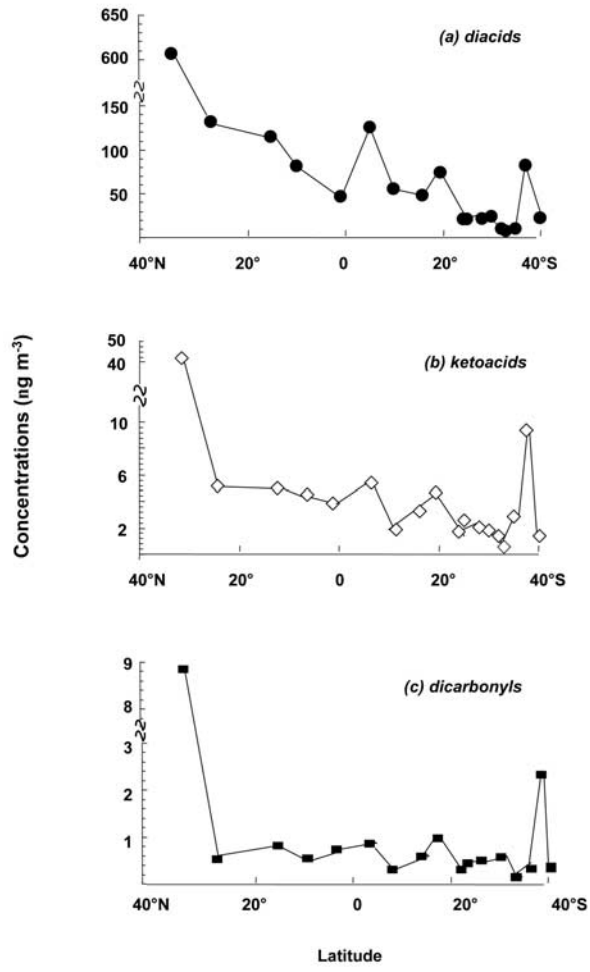

Figure 4. Latitudinal distribution of (a) total diacid, (b) ketoacid, and (c) dicarbonyl concentrations in the western Pacific aerosol samples.

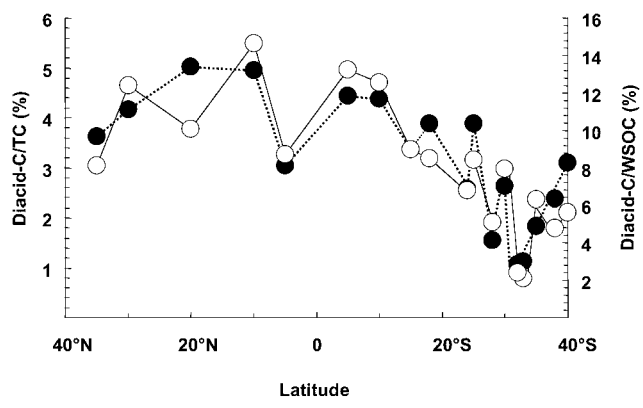

Figure 5. Latitudinal distribution of diacid-C/TC (solid circles) and diacid-C/WSOC (open circles) ratios in the western Pacific aerosol samples.

was observed for other samples, particularly for the southernmost samples. Dicarbonyls are moderately soluble and largely present in the gas phase [*Betterton*, 1992]. Methylglyoxal and glyoxal are tracers of the photochemical oxidation of a number of aromatic or straight chain unsaturated hydrocarbons such as benzene, toluene and isoprene [*Bandow et al.*, 1985; *Munger et al.*, 1995]. These compounds may be intermediates in the photochemical oxidation reactions of aromatic hydrocarbons to oxalic acid [*Norton et al.*, 1983], and are removed by photolysis and reaction with OH radicals [*Atkinson et al.*, 1993]. *Munger et al.* [1995] reported that 50% glyoxal is partitioned to the aqueous phase during cloudy periods and glyoxal and methylglyoxal have been reported in the marine air [*Zhou and Mopper*, 1990], rain and fog samples [*Grosjean et al.*, 1990], and snow and ice samples from Greenland [*Kawamura et al.*, 2001a].

[17] Glyoxal was more abundant than methylglyoxal in the southernmost South Pacific and *vice versa* in the tropical

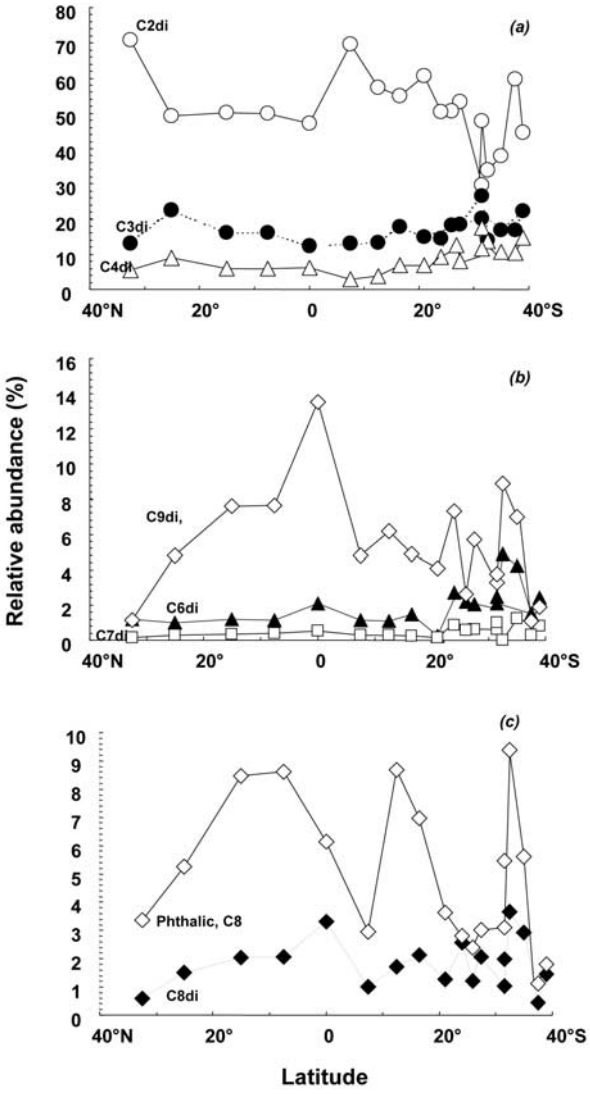

Figure 6. Latitudinal changes in the relative abundance of the most abundant individual α, ω-dicarboxylic acids in the western Pacific aerosol samples. (a) Oxalic (C_2di), malonic (C_3di) and succinic (C_4di) acids; (b) adipic (C_6di), pimelic (C_7di) and azelaic (C_9di) acids; and (c) suberic (C_8di) and phthalic (C_8di) acids.

and subtropical South Pacific (Figure 9) which was also observed for the rainwaters collected during the same cruise [*Sempéré and Kawamura*, 1996]. Methylglyoxal is also an important precursor of peroxyacetylnitrate (PAN) [*Munger et al.*, 1995]. Although we do not have decisive evidence, glyoxal may be significantly produced by photochemical oxidation of aromatic structures in the open ocean such as the southernmost South Pacific. *Carlson* [1982] reported enrichment of phenolic compounds in the sea surface slicks. The phenolic compounds could be emitted to the air from the microlayer of sea surface waters and oxidized in the marine atmosphere to form glyoxal. It is interesting to note that glyoxal is generally the more abundant (dicarbonyl) than methylglyoxal in the ice core (H-15) taken from the Antarctic near the coast (H. Kasukabe and K. Kawamura, unpublished results, 1995).

3.3. Depositions of Total and Water-Soluble Organic Carbon Over the Western Pacific

[18] Diacids comprised a significant fraction of aerosol TC (1–5%) and WSOC (2–15%). Clearly our results indicated that the concentrations of diacids and related polar compounds, and the WSOC and the diacid-C/WSOC ratio largely varied with latitude. The highest concentrations of diacids were found near the Japanese Islands and Australia. This can be explained as the main sources of these compounds are the direct emission from incomplete combustion of fossil fuels and photochemical oxidation of organic pollutants of continental origin as well as biomass burning [*Kawamura and Ikushima*, 1993; *Stephanou and Stratigakis*, 1993; *Narukawa et al.*, 1999]. Although the concentrations are much lower in remote areas than in urban atmosphere, water-soluble organic compounds are still enriched in the remote Pacific atmosphere, probably due to enhanced photochemical production of polar compounds such as dicarboxylic acids. As WSOC did not show any spectacular concentration decrease and since a short life time has been reported for diacids [*Grosjean*, 1989], it is likely that these compounds are continuously produced and scavenged in the remote atmosphere. It is of importance to discuss the deposition of diacids in order to better understand biogeochemical cycles of water-soluble organic carbon.

3.3.1. Wet Deposition of Oxalate

[19] These results are in good agreement with rainwater studies conducted in the same areas indicating that they

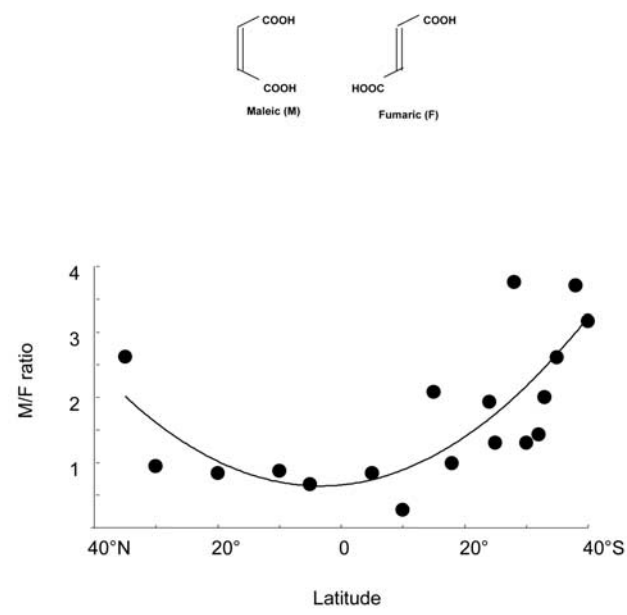

Figure 7. Latitudinal changes in C_4-unsaturated α, ω-dicarboxylic acids (maleic (M: *cis* configuration) and fumaric acid (F: *trans* configuration)) in the western Pacific aerosol samples.

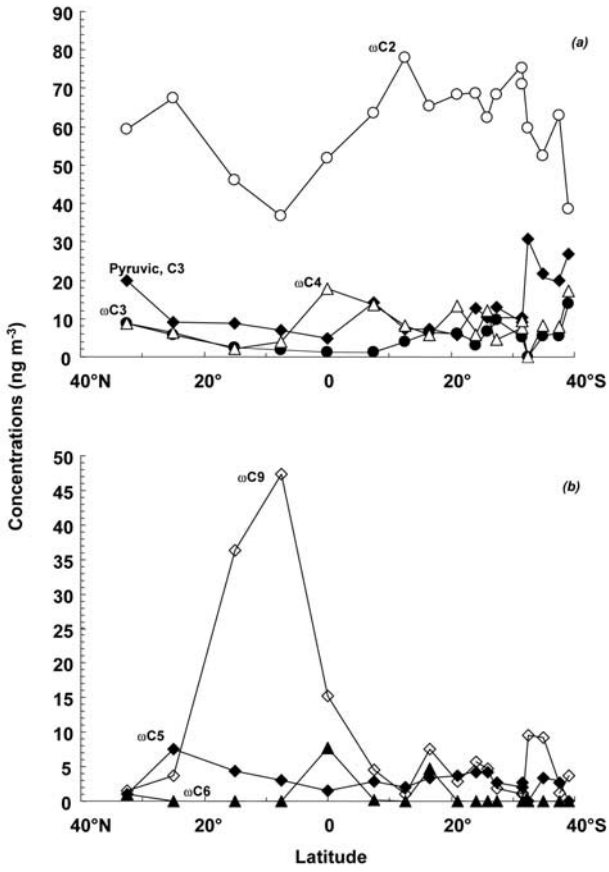

Figure 8. Latitudinal changes in the relative abundance of the ω-oxoacids, dicarbonyls and pyruvic acid in the western Pacific aerosol samples. (a) Glyoxylic (ωC_2), 3-oxopropanoic (ωC_3), 4-butananoic (ωC_4) and pyruvic acids; and (b) 5-oxopentanoic (ωC_5), 6-oxohexanoic (ωC_6) and 9-oxononanoic (ωC_9) acids.

comprised up to 5% (average 3%) of rainwater DOC [*Sempéré and Kawamura*, 1996]. Among the total diacids, it has been proposed that oxalate plays an important role in condensation nuclei growth [*Baudet et al.*, 1990; *Kerminen et al.*, 1999; *Hara et al.*, 2002, and references therein]. Oxalic acid was found to be predominantly distributed in atmospheric aerosols through the uptake of gaseous oxalic acid into fine or coarse particles or sea salts [*Kerminen et al.*, 1999]. A strong Aitken mode has been reported for oxalic acid, indicating that the growth of secondary particles to cloud condensation nuclei may be affected by oxalic acid, especially of marine origin [*Kerminen et al.*, 1999]. To better understand the relationship between the oxalic acid concentration in aerosols and rainwater, we can consider a simple case of in-cloud scavenging of a pre-existing oxalic acid in aerosol. The oxalic acid concentration in rainwater is described by the following equation [*Charlson and Rhode*, 1982, and references therein]:

$$\left[C_2O_4^{2-}\right]\text{rain} = \left[C_2O_4^{2-}\right]\text{aerosol} \times \varepsilon\,\text{DE}/90\text{L}, \qquad (1)$$

where ε is the scavenging efficiency for $C_2O_4^{2-}$ aerosol particles in the cloud, 90 is the oxalic acid molecular weight (g mol^{-1}) and L is the liquid water content (1 m^3) of the cloud. For soluble particles of 0.1–1 μm radius, ε is expected to be 0.5–1.0 [*Junge*, 1963]. In fact, oxalic acid was found to be enriched in submicron range particles around 0.5 μm in the North Pacific [*Mochida et al.*, 2003b]. D and E are the dilution and the evaporation of the cloud and rainwater. For the long-range transport of air pollutants, ε DE/L is in the range of 0.6–1.6 × 10^3 m^3 kg^{-1}; average 1.1 10^3 m^3 kg^{-1} [*Charlson and Rhode*, 1982]. On the basis of the aerosol oxalic acid concentrations we measured, and by using a cloud liquid water content of 1 g m^{-3} [*Charlson and Rhode*, 1982], a rough calculation predicts a concentration of oxalic acid in the marine rainwater of 45–471 μg L^{-1} (average 163; n = 4) and 2.6–96 μg L^{-1} (average 26; n = 14) for the North and South Pacific, respectively. These values are in the same order of magnitude as 19–461 μg L^{-1} (average 134; n = 4) and 82–106 μg L^{-1} (average 103; n = 10) as found for North and South Pacific rainwaters collected during the same cruise [*Sempéré and Kawamura*, 1996]. We may expect some limitations to the partition of oxalic acid into the aqueous phase under conditions such as highly acidic aerosol, low relative humidity, and an ambient temperature greater than 15°C; except for temperature, the others factors are not likely to occur in remote marine area. On the other hand, photochemical production of oxalic acid is very likely in cloud [*Warneck*, 2003]. This could enhance the theoretical concentrations of oxalic acid. These results suggest a contribution of oxalate to CCN may be significant in the western Pacific atmosphere.

3.3.2. Dry Deposition of Diacids

[20] Assuming that diacids are equally distributed in the lower troposphere, diacid standing masses in the first 3000 m were estimated at 243–1814 μg m^{-2} (average 699; n = 4) and 21–376 μg m^{-2} (average 127; n = 14) in the Northern

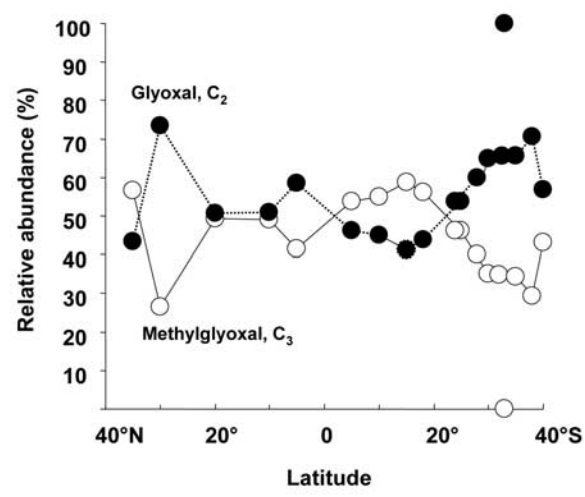

Figure 9. Latitudinal changes in the relative abundance of the dicarbonyls (methylglyoxal: C_3 and glyoxal: C_2) in the western Pacific aerosol samples.

Table 3. Standing Masses for Total Carbon and Total Nitrogen (TC and TN), and Diacids, Ketoacids, and Oxalic Acids, and Dry Depositions of Total Diacid and Oxalic Acid in North (0°–35°) and South (0°–40°) Western Pacific[a]

	North Western Pacific	South Western Pacific
	Standing Masses	
TC; (av.), mg m^{-2}	1.79–15.5; (5.77)	0.06–2.7; (1.46)
TN; (av.), mg m^{-2}	0.23–4.38; (1.37)	0.05–0.74; (0.22)
Diacids, μg m^{-2}	243–1814; (699)	21–376; (127)
Oxalic acid, μg m^{-2}	122–1286; (443)	7.2–262; (72)
Ketoacids, μg m^{-2}	13.6–124.8; (42)	1.7–24.8; (8.8)
	Dry Depositions	
Diacids; (av.), μg m^{-2} yr^{-1}	256–1907; (735)	22–396; (134)
Oxalic acid; (av.), μg m^{-2} yr^{-1}	18–1351; (466)	7.5–275; (75)

[a]Dry depositions were calculated by using a dry deposition velocity of 0.01 cm s^{-1} [*Slinn and Slinn*, 1980].

and Southern Pacific, respectively (Table 3). Similarly, ketoacid standing masses would be 14–125 μg m^{-2} (average 42; n = 4) and 1.7–25 μg m^{-2} (average 9; n = 14) in the Northern and Southern Pacific, respectively. The standing mass of oxalic acid in the Northern and Southern Pacific is something around 122–1286 μg m^{-2} (average 443; n = 4) and 7.2–262 μg m^{-2} (average 72; n = 14), respectively.

[21] In order to compare the importance of dry deposition to the surface ocean, we estimated a dry deposition flux for oxalic acid and total diacids. Assuming a dry deposition velocity of 0.01 cm s^{-1} for aerosol particles [*Slinn and Slinn*, 1980] obtained from an aerosol size of oxalic acid of 0.5 μm [*Kerminen et al.*, 1999; *Mochida et al.*, 2003b], we evaluated the air-to- sea fluxes of the diacids by dry deposition to be 256–1907 μg m^{-2} (average 735; n = 4) and 22–396 μg m^{-2} yr^{-1} (average 134; n = 14) for the Northern and Southern Pacific, respectively. These calculations give rise to a dry deposition for oxalic acid of 128–1351 μg m^{-2} yr^{-1} (average 466; n = 4) and 7.5–275 μg m^{-2} yr^{-1} (average 75; n = 14) for the Northern and Southern Pacific, respectively (Table 3). Diacid dry depositions are 2 orders of magnitude higher than the estimated dry depositions of alkanes, n-alcohols and fatty acids measured in the North Pacific [*Kawamura et al.*, 2003].

3.4. Photochemical Production of Water-Soluble Organic Compounds Total Diacids

[22] The spatial distribution of diacid-C/TC and diacid-C/WSOC ratios shows higher values at low latitudes (Figure 5) and in the Northern Pacific atmosphere where highest temperatures were recorded. The Northern Pacific maxima in the diacid-C/WSOC ratios suggested that in the Western Pacific, the diacids are produced in the atmosphere by photochemically induced secondary reactions or that they are preferentially injected to the atmosphere at these latitudes. Interestingly, a positive correlation was found between the diacid-C/WSOC ratios (r = 0.75; p = 0.005) and the air temperature (Figure 10) suggesting that secondary photochemical reactions (gas-to-particle conversion), and oxidation of hydrocarbons and other organic precursors are the main sources of diacids in this area. For many oxidation reactions, several sources and sinks have been proposed. Dicarboxylic acids have been considered to be mainly produced by secondary photochemical oxidation of anthropogenic and natural organic compounds such as biogenic fatty acids [*Kawamura and Gagosian*, 1987, 1990]. The present results seem to be consistent with previous studies which reported a diurnal distribution for C3–C6 diacid [*Satsumabayashi et al.*, 1990] with a maximum in daytime and summer maximum concentrations of C2–C6 diacids in the atmosphere [*Kawamura and Ikushima*, 1993]. Moreover, the diacid-C/WSOC relationship with temperature obtained in this study is consistent with the positive correlation obtained for diacid-C/TC versus temperature in Tokyo [*Kawamura and Ikushima*, 1993].

[23] Diacids can be produced through photochemical oxidation and through the action of HO radicals on unsaturated compounds such as fatty acids and aromatic compounds [*Kawamura and Gagosian*, 1987, 1990]. Reactions between free radicals and molecules have positive activation energies and their rates increase as temperature increase [*Graedel and Crutzen*, 1993, and references therein]. Interestingly, *Graedel and Crutzen* [1993] reported that atmospheric methane-hydroxyl reactions might be increased by nearly 30% between boundary layer and the lower troposphere (1 km) by a temperature difference of only 15°C. These observations suggest that the differences in temperature observed during the cruise might be explained in part by the temperature through photochemical oxidation reactions in the lower troposphere. Additionally, direct precursors of diacids such as unsaturated fatty acids are likely to be more enriched in warmer and slightly more productive waters [*Kawamura and Gagosian*, 1990] such as those encountered in the North Pacific rather than in the South Pacific at this period of the year [*Kennish*, 2000]. Those molecules might be further emitted from surface waters to the air and induce production of diacids through photochemical oxidation reactions.

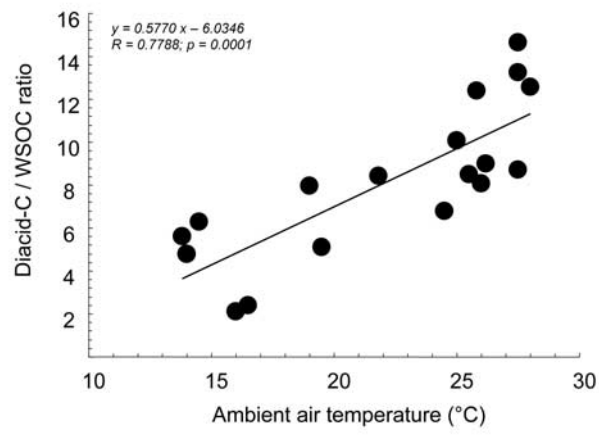

Figure 10. Diacid-C/WSOC ratio (in %) in the western Pacific aerosol samples as a function of the ambient air temperature measured on the upper deck of the R/V *Hakuho Maru* (~14 m above the sea level) during the cruise.

[24] It is important to note that primary sources are also important in the marine atmosphere near industrialized areas such as the Japanese Islands and Australia. It is now well established that LMW-diacids are produced by ozone and cycloalkene reaction [*Hatakeyama et al.*, 1987; *Kawamura and Ikushima*, 1993] as well as by the emissions from automobile exhausts [*Kawamura and Kaplan*, 1987] and from biomass burning [*Legrand and De Angelis*, 1996; *Narukawa et al.*, 1999]. The concentrations of diacids obtained here for the North Pacific are in good agreement with the previous work of *Kawamura and Usukura* [1993]. Those obtained at the site near the Japanese coasts (QFF 538) are much lower than those from the urban aerosols (90–3000 ng m^{-3} [*Kawamura and Ikushima*, 1993; *Sempéré and Kawamura*, 1994]). This study suggests (Figures 4 and 7) that the main source of diacids are of anthropogenic origin in the North Pacific. Diacid concentrations decrease toward the Southern Hemisphere during the sampling although the QFF 553 sample indicated high concentrations (85 ng m^{-3}). Thus concentration of diacids is driven by fossil fuel combustion and biomass burning and subsequent photochemical oxidation near the continent, whereas in remote areas, secondary photochemical reactions are probably the main sources.

3.4.1. Preferential Production of Oxalic Acid and Possible Mechanisms

[25] Although the relative abundance of total dicarboxylic acid-C in the water-soluble fraction increased with ambient temperature, part of the increase was found to depend on the carbon chain length and structure of the diacid species. Figures 11a–11b plot the individual relative abundance of succinic acid (C_4) and the oxalic/succinic acid (C_2/C_4) ratio as a function of air temperature. Interestingly, the relative abundance of succinic acid clearly shows a negative relationship with air temperature whereas the oxalic/succinic ratio stays relatively constant between 14° and 20°C and increases toward 28°C. The results again indicate that molecular distribution of short chain LMW-diacids is in relation with air temperature or very likely is enhanced by the photochemical reactions.

[26] It is of importance to note that succinic acid was found to be the most abundant diacids in some Antarctic aerosol samples [*Kawamura et al.*, 1996], in the spring snowpack [*Narukawa et al.*, 2002] and the Greenland ice core samples [*Kawamura et al.*, 2001b]. Interestingly, succinic acid was found to be more abundant than malonic acid in winter in Tokyo [*Sempéré and Kawamura*, 1994], in Southeast Asia [*Narukawa et al.*, 1999] and in most of the Arctic aerosol samples [*Kawamura et al.*, 1995; *Kerminen et al.*, 1999] as well as in Tokyo rain/snow/sleets [*Sempéré and Kawamura*, 1994], Los Angeles [*Kawamura et al.*, 2001b] and eastern Pacific rainwaters [*Sempéré and Kawamura*, 1996]. These results suggest a high relative abundance of C4 succinic acid is a common trend in cold environments. On the other hand, lower relative abundance of succinic diacid was generally found only for aerosol samples collected under sunny and hot conditions in urban area [*Kawamura and Ikushima*, 1993; *Sempéré and Kawamura*, 1994]. Although higher relative abundance of oxalic acid was observed for higher temperature, its linear relationship with the temperature is not significant. Thus the increase in the C_2/C_4 ratios and the decrease in C_4 relative abundance with temperature was mainly due to the low abundance of succinic acid at high temperature. This may suggest that succinic acid is a precursor of oxalic acid, which is further oxidized to CO and CO_2.

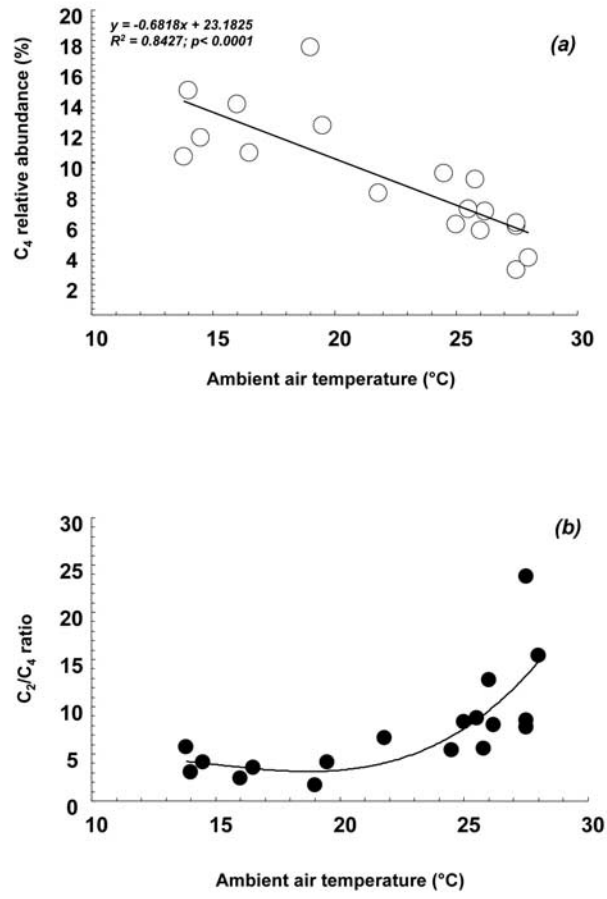

Figure 11. (a) Relative abundance of succinic diacid (C_4 di) and (b) the oxalic/succinic diacids (C_2/C_4) ratios in the western Pacific aerosol samples as the function of the ambient air temperature measured during the R/V *Hakuho Maru* cruise.

[27] The C_4–C_{10} α, ω-dicarboxylic acids are likely to be produced by the photo-oxidation of unsaturated fatty acids and their oxidation products [*Kawamura and Gagosian*, 1990; *Kawamura and Sakaguchi*, 1999]. Previous studies showed that longer chain diacids (e.g., C_8–C_{10}) are more stable in the atmosphere than shorter ones (e.g., C_5–C_6) which are likely to be precursors of the lower diacids. It was also proposed that photo-induced hydroxylation of succinic acid produces malic acid which may be further oxidize in the atmosphere to result in oxalic acid or malonic acid, the latter being further oxidize to oxalic acid through intermediate compounds such as hydroxymalonic acid or ketomalonic [*Kawamura and Ikushima*, 1993]. As a source of semivolatile organics, monocarboxylic acids are probably important in addition to the oxidation of cycloalkenes. It is important to note that midchain ketocarboxylic acids and

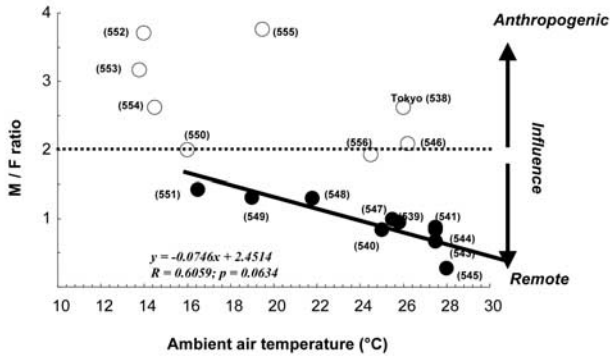

Figure 12. Distribution of C_4-unsaturated α, ω-dicarboxylic acids (maleic (M: *cis* configuration) and fumaric acid (F: *trans* configuration)) in the western Pacific aerosol samples as a function of the ambient temperature measured during the R/V *Hakuho Maru* cruise. Open circles are related to samples with M/F ratio of ∼2. Note that these samples correspond essentially to aerosol samples collected near Australia and the Japanese Islands. Solid circles are related to samples with M/F ratios <2 and correspond to samples collected in remote areas. Numbers in the figure correspond to QFF sample ID numbers (see also Figure 1). Possible anthropogenic and remote influences are also given in the figure.

hydroxy fatty acids have been reported in the marine atmosphere [*Kawamura and Gagosian*, 1990]. Interestingly, such relationships were not clearly found for relative abundances of other species including malonic acid (C_3), and C_5–C_{10} diacids.

3.4.2. *Cis*/*Trans* Configuration of Unsaturated Dicarboxylic Acids in Western Pacific Atmosphere

[28] Examination of the two configurations of C4 unsaturated diacid in relation with temperature may also provide useful information. Maleic acid (cis configuration) showed the highest concentrations at low air temperatures (QFF 550–552–554) and in samples collected near Australia (QFF 546, QFF 556) and the Japanese Islands (QFF 538) (Figures 12 and 1 for localization of the samples). By contrast, lower M/F ratios were observed for the most remote samples (QFF 539–543) and for the highest temperatures (QFF 547–549; 551). This is consistent with very low M/F ratios (0.06–1.3; average 0.26) already reported for the remote Pacific Ocean [*Kawamura and Sakaguchi*, 1999].

[29] The predominance of precursor *cis* configuration should be associated with the photochemical oxidation of benzene or toluene, whose *cis* configuration is preserved in the structure of the oxidation product. The maleic acid may further be isomerized photochemically to *trans* configuration (fumaric acid) in the atmosphere under solar radiation [*Kawamura and Ikushima*, 1993, and references therein]. These results seem in contrast with those obtained by *Kawamura and Ikushima* [1993] who reported higher M/F ratios for Tokyo samples collected in summer-autumn. However, Tokyo samples showed M/F ratios usually higher

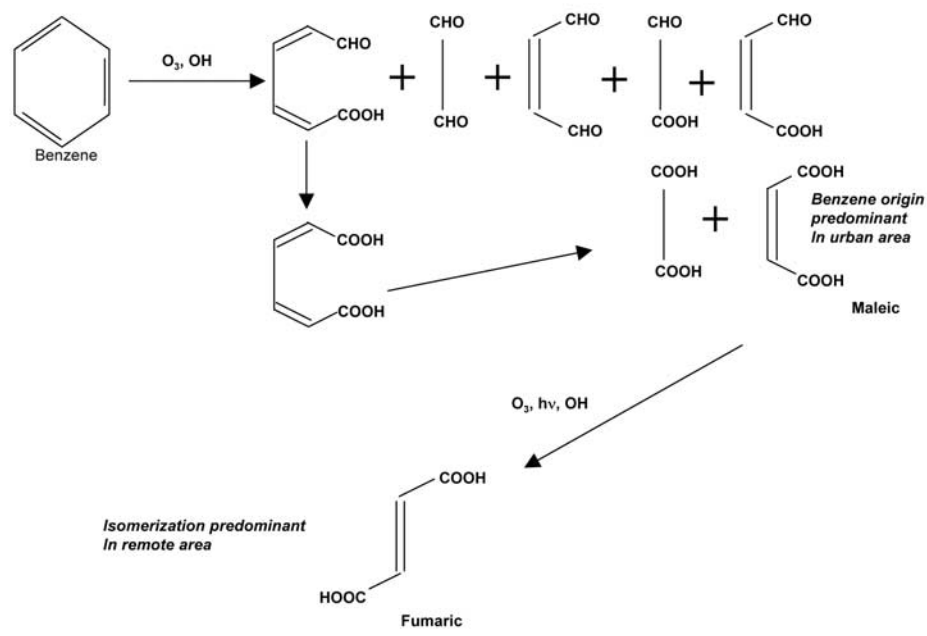

Figure 13. Reaction mechanisms (modified from *Kawamura and Kaplan* [1987]), proposed for the photochemical control of maleic and fumaric acid from the photo-oxidation production from benzene-type organic compound near continental area and from *cis*/*trans* isomerization in remote areas.

than 1 and were probably strongly dependant on the oxidation of benzene-type structures, whereas Western Pacific samples were not only dependant on the source of maleic acid but also for a large part, on the subsequent isomerization of maleic to fumaric acid. It is interesting to note that we observed a negative relationship between M/F ratios and air temperature for the most remote samples which showed a M/F ratio close to or lower than 1, indicating that isomerization and then the photochemical processes control the M/F ratio. Fumaric acid is an intermediate product of photochemical isomerization of maleic acid (Figure 13). Because of the double bond, fumaric acid would be further oxidized by ozone and other oxidizing agents like OH radicals to produce smaller diacids such as oxalic acid (Figure 13).

3.4.3. Azelaic Acid Distribution in Relation to the Air Temperature

[30] The relative abundance of other diacids did not show a clear relationship with air temperature. However, the concentrations of C_9 azelaic acid clearly show a positive hyperbolic relationship with air temperature (Figure 14a). The azelaic concentrations remained rather constant around 1 or 2 ng m^{-3} between 13° and ~21°C. In contrast, we observed large concentration variations of this acid for temperatures above 24°C. Interestingly, a logarithmic relationship was found between C_9-azelaic acid and 9-oxononanoic acid (Figure 14b) which has been proposed as a precursor of azelaic acid [*Kawamura and Gagosian*, 1987]. As indicated above, longer chain-diacids are likely produced by the photo-oxidation of unsaturated fatty acids and their oxidation products such as semivolatile and midchain ketocarboxylic acids [*Kawamura and Gagosian*, 1990]. The unsaturated fatty acids are abundant in terrestrial higher plant leaves and marine phytoplankton and are enriched in the seawater microlayer. After their emission into the atmosphere, they are photochemically oxidized form diacids dominated by azelaic acid, and to a lesser extent, 9-oxononanoic acid because of the double bond predominantly at C_9 position [*Kawamura and Gagosian*, 1987].

[31] Relationships between azelaic acid concentrations with temperature suggests either enhanced production of HO radicals in the lower troposphere and/or increased fatty acid emission of biological origin [*Kawamura and Gagosian*, 1990] from warm marine surface waters (and more productive waters at this period of the year [*Kennish*, 2000]), in the North Pacific. This process could induce higher production of azelaic acid in the North Pacific (where warmer water was encountered) than in Southern Pacific. Higher concentrations of C_9-diacid compared to ωC_9-ketoacid in warmer temperatures and higher solar radiation strongly suggest that the lower stability of the ketoacid may act as a precursor of azelaic acid.

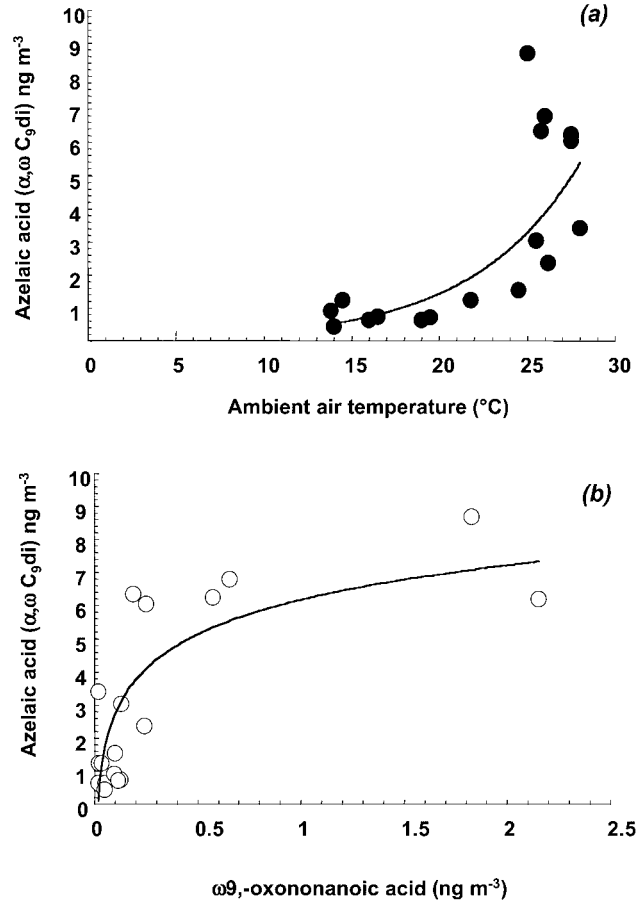

Figure 14. (a) Azelaic acid (C_9 α, ω-dicarboxylic acid) versus ambient temperature measured during the R/V *Hakuho Maru* cruise. (b) Azelaic acid (C_9 α, ω-dicarboxylic acid) versus 9-oxononanoic acid (ωC_9) in the western Pacific aerosol samples.

4. Summary and Conclusion

[32] Molecular distribution of water-soluble dicarboxylic acids in the marine aerosols samples collected from Western Pacific showed a predominance of oxalic acid (C_2) followed by malonic (C_3) and succinic acid (C_4). Diacids accounted for 3.2% (average) of TC and 8.2% (average) of WSOC, indicating that they are a major component of the water-soluble organic fraction of marine aerosols in Western Pacific. Our results indicated that although the level of aerosol mass was similar in the Northern and Southern Pacific, highest concentrations of organic components including diacids were observed in the North Pacific. Although the highest concentrations of oxalic diacid and its homologues were found near Asian or Australian continents (up to 604 ng m^{-3}). These results showed that diacids are still significantly abundant in remote marine atmosphere (7–81 ng m^{-3}), suggesting that diacids are continuously produced from organic precursors.

[33] We also found that the fraction of diacid in the water-soluble organic carbon increased linearly with air temperature. Diacids should act as cloud condensation nuclei, and play a role in the radiative balance by increasing the light backscattering and cooling the atmosphere. Because of their continuous production in remote areas under high solar radiation, their role is probably not limited by the continent and their urban sources. This report confirmed that concentration levels and relative abundance of diacids is controlled by the continental and anthropogenic sources as well as by

photochemistry in remote areas. However, this study highlights that the signature of the photochemical oxidation could be followed by the maleic/fumaric acid and on the oxalic/succinic acid ratios suggesting that these compounds might be useful tools for better understanding the present or past atmospheric photochemical reactions in the lower troposphere. Further studies are necessary to evaluate the significance of these compounds as tracers of atmospheric temperature or sunlight intensity; however, this study also suggests that a water-soluble fraction of the aerosol could be parameterized for global model calculations or for long term projections in relation to global change.

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References

Andreae, M. O., Raising dust in the greenhouse, *Nature*, *380*, 389–390, 1996.

Andreae, M. O., and P. J. Crutzen, Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, *Science*, *276*, 1052–1058, 1997.

Andreae, M. O., et al., Biomass burning: Its history, use and distribution and its impact on environmental quality and global climate, in *Global Biomass Burning, Atmospheric Climate and Biospheric Implications*, edited by J. S. Levine, pp. 3–21, MIT Press, Cambridge, Mass., 1991.

Atkinson, R., D. L. Baulch, A. R. Cox, R. F. Hampson Jr., J. A. Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement IV: IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, *21*, 1125–1568, 1993.

Ayers, G. P., and J. L. Gras, Seasonal relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air, *Nature*, *353*, 834–835, 1991.

Bandow, H., N. Washida, and H. Akimoto, Ring cleavage reactions of aromatic hydrocarbons studied by FT-IR spectroscopy: I. Photooxidation of toluene and benzene in the NO_x-air system, *Bull. Chem. Soc. Jpn.*, *58*, 2531–2540, 1985.

Baudet, J. G. R., J. P. Lacaux, J. J. Bertrand, F. Desalmand, J. Servant, and V. Yobué, Presence of an atmospheric oxalate source in the intertropical zone: Its potential action in the atmosphere, *Atmos. Res.*, *25*, 465–477, 1990.

Betterton, E. A., Henry's law constants of soluble and moderately soluble organic gases: Effects on aqueous phase chemistry, in *Gaseous Pollutants: Characterization and Cycling*, edited by J. O. Nriagu, pp. 1–50, John Wiley, New York, 1992.

Cadle, S., and P. J. Groblicki, An evaluation of methods for the determination of organic acid elemental carbon, in *Particulate Carbon-Atmospheric Life Cycle*, edited by G. T. Wolf and R. L. Klomisch, pp. 89–109, Plenum, New York, 1982.

Carlson, D. J., Surface microlayer phenolic enrichments indicate sea surface slicks, *Nature*, *296*, 426–429, 1982.

Charlson, R. J., and H. Rhode, Factors controlling the acidity of natural rainwater, *Nature*, *295*, 683–685, 1982.

Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Waren, Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate, *Nature*, *326*, 655–661, 1987.

Charlson, R. J., S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Coakley Jr., J. E. Hansen, and D. J. Hofmann, Climate forcing by anthropogenic aerosols, *Science*, *255*, 423–430, 1992.

Gagosian, R. B., E. T. Peltzer, and J. T. Merril, Long range transport of terrestrially derived lipids in aerosols from the South Pacific, *Nature*, *291*, 800–803, 1987.

Graedel, T. E., and P. J. Crutzen, The water cycle and climate, in *Atmospheric Change: An Earth System Perspective*, chap. 6, W. H. Freeman, New York, 1993.

Grosjean, D., Organic acids in southern California air: Ambient concentrations, mobile source emissions, in situ formation and removal processes, *Environ. Sci. Technol.*, *23*, 1506–1514, 1989.

Grosjean, D., K. Van Cauwenberghe, J. P. Schmid, P. E. Kelley, and J. N. Pitts Jr., Identification of C_3–C_{10} aliphatic dicarboxylic acids in airborne particulate matter, *Environ. Sci. Technol.*, *12*, 313–317, 1978.

Grosjean, D., A. H. Miguel, and T. M. Tavares, Urban air pollution in Brazil: Acetaldehyde and other carbonyls, *Atmos. Environ.*, *24*, 101–106, 1990.

Hara, K., K. Osada, K. Matsunaga, T. Sakai, Y. Iwasaka, and K. Furuya, Concentration trends and mixing states of particulate oxalate in Arctic boundary layer in winter/spring, *J. Geophys. Res.*, *107*, 4399, doi:10.1029/2001JD001584, 2002.

Hashimoto, Y., H. K. Kim, T. Otoshi, and Y. Sekine, Air quality at Seoul, Lorea, May–March 1989, *J. Jpn. Soc. Air Pollut.*, *26*, 51–58, 1991.

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

Hegg, D. A., L. F. Radke, and P. V. Hobbs, Measurements of Aitken nuclei and cloud condensation nuclei in the marine atmosphere and their relation to the DMS-cloud-climate hypothesis, *J. Geophys. Res.*, *96*, 18,727–18,733, 1991a.

Hegg, D. A., R. J. Fereck, P. V. Hobbs, and L. F. Radke, Dimethyl sulfide and cloud condensation nucleus correlation in the northeast Pacific Ocean, *J. Geophys. Res.*, *96*, 13,189–13,191, 1991b.

Houghton, J. M., L. G. Meira Filho, B. A. Callendar, N. Harris, A. Kattenberg, and K. Maskell (Eds.), *Climate Changes: The Science of Climate Change*, Cambridge Univ. Press, New York, 1995.

Junge, C. E., *Air Chemistry and Radioactivity*, Academic, San Diego, Calif., 1963.

Kawamura, K., and R. B. Gagosian, Implications of ω-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids, *Nature*, *325*, 330–332, 1987.

Kawamura, K., and R. B. Gagosian, Mid-chain ketocarboxylic acids in the remote marine Atmosphere: Distribution patterns and possible formation mechanisms, *J. Atmos. Chem.*, *11*, 107–122, 1990.

Kawamura, K., and K. Ikushima, Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, *27*, 2227–2235, 1993.

Kawamura, K., and I. R. Kaplan, Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air, *Environ. Sci. Technol.*, *21*, 105–110, 1987.

Kawamura, K., and F. Sakaguchi, Molecular distribution of water-soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, *104*, 3501–3509, 1999.

Kawamura, K., and K. Usukura, Distributions of low molecular weight dicarboxylic acids in the North Pacific Ocean aerosol samples, *J. Oceanogr.*, *49*, 271–283, 1993.

Kawamura, K., and O. Yasui, Organic acids and aldehydes in the ice samples from Site-J, Greenland, *Bull. Glacier Res.*, *9*, 59–63, 1991.

Kawamura, K., H. Kasukabe, O. Yasui, and L. A. Barrie, Production of dicarboxylic acids in the Arctic atmosphere at polar sunrise, *Geophys. Res. Lett.*, *22*, 1253–1256, 1995.

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

Kawamura, K., K. Yokohama, Y. Fujii, and O. Watanabe, A Greenland ice core record of low molecular weight dicarboxylic acids, and α-dicarbonyls: A trend from little ice age to the present (1540–1989 AD), *J. Geophys. Res.*, *106*, 1331–1345, 2001a.

Kawamura, K., S. Steinberg, L. Ng, and I. R. Kaplan, Wet deposition of low molecular weight mono-and di-carboxylic acids, aldehydes and inorganic species in Los Angeles, *Atmos. Environ.*, *35*, 3917–3926, 2001b.

Kawamura, K., Y. Ishimura, and K. Yamasaki, Four-year observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific, *Global Biogeochem. Cycles*, *17*(1), 1003, doi:10.1029/2001GB001810, 2003.

Kennish, M. J., *Practical Handbook of Marine Science*, edited by M. J. Kennish, CRC, Boca Raton, Fla., 2000.

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

Kerminen, V. M., C. Ojanen, T. Pakkanen, R. Hillano, M. Aurela, and J. Merilaïnen, Low molecular weight dicarboxylic acids in an urban and rural atmosphere, *J. Aerosol Sci.*, *31*, 349–362, 2000.

Khwaja, H. A., Atmospheric concentrations of carboxylic acids and related compounds at a semiurban site, *Atmos. Environ.*, *29*, 45–48, 1995.

Krishnamurti, B. T., B. Jha, J. Prospero, A. Jayaraman, and V. Ramanathan, Aerosol and pollutant transport and their impact on radiative forcing over the tropical Indian Ocean during the January–February 1996 pre-INDOEX cruise, *Tellus, Ser. B*, *50*, 521–542, 1998.

Legrand, M., and M. De Angelis, Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone, *J. Geophys. Res.*, *101*, 4129–4145, 1996.

Li, S. M., and J. W. Winchester, Water-soluble organic constituents in Arctic aerosols and snow pack, *Geophys. Res. Lett.*, *20*, 45–48, 1993.

Li, X., H. Maring, D. Savoie, K. Voss, and J. M. Prospero, Dominance of mineral dust in aerosol light-scattering in the North Atlantic trade winds, *Nature*, *380*, 416–419, 1996.

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

Mochida, M., A. Kawabata, K. Kawamura, H. Hatsushika, and K. Yamazaki, Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific, *J. Geophys. Res.*, *108*, 4193, doi:10.1029/2002JD002355, 2003a.

Mochida, M., K. Kawamura, N. Umemoto, M. Kobayashi, S. Matsunaga, H. Lim, B. J. Turpin, T. S. Bates, and B. R. T. Simoneit, Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off coasts of East Asia: Continental outflow of organic aerosols during the ACE-Asia campaign, *J. Geophys. Res.*, doi:10.1029/2002JD003249, in press, 2003b.

Mueller, P. K., K. K. Fung, S. L. Heisler, D. Grosjean, and G. M. Hidy, Atmospheric particulate carbon observations in urban and rural areas of the United States, in *Particulate Carbon-Atmospheric Life Cycle*, edited by G. T. Wolf and R. L. Klimisch, pp. 343–370, Plenum, New York, 1982.

Munger, J. W., D. J. Jacob, B. C. Daube, and L. W. Horowitz, Formaldehyde, glyoxal and methylglyoxal in air and cloudwater at a rural mountain site in central Virginia, *J. Geophys. Res.*, *100*, 9325–9333, 1995.

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

Narukawa, M., K. Kawamura, S.-M. Li, and J. W. Bottenheim, Dicarboxylic acids in the Arctic aerosols and snowpacks collected during ALERT 2000, *Atmos. Environ.*, *36*, 2491–2499, 2002.

Neususs, C., M. Pelzing, A. Plenwka, and H. Herrmann, A new analytical approach for size resolved speciation of organic compounds in atmospheric aerosol particles: Method and first results, *J. Geophys. Res.*, *105*, 4513–4527, 2000.

Norton, R. B., J. M. Roberts, and B. J. Huebert, Tropospheric oxalate, *Geophys. Res. Lett.*, *10*, 517–520, 1983.

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

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

Peltzer, E. T., and R. B. Gagosian, Organic geochemistry of aerosols over the Pacific Ocean, in *Chemical Oceanography*, vol. 10, pp. 281–338, Academic, San Diego, Calif., 1989.

Plumb, R. A., and D. A. McConalong, On the Meridional structure of long-lived tropospheric constituents, *J. Geophys. Res.*, *93*, 15,897–15,913, 1988.

Prospero, J. M., and D. L. Savoie, Effects of continental sources on nitrate concentrations over the Pacific Ocean, *Nature*, *339*, 687–689, 1989.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit, Sources of fine organic aerosols: 1. Charbroilers and meat cooking operations, *Environ. Sci. Technol.*, *25*, 1112–1125, 1991.

Satsumabayashi, H., H. Kurita, Y. Yokouchi, and H. Ueda, Photochemical formation of particulate dicarboxylic acids under long-range transport in central Japan, *Atmos. Environ.*, *24*, 1443–1450, 1990.

Saxena, P., and L. M. Hildemann, Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, *24*, 57–109, 1996.

Saxena, P., L. M. Hildemann, P. H. McHurry, and J. H. Seinfeld, Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, *100*, 18,755–18,770, 1995.

Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit, Measurement of emissions from air pollution sources: 1. C_1 through C_{29} organic compounds from meat charbroiling, *Environ. Sci. Technol.*, *22*, 1566–1577, 1999.

Schuetzle, D., D. Cronn, and A. I. Crittenden, Molecular composition of secondary aerosols and its possible origin, *Environ. Sci. Technol.*, *9*, 838–845, 1975.

Sekine, Y., Y. Hashimoto, T. Nakamura, Z. Chen, and S. Maitsuzawa, Characterization of atmospheric aerosol components at Beijing, China, *J. Jpn. Soc. Air Pollut.*, *27*, 237–245, 1992.

Sempéré, R., and K. Kawamura, Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere, *Atmos. Environ.*, *28*, 449–459, 1994.

Sempéré, R., and K. Kawamura, Low molecular weight dicarboxylic acids and related polar compounds in the remote marine rain samples collected from western Pacific, *Atmos. Environ.*, *30*, 1609–1619, 1996.

Sicre, M. A., J. C. Marty, and A. Saliot, *n*-Alkanes, fatty acid esters, and fatty acid salts in size fractionated aerosols collected over the Mediterranean Sea, *J. Geophys. Res.*, *95*, 3649–3657, 1990.

Slinn, S. A., and W. G. N. Slinn, Predictions for particle deposition on natural waters, *Atmos. Environ.*, *14*, 1013–1016, 1980.

Stephanou, E. G., α, ω-Dicarboxylic acid salts and α, ω-dicarboxylic acids: Photo-oxidation products of unsaturated fatty acids, present in marine aerosols and marine sediment, *Naturwissenschaften*, *79*, 128–131, 1992.

Stephanou, E. G., and N. Stratigakis, Oxocarboxylic and α, ω-dicarboxylic acids: Photooxidation products of biogenic unsaturated fatty acids present in urban aerosols, *Environ. Sci. Technol*, *27*, 1403–1407, 1993.

Talbot, R. W., A. S. Vijgen, and R. C. Harriss, Soluble species in the Arctic summer troposphere: Acidic gases, aerosols, and precipitations, *J. Geophys. Res.*, *97*, 16,531–16,543, 1992.

Tegen, I., A. Lacis, and I. Fung, The influence on climate forcing of mineral aerosols from disturbed soils, *Nature*, *380*, 419–422, 1996.

Tran, N. K., S. M. Steinberg, and B. J. Johnson, Volatile aromatic hydrocarbons and dicarboxylic acid concentration in air at an urban site in the Southwestern US, *Atmos. Environ.*, *34*, 1845–1852, 2000.

Uematsu, M., R. A. Duce, and J. M. Prospero, Deposition of atmospheric mineral particles in the North Pacific Ocean, *J. Atmos. Chem.*, *3*, 123–138, 1985.

Warneck, P., In-cloud chemistry opens pathway to the formation of oxalic acid in the atmosphere, *Atmos. Environ.*, *37*, 2423–2427, 2003.

Yao, X., M. Fang, and C. K. Chan, Size distribution and formation of dicarboxylic acids in atmospheric particles, *Atmos. Environ.*, *36*, 2099–2107, 2002.

Zhou, X., and K. Mopper, Measurements of sub-parts-per-billion levels of carbonyl compounds in marine air by a simple cartridge trapping procedure followed by liquid chromatography, *Environ. Sci. Technol.*, *24*, 1482–1485, 1990.

Zuo, Y., and J. Hoigné, Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes, *Environ. Sci. Technol.*, *26*, 1014–1022, 1992.

K. Kawamura, Institute of Low Temperature Science, Hokkaido University, N19 W8, Kita-ku, 060-0819 Sapporo, Japan. (kawamura@owtem.hokudai.ac.jp)

R. Sempéré, Laboratoire de Microbiologie Marine, UMR CNRS/INSU 6117, Case 907, Centre d'Océanologie de Marseille, Université de la Méditerranée, F-13288 Marseille Cedex 9, France. (sempere@com.univ-mrs.fr)