

Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: Continental outflow of organic aerosols during the ACE-Asia campaign

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[1] Aerosol sampling for major oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) was conducted from 15 March to 19 April 2001 on board the National Oceanic and Atmospheric Administration R/V *Ronald H. Brown* over the western North Pacific, the East China Sea, and the Sea of Japan, as part of the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) campaign. During the cruise, aerosol particles were collected on quartz fiber filters using a high-volume air sampler. Diacids were also collected using an annular denuder sampling system to assess their gas-particle partitioning. Concentrations of total diacids, total fatty acids, and levoglucosan were found to be higher off the coasts of East Asia than in the remote Pacific. Contributions of these organic compounds to total organic carbon and total organic matter (OM) were calculated to be $9.8 \pm 2.3\%$ and $19.0 \pm 4.8\%$, respectively, assuming OM to be organic carbon \times 1.6. Diacid concentrations were highly correlated with nss-SO_4^{2-} and NO_3^- , which originate from anthropogenic sources over East Asia. The temporal variations and chain-length distributions of fatty acids suggest that atmospheric transport of terrestrial organic materials is important off the coast of the continent. $\text{C}_2 - \text{C}_5$ diacids were present predominantly in the particulate phase. The relative abundances of $\text{C}_2 - \text{C}_5$ diacids stayed almost unchanged throughout the cruise, suggesting that deposition is more important than chemical decomposition as a sink of diacids and that they are relatively stable end products in the atmosphere.

INDEX TERMS:

0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 1610 Global Change: Atmosphere (0315, 0325); KEYWORDS: organic aerosol, East Asia, transport, dicarboxylic acids, fatty acids, levoglucosan

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1. Introduction

[2] Atmospheric aerosols contain substantial amounts of organic compounds, which potentially alter their physical

and chemical properties. The sources of organic aerosols include fossil-fuel combustion and biomass burning, whose global emission rates are estimated to be 28.5 and 44.6 Tg yr⁻¹, respectively [Lioussé *et al.*, 1996]. The contribution of biogenic VOCs to the formation of secondary organic aerosols may also be substantial, and the estimates of the global production rates range from 7.8 to 79 Tg yr⁻¹ [Lioussé *et al.*, 1996; Griffin *et al.*, 1999; Kanakidou *et al.*, 2000]. Organic compounds as well as sulfates are major components in sub-micron aerosols, contributing significantly to the scattering of sunlight (direct effect) under various circumstances [Mazurek *et al.*, 1991; Penner, 1995]. Furthermore, polar organic compounds are hypothesized to make aerosol particle surfaces hydrophilic, which enhances the parti-

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cle's ability to serve as cloud condensation nuclei (CCN) [Novakov and Penner, 1993; Rivera-Carpio et al., 1996; Andrews et al., 1997; Matsumoto et al., 1997; Yu, 2000]. The number of CCN affects cloud radiative properties (indirect effect).

[3] Organic acids are an important class of compounds in atmospheric aerosol particles. In particular, dicarboxylic acids (DCAs) and fatty acids (FAs) are present predominantly in particles rather than in the gas phase [Schauer et al., 1999; Baboukas et al., 2000; Limbeck et al., 2001] because of the low vapor pressures ($\leq 10^{-4}$ Torr). DCAs have been shown to be major constituents of water-soluble organic compounds in aerosols [Saxena and Hildemann, 1996] and have been found in cities, rural areas, marine environments and polar regions [Kawamura et al., 1996]. Primary sources of DCAs are fossil-fuel combustion including motor vehicle exhaust [Kawamura and Kaplan, 1987], meat-cooking operations [Rogge et al., 1991], and biomass burning [Rogge et al., 1998]. It is also speculated from their diurnal variation that these compounds are produced photochemically in the air [Satsumabayashi et al., 1990]. FAs are found in atmospheric aerosols in residential areas [Cautreels and Van Cauwenberghe, 1977], rural sites [Ketserides et al., 1976; Yokouchi and Ambe, 1986], and remote sites [Simoneit et al., 1977, Gagosian et al., 1981]. They are emitted to the atmosphere from plants [Rogge et al., 1993a, Simoneit et al., 1977, 1991] and soil [Matsumoto and Hanya, 1980] as well as marine sources. They are also released to the atmosphere by various anthropogenic operations including combustion of organic materials [Rogge et al., 1991, 1993b, 1993c, 1993d, 1994, 1998]. Saccharides are another class of oxygenated organic compounds with substantial atmospheric concentrations [e.g., Graham et al., 2002; Pashynska et al., 2002]. Levoglucosan (1,6-anhydro- β -D-glucopyranose), formed during the pyrolysis of cellulose, is emitted in large quantities during wood combustion [Schauer et al., 2001; Nolte et al., 2001; Simoneit, 2002], and detected in biomass burning plumes [Graham et al., 2002] and in urban areas [Zdráhal et al., 2002]. Levoglucosan is stable under simulated atmospheric conditions [Fraser and Lakshmanan, 2000], and was detected even in the remote ocean far from combustion sources [Simoneit and Elias, 2000]. Saccharides also have low vapor pressures [Oja and Suuberg, 1999] and thus are present in the particulate phase.

[4] The Asian continent is an important source region of atmospheric aerosols with different origins including biomass burning, dust storms, and industrial and residential emissions. In this study, we focused on the chemical speciation of organic fractions in marine atmospheric aerosols influenced by the outflow of the Asian air masses. In order to better understand characteristics of organic aerosols and their long-range transport, we measured the temporal and spatial variation of DCAs, FAs, and levoglucosan over the western North Pacific, the East China Sea, and the Sea of Japan. Our chemical characterization has revealed that identified oxygenated organic compounds contribute substantially to the mass of total organic matter because of the large oxygen contents. Furthermore, gas/particle partitioning of DCAs were measured for the first time in the Asian Pacific region. On the basis of the temporal and spatial

distributions, their possible sources and sinks during long-range transport are discussed.

2. Experiment

2.1. Aerosol Sampling and Analysis

[5] Aerosol sampling was conducted from 15 March to 19 April 2001 on board the National Oceanic and Atmospheric Administration (NOAA) R/V *Ronald H. Brown*, as part of the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) campaign. A high-volume air sampler (Kimoto AS810) and an annular denuder system (URG Corp.) were used for bulk aerosol sampling and DCA gas/particle sampling, respectively. The cruise track is presented in Figure 1.

[6] Aerosol samples were collected on pre-combusted (450°C , 3–6 hrs) quartz fiber filters (20×25 cm, Pallflex 2500QAT-UP) in the high-volume air sampler. To prevent any possible contamination from ship exhausts, the sampler was controlled by a wind sector/wind speed system that automatically shuts off the sampling pumps at low wind speed (< 2.5 m s $^{-1}$) or when air came from abaft the beam. Air was sampled for 0.5–1 day at a flow rate of 800 L min $^{-1}$ (corresponding to a filter surface velocity of ~ 33 cm s $^{-1}$). The pumping time was $60 \pm 31\%$ of the sampling period on average with one standard deviation. Fifty aerosol samples were collected using the high-volume air sampler. The annular denuder sampling system used a Na $_2$ CO $_3$ coated denuder to trap gaseous organic acids and a Na $_2$ CO $_3$ impregnated quartz fiber filter to collect particles. A backup denuder coated with Na $_2$ CO $_3$ was used to assess volatilization of organic acids from the collected particles. A cyclone inlet removed large particles (50% cutoff diameter $> 2.5\mu\text{m}$). Thirty denuder samples were collected during the cruise. The sampling periods ranged 0.5–2 days, the flow rate was 10 L min $^{-1}$, and the pumping time was $61 \pm 24\%$ of the sampling period. Only DCAs were measured in the denuder samples because concentration levels of FAs were lower than the laboratory blank levels.

[7] Analysis of DCAs and FAs was conducted by the method described by Kawamura and Ikushima [1993] with some modification. In this study, samples were extracted with water (3×5 ml) to remove organic acids followed by ethyl acetate (3×5 ml) to extract FAs. The water extracts and ethyl acetate extracts were combined, concentrated to about 0.1 ml, and then reacted with 14% BF $_3$ /n-butanol. The mixture was heated for 1h to esterify carboxyl groups. The butyl esters of DCAs and FAs were extracted with n-hexane, and then quantified using GC-FID and GC-MS. It should be noted that carboxylic acid esters in aerosol particles, such as phthalic acid esters and fatty acid esters, may also be transesterified to butyl esters by this method. Hence carboxylic acids presented here include those in the form of esters in the atmosphere.

[8] Analysis of levoglucosan was conducted by GC-FID and GC-MS, and is fully described by M. Kobayashi et al. (manuscript in preparation, 2003). Briefly, levoglucosan was extracted from the samples with a methylene chloride/methanol 2:1 mixture. The samples were concentrated and

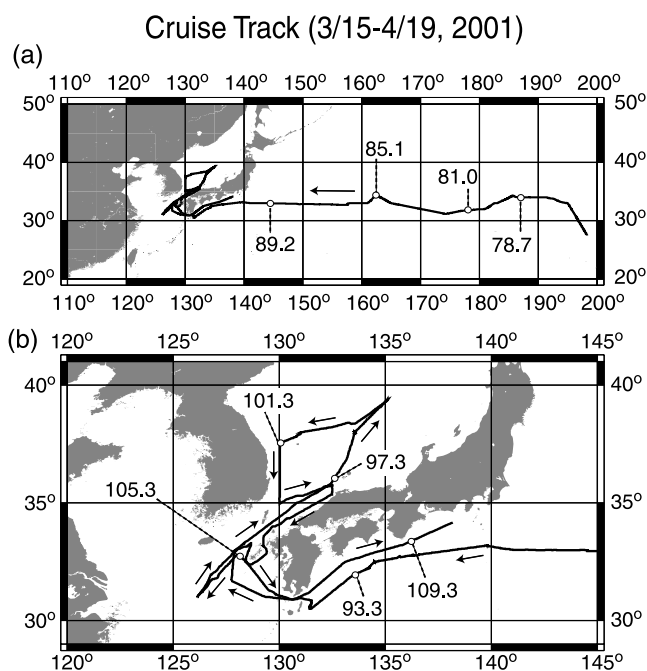


Figure 1. Cruise track of the R/V *Ronald H. Brown* (15 March to 19 April 2001). The days of year (DOY) are presented at the corresponding locations of the ship.

sonicated with methylene chloride. Sugars in the solution were oximated with hydroxylamine in pyridine, and derivatized with 99% *N,N*-bis(trimethylsilyl)fluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS), and then quantified with GC-FID and GC-MS.

[9] Inorganic ion species were quantified by ion chromatography (Dionex 500) after the extraction of quartz filter samples with pure water.

[10] This study focused on the compounds that contribute substantially to the total organic aerosol mass. Although organic compounds are not fully reported in this study, many other compounds were also detected in the marine aerosol samples. For example, fructose, glucose, inositol, and sucrose were detected in the course of the levoglucosan analysis. Size-segregated aerosol measurements in Sapporo, Japan ($43^{\circ}05'N$, $141^{\circ}21'E$) showed that while levoglucosan was mainly present in accumulation mode aerosols, fructose, glucose, inositol and sucrose were present mostly in very large ($>10 \mu\text{m}$) particles (Mochida, unpublished data). Since this size distribution is quite different from that of the major organic fractions represented by organic carbon (OC), these additional sugars were not reported in this study. *N*-alkanes and PAHs were quantified for a limited number of samples by GC-FID and GC-MS analysis. Their concentrations were in general lower than that of FAs and the results are not presented in this study. The UCM fraction (unresolved complex mixture of branched and cyclic hydrocarbons) accounted for 1–6% (average 4%) and 0.1–12.1% of the total carbon in aerosols in Tokyo and off the coast of Japan, respectively [Kawamura *et al.*, 1995; Kawamura, 2001]. Although not measured, the relative abundances of the UCM in the aerosol samples analyzed in this study

may be similar to the values measured in Tokyo and off the coast of Japan.

2.2. Comparison of High-Volume Air Sampling and Annular Denuder Sampling

[11] In this study, an inter-comparison was conducted between the high-volume (HV) and the annular denuder (AD) samplers for some DCAs. A high-volume air sampler is simple to handle and applicable for the analysis of trace compounds because of the large sampling volume and low blank levels of pre-combusted quartz fiber filters. In addition, these advantages make it possible to collect samples with high frequency. However, samples are subjected to potential artifacts, particularly adsorption of gas phase species and the evaporation of semi-volatile compounds from particles. Such artifacts can be minimized by annular denuder sampling although it is not suitable for the analysis of trace compounds because of lower sampling volume and higher blank levels of the reagents (Na_2CO_3 for DCA sampling).

[12] Figure 2 presents plots of HV versus AD data for $\text{C}_2 - \text{C}_5$ DCAs. The AD data presented here mean the particulate DCAs that were collected on filters and backup filter. HV air sampling was more frequent than AD sampling, thus some AD data were plotted against average

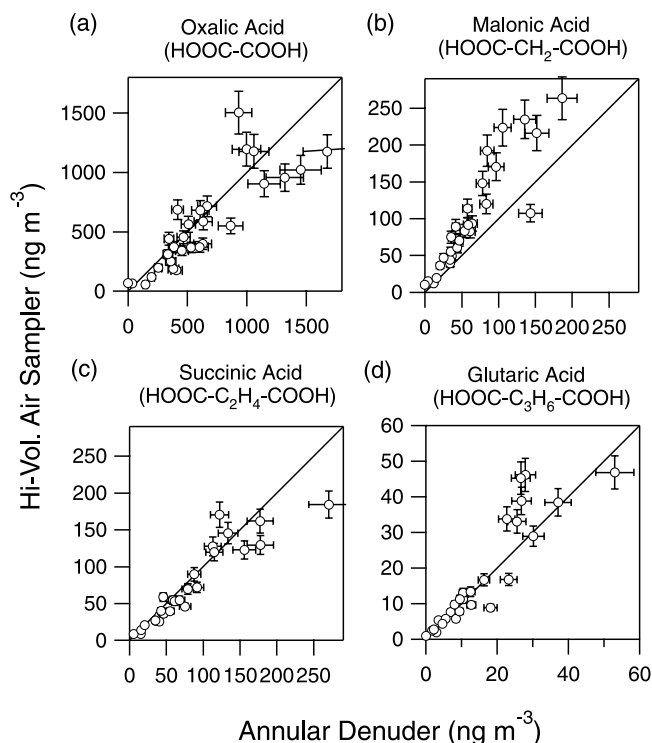
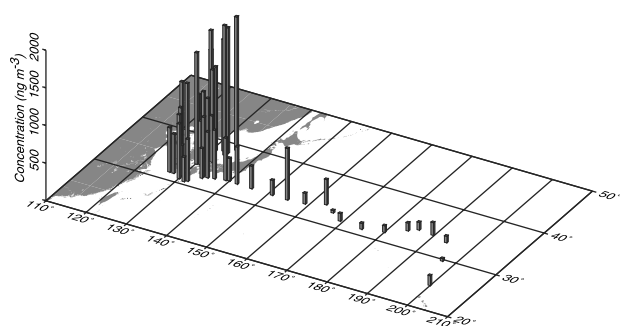
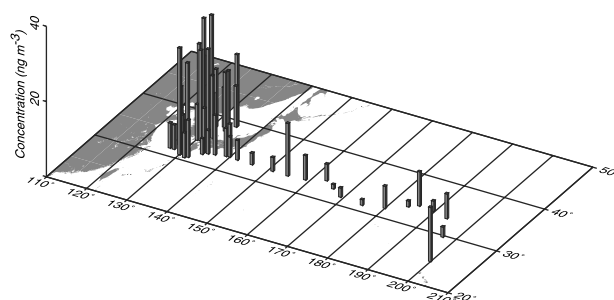


Figure 2. Plots of data for the high-volume (HV) air sampler versus the annular denuder (AD) system for (a) oxalic, (b) malonic, (c) succinic, and (d) glutaric acids. For the AD sampling, sums of the compounds collected on the filter and the backup denuder were presented. Each data point for the AD sampling is based on single sample whereas that for HV means an average of 2–4 aerosol samples.

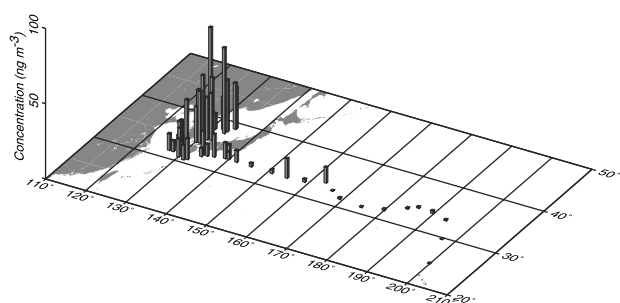
(a) Total DCAs



(b) LFAs



(c) HFAs



(d) Levoglucosan

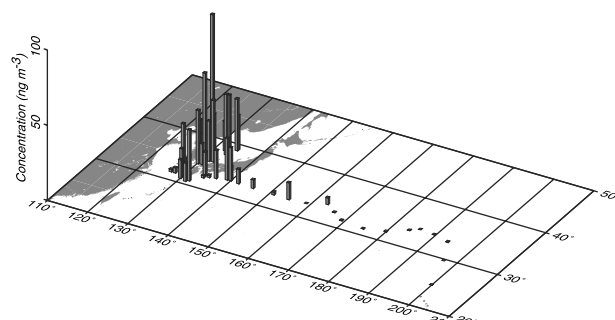


Figure 3. Spatial distribution of (a) total DCAs, (b) total LFAs, (c) total HFAs, and (d) levoglucosan during the cruise (15 March to 19 April 2001).

values of several HV samples. As can be seen in the figure, there are some variations between two sampling methods that are not within the analytical errors in the procedure (about 10%). Oxalic acid (C_2) concentrations obtained by HV sampling were systematically lower than those obtained by AD sampling, whereas malonic acid (C_3) showed an opposite trend. The systematic differences were less significant for succinic and glutaric acids. The AD system has negligible adsorption/volatilization problem in the measurement of particulate DCAs, whereas HV sampler has potential problems such as adsorption of gaseous DCAs to filters and volatilization of particulate DCAs during sampling. Although concentrations of DCAs did not change significantly during 1–5 days of sampling [Mochida *et al.*, 2003], they may be affected by chemical artifacts such as ozone oxidation on the filter substrate. Differences between the two samplers could also be due to the size cut on the AD sampler. If the amount of DCAs in supermicron sizes was substantial, the plots in Figure 2 should shift upward. On the basis of the data shown in Figure 2, the $C_2 - C_5$ DCA concentration ratios of $[C_n \text{ by HV sampler}]/[C_n \text{ by AD sampler}]$ ($n = 2-5$) were 0.80 ± 0.31 , 1.44 ± 0.49 , 0.89 ± 0.23 , and 1.10 ± 0.31 for oxalic, malonic, succinic and glutaric acids, respectively (average values with one standard deviation).

[13] The agreement between HV and AD samplings leads to a conclusion that HV data can be treated as the concentrations of particulate DCAs. In this sense, the standard deviations presented above are guides for assessing the uncertainty of the particulate DCA concentrations obtained by the HV aerosol sampling methods used. This inter-

comparison was not conducted for FAs and levoglucosan. However, their low vapor pressures suggest that HV data may also well represent their particulate concentrations. Hence concentrations of DCAs, FAs, levoglucosan obtained by HV sampler are interpreted as those present in aerosol particles.

3. Results and Discussion

3.1. Spatial Distribution of DCAs, FAs, and Levoglucosan During RB01-02 Cruise

[14] Figure 3a presents the spatial distribution of total DCAs obtained by HV sampling, where total DCAs is defined here as the sum of saturated $C_2 - C_{10}$ straight-chain DCAs, maleic and fumaric acids, and phthalic acid. Oxalic acid was the most abundant DCA measured during the cruise and accounted for approximately 70 wt% of the total DCAs. The relative abundances of malonic and succinic acids were 13 wt% and 10 wt%, respectively. Therefore total DCA distributions shown in Figure 3a largely depend on oxalic acid. As seen in the figure, total DCA concentrations are higher over off the coasts of East Asia than over the remote Pacific. In particular, very high concentrations of DCAs exceeding $1 \mu\text{g m}^{-3}$ were obtained over the Sea of Japan and the East China Sea where heavily polluted air masses were encountered. Such high concentrations are comparable to those observed in Tokyo ($90-1400 \text{ ng m}^{-3}$, average 480 ng m^{-3} [Kawamura and Ikushima, 1993]). In contrast, total concentrations of DCAs over the Pacific were low (usually $<100 \text{ ng m}^{-3}$). This concentration range is consistent with a previous study

Table 1. Summary of Concentrations of Dicarboxylic Acids, Fatty Acids, and Levoglucosan Observed During the RB01-02 Cruise^a

	Pacific (>140°E), n = 18		Pacific (<140°E), n = 8		East China Sea, n = 9		Sea of Japan, n = 15	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
DCAs	34–690	200	330–730	540	410–1500	850	480–2100	1200
LFAs	1.2–14	5.5	4.2–28	10	6.0–16	9.7	8.3–31	18
HFAs	0.2–13	3.3	5.5–15	10	7.9–41	18	10–68	32
Levoglucosan ^b	BDL–22	3.6	1.5–34	14	1.6–36	15	BDL–91	29
Total	36–720	220	350–780	580	430–1500	890	520–2200	1300

^aConcentrations are given in ng m⁻³.

^bThe concentration of levoglucosan in five samples were below detection limit (BDL, 0.02–1 ng m⁻³ depending on samples).

reported for the Pacific aerosol samples collected in autumn 1990 by *Kawamura and Sakaguchi* [1999].

[15] Spatial distributions of lower molecular weight C₁₆ + C₁₈ fatty acids (LFAs) and higher-molecular-weight C₂₀ – C₃₂ fatty acids (HFAs) are shown in Figures 3b and 3c, respectively. Their distributions were consistent with that of total DCAs; higher concentrations were observed off coast of East Asia than in the remote marine boundary layer. The combined concentrations of LFAs and HFAs approached 100 ng m⁻³ off the coast of East Asia. A strong even carbon number predominance was observed in the FAs (data not shown), as reported for marine aerosols in the northern North Pacific [e.g., *Mochida et al.*, 2002]. While concentrations of LFAs were in many cases lower than HFAs off the coast of East Asia, LFAs were more abundant than HFAs in the marine boundary layer of the central Pacific. Throughout the cruise, the FA concentrations were roughly 1 order of magnitude lower than that of total DCAs. Spatial distribution of levoglucosan is presented in Figure 3d, which is comparable to those of total LFAs and HFAs. Table 1 summarizes the concentration ranges and mean concentrations of DCAs, LFAs, HFAs and levoglucosan in the remote Pacific (>140°E), the coastal Pacific (<140°E), the East China Sea, and the Sea of Japan.

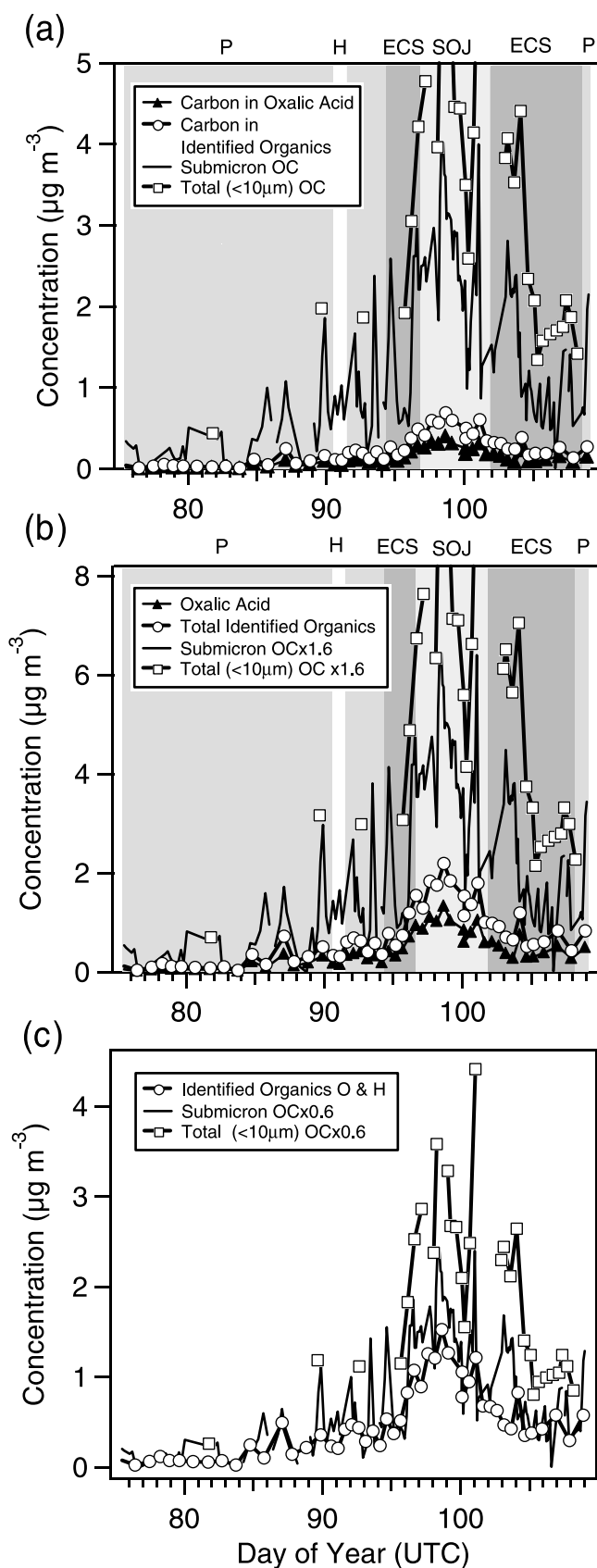
3.2. Contribution of DCAs, FAs, and Levoglucosan to Aerosol Organic Matter

[16] Figure 4a presents concentrations of organic carbon (OC) in size ranges of $D_p < 1$ and 10 μm , oxalic acid carbon, and total oxygenated carbon concentrations of the identified species (DCAs, FAs, and levoglucosan). Concentrations of identified compounds are from HV sampling, whereas OC in size ranges of $D_p < 1$ and $D_p < 10 \mu\text{m}$ were obtained using a semi-continuous automated carbon analyzer and impactor filter sampler, respectively [*Mader et al.*, 2003]. Both methods used the ACE-Asia standard thermal-optical technique [*Schauer et al.*, 2003]. Although sampling frequency and particle size ranges are different between two OC data sets ($D_p < 1$ and 10 μm) and HV data set for chemical speciation, general trends of the profile are similar; highest concentrations were observed between day of year (DOY) 95–100 off the coast of East Asia. Assuming that concentrations of OC in the size range of $D_p < 10 \mu\text{m}$ are nearly equal to that in whole size range as sampled by the HV sampler, DCAs, FAs and levoglucosan comprised $9.8 \pm 2.3\%$ of total OC (TOC). The contribution of carbon in total DCAs was largest among the identified compound classes, which was $8.8 \pm 2.4\%$ of TOC. An averaged ratio of [total DCA carbon]/[total carbon (TC)] over the North

Pacific and Tropical Pacific in 1990 was reported to be 8.8% [*Kawamura and Sakaguchi*, 1999], being in close agreement with the data reported here.

[17] Although OC is a typical parameter directly measured to quantify the organic fraction in aerosols, organic aerosol mass (or volume) is more important to the chemical and physical properties of aerosols. As opposed to hydrocarbons that consist of only carbon and hydrogen atoms, oxygenated organic compounds such as organic acids contain oxygen atoms whose mass and volume are substantial. Organic acids in aerosols have large [organic matter]/[organic carbon] ratios (OM/OC) because they contain oxygen atoms as -COOH. Particularly, the OM/OC ratios of low-molecular-weight DCAs are high because of four oxygen atoms in two carboxyl groups. Therefore contributions of DCAs to the aerosol mass should be larger than those on carbon basis. Table 2 shows the OM/OC ratios of some major DCAs, FAs, and levoglucosan, as well as proposed OM/OC ratios for urban and remote aerosols. The OM/OC ratios of oxalic acid (C₂ DCA), malonic acid (C₃ DCA), succinic acid (C₄ DCA), and levoglucosan are 3.8, 2.9, 2.5, and 2.3 respectively. For oxalic acid, more than 70% of the mass come from oxygen atoms, indicating that their contributions to the aerosol mass and volume are significant. The OM/OC ratios for FAs (e.g., 1.3 for C₁₆ FA) are much lower than those for low-molecular-weight DCAs because of the presence of long alkyl chains.

[18] OM/OC ratios in urban aerosols range from 1.4 to 1.7 (1.6 recommended), whereas at remote site, ratios range from 1.8 to 3.0 (2.1 recommended) [*Turpin and Lim*, 2001]. As seen in Table 2, OM/OC ratios of these low-molecular-weight DCAs are higher than the recommended OM/OC ratios for remote and urban aerosols. Particularly, the OM/OC ratios of DCAs in Table 2 are more than twice that proposed for urban aerosols. Figure 4b presents concentrations of estimated aerosol organic matter (OC \times 1.6) as well as sum of DCAs, FAs and levoglucosan. Using the estimate of total OM of OC \times 1.6 ($D_p < 10 \mu\text{m}$), the identified oxygenated organic compounds account for $19.0 \pm 4.8\%$ of total OM (see Figure 4b). Size-segregated aerosol sampling conducted in this study showed that substantial fraction of C₂ – C₄ DCAs were present in accumulation mode aerosols (*Mochida*, unpublished data). Therefore, being not quantified in this study, their contribution to submicron organic aerosol mass (see Figure 4b) should be substantial. Significant contribution of such oxygenated compounds to the organic aerosol mass should be taken into account for assessing the organic aerosol mass and volume.



[19] The contribution of oxygen and hydrogen contained in the identified organic compounds to the total organic aerosol mass can be evaluated by comparing non-carbonaceous mass (oxygen and hydrogen) in identified organic compounds and those estimated in total organic matter (Figure 4c). The non-carbonaceous mass in total organic matter was assumed to be $\text{OC} \times 0.6$, which corresponds to total organic matter ($\text{OC} \times 1.6$) – OC. The contribution of identified organic compounds to the non-carbonaceous components in organics ($D_p < 10 \mu\text{m}$) was $34.9 \pm 9.0\%$, indicating even larger contribution than that on an organic mass basis. This non-carbonaceous mass in the identified organic compounds is roughly 1/5 of the OC mass, suggesting that the mass of total organic matter should be at least $\text{OC} \times 1.2$. The actual OM/OC ratio in the aerosol samples depends on the elemental composition of species other than DCAs, FAs, and levoglucosan. The remainder of the OM in aerosols includes hydrocarbons such as n-alkanes, PAHs and UCM, but their contribution to OC may be insignificant. There are reports that humic-like substances contribute significantly to the organic aerosol mass [Simoneit, 1980; Krivácsy *et al.*, 2001] in various circumstances. Because these substances should contain oxygenated compounds, they possibly contribute to total non-carbonaceous masses reported in this study.

[20] Another important role of organic acids in the contribution to aerosol mass is a formation of salts. They are possibly present as ammonium salts because both organic acids and NH_4^+ are predominantly present in submicron size particles. When the sum of organic acids and NH_4^+ is defined as OM-salt, the OM-salt/OC ratios is 5.2 for oxalic acid which is present as $(\text{COONH}_4)_2$ (see Table 2). This ratio is significantly larger than the OM/OC ratio (3.8) of free oxalic acid. If all organic acids detected in this study were assumed to be present as ammonium salts, the contribution of DCAs, FAs and levoglucosan to the total aerosol mass would increase by about 30%.

3.3. Sources of DCAs, FAs, and Levoglucosan

[21] High concentrations of DCAs have been reported in urban atmosphere, as well as in plumes from biomass burning [Lefer *et al.*, 1994; Narukawa *et al.*, 1999; Graham *et al.*, 2002]. Our recent study on the marine aerosols collected in Chichi-jima Island, the western North Pacific, based on factor analysis and trajectory analysis demonstrated that the dominant source regions for $\text{C}_2 - \text{C}_5$ DCAs and

Figure 4. (opposite) (a) Concentrations of organic carbon (OC) in size ranges of $D_p < 1 \mu\text{m}$ and $D_p < 10 \mu\text{m}$, and carbon in oxalic acid and in total DCAs, FAs and levoglucosan. (b) Estimated organic aerosol mass ($\text{OC} \times 1.6$) in size ranges of $D_p < 1 \mu\text{m}$ and $D_p < 10 \mu\text{m}$, and concentrations of oxalic acid and sums of DCAs, FAs and levoglucosan. (c) Estimated non-carbon mass in organic fraction ($\text{OC} \times 0.6$) in size ranges of $D_p < 1 \mu\text{m}$ and $D_p < 10 \mu\text{m}$, and in sum of DCAs, FAs and levoglucosan. Organic carbon data in size range of $D_p < 10 \mu\text{m}$ are from impactor/filter sampling/thermal-optical analysis of NOAA/PMEL, and submicron OC is from the semi-continuous automated carbon analyzer of Rutgers University [Lim *et al.*, 2003]. Annotations on top of the figures are as follows: P, Pacific; H, Hachijo Island; ECS, East China Sea; SOJ, Sea of Japan.

Table 2. OM/OC Ratios of Organic Acids, Levoglucosan, and Organics in Aerosols^a

	Mass/OC Ratios	NH ₄ -Salt/OC Ratios
Oxalic acid (HOOC-COOH)	3.8	5.2
Malonic acid (HOOC-CH ₂ -COOH)	2.9	3.8
Succinic acid (HOOC-C ₂ H ₄ -COOH)	2.5	3.2
C ₁₆ Fatty acid (CH ₃ -(CH ₂) ₁₄ -COOH)	1.3	1.4
Levoglucosan (C ₆ H ₁₀ O ₅)	2.3	–
Urban (Los Angeles, USA) ^b	1.4–1.7 (1.6 recommended)	–
Remote (San Joaquin Valley) ^b	1.8–3.0 (2.1 recommended)	–
Wood Combustion ^b	1.9–2.1	–

^aOM, organic matter; OC, organic carbon.

^bTurpin and Lim [2001].

their precursors are populated regions of the Asian continent, suggesting that they are derived from anthropogenic sources including fossil- and wood-fuel combustion [Mochida *et al.*, 2003]. The spatial distribution of total DCAs shown in Figure 3a is consistent with this interpretation. Because of the westerly winds, DCAs emitted in the East Asian regions and/or produced photochemically from anthropogenic precursors are transported over the western North Pacific. For oxalic acid, this hypothesis is consistent with previous studies, in which a positive correlation between nitrate and oxalate was observed at a remote Colorado mountain site [Norton *et al.*, 1983] and over the remote Atlantic Ocean [Baboukas *et al.*, 2000].

[22] In order to further evaluate this hypothesis, correlations of total DCAs (nearly equivalent to the sum of C₂ – C₅ DCAs) to the concentrations of non sea salt (nss)-SO₄²⁻ and filterable NO₃⁻ were examined (Figures 5a and 5b). A strong correlation can be seen in the figures. Although such correlations were also seen for LFAs, HFAs and levoglucosan whose concentrations are also regulated by the Asian outflow, the *R*² value of the correlation of log[DCAs] with log[nss-SO₄²⁻] (0.84) is higher than those for log[HFAs] (0.76), log[LFAs] (0.47) and log[levoglucosan] (0.63). This indicates, in terms of source regions, that DCAs are more tightly linked to nss-SO₄²⁻ than those for FAs and levoglucosan. The slope of the regression line for the log-log plot of DCAs versus nss-SO₄²⁻ shown in Figure 5a is close to unity (0.97), suggesting that the DCA concentrations relative to nss-SO₄²⁻ are almost constant from the coastal to the remote ocean. Because of the short lifetime of SO₂ in polluted air, new formation of nss-SO₄²⁻ is limited during the atmospheric transport over the remote Pacific. Therefore the consistency of [DCAs]/[nss-SO₄²⁻] ratios suggests that photochemical formation of DCAs during a long-range transport from coastal to remote Pacific is not significant. The slope of the regression line for total DCAs versus NO₃⁻ was less than unity (0.77), indicating that concentrations of total DCAs relative to those of NO₃⁻ were higher in the remote ocean than off the coast of East Asia. This can probably be related to the difference in removal processes of aerosols with different sizes: NO₃⁻ was present in the coarse mode whereas major DCAs were present in the fine mode aerosols.

[23] Biomass burning in South and Southeast Asia potentially contributes to the organic aerosols in the East Asia region, but the highest concentrations of total DCAs were not obtained when air masses come from South and Southeast Asia based on the trajectory analysis.

[24] Little is known about the photochemical formation pathway of DCAs. Ozone oxidation of cyclic olefins has

been suggested by laboratory studies [e.g., Hatakeyama *et al.*, 1987], but their actual significance in the atmosphere has not been evaluated. Oxidation of glyoxal (OHC-CHO) and glyoxalic acid (OHC-COOH) in particles as well as in the gas phase has been suggested as a source of oxalic acid [Beck *et al.*, 2000]. For glyoxal, there are several proposed formation pathways in gas phase photochemical reactions.

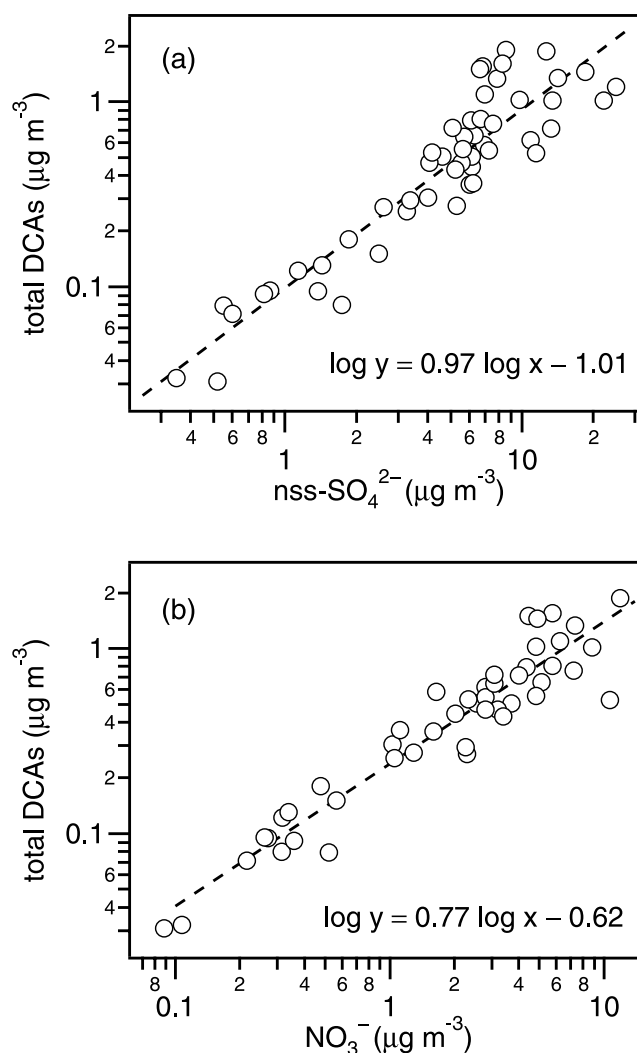


Figure 5. Log-log plots of the DCA concentrations against the concentrations of (a) nss-SO₄²⁻ and (b) filterable NO₃⁻. For NO₃⁻, five samples showing significantly lower concentrations than those from NOAA/PMEL were omitted from the analysis.

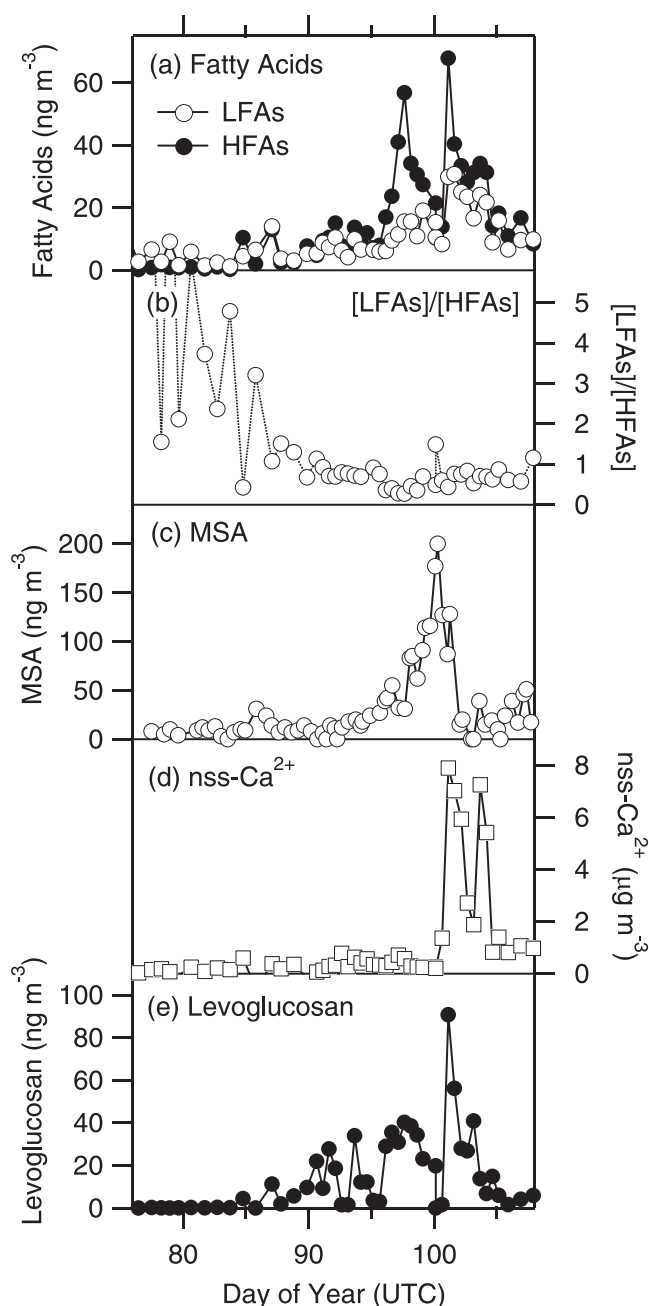


Figure 6. Temporal variation of (a) LFAs and HFAs, (b) [LFA]/[HFA] ratios, (c) MSA, (d) nss-Ca^{2+} , and (e) levoglucosan in aerosols during the cruise.

For instance, aromatic hydrocarbons, which are abundant in the polluted air, are emitted by combustion processes. They may be oxidized to form glyoxal in the atmosphere [e.g., Stockwell *et al.*, 1997, and references therein]. Further studies including laboratory studies are required to identify the major formation pathways of DCAs.

[25] The time series of LFA and HFA concentrations and ratios of LFAs to HFAs (L/H ratios) are shown in Figures 6a and 6b. It is generally recognized that LFAs are more abundant than HFAs in the marine atmosphere because of their emissions from marine sources [Peltzer *et al.*, 1984]. On the other hand, continental air masses contain FAs

derived from plant waxes, soils, and fossil fuel combustion [Simoneit and Mazurek, 1982]. As stated before, L/H ratios were higher over the remote ocean during this cruise, which is consistent with the fact that LFAs are major FAs in seawater and in aerosols in the remote marine boundary layer [Mochida *et al.*, 2002]. During the high-FA event of DOY 95–105 (see Figure 2a), the L/H ratios decreased to less than unity (Figure 2b). The low L/H ratio around unity is characteristic of terrestrial FAs, suggesting that terrestrial FAs are transported from the continent to the coastal regions of East Asia. During DOY 98–101, concentrations of methanesulfonic acid (MSA) (Figure 6c), which is produced by the atmospheric oxidation of dimethylsulfide (DMS) released as a gas from the marine biological activity in the ocean, increased significantly, while the L/H ratios stayed low. This indicates that the FA input from marine sources was insignificant off the coast of East Asia compared to the Asian outflow of terrestrial FAs, although marine biological activity is very high in the region. Sea salt concentrations were low ($[\text{Na}^+] < 4 \mu\text{g m}^{-3}$) around DOY 98–101 because of calm weather conditions, which may result in the small contribution from marine sources. While apportionment to different terrestrial sources (anthropogenic combustion processes, plant wax, soil) is usually difficult for FAs, their temporal variation during the cruise implies an influence of FAs released to the atmosphere with mineral dust particles. The highest concentrations of FAs were observed during the dust event, which can be seen from the high nss-Ca^{2+} concentrations at DOY 101–104 (Figure 6d). Some co-variations of nss-Ca^{2+} and FAs, in particular LFAs, are present, suggesting the contribution of soil dust emissions to the atmospheric FAs. This is consistent with the hypothesis by Matsumoto *et al.* [2001], who recently suggested that soil dust emission is an important source of atmospheric FAs on the basis of ^{14}C measurement of FAs in aerosols.

[26] Figure 6e shows the time series of the concentration of levoglucosan. A large increase in the concentration was also seen during the heavy dust event at DOY 102. However, when the second peak of nss-Ca^{2+} appeared at DOY 104, the concentration of levoglucosan stayed low ($< 20 \text{ ng m}^{-3}$). Therefore the emission of Asian soil dust to the atmosphere and its transport by the westerly winds is not likely responsible to the variation of levoglucosan. There is little doubt that biomass burning is an important source of levoglucosan in the atmospheric aerosols studied. Concentrations of levoglucosan have been reported to be comparable to that of oxalic acid in the plumes of biomass burning that is close to the sources [Graham *et al.*, 2002]. In this study, the concentrations of levoglucosan were found to be 1–2 orders of magnitude lower than those of oxalic acid. This does not imply that the contribution of biomass burning including wood-fuel combustion is small to the total organic aerosols collected. The production of oxalic acid due to photochemical processes and the decomposition of levoglucosan during long-range transport, as suggested by Gao *et al.* [2003] in a study of biomass burning events in Africa, may account for the high ratio of oxalic acid to levoglucosan. It is unlikely that a dehydrosaccharide such as levoglucosan can be formed photochemically from other forms of sugars during transport in the atmosphere. Therefore levoglucosan must result from primary emissions.

Biomass and bio-fuel burning in South, Southeast, and East Asia is a potential source of levoglucosan in the air over the western North Pacific. Wood-fuel combustion is substantial in East Asia, which may contribute strongly the enhanced concentrations of levoglucosan in the marine air off the coasts of Asia.

[27] To assess the role of Asian soil dust as a source of organic aerosols, we measured DCAs, FAs and levoglucosan in the simulated Asian dust (CJ-2, prepared by National Research Center for Environmental Analysis and Measurement, China, and National Institute for Environmental Studies, Japan), whose mode diameter is $26 \mu\text{m}$ [Nishikawa *et al.*, 2000]. Applying the same procedure of extraction and analysis, the concentrations of oxalic (C_2 DCA), malonic (C_3 DCA) and stearic (C_{18} FA) acids and levoglucosan in CJ-2 were determined to be 42.5, 2.4, 4.8, and $<0.1 \text{ ng per } 1 \text{ mg}$ of sample, respectively. During the heavy dust event at DOY 102 and 104, the dust concentrations were estimated to be more than $100 \mu\text{g m}^{-3}$ on the basis of the concentrations of nss Ca^{2+} in the aerosol samples and CJ-2 (5.3 wt%) [Nishikawa *et al.*, 2000]. The concentrations of oxalic, malonic, and stearic acids and levoglucosan have been estimated to be 8300, 1200, 84, and 640 ng per 1 mg of sample of airborne dust at DOY 102. In the case of FAs, the estimated amount of stearic acid in the dust aerosols is 1 order of magnitude higher than that of simulated dust (CJ-2), which is inconsistent with the hypothesis above. Soil dust in other sites might contain larger amount of FAs and that the different particle sizes between the aerosols and simulated dust samples may result in the different abundance of FAs. The latter case is likely because concentrations of FAs in CJ-2 were 1 order of magnitude larger than that of another dust simulated sample (CJ-1) which was collected in the same location as CJ-2 but contained larger particles (mode diameter $49 \mu\text{m}$).

[28] While comparison of dust aerosols with CJ-2 was not conclusive for FAs, the importance of dust-derived DCAs and levoglucosan may be ruled out. Concentrations of C_2 and C_3 DCAs and levoglucosan in the aerosols were 2 orders of magnitude or more higher than that of simulated dust sample (CJ-2). Assuming that relative abundance of organic acids in CJ-2 represents their relative emission rates from dust in China, the contribution of DCAs and levoglucosan from the soil dust is relatively small even if all the FAs measured in the air samples originated from desert dust particles. In the case of DCAs, there is still a possibility that precursors of DCAs are abundant on dust particles and are oxidized to form DCAs during atmospheric transport. However, in contrast to FAs, no significant increase was found in the concentrations of total DCAs during the dust event (DOY 101–104) (see Figure 4b for oxalic acid), being consistent with the results obtained by the analysis of CJ-2.

3.4. Gas/Particle Partitioning of DCAs

[29] Although DCAs have low vapor pressures, they may be partitioned between gas phase and particles in the atmosphere [Baboukas *et al.*, 2000; Limbeck *et al.*, 2001]. To assess the partitioning, DCAs in gas and particulate phases were collected separately using the annular denuder system. Figure 7 presents the ratios of $\text{C}_2 - \text{C}_5$ DCAs collected on filters and backup denuders relative to those

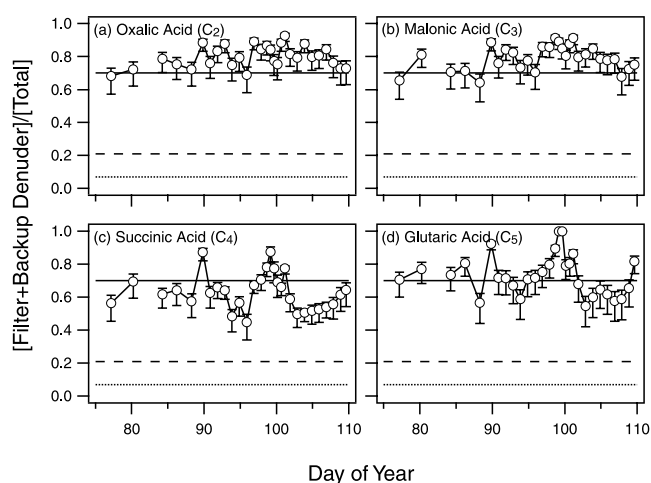


Figure 7. (a–d) Relative abundances of particulate $\text{C}_2 - \text{C}_5$ DCAs in air, obtained by the annular denuder sampling. Possible biases due to the breakthrough of gaseous DCAs from the front denuder are included in error bars. The solid, dashed, and dotted lines indicate averaged values for oxalic, acetic and formic acids, respectively, reported by Baboukas *et al.* [2000].

collected in total (filters and front and backup denuders). The ratios in Figure 7 represent the proportions of $\text{C}_2 - \text{C}_5$ DCAs in aerosol particles. The results show that they are predominantly present in particles rather than in the gas phase. However, the values may be underestimated because of the cut-off of large particles and possible deposition of very small particles on denuders due to high diffusion rates. While the concentrations of DCAs and total particulate matter fluctuated over 2 orders of magnitude during the cruise, the proportions shown in Figure 7 did not change significantly. This may suggest that the actual fractions in particles are close to unity. The average proportion of oxalic acid in aerosol particles over the Atlantic ocean was reported to be 70% by Baboukas *et al.* [2000]. This value is within the range of values measured in our study. Baboukas *et al.* [2000] also measured the proportion of particulate formic and acetic acids, with values of 7% and 21%, respectively. Although the ratios presented in Figure 7 may have fluctuated from the actual proportions in particles because of the artifacts described above, there is little doubt that proportions of $\text{C}_2 - \text{C}_5$ DCAs in particles were significantly larger than the values reported for acetic and formic acids.

3.5. Sink of DCAs of Continental Origin in the Marine Atmosphere

[30] Figure 8 presents the abundance of $\text{C}_2 - \text{C}_9$ DCAs, as well as $\text{C}_{16} + \text{C}_{18}$ fatty acids (LFAs), $\text{C}_{20} - \text{C}_{32}$ fatty acids (HFAs), and levoglucosan relative to oxalic acid (C_2), which was the most abundant species. The relative abundances for $\text{C}_3 - \text{C}_5$ DCAs stay almost constant in spite of the large fluctuation of the oxalic acid concentrations. On the other hand, the abundances for $\text{C}_6 - \text{C}_9$ DCAs, LFAs, HFAs, and levoglucosan relative to oxalic acid showed a large variability, which may be related to different source

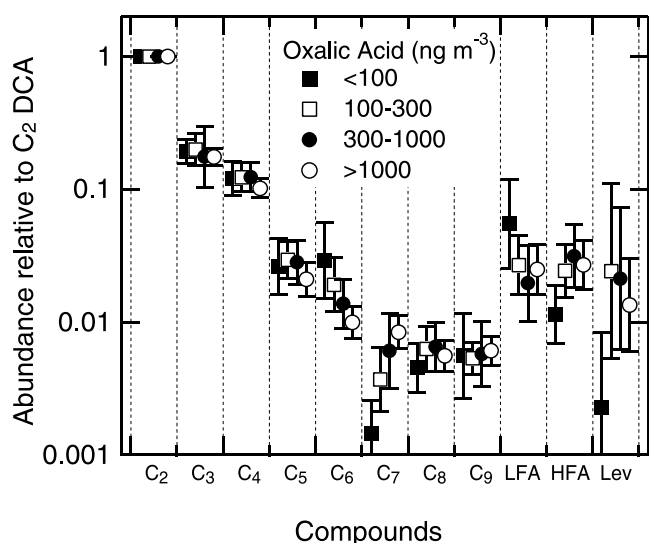


Figure 8. Relative abundances of $C_2 - C_9$ DCAs, LFAs, HFAs and levoglucosan to oxalic acid. Averaged values when oxalic acid concentration were <100 (solid squares), $100-300$ (open squares), $300-1000$ (solid circles) and >1000 ng m^{-3} (open circles) are plotted separately with one standard deviation. Averages and one standard deviations were calculated on the log-scale basis. C_n ($n = 2-9$): C_n DCAs. Lev: levoglucosan.

regions and/or fractionation due to different lifetimes during the atmospheric transport. $C_2 - C_5$ DCAs may be strongly associated with anthropogenic sources, while LFAs be with marine biogenic sources [Mochida *et al.*, 2002, 2003]. In fact, the highest relative abundance of LFAs was obtained when oxalic acid was the lowest (i.e., over the remote ocean), indicating the importance of marine sources.

[31] In Figure 9, the abundances of malonic (C_3), succinic (C_4) and glutaric (C_5) acids relative to oxalic (C_2) acid, expressed by $[C_n \text{ DCA}]/[C_2 \text{ DCA}]$ ($n = 3, 4, 5$), are plotted for all samples. Although the $[C_n \text{ DCA}]/[C_2 \text{ DCA}]$ ratios showed some variability, there was no significant trend throughout the cruise. This homogeneity reveals information about the fate of DCAs that are transported from the continent to the remote Pacific. In general, the sink of particulate organic compounds includes dry/wet deposition as well as decomposition in the atmosphere. The latter process in both gas phase and particles [Zuo and Hoigné, 1992, 1994] generally accompanies molecular fractionation due to the different reaction rates of the compounds, whereas the former processes are less involved with molecular fractionation and are similar for aerosols with similar properties (e.g., size and hygroscopicity). While the high correlation of DCA and SO_4^{2-} is strong evidence of the long chemical lifetime of DCAs, the homogeneity of $C_2 - C_5$ DCAs also suggests that chemical decomposition during transport from the continent to the remote Pacific is not important.

[32] To examine this hypothesis quantitatively, trends expected by the chemical fractionations are shown in the lower right of Figure 9. The ratios of the pseudo-first-order decomposition rate constants $k(C_n \text{ DCA})/k(C_2 \text{ DCA})$ are 1, 1.5, 2.7, and 4.0, which are equivalent to the ratios of gas

phase OH reaction rate constants for $C_2 - C_5$ DCAs (estimated by the model of Kwok and Atkinson [1995]). The slopes of the regression lines for the measured $[C_n \text{ DCA}]/[C_2 \text{ DCA}]$ are not as significant as the calculated fractionation slopes, again indicating that the contribution of chemical decomposition to the decrease in DCA concentrations during the long-range transport is minor. Therefore deposition and dilution should mainly regulate the concentrations of DCAs. On the basis of the backward trajectory analysis, the residence time of air masses over the ocean was up to 5 days. Organic aerosols are thought to have residence times of about one week [Takemura *et al.*, 2000], but should be much shorter for air masses measured in this study because of the repeated precipitation (from trajectory analysis). We therefore conclude that deposition is the major sink of $C_2 - C_5$ DCAs. We also conclude that DCAs are relatively stable end products in the oxidation of organic compounds over the remote ocean.

4. Summary and Conclusion

[33] Temporal and spatial distributions of dicarboxylic acids (DCAs), fatty acids (FAs) and levoglucosan were obtained in the western North Pacific, the East China Sea, and the Sea of Japan during the ACE-Asia campaign. Concentrations of total DCAs, FAs and levoglucosan were higher off the coasts of East Asia than the remote Pacific. DCAs were very abundant in the marine aerosols with concentrations that sometimes exceeded $1 \mu\text{g m}^{-3}$ in the Sea of Japan and the East China Sea. Spatial distributions of levoglucosan on regional scale were reported for the first time, showing long-range transport from Asian continent to the central Pacific. Comparison of total concentrations of DCAs, FAs and levoglucosan with total organic carbon showed a substantial contribution of those compounds to the organic carbon mass. When organic mass was assumed to be organic carbon $\times 1.6$, the identified organic species accounted for $19.0 \pm 4.8\%$ and $34.9 \pm 9.0\%$ of the total

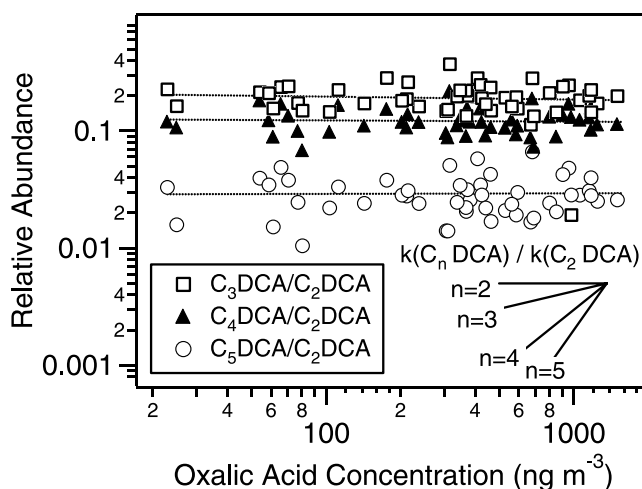


Figure 9. Relative abundances of $C_3 - C_5$ DCAs acids to oxalic acid for all samples measured during the cruise. The slope shown on the right side of the figure denotes the fractionation line when the decomposition rate constants $k(C_n \text{ DCA})/k(C_2 \text{ DCA})$ are 1, 1.5, 2.7, and 4.0 (see the text).

organic mass and non-carbonaceous (oxygen and hydrogen) organic mass, respectively. These results emphasize the importance of non-carbon mass in organics and suggest further study on the chemical speciation to determine this mass. Positive relationships between total DCAs and nsSO_4^{2-} or NO_3^- support the hypothesis that $\text{C}_2 - \text{C}_5$ DCAs and/or their precursors over the western North Pacific are of anthropogenic origin. The high abundance of LFAs relative to HFAs showed that high concentrations of FAs in the coastal oceans off East Asia (up to 100 ng m^{-3}) were regulated mainly by terrestrial sources despite the high marine biological productivity in the Pacific rim region. Although soil dust emission possibly affect on the atmospheric concentrations of FAs during the heavy dust event, its influence was minimal on DCAs and levoglucosan. The gas/particle studies showed that DCAs exist predominantly in particles. Homogeneity of $\text{C}_2 - \text{C}_5$ DCAs suggested that they are relatively stable end products in the atmospheric oxidation processes and that deposition is the major sink of DCAs.

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