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Dicarboxylic acids, ketocarboxylic acids and glyoxal in the marine aerosols collected during a round-the-world cruise

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Abstract

This study investigated spatial distributions of water-soluble dicarboxylic acids and related compounds in the marine aerosols collected at low- to mid-latitudes in the Northern Hemisphere for a better understanding of the photochemical aging of organic aerosols during long-range transport. Their molecular distributions were characterized by the predominance of oxalic acid (C_2) followed by malonic (C_3) and succinic (C_4) acids, except for one sample (QFF114, $C_2 > C_4 > C_3$) that was collected in the western North Pacific with a heavy influence of biomass burning. Concentration ranges of diacids, ketoacids (including glyoxylic acid and pyruvic acid), and glyoxal were 17-718 ng m^{-3} (average 218 ng m^{-3}), 0.40-72 ng m^{-3} (23 ng m^{-3}), and 0.16-19 ng m^{-3} (3.3 ng m^{-3}), which account for 3.6-23% (14%), 0.09-2.3% (1.3%), and 0.04-0.45% (0.19%) of organic carbon (OC) in the marine aerosols, respectively. Positive correlations were observed between OC and diacids/ketoacids. Positive correlations were also found between biogenic secondary organic aerosol (SOA) tracers (e.g., 2-methylglyceric acid) and diacids/ketoacids, suggesting a significant contribution of biogenic secondary source. The spatial distributions of diacids exhibited higher loadings over the coastal/tropical regions than the open oceans, which are similar to those of the concentration ratios of malonic/succinic (C_3/C_4) and adipic/azelaic (C_6/C_9), indicating a more significant influence of anthropogenic sources over the coastal regions than the remote oceans. However, the concentration ratios of oxalic acid to levoglucosan, a biomass-burning tracer, and to C_{29} *n*-alkane, a tracer for terrestrial biogenic emission showed higher values over the open oceans than the coastal regions, suggesting a continuous production of oxalic acid during long-range atmospheric transport. This study indicates that the long-range transport of primary and secondary aerosols of continental origin and photooxidation/aerosol aging are important factors controlling the organic chemical composition of aerosol particles in the marine atmosphere.

Keywords: Marine organic aerosols; Dicarboxylic acids; Oxalic acid; Glyoxylic acid; Glyoxal; Secondary organic aerosols

1. Introduction

Organic aerosols are one of the major fractions of atmospheric aerosol particles (Kanakidou et al., 2005), which affect the radiative balance on the earth directly by scattering sunlight and indirectly by acting as cloud condensation nuclei (CCN) (Novakov and Penner, 1993). Their chemical characterization has been widely conducted on regional and global scales (Kanakidou et al., 2005; Hallquist et al., 2009), which is important to understand the hygroscopicity and CCN activity of aerosol particles. However, organic aerosols in the marine atmosphere have rarely been studied, although the oceans cover more than 70% of the Earth's surface. So far, their chemical nature remains poorly understood in the marine atmosphere due to their diverse sources and formation mechanisms (O'Dowd and de Leeuw, 2007), as well as the difficulty/inconvenience of obtaining marine aerosol samples.

Marine organic aerosols are composed of water-insoluble (WIOC) and water-soluble organic carbon (WSOC) (O'Dowd et al., 2004; O'Dowd and de Leeuw, 2007; Sciare et al., 2009; Russell et al., 2010). WIOC is predominantly produced by primary emissions of biogenic organic matter such as bacterial and viral debris as well as phytoplankton debris via wave breaking. Emissions of terrestrial higher plant waxes also contribute to WIOC in the marine aerosols (Gagosian et al., 1987). In contrast, the majority of WSOC is produced by the atmospheric oxidation of volatile organic compounds (VOCs) emitted from the ocean (O'Dowd and de Leeuw, 2007), or is transported from the continents having originated from the primary emissions and secondary processing. Photochemical processing of organic aerosols in the atmosphere during long-range transport (i.e., aerosol aging) can largely alter the chemical composition of water-soluble organic aerosols (Rudich et al., 2007). These atmospheric processing can increase CCN concentrations in remote oceans.

Low molecular weight (LMW) dicarboxylic acids and related polar compounds are one of the most abundant compound classes in organic aerosols. They are highly water-soluble and thus may significantly enhance the hygroscopicity of aerosol particles. Previous studies (Cruz and Pandis, 1998; Brooks et al., 2002) have shown that the presence of dicarboxylic acids may affect both deliquescence relative humidity and hygroscopicity of aerosol particles.

Although LMW diacids can be emitted from primary sources such as biomass burning (Narukawa et al., 1999), vehicular exhausts (Kawamura and Kaplan, 1987), cooking (Schauer et al., 2002), and natural marine sources (Rinaldi et al., 2011), they are mainly produced from the atmospheric photooxidation of various organic precursors (Kawamura and Gagosian, 1987; Stephanou, 1992; Kawamura and Sakaguchi, 1999). Specifically, there is growing evidence that oxalic acid, one of the most abundant organic species in the atmosphere, is a product of cloud processing (Sorooshian et al., 2006). Furthermore, dicarboxylic acids can form strong organic complexes with metals (Gamble et al., 1980; Santana-Casiano et al., 2000). Thus, the atmospheric transport, marine primary emission, as well as in situ formation of dicarboxylic acids in the atmosphere may influence the biogeochemical cycles of heavy metals (e.g., Fe and Hg). LWM dicarboxylic acids and related compounds can contribute to 0.3-4.5% of total carbon (TC) in urban regions (Kawamura and Ikushima, 1993) and more than 10% of TC in remote oceans (Kawamura and Sakaguchi, 1999; Wang et al., 2006b), highlighting their importance in marine aerosols.

In this study, we report the molecular distributions, abundances and spatial distributions of dicarboxylic acids and related compounds (e.g., glyoxylic acid, pyruvic acid and glyoxal) that are potential intermediate precursors of oxalic acid in the marine aerosol samples that were collected at low- to mid-latitudes of the Northern Hemisphere during a round-the-world cruise. Molecular compositions of these organic species are discussed in relation to the sources, formation processes, and the influence of long-range transport of continental aerosols to the remote marine atmosphere.

2. Sample and method

2.1. Sample collection

Total suspended particles (TSP) were collected using a high-volume air sampler at a flow rate of $1.2 \text{ m}^3 \text{ min}^{-1}$ on board of the R/V *Hakuho Maru* during a round-the-world cruise (KH89-2, Figure 1) from October 30, 1989 to March 3, 1990. Detailed sample information is

presented in Table 1. Possible contamination from ship exhaust was prevented using a wind speed/wind sector controller by shutting off the sampling pump during beam-side airflow ($>45^\circ$) and/or low wind speed ($<5 \text{ m s}^{-1}$). Aerosol samples were collected onto pre-combusted (450 °C for 6 h) quartz fiber filters (20 cm \times 25 cm, Pallflex). After sampling, each filter was stored individually in a pre-combusted glass jar (150 ml) with a Teflon-lined screw cap in darkness at -20°C until analysis.

In the present study, we collected the marine aerosol samples on a two- to three-day basis. This time scale is reasonable to use the high-volume air sampler in order to collect enough material for a detailed organic analysis using GC/MS technique, especially in the marine atmosphere. It should be noted that sampling artifacts might occur due to the evaporation/adsorption processes of semi-volatile organics on the filter or particle surface during sampling (Turpin et al., 2000). For example, semi-volatile organic compounds can be lost from the aerosol particles on the filter. Thus, the reported concentrations may be underestimated. However, we consider that the evaporative loss of diacids and related compounds should be minimal due to their low vapor pressures (Saxena and Hildemann, 1996).

2.2. Dicarboxylic acids and related water-soluble compounds

Filter samples were analyzed for water-soluble diacids, ketoacids and glyoxal using a method described in Kawamura and Ikushima (1993) and Kawamura (1993). Briefly, filter aliquots were extracted under ultrasonication with organic-free pure water (5 ml \times 3). The water extracts were concentrated down to ca. 0.5 ml in a pear-shaped flask by using a rotary evaporator under a vacuum and dried in a nitrogen air stream. The dried samples were then reacted with 14% BF_3/n -butanol at 100 °C for 30 min. During this procedure, the carboxyl functional group was derivatized to butyl ester, and the aldehyde and keto groups were derived to dibutoxy acetal (Kawamura, 1993). The derivatives were extracted with 5 ml of *n*-hexane after adding pure water (3 ml) and a small amount (0.2 ml) of acetonitrile, the latter makes the excess butanol transfer into the aqueous phase more effectively. The hexane layer was further washed with pure water (3 ml \times 2). The extracts were dried by using a rotary

evaporator and a nitrogen blow-down system again and were then dissolved in 50 μl of *n*-hexane. The butyl esters and acetals were determined with a Hewlett Packard (HP) 5890 gas chromatograph (GC) equipped with a split/splitless injector, a fused silica capillary column (HP-5, 0.2 mm ID \times 25 m \times 0.52 μm film thickness), and a flame ionization detector (FID). Peak identification was performed by a comparison of GC retention times with those of authentic standards. The identification of diacids and related compounds was confirmed by mass spectral analysis using a Finnigan-MAT ITS-40 GC-MS system (Kawamura, 1993). Recovery experiments were performed by spiking free diacids onto precombusted quartz fiber filters. Results showed that the recoveries were better than 70% for oxalic acid and 90% for malonic, succinic and adipic acids. Field blanks showed small peaks of oxalic and phthalic acids; however, they were less than 5% of the real samples. Duplicate analysis of the field samples showed that the analytical error of this method was less than 10% for major species. Concentrations of diacids and related compounds reported here were corrected for the blanks but not for recoveries. The GC measurements of diacids and related compounds were completed in 1991.

Organic carbon (OC) was determined using a Sunset Lab EC/OC Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocol. Typically, a 1.54 cm^2 punch (Φ 14 mm) of the filter was placed in a quartz tube inside the thermal desorption chamber of the analyzer, and then stepwise heating was applied (Wang et al., 2005a). Duplicate analyses of filter samples for OC showed uncertainties of $\pm 10\%$.

3. Results and discussion

3.1. Molecular distributions of diacids and related compounds, and their contributions to organic carbon

A homologous series of dicarboxylic acids ($\text{C}_2\text{-C}_{10}$) and ketoacids ($\text{C}_2\text{-C}_9$), and one α -dicarbonyl (glyoxal) were detected in the marine aerosols. Their chemical structures are

given in Figure 2. Table 1 summarized their concentrations as well as their contributions to organic carbon (OC). Concentration ranges of diacids and ketoacids were 17-718 ng m⁻³ (average 218 ng m⁻³) and 0.40-72 ng m⁻³ (23 ng m⁻³), respectively. Glyoxylic acid (α C₂) was the most abundant ketoacid (0.20-31 ng m⁻³, 11 ng m⁻³), followed by pyruvic acid (Pyr) (0.19-25 ng m⁻³, 6.8 ng m⁻³). Glyoxylic acid is a precursor of oxalic acid (Kawamura et al., 1996a). Glyoxal was also detected in the marine aerosols with a concentration range of 0.16-19 ng m⁻³ (3.3 ng m⁻³). It is a precursor for secondary organic aerosol (SOA) formation via heterogeneous processes (Kroll et al., 2005).

Oxalic acid (C₂) was found to be the most abundant diacid species (10-338 ng m⁻³, average 132 ng m⁻³), followed by malonic (C₃) (2.1-142 ng m⁻³, 40 ng m⁻³) and succinic acids (C₄) (1.5-81 ng m⁻³, 19 ng m⁻³) (Figure 3a). Oxalic acid accounts for 47-70% (average 58%) of the quantified diacid mass. The predominance of oxalic acid has been reported in atmospheric aerosols collected from different locations in the world including Chinese and Indian megacities (Ho et al., 2007; Miyazaki et al., 2009; Pavuluri et al., 2010), the western North and Central Pacific (Kawamura and Sakaguchi, 1999; Mochida et al., 2003b), Amazonia (Kundu et al., 2010), Europe (Legrand et al., 2007) and the Arctic (Kawamura et al., 2005), as well as the southern Ocean (Wang et al., 2006b). This is reasonable because oxalic acid is the end-product of various oxidation/decomposition pathways in the atmosphere (Kawamura and Sakaguchi, 1999; Lim et al., 2005). Abundances of the individual diacid species generally decreased with an increase in carbon chain length, although adipic (C₆) and azelaic (C₉) acids were relatively abundant (Figure 3a).

The total measured polar organic compounds accounted for 3.7-24% (15%) of OC, among which diacids were the major contributor, accounting for 3.6-23% (average 14%) of OC. Total ketoacids accounted for 0.09-2.3% (1.3%) of OC. The contribution of diacids to OC (diacid-C/OC ratio) is consistent with a similar field measurement conducted in the southern ocean (Sempéré and Kawamura, 2003), and is higher than those reported in urban regions (Table 2). For example, the diacid-C/OC ratio in Sapporo, Japan is 4.8%. Lower ratios are reported in New Delhi, India (1.0%) (Miyazaki et al., 2009) and Ulaanbaatar,

Mongolia (0.9%) (Jung et al., 2010). In biomass burning aerosols from Rondônia, Brazil, such ratios were 1.7% and 1.4% during the daytime and nighttime, respectively (Kundu et al., 2010). Thus, the higher diacid-C/OC ratio indicates that diacids in the marine atmosphere are consistent with the photochemical aging of continental organic aerosols during long-range atmospheric transport. This concept will be discussed in more detail as below.

3.2. Spatial distributions of diacids

Figure 4 presents the spatial distributions of total measured diacids in the marine aerosols collected during the round-the-world cruise of R/V *Hakuho Maru*, compared with those reported in the continental aerosols. In general, diacids reported in continental aerosols are higher than those in marine aerosols. In the present study, higher levels of diacids were observed off the coasts of East Asia and western North/Central America than those in the open ocean (Figure 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 (Streets et al., 2003; Zheng et al., 2005; Fu et al., 2008). The decrease in the concentrations of diacids from the Asian coastal region to the central North Pacific Ocean indicates that the Asian continent is a significant “emitter” of organic aerosols including diacids and their precursors, which can be transported long distances by the westerly winds in winter/spring. Such a pattern may also suggest that dry and wet depositions of aerosol particles can remove diacids and other organics from the atmosphere. Another possible reason for the lower concentrations over the open oceans than the coastal regions is the atmospheric dilution of organics including oxalic acid during long-range transport. Similarly, lower levels of diacids were found in the central North Atlantic than those off the coasts of the western North/Central America (Figure 4). A similar spatial pattern was found for bisphenol A (BPA) during the same campaign (Fu and Kawamura, 2010). Atmospheric BPA is proposed to be derived from anthropogenic activities including the burning of plastic wastes (Fu and Kawamura, 2010).

3.3 Correlations between OC and diacids/ketoacids, and the influence of biomass burning

Figure 5a shows a linear correlation between the concentrations of OC and diacids ($R^2=0.70$) in the marine aerosols. A more significant correlation ($R^2=0.95$) was observed between OC and ketoacids (Figure 5a). Diacids and related compounds are formed from the oxidation of volatile organic species (VOCs, e.g., isoprene), long-chain unsaturated fatty acids (e.g., oleic acid) (Kawamura and Gagosian, 1987), as well as from biomass burning (Narukawa et al., 1999; Gao et al., 2003; Kundu et al., 2010), fossil fuel combustion (Kawamura and Kaplan, 1987; Wang et al., 2006a) and marine emission (Rinaldi et al., 2011).

On a global scale, biomass burning, biogenic SOA formation, as well as anthropogenic emissions have been well recognized as major sources of organic aerosols (de Gouw and Jimenez, 2009). Organic aerosols in the marine atmosphere are influenced not only by oceanic emissions, but also by continental emissions through long-range atmospheric transport (Facchini et al., 2008; Hawkins et al., 2010; Myriokefalitakis et al., 2010). With regard to the influence of biomass burning, no significant correlations (Figure 5b) were observed between the measured organic species ($R^2 = 0.09$ for diacids and 0.35 for ketoacids) and levoglucosan, a specific tracer for biomass burning (Simoneit et al., 1999). This indicates that biomass burning is not a major source of diacids and related compounds in our samples.

Interestingly, the molecular distribution of diacids in one sample (QFF114) collected in the western North Pacific is dominated by C_2 , followed by C_4 and then C_3 (Figure 3b). Such a distribution is different from the other samples that show $C_3 > C_4$ (Table 1), but is consistent with those reported for biomass burning aerosols. For example, the pattern of $C_4 > C_3$ was reported for ambient aerosols collected during the 1997 Indonesian forest fires (Narukawa et al., 1999) and during an intensive biomass burning season in Rondônia, Amazonia (Kundu et al., 2010). Our previous study (Fu et al., 2011) has shown that the sample of QFF114 contains a significantly higher level of levoglucosan (27 ng m^{-3}) than those ($0.01\text{-}5.2 \text{ ng m}^{-3}$) for the rest of the samples. QFF114 was collected close to Japan and China during late winter/early spring (Table 1) when westerly winds dominate over the western North Pacific. Thus, the specific molecular characteristic of diacids in QFF114 suggests that it was heavily influenced

by biomass burning in the upwind regions. In addition, ketoacids in QFF114 showed a strong predominance of glyoxylic acid (ωC_2), which is even more abundant than C_3 and C_4 (Figure 3).

3.4 Concentration ratios of selected diacid species: primary versus secondary contribution

Kawamura and Ikushima (1993) proposed that the C_3/C_4 ratio can be used as an indicator of enhanced photochemical production of diacids, because C_4 can be degraded to C_3 due to the abstraction of its hydrogen by OH radicals and subsequent decarboxylation reactions. Lower C_3/C_4 ratios (0.25-0.44, average 0.35) were reported in anthropogenic aerosols from automobile emission (Kawamura and Kaplan, 1987), which has been interpreted due to a selective degradation of C_3 over C_4 during combustion (Kawamura and Ikushima, 1993). The ratios are higher in ambient urban aerosols in Chinese megacities (0.6-1.1, 0.74) (Ho et al., 2007), Tokyo (0.56-2.9, 1.6) (Kawamura and Ikushima, 1993), and Los Angeles (0.31-1.4) (Kawamura and Kaplan, 1987). In New Delhi, the C_3/C_4 ratios were found to be 0.40-1.1 with higher ratios in daytime (average 0.66) than in nighttime (0.58) (Miyazaki et al., 2009). Figure 6a shows the spatial distribution of C_3/C_4 ratios during the cruise. The C_3/C_4 ratios varied from 0.9 to 5.8 with an average of 2.3, which are about three times higher than those in above-mentioned urban aerosols. Higher ratios in the marine aerosols than in the urban aerosols suggest that malonic acid (C_3) is photochemically produced during long-range transport from continents to the marine atmosphere.

Relatively lower C_3/C_4 ratios were observed in the mid-latitudes than those in the subtropical regions (Figure 6a). This pattern suggests an enhanced photochemical production in warmer regions. This is consistent with those reported in marine aerosols collected at Gosan site, Jeju Island in the western North Pacific, showing higher C_3/C_4 ratios in summer than other seasons (Kundu et al., 2010). The summer maxima of C_3/C_4 ratios (spring, 2.0; summer, 3.8; autumn, 1.6; winter, 1.2) were also found in marine aerosols at Chichi-Jima Island in the western North Pacific, Japan (Mochida et al., 2003a). High C_3/C_4 ratios (up to 10) were reported in remote marine aerosols from the equatorial central Pacific (Kawamura and Sakaguchi, 1999). In addition, high C_3/C_4 ratios (3-5) were reported in rural aerosols

collected from a background site in South Africa (Limbeck et al., 2001).

Azelaic acid (C_9) has been proposed as a secondary reaction product by photooxidation of biogenic unsaturated fatty acids containing a C=C bond predominantly at the C_9 position (e.g., oleic acid) (Kawamura and Gagosian, 1987). In contrast, adipic acid (C_6) is proposed to be of anthropogenic origin (Kawamura and Kaplan, 1987). Thus, the C_6/C_9 ratio can provide their source strength from biogenic and anthropogenic emissions. The higher the C_6/C_9 ratios, the stronger the influences of anthropogenic emissions. In Figure 6b, the lowest value was observed in the central North Pacific, which can be interpreted by the lesser contribution of anthropogenic aerosols including C_6 diacids and a significant influence of marine primary organic aerosols that contains biogenic unsaturated fatty acids, the precursors of C_9 . The highest C_6/C_9 ratio was observed in the Bay of Bengal near India followed by coastal regions off East Asia (Figure 4). It should be noted that unsaturated fatty acids such as oleic acid can also be emitted by biomass burning and meat cooking (Rogge et al., 1991) as well as terrestrial plants (Kawamura and Gagosian, 1987). Oleic acid can be rapidly oxidized into C_9 and other compounds (Matsunaga et al., 1999), which can be further decomposed to C_5 and C_4 . In this study, we observed positive correlations between oleic acid and diacids ($R^2=0.71$) or ketoacids ($R^2=0.52$) (Figure 5c), which suggests that biogenic emission should be an important contributor to diacids and related compounds.

Maleic acid (M) can be photochemically isomerized to *trans* configuration (fumaric acid, F) in the atmosphere under solar radiation. Lower M/F ratios (0.1-1.5) were observed for the marine aerosols in the present study than those reported in urban (0.9-2.3) regions (Table 2). The predominance of precursor *cis* configuration in urban aerosols should be associated with the photochemical oxidation of benzene or toluene, whose *cis* configuration is preserved in the structure of the oxidation products (Sempéré and Kawamura, 2003). The lower M/F ratios observed in the marine aerosols indicate that further isomerization of maleic acid (M) to fumaric acid (F) occurs in the marine atmosphere during long-range transport. Interestingly, the ratios were generally lower in the subtropical regions than in the mid-latitudinal regions (Figure 6c), which is probably due to an enhanced isomerization of M

to F under warmer temperature and stronger sunlight irradiation near the equator. A negative linear correlation between M/F ratio and ambient temperature has been reported by Sempéré and Kawamura (2003). Fumaric acid (F) is an intermediate product of photochemical isomerization of maleic acid (M), and can be further oxidized by OH radicals and other oxidizing agents to produce smaller diacids such as oxalic acid (Sempéré and Kawamura, 2003).

3.5 Concentration ratios of oxalic acid to levoglucosan and C₂₉ n-alkane

Oxalic acid (C₂), the end-product of oxidative decomposition of various organic precursors, contributed 1.6-14% (average 6.4%) of OC in the marine aerosols. The spatial distribution of C₂ showed a gradual decrease from coastal to remote oceans (Table 1), which is similar to the spatial trends of total diacids (Figure 4) and BPA (Fu and Kawamura, 2010).

As mentioned above, levoglucosan is a specific tracer for biomass burning. This anhydrosugar compound has been reported in both continental and marine aerosols all over the world (Simoneit and Elias, 2000; Simoneit et al., 2004; Fu et al., 2009; Mochida et al., 2010; Fu et al., 2011), indicating the importance of biomass burning as the source of organic aerosols on a global scale. Figure 6d shows the spatial distribution of mass concentration ratios of oxalic acid to levoglucosan. Lower ratios were observed off the coast of East Asia with higher ratios in the open oceans, which could be partly explained by the photochemical production of oxalic acid and the potential degradation of levoglucosan during long-range transport. In a previous study, Gao et al. (2003) examined the mass concentration ratio of total diacids to levoglucosan in smoke and haze aerosols collected at various altitudes in South Africa, and found that the ratio systematically increases with increasing altitude. They suggested that levoglucosan could have been chemically converted to diacids during upward transport. Recently, several laboratory studies have shown that levoglucosan in the atmosphere can be oxidized by OH radicals (Hennigan et al., 2010; Hoffmann et al., 2010; Kessler et al., 2010), especially under high relative humidity conditions (Hoffmann et al., 2010). Other factors such as dry/wet scavenging of aerosols during long-range transport, as well as the natural marine source of oxalic acid (Rinaldi et al., 2011) may also contribute the

spatial patterns of oxalic acid to levoglucosan.

Homologous series of high molecular weight (HMW) *n*-alkanes ($>C_{27}$) are typical biomarkers that originate from terrestrial higher plant waxes (Simoneit et al., 2004). They are one of the major lipid compounds in primary organic aerosols (POA). We chose C_{29} *n*-alkane as a tracer for biogenic POA, and examined the mass concentration ratio of oxalic acid to C_{29} *n*-alkane. The spatial distribution of the ratio of oxalic acid to C_{29} *n*-alkane (Figure 6e) was characterized by a gradual increase from the Asian coastal region to the central North Pacific Ocean (QFF100-QFF103), indicating that the increasing ratio is consistent with changes in chemical compositions of the marine organic aerosols due to photochemical aging and the marine emission of dicarboxylic acids.

3.6. Correlations between biogenic SOA tracers and diacids/ketoacids

Sea-spray aerosol, or primary marine aerosol, is a well-known source to the global natural aerosol mass budget. In recent years, however, significant efforts have been made into the study of secondary organic aerosol (SOA) in the marine boundary layer. For example, Facchini et al. (2008) reported that dimethyl and diethyl-ammonium salts (DMA^+ and DEA^+) are important submicron marine SOA components over the North Atlantic during a period of high biological activity. Claeys et al. (2010) proposed that organosulfates (sulfate esters of C_9 - C_{13} hydroxyl carboxylic acids) can be considered as marine SOA tracers for the oxidation of unsaturated fatty acids derived from marine algae. Series of C_7 - C_{15} monohydroxy fatty acids with OH group at C-5 to ω -1 positions have been reported as oxidation products of unsaturated fatty acids in the remote marine aerosols from the Pacific (Kawamura and Gagosian, 1988). Laboratory experiments (Ekström et al., 2009) have shown that 2-methyltetrols, tracers for isoprene SOA (Claeys et al., 2004), and related isoprene oxidation products can increase CCN levels in the pristine marine atmosphere that is limited in CCN.

In a previous study, we have reported abundances of biogenic SOA tracers from the photooxidation of isoprene and α -/ β -pinene during the same cruise of KH89-2 (Fu et al., 2011). Our samples were mainly collected in winter when marine emissions of biogenic VOCs such as isoprene should be negligible (Shaw et al., 2010); the major source of biogenic

SOA tracers during the cruise is assumed to be of terrestrial origin. Concentration ranges of 2-methyltetrols were 0.07-15 ng m⁻³ (2.4 ng m⁻³). Pinonic and pinic acids are tracers for the oxidation of α -/ β -pinene with O₃ and OH radicals (Kavouras et al., 1998). 2-Methylglyceric acid (2-MGA) and 3-hydroxyglutaric acid (3-HGA) are higher-generation products of isoprene and α -pinene oxidation, respectively (Kourtchev et al., 2009).

Based on the dataset of biogenic SOA tracers (Fu et al., 2011) and the water-soluble organic acids listed in Table 1, a weak correlation ($R^2=0.26$) was found between 2-methyltetrols and diacids (Figure 7a), and no correlation ($R^2=0.09$) between 2-methyltetrols and ketoacids. However, 2-MGA, the higher-generation product of isoprene oxidation, showed a strong positive correlation with diacids ($R^2=0.84$), and a relatively weak correlation with ketoacids ($R^2=0.42$) (Figure 7b). Such differences may suggest that 2-MGA can readily serve as an organic precursor for the production of diacids and ketoacids under ambient conditions, rather than 2-methyltetrols. 2-Methyltetrols are proposed to be formed through diepoxy derivatives of isoprene through acid-catalyzed hydrolysis (Wang et al., 2005b), while 2-MGA is possibly formed by further oxidation of methacrolein and methacrylic acid from isoprene (Claeys et al., 2004b; Surratt et al., 2006). In contrast, both first- (pinonic + pinic acids, Figure 7c) and higher-generation (3-hydroxyglutaric acid, Figure 7d) products from α -/ β -pinene oxidation exhibited good correlations with diacids or ketoacids, indicating that both first- and higher-generation products can serve as precursors to result in diacids and ketoacids.

Recently, it has been proposed that oxalic acid is produced by the oxidation of isoprene and other VOCs via in-cloud photochemical processing using 3D models (Myriokefalitakis et al., 2011). The chemical mechanisms for SOA formation and photochemical aging processes in the marine atmosphere should differ among the different sampling locations with different air mass compositions (e.g. different OH, ozone, and NO_x levels), as well as the aerosol acidity and relative humidity. Further works are needed to elucidate the complexity and dynamic nature of oxidation and formation mechanisms of marine organic aerosols.

4. Conclusions

The molecular distribution of water-soluble dicarboxylic acids in the marine aerosols collected during a round-the-world cruise showed a predominance of oxalic acid (C_2) followed by malonic acid (C_3) and succinic acid (C_4), except one sample (QFF114) that was heavily influenced by biomass burning. Diacids and ketoacids accounted for 14% (average) and 1.3% of OC, respectively, indicating that they are a major component of the water-soluble fraction of marine organic aerosols. Although the spatial distributions of diacids exhibited higher loadings over the coastal/tropical regions than the remote oceans, the relative abundances of these compounds is controlled by continental biogenic and anthropogenic sources as well as by photochemical oxidation processes during long-range transport to the open oceans. The levels of diacids have good correlations with polar organic marker compounds for isoprene and α -/ β -pinene, suggesting that the emissions of biogenic VOCs followed by photochemical oxidation are important sources of diacids in the marine atmosphere. Furthermore, diacids together with biogenic SOA tracers might be useful for better understanding the photooxidation/decomposition pathways and/or aerosol aging processes in the marine atmosphere.

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Table 1. Concentrations of dicarboxylic acids and other organic compounds identified in marine aerosols (ng m⁻³)

Location	Sample														
	North Pacific ^a					California Coast			North Atlantic		Indian Ocean	South China Sea		Western North Pacific	
Sample ID	QFF100	QFF101	QFF102	QFF103	QFF104	QFF105	QFF106	QFF107	QFF108	QFF109	QFF110	QFF111	QFF112	QFF113	QFF114
Date/Month	30/10-2/11	4-6/11	6-9/11	9-12/11	12-15/11	23-24/11	27-30/11	30/11-2/12	17-19/12	21-25/12	4-6/2	19-22/2	23-26/2	26-28/2	2-3/3
Year	1989	1989	1989	1989	1989	1989	1989	1989	1989	1989	1990	1990	1990	1990	1990
Air volume (m ³)	3540	1005	2465	3550	3925	2340	3255	2845	1780	4470	3060	3530	4210	1925	1865
OC (μgC m ⁻³) ^b	0.50	-	0.16	0.06	0.08	1.7	0.46	0.44	0.23	0.18	0.71	0.82	-	0.82	1.3
	I. Diacids														
Oxalic, C ₂	88.5	24.9	10.0	18.3	25.5	338	247	112	50.3	45.4	173	299	90.7	173	139
Malonic, C ₃	34.5	5.66	2.12	3.45	5.93	142	68.1	41.8	21.0	20.8	49.9	81.3	25.3	33.2	18.9
Succinic, C ₄	21.6	10.1	1.52	4.02	2.99	80.5	11.8	11.3	9.87	6.13	24.4	30.1	17.3	25.2	20.8
Glutaric, C ₅	4.72	1.87	0.32	0.62	0.65	20.0	1.75	2.37	2.43	3.69	3.26	4.50	2.92	7.11	5.12
Adipic, C ₆	6.04	1.67	0.43	0.46	0.40	15.5	2.96	3.93	3.25	2.97	9.77	14.2	3.00	4.97	7.90
Pimelic, C ₇	1.15	0.60	0.05	0.14	0.10	9.50	0.63	2.06	1.08	0.91	0.80	3.04	1.13	2.72	3.07
Suberic, C ₈	0.66	0.64	0.10	0.22	0.15	nd ^c	1.25	2.11	1.23	0.67	0.84	1.56	0.67	1.56	2.01
Azelaic, C ₉	1.34	1.71	0.27	0.54	0.22	4.19	3.11	4.05	1.70	1.01	1.02	2.17	1.00	1.34	2.62
Sebacic, C ₁₀	0.15	nd	0.55	0.08	0.05	2.53	0.30	1.13	nd	nd	0.29	0.94	nd	nd	nd
Methylmalonic, iC ₄	1.32	0.52	0.12	0.20	0.31	6.38	0.95	1.02	1.23	1.16	0.89	1.95	0.68	1.53	0.86
Maleic, M	1.37	1.26	0.07	0.29	0.31	0.39	0.34	0.57	0.55	0.44	0.50	0.77	2.37	2.11	3.74
Fumaric, F	0.91	0.83	0.16	0.39	0.37	2.84	1.10	1.10	1.11	1.01	1.92	1.46	1.75	2.32	3.95
Malic, hC ₄	1.13	0.50	0.11	0.15	0.19	43.0	9.87	13.6	4.06	4.39	27.0	36.8	10.3	13.0	7.63
Oxomalonic, kC ₃	-	-	-	-	-	2.47	0.57	0.57	0.46	0.19	2.96	3.10	0.48	2.40	0.83
4-Oxopimelic, kC ₇	-	-	-	-	-	11.8	1.87	3.31	0.59	0.71	2.83	5.07	1.81	2.59	1.72
Phthalic, Ph	0.72	1.97	0.65	0.72	0.36	38.8	0.83	2.04	0.84	0.50	1.71	3.02	1.83	11.9	7.11
subtotal	167	53.2	17.1	30.7	38.3	718	352	203	99.7	89.9	301	489	161	285	225
Diacids in OC (%) ^d	11.0	-	3.6	16.8	14.9	14.5	22.9	15.0	14.4	16.5	13.5	18.7	-	11.3	5.7
	II. Ketoacids														
Pyruvic, Pyr	0.55	nd	nd	nd	0.19	15.4	2.20	3.18	1.99	4.60	6.02	7.80	1.08	8.22	24.6
Glyoxylic, ωC ₂	6.02	0.38	0.20	0.63	1.32	30.4	6.03	5.28	3.51	4.18	15.3	22.2	2.03	19.6	31.3
3-Oxopropanoic, ωC ₃	0.53	0.32	0.03	0.16	0.08	3.92	0.87	0.76	0.31	0.25	1.63	1.33	0.27	1.69	1.16
4-Oxobutanoic, ωC ₄	0.69	1.85	0.11	0.30	0.13	3.26	0.72	0.91	0.63	0.48	1.57	2.17	0.82	1.56	1.70
6-Oxohexanoic, ωC ₆	-	-	-	-	-	7.02	0.78	1.75	0.74	0.54	2.44	3.08	nd	4.54	2.22
7-Oxoheptanoic, ωC ₇	-	-	-	-	-	4.34	0.32	1.07	0.34	0.32	0.50	1.85	0.49	nd	nd
8-Oxooctanoic, ωC ₈	-	-	-	-	-	1.62	0.18	0.51	nd	nd	0.51	nd	0.26	nd	nd
9-Oxononanoic, ωC ₉	0.14	0.08	0.02	0.04	0.05	6.19	0.45	1.59	0.19	0.22	1.68	3.17	0.39	1.13	0.94
Subtotal	7.94	3.11	0.40	1.20	1.60	72.2	11.5	15.1	7.72	10.6	29.7	41.6	5.34	36.7	61.9
Ketoacids in OC (%) ^d	0.56	-	0.09	0.72	0.79	1.8	1.0	1.5	1.4	2.3	1.7	2.0	-	1.8	1.8
	III. Dicarbonyl														
Glyoxal, Gly	0.91	0.49	0.16	0.24	0.59	18.5	0.52	0.76	0.58	1.76	1.65	2.49	0.54	4.76	10.2
Glyoxal in OC (%) ^d	0.07	-	0.04	0.17	0.31	0.45	0.05	0.07	0.10	0.40	0.10	0.13	-	0.24	0.32
Total in OC (%) ^d	11.6	-	3.7	17.7	16.0	16.7	24.0	16.6	15.9	19.2	15.2	20.9	-	13.3	7.8

^a Diacid concentrations of the samples collected in the North Pacific (QFF100-104) were obtained from a previous study (Kawamura and Usukura, 1993); ^bThe filter samples of QFF101 and QFF112 were not available for the analysis of OC and other organic species; ^c nd = not detected; ^d All the quantified organic compounds were converted to their carbon contents to calculate the OC ratios.

Table 2. Comparison of dicarboxylic acid concentrations in atmospheric aerosols from different locations.

Sampling location	Sampling period	Size	Oxalic ng m ⁻³	Glyoxal ng m ⁻³	M/F	C ₃ /C ₄	Total diacids (mean), ng m ⁻³	Diacid-C/OC ^a , % (Diacid-C/WSOC, %)	References
I. Urban Site									
Tokyo, Japan	Apr 1988–Feb 1989	TSP	270	-	1.5	1.5	90-1360 (480)	-	(Kawamura and Ikushima, 1993)
Sapporo, Japan	May-Jul 2005	TSP	192	4.6	2.0	1.4	106-787 (406)	(4.8)	(Aggarwal and Kawamura, 2008)
Chinese megacities	Jan 2003	PM _{2.5}	558	3.02	2.2	0.61	319-1940 (904)	1.3	(Ho et al., 2007)
	Jun-Jul 2003	PM _{2.5}	513	2.72	2.0	0.86	211-2162 (892)	2.3	(Ho et al., 2007)
Beijing, China	Aug-Sept 2006	PM _{2.5}	449	4.7	2.3	0.53	294-1440 (760)	(6.5)	(Ho et al., 2010)
Hong Kong, China	2003-2005	PM _{2.5}	182-3073	3.4-83	0.9-1.9	1.3-5.2	404-4490	1.2-11.4 (2.6-15.5)	(Li and Yu, 2010)
Chennai, India	Jan-Jun 2007	PM ₁₀	360	4.6	1.5	1.4	227-1030 (612)	(5.9)	(Pavuluri et al., 2010)
New Delhi, India	Winter 2006-2007	TSP	1430	1-72	2.0-3.6	0.6	835-6030 (2330)	-	(Miyazaki et al., 2009)
II. The Polar Region									
Alert, Arctic	1987-1988	TSP	14	0.54	0.5-1.0	0.1-1.0	4.3-97 (25)	-	(Kawamura et al., 1996a)
Alert, Arctic	Jan-Apr 1992	PM ₂	26	1.8	1.5	1.0	18-146 (64)	-	(Kawamura et al., 2005)
Syowa, Antarctica	1991	PM _{0.7}	1.6-10	0.05-0.16	0.9-4.9	0.04-0.2	6.0-89 (30)	-	(Kawamura et al., 1996b)
III. Marine Region									
Pacific Ocean	Oct-Dec 1990	TSP	40	-	0.3	4.0	10-248 (62)	-	(Kawamura and Sakaguchi, 1999)
Pacific Ocean	Aug-Oct 1992	TSP	2.8	0.07	2.0	1.3	7.1-605 (7.3)	(2.1-15)	(Sempéré and Kawamura, 2003)
East China Sea	Mar-Apr 2001	TSP	-	-	-	-	410-1500 (850)	-	(Mochida et al., 2003b)
Japan Sea	Mar-Apr 2001	TSP	-	-	-	-	480-2100 (1200)	-	(Mochida et al., 2003b)
Chichi-Jima Island	Apr 1990–Nov 1993	TSP	-	-	-	-	6-550 (139)	-	(Mochida et al., 2003b)
Southern Ocean	Nov 1994–Feb 1995	TSP	2.4	0.07	1.7	1.7	2.9-7.2 (4.5)	-	(Wang et al., 2006b)
North Pacific	Oct-Nov 1989	TSP	10-89	0.16-0.91	0.4-1.5	0.6-2.0	17-167 (61)	3.6-16.8	This study
California Coast	Nov-Dec 1989	TSP	112-338	0.52-19	0.1-0.5	1.8-5.8	203-718 (424)	14.5-22.9	This study
Atlantic Ocean	Dec 1989	TSP	45-50	0.58-1.8	0.4-0.5	2.1-3.4	90-100 (95)	14.4-16.5	This study
Indian Ocean	Feb 1990	TSP	173	1.7	0.3	2.1	301	13.5	This study
South China Sea	Feb 1990	TSP	91-299	0.54-2.5	0.5-1.4	2.7	161-489 (325)	18.7	This study
Western North Pacific	Feb–Mar 1990	TSP	139-173	4.8-10	0.9	0.91-1.5	225-285 (255)	5.7-11.2	This study

^aDiacid-C, total diacid carbon.

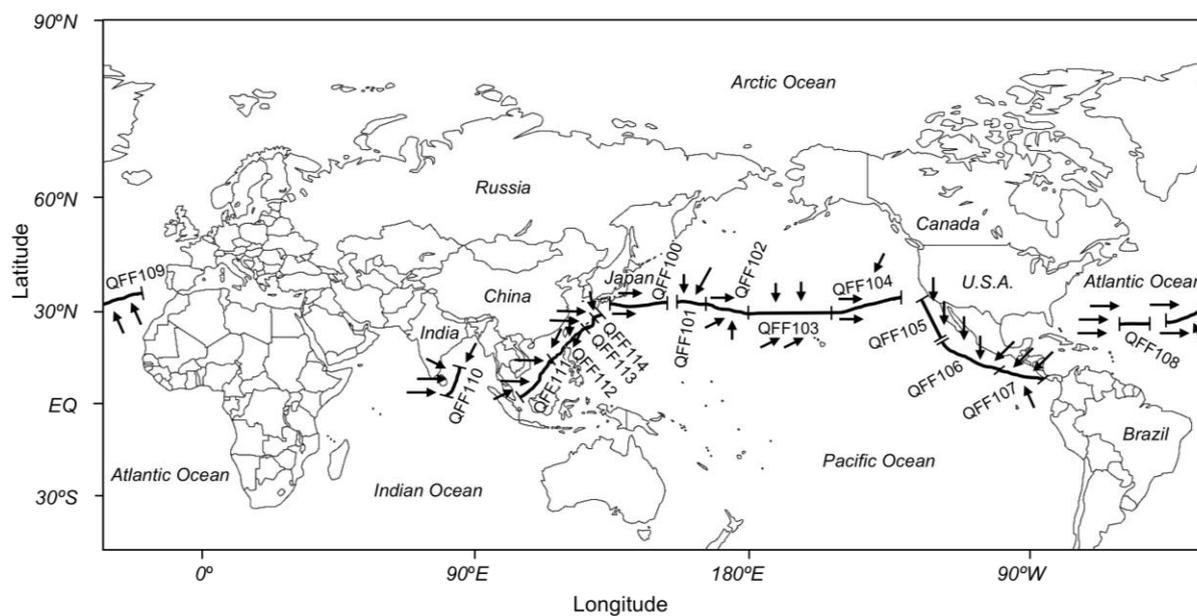


Fig. 1. Cruise track of KH89-2 and surface wind conditions. The cruise started from west Japan on October 30, 1989 via the North Pacific (QFF100-104), California Coast (QFF105-107), North Atlantic (QFF108-109), Indian Ocean (QFF110), South China Sea (QFF111-QFF112), and ended in the western North Pacific (QFF113-114) on March 3, 1990. The quartz fiber filter identification numbers used in the corresponding cruise periods are shown in the map. Arrows indicate surface wind directions with wind speeds above 7 m s^{-1} (data from the R/V *Hakuho Maru*).

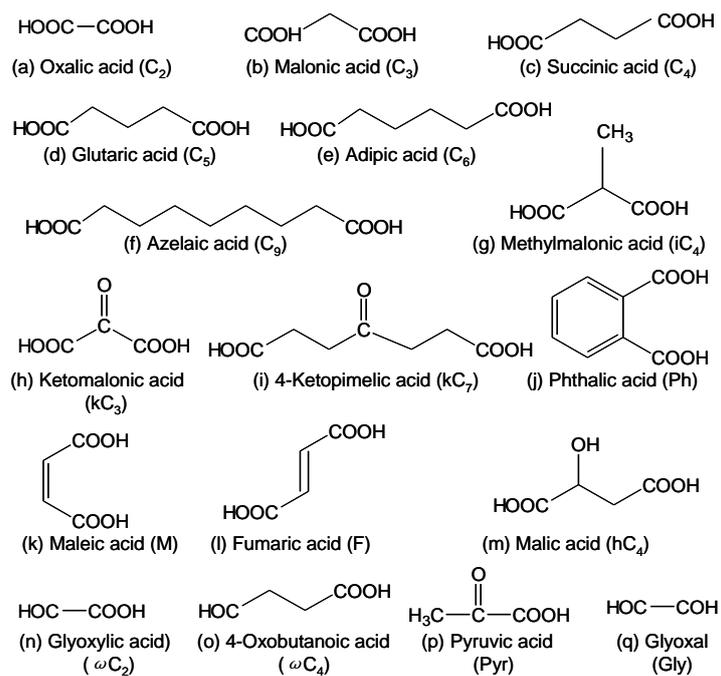


Fig. 2. Chemical structures of selected dicarboxylic acids and other major organic compounds detected in the marine aerosols.

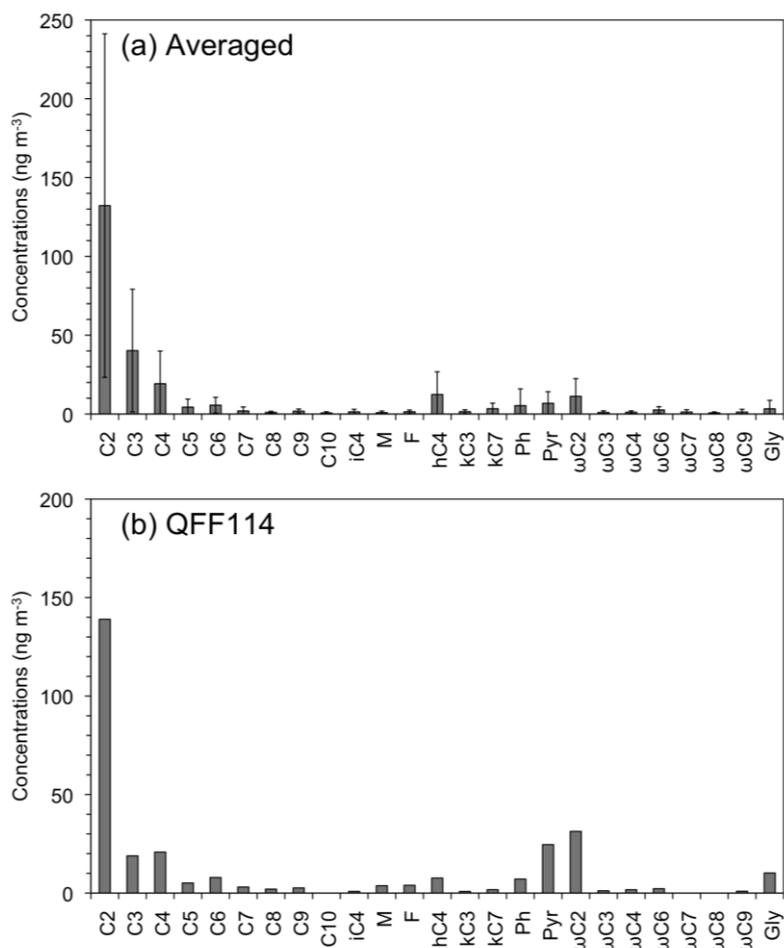


Fig. 3. Molecular distributions of diacids and related compounds in the marine aerosols. (a) averaged concentrations of the measured polar organic species with bars of standard deviation ($n=15$); (b) molecular distributions of the measured compounds in the sample of QFF114, which was collected in the western North Pacific in spring and was influenced by biomass burning.

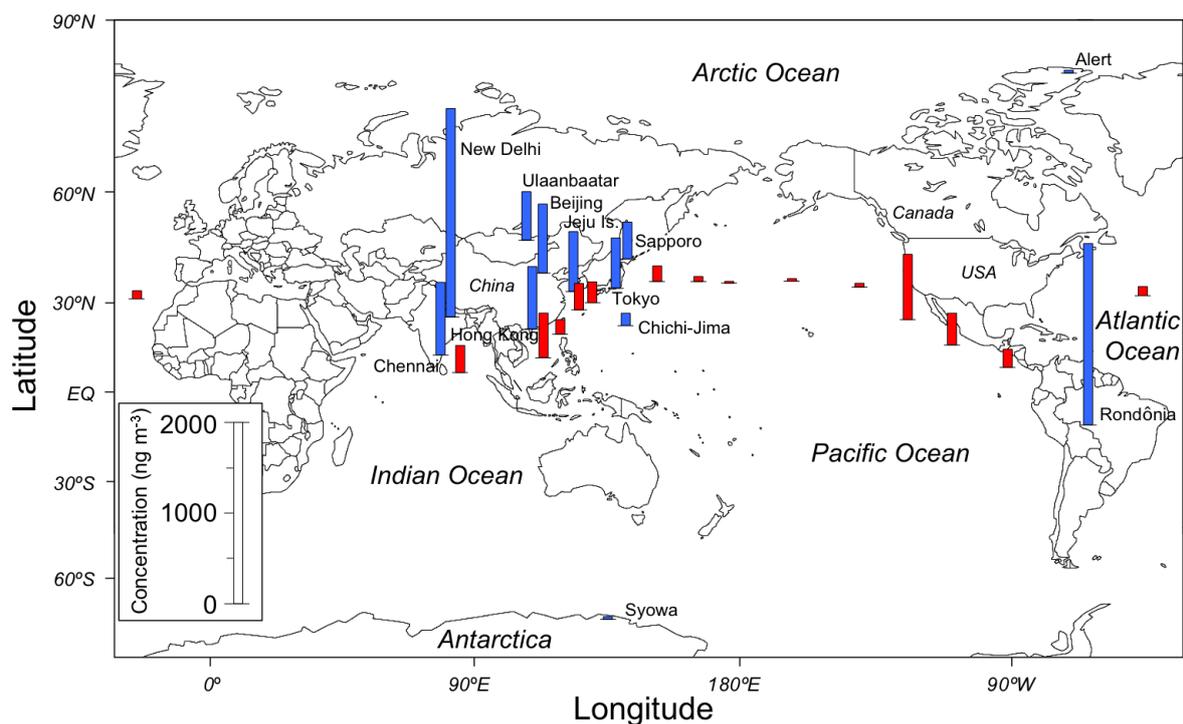


Fig. 4. Total concentrations of dicarboxylic acids in the marine aerosols collected during KH89-2 (red bars), compared with those (mean values, blue bars) reported in urban aerosols from Chennai (Pavuluri et al., 2010), New Delhi (Miyazaki et al., 2009), Hong Kong (Li and Yu, 2010), Beijing (Ho et al., 2010), Ulaanbaatar (Jung et al., 2010), Tokyo (Kawamura and Ikushima, 1993), Sapporo (Aggarwal and Kawamura, 2008), rural aerosols from Rondônia (Kundu et al., 2010), marine aerosols from Chichi-Jima Island in the western North Pacific (Mochida et al., 2003b), and the polar region aerosols from Alert in the Arctic (Kawamura et al., 1996a; Kawamura et al., 2005) and Syowa Station in Antarctica (Kawamura et al., 1996b).

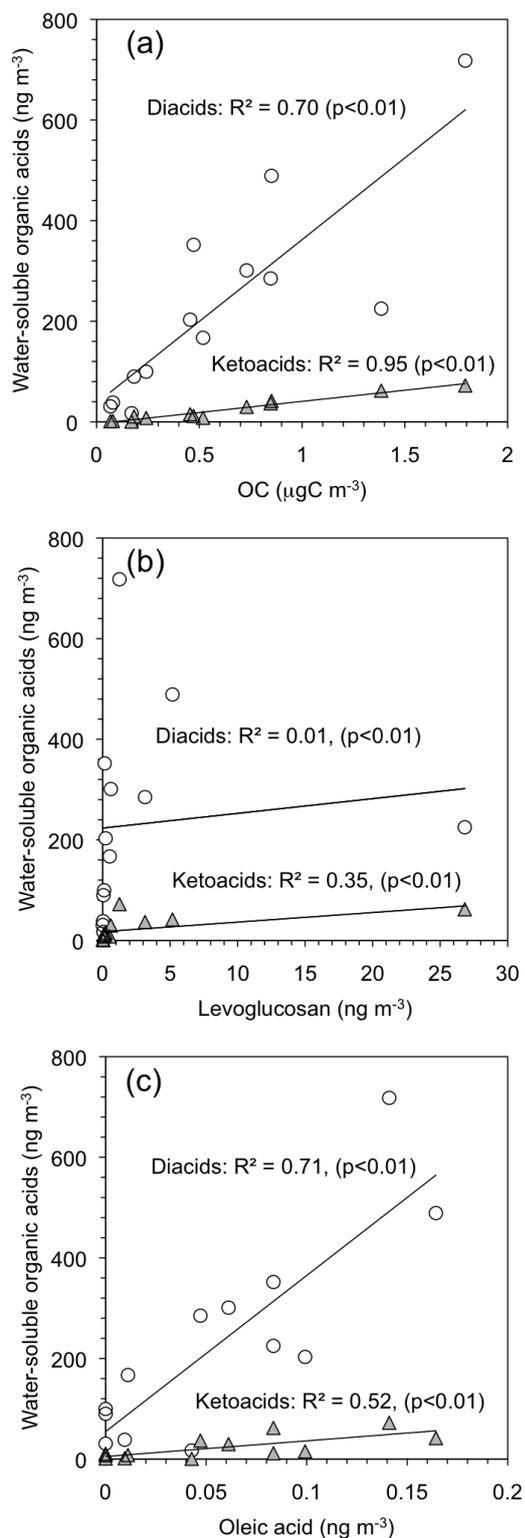


Fig. 5. Relationship between the concentrations of water-soluble organic acids (diacids and ketoacids) and (a) organic carbon (OC), (b) levoglucosan, and (c) oleic acid (C_{18:1} fatty acid).

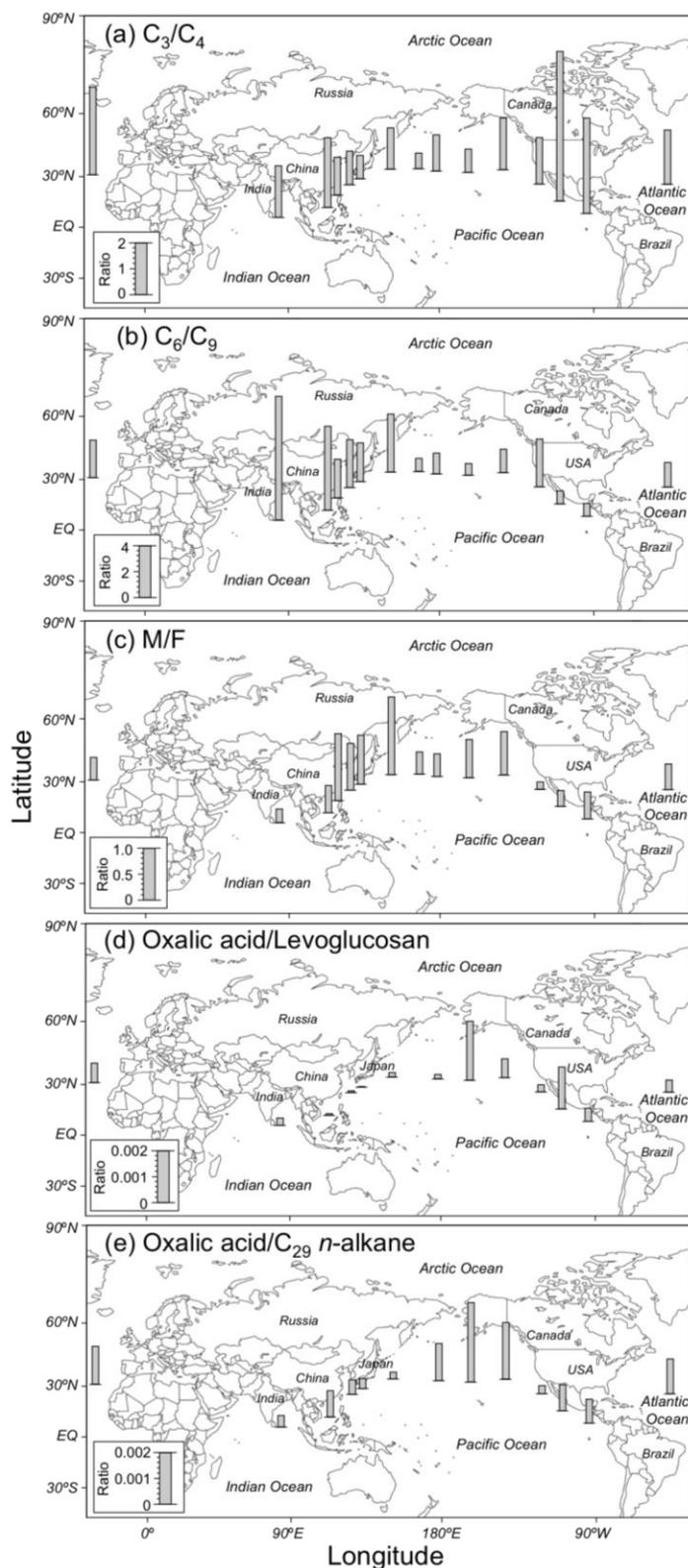


Fig. 6. Depiction of the concentration ratios of (a) malonic/succinic (C_3/C_4), (b) adipic/azelaic (C_6/C_9), (c) maleic/fumaric (M/F), (d) oxalic acid/levoglucosan, and (e) oxalic acid/ C_{29} *n*-alkane measured in the marine aerosols. The dataset of *n*-alkanes, levoglucosan, and other organic marker compounds can be found in a previous study (Fu et al., 2011).

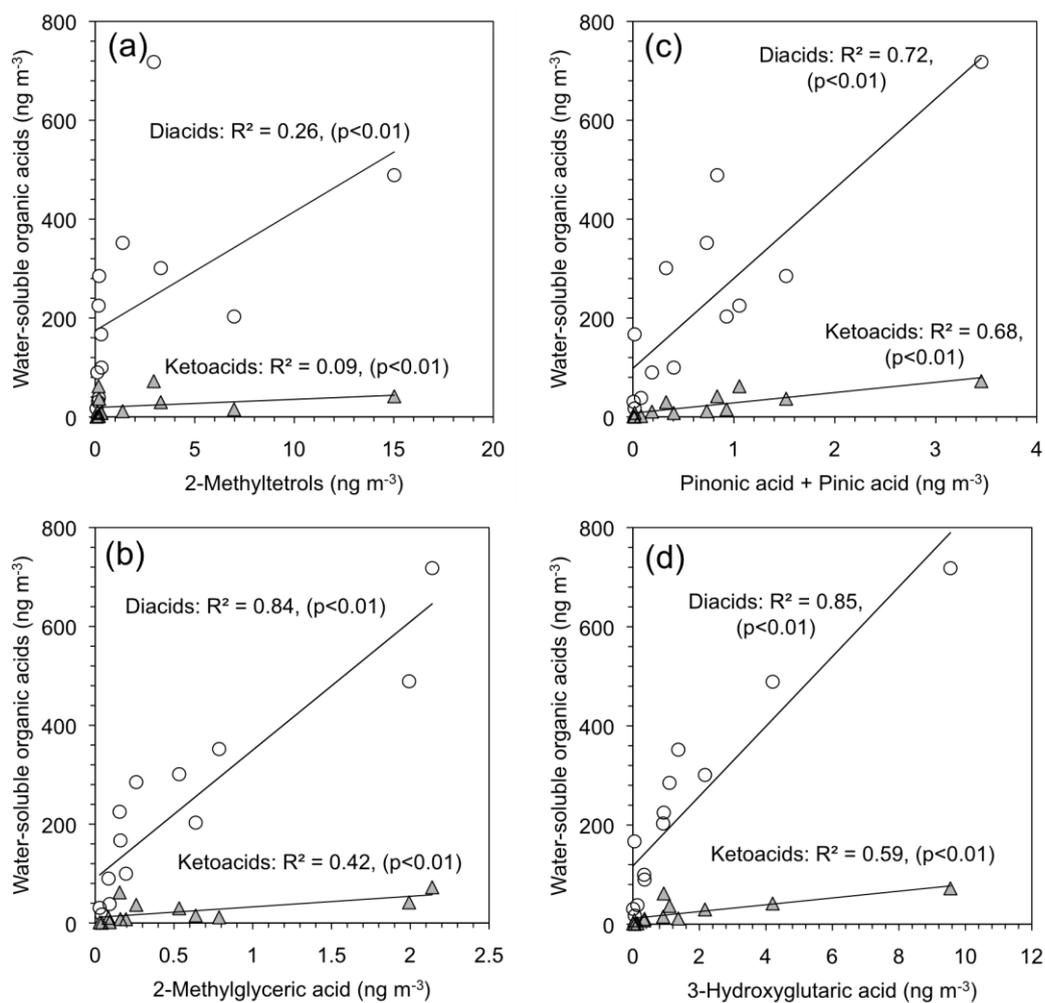


Fig. 7. Relationship between the concentrations of biogenic SOA tracers and total measured diacids and ketoacids. 2-Methyltetrols and 2-methylglyceric acid are tracers for isoprene oxidation; pinonic, pinic and 3-hydroxyglutaric acids are tracers for α -/ β -pinene oxidation.