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## RESEARCH ARTICLE

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## Key Points:

- Biogenic unsaturated fatty acids and isoprene are sources of atmospheric diacids
- Photochemical oxidation of these precursors produces oxalic and other diacids
- This study signifies a crucial role of marine source over continental ones

## Supporting Information:

- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5
- Figure S6
- Figure S7
- Figure S8
- Figure S9
- Table S1

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## Latitudinal distributions of atmospheric dicarboxylic acids, oxocarboxylic acids, and $\alpha$ -dicarbonyls over the western North Pacific: Sources and formation pathways

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**Abstract** The present study aims to assess the molecular distributions of water-soluble dicarboxylic acids (diacids:  $C_2$ – $C_{12}$ ), oxocarboxylic acids ( $C_2$ – $C_9$ ), and  $\alpha$ -dicarbonyls (glyoxal and methylglyoxal) in aerosols collected over the western North Pacific (WNP) during a summer cruise (August to September 2008). The measured water-soluble organics show pronounced latitudinal distributions with higher concentrations in the region of 30°N–45°N (average 63 ng m<sup>-3</sup>) than 10°N–30°N (18 ng m<sup>-3</sup>). Mass fraction of oxalic acid ( $C_2$ ) in total aliphatic diacids ( $\Sigma C_2$ – $C_{12}$ ) showed higher values (72 ± 10%) in lower latitude (10°N–30°N) than that (56 ± 16%) in higher latitude (30°N–45°N), suggesting a photochemical production of  $C_2$  due to an increased insolation over the tropical WNP. A similar trend was found in other diagnostic ratios such as oxalic to succinic ( $C_2/C_4$ ) and oxalic to glyoxylic acid ( $C_2/\omega C_2$ ), which further corroborate an enhanced photochemical aging over the WNP. In addition, relative abundances of oxalic acid in total diacids showed a marked increase as a function of ambient temperature, supporting their photochemical production. Constantly low concentration ratios of adipic and phthalic acids relative to azelaic acid suggest a small contribution of anthropogenic sources and an importance of oceanic sources during the study period. Significant production of  $C_2$  through oxidation of biogenic volatile organic compounds emitted from the sea surface is also noteworthy, as inferred from the strong linear correlations among water-soluble organic carbon, methanesulphonic acid, and oxalic acid. Sea-to-air emission of unsaturated fatty acids also contributes to formation of diacids over the WNP.

### 1. Introduction

Oceans contribute significantly (>50%) to the global aerosol burden (1000–3000 Tg yr<sup>-1</sup>) [Erickson and Duce, 1988], exerting considerable influence on the Earth's radiation budget [Haywood *et al.*, 1999]. Despite their global significance, composition of marine aerosols remains poorly understood, thus leading to a large uncertainty in assessing the aerosol radiative forcing [Sathesh and Krishna Moorthy, 2005]. Marine aerosol is a complex mixture of sea-salt particles and organics [Cavalli *et al.*, 2004; Facchini *et al.*, 2008b; O'Dowd and de Leeuw, 2007]. The studies carried out over the remote oceanic regions have focused mainly on atmospheric abundance and distributions of sulfates (nonsea salt/sea salt) [Charlson *et al.*, 1987; Charlson *et al.*, 1992] and mineral dust [Duce *et al.*, 1980; Schulz *et al.*, 2012; Uematsu *et al.*, 1985]. However, studies of organic aerosols over the open ocean have been limited in the literature in spite of their importance in cloud-aerosol interactions and dominance of mass concentration.

Water-soluble organics have gained considerable attention in recent years owing to their potential impacts on climate via the ability to act as cloud condensation nuclei (CCN). Among them, dicarboxylic acids and related polar compounds (oxocarboxylic acids and  $\alpha$ -dicarbonyls) are extensively studied chemical constituents in ambient particulate matter. In particular, low molecular weight (LMW) diacids are important constituents of organic aerosols, which can contribute to the water solubility of atmospheric particles and, thus, have an impact on climate [Kawamura *et al.*, 2013b]. Meanwhile, LMW monocarboxylic acids are largely present in gaseous phase [Kawamura *et al.*, 1985]. These dicarboxylic acids and related polar compounds have been detected in urban [Kawamura *et al.*, 2003; Legrand *et al.*, 2007; Miyazaki *et al.*, 2009; Sempéré and Kawamura, 1994], remote continental and marine [Fu *et al.*, 2013b; Kundu *et al.*, 2010; Miyazaki *et al.*, 2010; Mochida *et al.*, 2003a; Sempéré and Kawamura, 2003; Simoneit *et al.*, 2004], and polar regions [Kawamura *et al.*, 1996a; Kawamura *et al.*, 1996b; Narukawa *et al.*, 2002]. The abundances and mass concentration ratios of these oxygenated species to the water-soluble organics could provide pivotal

information on photochemical aging of aerosols during the long-range atmospheric transport [Fu *et al.*, 2013b; Kawamura and Usukura, 1993; Miyazaki *et al.*, 2010; Mochida *et al.*, 2003a; Sempéré and Kawamura, 2003]. However, this information is still limited in the literature for the remote marine aerosols compared with continental aerosols primarily due to inaccessibility of ship-based observations.

Based on the earlier observations, it is noteworthy that the molecular distributions of diacids in marine aerosols are characterized by the predominance of low molecular weight (LMW) diacids among which oxalic acid ( $C_2$  diacid or  $(COOH)_2$ ) is dominant followed by malonic ( $C_3$  diacid or  $CH_2(COOH)_2$ ) and succinic acids ( $C_4$  diacid or  $(CH_2)_2(COOH)_2$ ) [Fu *et al.*, 2013b; Kawamura and Sakaguchi, 1999]. These distributions are contrary to those documented for aerosols collected from urban and rural continental sites, where  $C_4$  diacid is more abundant than  $C_3$  diacid [Kawamura and Kaplan, 1987; Kawamura and Yasui, 2005; Miyazaki *et al.*, 2009]. Furthermore, these chemical species can contribute to total carbon in polluted continental (up to 2% [Kawamura and Ikushima, 1993]) and marine regions (up to ~16% [Kawamura and Sakaguchi, 1999]). The particles enriched with LMW diacids and related compounds have been hypothesized to act as CCN owing to their hygroscopic nature and thus important to study [Yu, 2000]. A piece of evidence in favoring this argument has been provided recently by Sorooshian *et al.* [2007], who found the existence of an intense layer of diacids (mainly oxalic acid) over cirrus cloud in the Gulf of Mexico and Houston region.

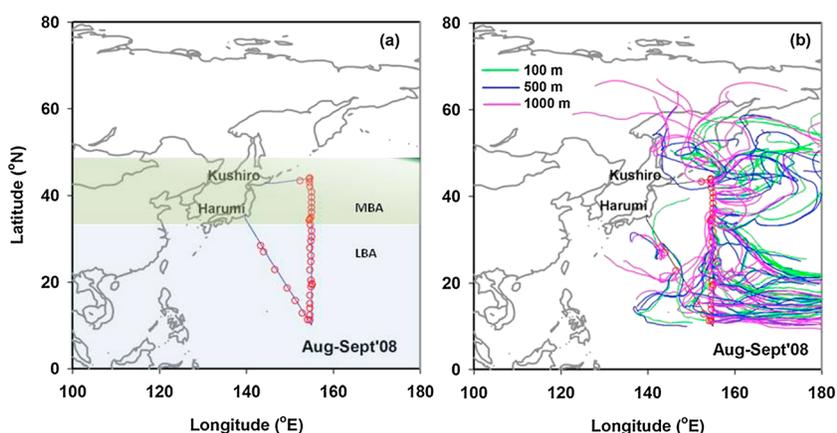
LMW diacids in the marine atmosphere can result from both primary and secondary sources. Over the open ocean, the primary emission of these water-soluble organics, mainly come from the biological and photochemical activities in the sunlit surface waters, emitted into the marine atmospheric boundary layer along with sea spray [Steinberg and Bada, 1984; Tedetti *et al.*, 2006]. However, the photochemical and aqueous phase oxidation of biogenic unsaturated fatty acids and volatile organic compounds (VOCs) such as isoprene emitted from the ocean surface can also serve as an important source of water-soluble organics [Bikkina *et al.*, 2014; Sempéré and Kawamura, 2003]. In this study, the bulk aerosol samples (i.e., total suspended particulate matter (TSP)) collected from the remote Pacific Ocean were investigated for their atmospheric abundances of water-soluble dicarboxylic acids, oxocarboxylic acids, and  $\alpha$ -dicarbonyls. In addition, their spatiotemporal distribution pattern and the photochemical aging of air masses have been assessed through certain diagnostic mass ratios of these organic species. Abundances of water-soluble organics and their diagnostic mass ratios (or characteristic of particular sources) will be compared between this study and those from other oceanic regions to better understand the chemical aging of marine aerosols over the Pacific Ocean.

## 2. Methodology

### 2.1. Cruise Track and Meteorological Conditions

Based on the modeling and field studies, it has been demonstrated that the continental air masses from East Asia significantly influence the chemical composition of aerosols [Prospero, 1996] and trace gases [Bey *et al.*, 2001; Walker *et al.*, 2010] over the western North Pacific (WNP) during winter and spring [Huebert *et al.*, 2003]. By comparing the long-term chemical composition data of marine aerosols (i.e., sugars and anhydrosugars, tracers for assessing the impact of biomass burning emissions) collected from a remote Island (Chichi-Jima), Chen *et al.* [2013] reported that the long-range atmospheric transport from East Asia is particularly higher in winter and spring and lower in summer and fall seasons. In contrast to winter and spring, the pristine maritime air masses from the south and southeast Pacific influence the chemical composition of aerosols over the WNP owing to prevailing high-pressure system, which develops during the course of summer. In addition, the persistent occurrence of phytoplankton blooms in the WNP during spring-late summer has also been documented by Kasai *et al.* [1998]. Likewise, consolidating the cruise data ( $N=176$ ) from the North Pacific, the occurrence of diatoms and *Trichodesmium* spp. (a dominant nitrogen fixer) in summer has been ascertained by Dore *et al.* [2008].

The present study is based on the second leg of a cruise (KH08) undertaken in the WNP during late August to early September (see more details for leg 1 cruise in the WNP [Miyazaki *et al.*, 2010]). These cruises are intended to study the chemical and isotopic compositions of pristine marine aerosols during which surface ocean is characterized by high biological activity. For this study, aerosol samples (TSP) were collected over the western North Pacific during 24 August to 13 September 2008 (i.e., on board R/V *Hakuho Maru*, Cruise: KH08-leg 2, from Kushiro to Tokyo). Figure 1 shows the cruise track. Meteorological parameters were



**Figure 1.** (a) Cruise track used for aerosol collection in the western North Pacific during August to September 2008 (b) air mass back trajectory cluster for the sampling days at arrival heights 100, 500, and 1000 m (MBA and LBA refer to more and less biologically influenced aerosols, respectively).

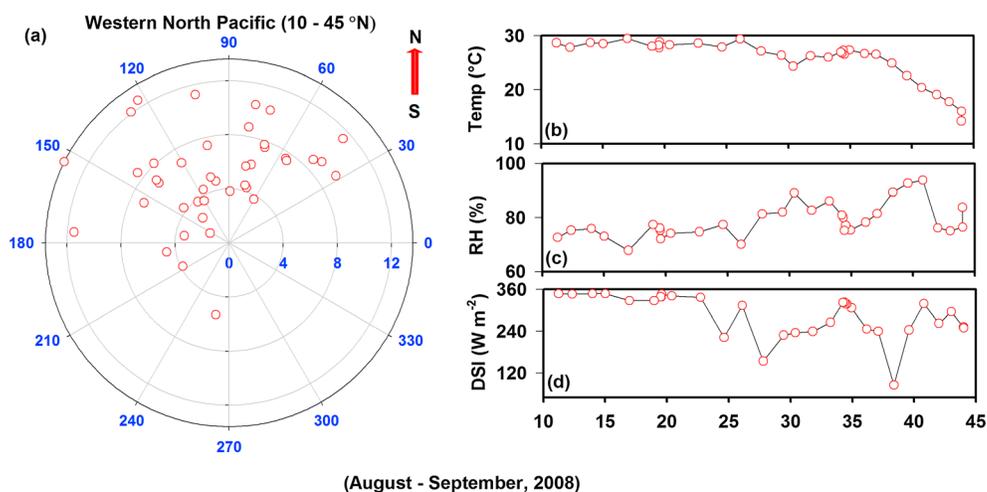
obtained from the onboard automatic weather station. During the cruise, ambient temperature and relative humidity varied from 14.2 to 29.4°C and 68 to 94%, respectively. Wind direction and speed were corrected for ship's motion. On average, wind directions were predominantly northeasterly/westerly, and the surface level wind speed ranged from 1.6 to 13.6 m s<sup>-1</sup> (average ± standard deviation 7.0 ± 3.0 m s<sup>-1</sup>). Daily averaged ambient temperature, relative humidity, wind speed and wind directions during the study period are given in Figure 2. More details regarding cruise track and meteorological conditions are described in Miyazaki *et al.* [2011].

## 2.2. Aerosol Collection and Analysis

For this study, a high-volume air sampler was set up on the front deck of the ship's navigation room and was operated at a flow rate of 1.0 m<sup>3</sup> min<sup>-1</sup> to collect total suspended particles (TSPs). In order to avoid the contamination from the ship's smoke stack, wind sector/wind speed controller was used for the aerosol sampling. All TSP samples were collected on precombusted (~450°C) quartz filter (25 cm × 20 cm, PALLFLEX<sup>TM</sup>, 2500 QAT-UP) substrates. The air volume ranged from 500 m<sup>3</sup> to 800 m<sup>3</sup> for most of the samples. After collection, filter samples were kept in clean glass jars with a Teflon-lined screw cap and stored at -20°C until the analyses for dicarboxylic acids (hereafter referred as diacids), oxocarboxylic acids (or oxoacids), and  $\alpha$ -dicarbonyls. The methodology used in this study to determine diacids and related compounds is similar to the protocols described in our earlier publications [Kawamura, 1993; Kawamura and Ikushima, 1993] but is slightly modified for better recovery [Hegde and Kawamura, 2012].

Briefly, an aliquot of aerosol filter cut was extracted with deionized ultrapure water (specific resistivity ≈ 18.2 MΩ-cm) by ultrasonic agitation (3 × 10 mL). The extracts were then passed through a Pasteur pipette containing quartz wool to remove the filter debris, and the pH of the solution was adjusted to ~8.5–9.0 with 0.05 M potassium hydroxide (KOH) solution. The water extracts were then concentrated using a rotary evaporator under vacuum. The concentrates were derivatized with 14% BF<sub>3</sub> in *n*-butanol in order to convert carboxyl groups to dibutyl esters and oxo and aldehyde groups to dibutoxy acetals. The derivatized products were then extracted into *n*-hexane and analyzed on capillary gas chromatograph (GC) equipped with a split/splitless injector, fused silica capillary column (HP-5, 0.2 mm I. D. × 25 m long × 0.5 μm film thickness), and flame ionization detector (FID). Concentrations of diacids, oxoacids, and  $\alpha$ -dicarbonyls in aerosol samples were ascertained by simultaneous analysis of the authentic standard solution containing dibutyl esters of oxalic, malonic, succinic, adipic, glutaric, phthalic, and azelaic acids. In addition, peak identification was confirmed by comparing the mass spectra obtained by GC-mass spectrometry (MS). More detailed analytical methods with respect to peak identification and confirmation are mentioned in our earlier laboratory protocols [Kawamura, 1993; Kawamura and Ikushima, 1993].

In order to support the inferences drawn in the present study, we have obtained the atmospheric abundances of water-soluble organic carbon (WSOC) and methanesulphonic acid (MSA) from Miyazaki *et al.* [2011]. Likewise, isoprene-secondary organic aerosol (SOA) tracers (2-methylglyceric acid and



**Figure 2.** (a) Wind rose showing the wind direction, wind speed (in  $\text{m s}^{-1}$ ) and latitudinal profiles, (b) ambient temperature, (c) relative humidity, and (d) downward solar irradiance (obtained from NCEP obtained from NOAA air resources laboratory).

methyltetrols) are measured by GC-MS following the method of *Fu et al.* [2013a], and their concentrations are published elsewhere [*Bikkina et al.*, 2014]. In order to assess the role of aerosol liquid water content (LWC) on secondary organic aerosol (or SOA) formation, we have estimated LWC using a thermodynamic equilibrium model, ISORROPIA-II [*Fountoukis and Nenes*, 2007; <http://nenes.eas.gatech.edu/ISORROPIA/>]. Inorganic compositions from *Miyazaki et al.* [2011] and measured onboard meteorological parameters (relative humidity and ambient temperature) were used as input parameters for estimating the aerosol LWC using ISORROPIA-II (as reverse problem in which aerosol composition is used).

### 2.3. Quality Assurance

In order to check the recovery, known amounts of free diacids were spiked on the blank filter and then extracted, derivatized, and determined with GC-FID in a similar way to that of real aerosol samples as described above. The recoveries of all diacids measured in this study are better than 85%, except for  $\text{C}_2$  diacid for which a modest recovery of 80% is achieved. The overall analytical uncertainties in the diacid measurements are less than  $\sim 10\%$  based on replicate analyses of the real samples. Statistical analyses were also carried out using two-tailed  $t$  score test wherever necessary comparisons are made.

## 3. Results and Discussion

### 3.1. Biological Activity and Continental Influence

The air mass back trajectory (AMBT) analyses provide crucial information on the source region of pollutants and their transport pathways (whether continental or marine influence). In this study, 7 day isentropic AMBTs were computed for all sampling dates at three arrival heights (100, 500, and 1000 m; see Figure 1) using Hybrid Single-Particle Lagrangian Integrated Trajectory model (version 4) [*Draxler et al.*, 1999] and Global Data Assimilation System reanalysis meteorological data sets from NOAA air resources laboratory. It is noteworthy that for most of the sampling days (except few, i.e., 3 days), the AMBTs show marine origin, consistent with the prevailing meteorology over North Pacific during summer.

During the study period, the aerosol samples collected from 30°N to 45°N were characterized by high contribution of marine-derived SOAs compared to that from 10°N to 30°N. This inference is drawn from higher ( $P < 0.05$ ) percentage contribution of MSA to total organic carbon (OC) in aerosols collected between 30 and 45°N (average  $\pm$  standard deviation  $6 \pm 2\%$ ) compared to that from 10°N to 30°N ( $2 \pm 1\%$ ). In the marine atmospheric boundary layer (MABL), MSA is produced by the oxidation of dimethyl sulphide (DMS), a gaseous precursor that is derived in the sunlit surface waters during biological activity and emitted to the air through sea-air interface. Thus, MSA can be used as a tracer to assess the qualitative contribution of DMS and other biogenic volatile organic compounds (BVOCs) from the marine environment [*Miyazaki et al.*, 2010].

The SOA formation from marine BVOCs can also be ascertained by the presence of diethylammonium (DEA<sup>+</sup>), a tracer for biogenic secondary organic aerosols over the open ocean waters characterized with high biological activity [Facchini *et al.*, 2008a]. In this regard, Miyazaki *et al.* [2011] have documented high and low concentrations of DEA<sup>+</sup> in more and less biologically influenced aerosols, respectively, over the WNP during the study period. Likewise, previous studies have documented isoprene emissions from the productive open ocean waters [Arnold *et al.*, 2009, and references therein]. However, the oxidation of isoprene in the MABL leads to the formation of variety of organic compounds such as methyltetrols and methylglyceric acid (also known as isoprene-SOA tracers), methylglyoxal, pyruvic, and glyoxylic acids [Carlton *et al.*, 2009, and references therein]. During the cruise, a significant increase in the atmospheric concentrations of isoprene-SOA tracers, methylglyoxal, pyruvic, and glyoxylic acids was recognized in more biologically influenced aerosols than less biologically influenced aerosols [Bikkina *et al.*, 2014].

The high biological activity in the WNP (30°N–45°N) during the study period is also confirmed by the relative increase in chlorophyll *a* concentrations in seawater (0.04–0.34 mg m<sup>-3</sup>; average 0.15 mg m<sup>-3</sup>) compared to that between 10°N and 30°N (0.03–0.06 mg m<sup>-3</sup>; average 0.04 mg m<sup>-3</sup>) [Miyazaki *et al.*, 2011]. During the cruise (KH08-2: August to September 2008), Jung *et al.* [2014] had documented a linear relationship between chlorophyll *a* concentration and atmospheric abundance of MSA and nonsea-salt sulphate, suggesting their formation from the DMS oxidation in the MABL. Their study also highlighted the occurrence of phytoplankton blooms over the high latitude (>30°N) than at low latitudes (<30°N). In this regard, the aerosols collected between 30°N–45°N and 10°N–30°N are categorized as “more and less biologically influenced aerosols (MBA and LBA),” respectively [Miyazaki *et al.*, 2011]. The latitudinal distribution of relevant parameters measured in this study is therefore discussed as “MBA-type” and “LBA-type.” In addition, to corroborate the inferences related to oceanic contribution of BVOCs to marine SOAs, latitudinal profiles of columnar chlorophyll *a* concentrations in seawater, atmospheric abundances of MSA, WSOC, and water-soluble dicarboxylic acids and related polar compounds are shown in Figure S1 in the supporting information obtained from our earlier publications [Bikkina *et al.*, 2014; Miyazaki *et al.*, 2011].

## 3.2. Latitudinal Distributions of Diacids, Oxoacids, and $\alpha$ -Dicarbonyls

### 3.2.1. Dicarboxylic Acids

A homologous series of diacids (from C<sub>2</sub> to C<sub>12</sub>), branched chain diacids, unsaturated diacids, and multifunctional diacids were detected in the marine aerosols (Table 1). All the diacids show pronounced spatiotemporal variability. In order to focus on the latitudinal distribution, we discuss here only those aerosol samples collected from the latitudinal transect of the cruise track that spans between 10°N and 45°N and at the longitude of ~155°E (see Figure 1).

In this study, the measured diacids show higher concentrations in the MBA-type than LBA-type (see Table 1). Owing to large variability, we have compared the median concentration of MBA with that of LBA for diacids and found to be consistent with that of mean values. Figure 3 depicts the latitudinal variations of selected diacids over the WNP during the study period. Similar temporal variability is observed between adipic acid and azelaic acid, suggesting the formation of adipic acid from azelaic acid which is in turn a photochemical oxidation product of biogenic unsaturated fatty acid (e.g., oleic acid) [Kawamura and Gagosian, 1987; Kawamura and Usukura, 1993; Satsumabayashi *et al.*, 1990]. This inference is further supported by the laboratory photooxidation experiment of azelaic acid solution with hydroxyl radical that resulted in the formation of adipic acid as an intermediate [Yang *et al.*, 2008a]. Therefore, we infer that adipic acid formed from the natural sources. However, previous studies suggested that adipic acid could also be formed from the oxidation of cyclic olefins with ozone in the polluted urban atmosphere [Grosjean, 1989; Kawamura and Ikushima, 1993]. Owing to the lack of continental outflow from East Asia to the WNP during summer, we presume that it is derived from marine origin.

Similar temporal trends are noteworthy for phthalic (Ph) and terephthalic acids (tPh) and are consistent with that of adipic and azelaic acids (Figure 3). Therefore, it is possible that these compounds also might have been originated from the natural sources over the WNP than that derived from anthropogenic sources. Similar to our study, a close resemblance in the temporal trend between phthalic acid and azelaic acid has been observed for pristine Arctic aerosols sampled during early summer by Kawamura *et al.* [2010] and, thus, suggested their natural source. In this regard, previous study by Carlson [1982] had shown that phthalates can also be formed from the photochemical oxidation of phenolic compounds, which are shown to be

**Table 1.** Statistical Description (Range, Average, Standard Deviation, Median, and Geometric Mean) About the Concentrations and Relative Abundance of Measured Water-Soluble Organics in Total Mass Concentration of Diacids and Related Compounds<sup>a</sup>

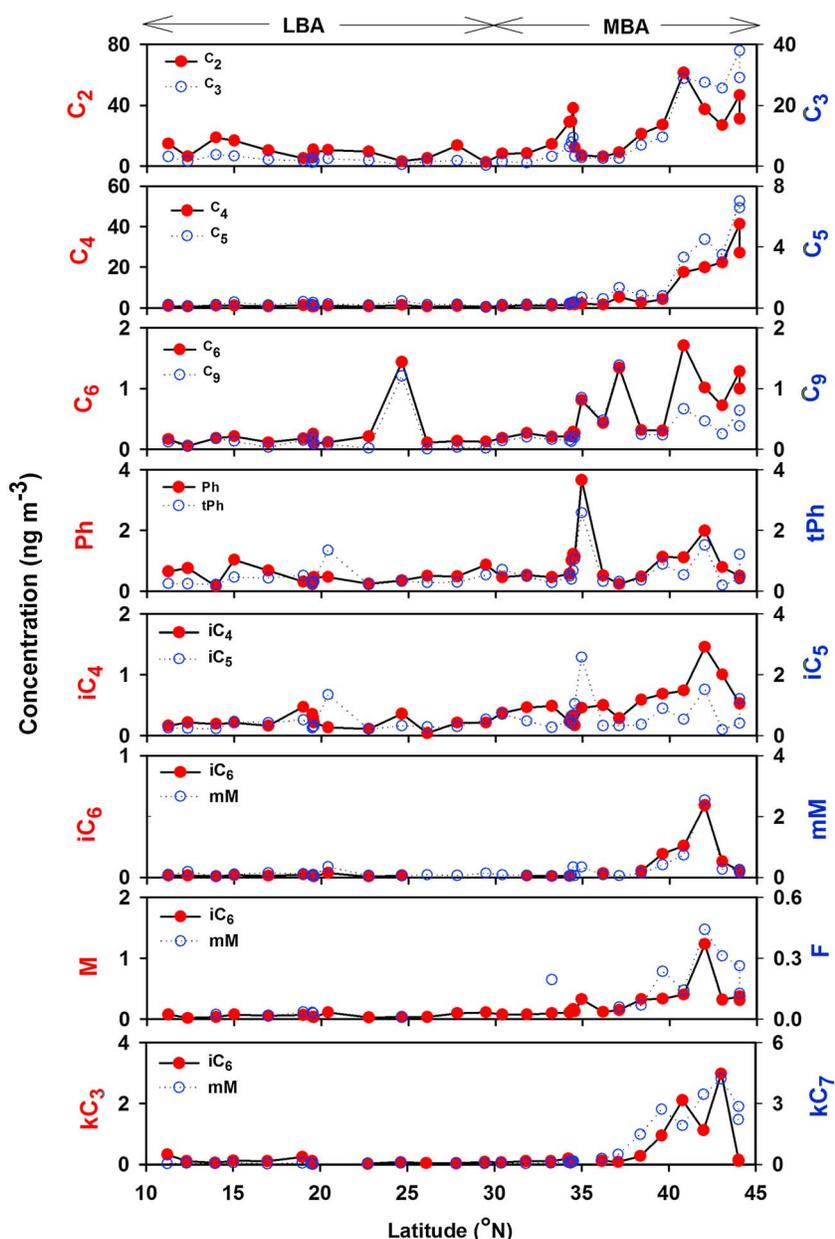
| Compound                            | MBA: 30°N–45°N |  | LBA: 10°N–30°N |                          |
|-------------------------------------|----------------|--|----------------|--------------------------|
|                                     | Range          | Avg ± SD (Median, Geometric Mean (GM)) | Range          | Avg ± SD (Median, GM)    |
| <i>Diacids</i>                      |                |  |                |                          |
| Oxalic (C <sub>2</sub> )            | 6.3–61.2       | 24.5 ± 14.9 (26.9, 20.2)               | 2.5–19.3       | 11.0 ± 5.2 (10.5, 9.6)   |
| Malonic (C <sub>3</sub> )           | 1.1–37.8       | 12.6 ± 11.6 (7.8, 7.6)                 | 0.2–4.7        | 2.0 ± 1.1 (1.8, 1.7)     |
| Succinic (C <sub>4</sub> )          | 0.9–41.2       | 9.8 ± 11.5 (2.7, 4.8)                  | 0.4–2.6        | 1.0 ± 0.5 (1.0, 0.9)     |
| Glutaric (C <sub>5</sub> )          | 0.2–7.0        | 2.1 ± 2.3 (0.8, 1.1)                   | 0.05–1.0       | 0.3 ± 0.2 (0.2, 0.2)     |
| Adipic (C <sub>6</sub> )            | 0.2–1.7        | 0.7 ± 0.5 (0.4, 0.5)                   | 0.1–1.6        | 0.3 ± 0.4 (0.2, 0.2)     |
| Pimelic (C <sub>7</sub> )           | 0.01–1.0       | 0.2 ± 0.3 (0.06, 0.1)                  | n.d.–0.25      | 0.04 ± 0.05 (0.03, 0.03) |
| Suberic (C <sub>8</sub> )           | n.d.–0.7       | 0.5 ± 0.5 (0.4, 0.3)                   | n.d.–0.86      | 0.20 ± 0.25 (0.12, 0.13) |
| Azelaic (C <sub>9</sub> )           | 0.1–1.8        | 0.5 ± 0.5 (0.2, 0.3)                   | 0.004–1.2      | 0.2 ± 0.2 (0.1, 0.1)     |
| Sebacic (C <sub>10</sub> )          | n.d.–0.2       | 0.1 ± 0.1 (0.08, 0.1)                  | n.d.–0.05      | 0.02 ± 0.01 (0.01, 0.01) |
| Undecanedioic (C <sub>11</sub> )    | 0.01–0.4       | 0.1 ± 0.1 (0.06, 0.1)                  | 0.02–0.49      | 0.08 ± 0.10 (0.01, 0.06) |
| Dodecanedioic (C <sub>12</sub> )    | n.d.–0.4       | 0.3 ± 0.2 (0.30, 0.2)                  | 0.01–0.07      | 0.03 ± 0.03 (0.02, 0.02) |
| Methylmalonic (iC <sub>4</sub> )    | 0.1–1.7        | 0.5 ± 0.4 (0.3, 0.4)                   | 0.03–0.24      | 0.11 ± 0.05 (0.10, 0.10) |
| Methylsuccinic (iC <sub>5</sub> )   | 0.2–1.5        | 0.5 ± 0.3 (0.5, 0.4)                   | 0.04–0.55      | 0.22 ± 0.13 (0.21, 0.19) |
| Methylglutaric (iC <sub>6</sub> )   | n.d.–0.6       | 0.1 ± 0.2 (0.05, 0.1)                  | n.d.–0.04      | 0.02 ± 0.01 (0.01, 0.01) |
| Maleic (M)                          | 0.1–1.2        | 0.3 ± 0.3 (0.2, 0.2)                   | 0.02–0.1       | 0.05 ± 0.03 (0.04, 0.05) |
| Fumaric (F)                         | n.d.–0.4       | 0.2 ± 1.2 (0.2, 0.2)                   | n.d.–0.09      | 0.04 ± 0.03 (0.03, 0.03) |
| Methylmaleic (mM)                   | 0.1–2.5        | 0.3 ± 0.6 (0.1, 0.2)                   | 0.02–0.35      | 0.10 ± 0.07 (0.09, 0.08) |
| Phthalic (Ph)                       | 0.2–3.7        | 0.9 ± 0.8 (0.6, 0.7)                   | 0.2–1.0        | 0.5 ± 0.2 (0.5, 0.4)     |
| Isophthalic (iPh)                   | 0.01–0.8       | 0.2 ± 0.2 (0.1, 0.1)                   | 0.03–0.38      | 0.14 ± 0.09 (0.10, 0.11) |
| Terephthalic (tPh)                  | 0.2–2.6        | 0.7 ± 0.6 (0.6, 0.6)                   | 0.1–1.3        | 0.4 ± 0.3 (0.3, 0.3)     |
| Hydroxy succinic (hC <sub>4</sub> ) | 0.04–0.96      | 0.23 ± 0.24 (0.13, 0.15)               | n.d.–0.09      | 0.03 ± 0.02 (0.02, 0.02) |
| Ketomalonic (kC <sub>3</sub> )      | n.d.–3.0       | 0.5 ± 0.8 (0.1, 0.2)                   | n.d.–0.32      | 0.10 ± 0.07 (0.09, 0.08) |
| Ketopimelic (kC <sub>7</sub> )      | n.d.–4.2       | 1.1 ± 1.4 (0.2, 0.3)                   | n.d.–0.23      | 0.05 ± 0.04 (0.04, 0.04) |
| Total diacids                       | 13–153         | 56 ± 41 (42, 43)                       | 4.6–31.0       | 16.7 ± 6.7 (15.3, 15.3)  |
| <i>Oxoacids</i>                     |                |  |                |                          |
| Glyoxylic (ωC <sub>2</sub> )        | 0.6–4.7        | 1.9 ± 1.4 (1.3, 1.5)                   | 0.1–0.7        | 0.3 ± 0.2 (0.2, 0.2)     |
| 3-Oxopropanoic (ωC <sub>3</sub> )   | 0.02–1.9       | 0.3–0.5 (0.1, 0.1)                     | 0.01–0.07      | 0.03 ± 0.02 (0.03, 0.03) |
| 4-Oxobutanoic (ωC <sub>4</sub> )    | 0.05–2.9       | 0.6 ± 0.7 (0.3, 0.3)                   | n.d.–0.26      | 0.15 ± 0.07 (0.14, 0.13) |
| 5-Oxopentanoic (ωC <sub>5</sub> )   | 0.05–0.9       | 0.2 ± 0.2 (0.1, 0.2)                   | 0.02–0.13      | 0.07 ± 0.03 (0.07, 0.07) |
| 7-Oxoheptanoic (ωC <sub>7</sub> )   | 0.1–3.8        | 0.8 ± 1.0 (0.4, 0.4)                   | 0.03–0.30      | 0.13 ± 0.06 (0.12, 0.12) |
| 8-Oxooctanoic (ωC <sub>8</sub> )    | n.d.–5.4       | 0.9 ± 1.4 (0.3, 0.3)                   | n.d.–0.22      | 0.06 ± 0.05 (0.04, 0.05) |
| 9-Oxononanoic (ωC <sub>9</sub> )    | n.d.–1.9       | 0.4 ± 0.6 (0.1, 0.2)                   | n.d.–0.10      | 0.02 ± 0.02 (0.02, 0.02) |
| Total ω-oxoacids                    | 1.1–21.2       | 5.0 ± 5.2 (3.3, 3.3)                   | 0.3–1.6        | 0.7 ± 0.3 (0.6, 0.6)     |
| Pyruvic (Pyr)                       | 0.1–3.4        | 0.7 ± 0.9 (0.4, 0.4)                   | 0.04–0.75      | 0.22 ± 0.14 (0.21, 0.18) |
| <i>α-Dicarbonyls</i>                |                |  |                |                          |
| Glyoxal (Gly)                       | 0.1–0.6        | 0.2 ± 0.1 (0.2, 0.2)                   | 0.00–1.8       | 0.2 ± 0.4 (0.07, 0.1)    |
| Methylglyoxal (MeGly)               | 0.002–1.0      | 0.3 ± 0.2 (0.2, 0.2)                   | 0.03–1.5       | 0.1 ± 0.3 (0.06, 0.1)    |
| Total α-dicarbonyls                 | 0.2–1.3        | 0.5 ± 0.3 (0.4, 0.4)                   | 0.04–3.3       | 0.3 ± 0.7 (0.13, 0.1)    |

<sup>a</sup>All concentrations are in ng m<sup>-3</sup>; n.d. refers to “not detected.” MBA and LBA refer to more and less biologically influenced aerosols, respectively.

enriched in sea surface microlayer slicks. In addition, recent study by *Bahadur et al.* [2010] have suggested that phenolic compounds in marine aerosols, collected from the remote North Atlantic, are mainly associated with primary emissions along with sea spray. Their emissions into the MABL along with biogenic unsaturated fatty acids and subsequent photooxidation have been suggested as a source of phthalate over pristine oceanic regions [*Kawamura et al.*, 2010].

Taken together, by looking at the observed similar temporal trends among azelaic, adipic, and phthalic acids, we attribute their formation from the photochemical oxidation of biogenic unsaturated fatty acids and phenols which are emitted to the MABL from the ocean surface. However, their concentrations (C<sub>6</sub>, Ph, and tPh) over the WNP are 10 to 30 times lower than those reported in the urban atmosphere such as Tokyo and Sapporo [*Bikkina et al.*, 2014], suggesting that marine-derived contributions are relatively low compared to those formed from anthropogenic sources.

It is important to note that although some trajectories (first three samples) computed at 1000 m above sea level over the WNP indeed look like passing over the continent (Figure 1), the air mass trajectory height over



**Figure 3.** Latitudinal distributions of saturated diacids (oxalic, malonic, succinic, glutaric, adipic, and azelaic acids:  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_5$ ,  $C_6$ , and  $C_9$ ), branched chain diacids (methylmalonic, methyl succinic, and methylglutaric acids:  $iC_4$ ,  $iC_5$ , and  $iC_6$ ), unsaturated diacids (methylmaleic, maleic, fumaric, phthalic, and terephthalic diacids:  $mM$ ,  $M$ ,  $F$ ,  $Ph$ , and  $tPh$ ), and multifunctional diacids (ketomalonic and ketopimelic acids:  $kC_3$  and  $kC_7$ ) in aerosols collected over the western North Pacific during August to September 2008. Temporal distributions of  $C_2$  and  $C_9$  are only used for comparison and obtained from *Bikkina et al.* [2014]. Here MBA and LBA refer to more and less biologically influenced aerosols that are sampled over the western North Pacific during high and low biological activities, respectively.

the source sites is more than 3000 to 5000 m (see Figure S2 in the supporting information). The long-range atmospheric transport of pollutants from East Asia at these heights is less likely during summer (see Figure S2 in the supporting information). Therefore, the observed lower (10–30 times) atmospheric abundances of anthropogenic tracers ( $Ph$ ,  $tPh$ ,  $C_6$ , and  $EC$ ) over the WNP compared to those over nearby continental urban sites in East Asia, indeed, prompt us to infer that minor or negligible impact of East Asian outflow occurred during the study period.

It is noteworthy that the higher mass concentrations of azelaic acid ( $C_9$ ) are also consistent with the high biological activity in  $30^\circ\text{N}$ – $45^\circ\text{N}$ . Based upon UV irradiation on an oleic acid and ozone system, *Matsunaga et al.* [1999] documented the production of  $C_2$  to  $C_9$  diacids among which azelaic acid is dominant. In this regard, a close resemblance of temporal variability between  $C_9$  diacid,  $C_6$  diacid, and total mass concentration of low molecular diacids (i.e., LMW diacids:  $C_2 + C_3 + C_4$ , see Figure S1 in the supporting information) suggests that photochemical oxidation of azelaic acid might explain the formation of shorter-chain homologues ( $C_6$ ,  $C_5$ , and  $C_4$  diacids), which eventually leads to the formation of  $C_2$  diacid over the WNP during summer. Therefore, it is inferred from Figure 3 that aerosols collected from the MABL of WNP has considerable influence of biogenic emissions from the ocean surface. However, its contribution to WSOC is diminished in  $10^\circ\text{N}$ – $30^\circ\text{N}$ , which is characterized by low biological activity and thus reflected by lower  $C_9$  concentration. As mentioned in section 3.1, this observation is also consistent with other chemical proxies such as chlorophyll *a*, MSA, and  $\text{DEA}^+$  [*Miyazaki et al.*, 2011], and hydroxy acids [*Miyazaki et al.*, 2014].

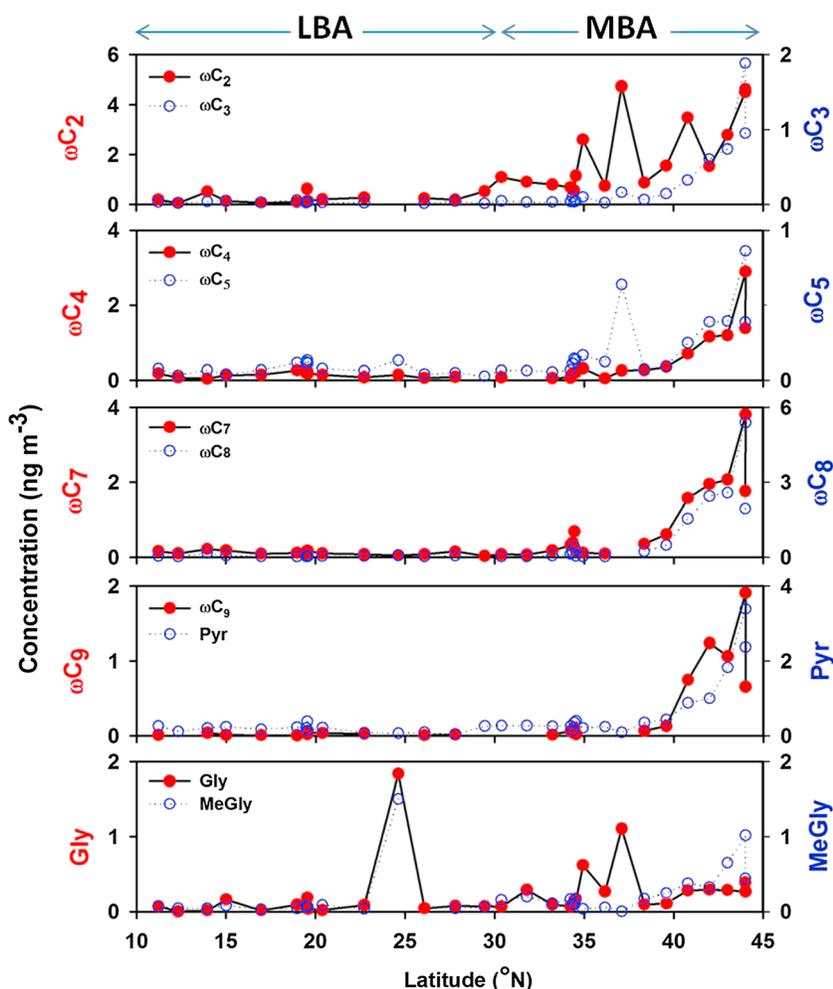
Total diacid concentrations over the open ocean waters of the WNP during the study period (August to September 2008) varied from 5 to  $153 \text{ ng m}^{-3}$  (average  $35 \pm 34 \text{ ng m}^{-3}$ ). The mean concentration of diacids from this study is found to be somewhat lower than those reported from the remote and coastal islands in the WNP, for example, Chichijima, Japan ( $139 \text{ ng m}^{-3}$ ) [*Mochida et al.*, 2003a] and Gosan, Jeju Island, South Korea ( $660 \text{ ng m}^{-3}$ ) [*Kawamura et al.*, 2004] and ( $636 \text{ ng m}^{-3}$ ) [*Kundu et al.*, 2010], and from the Sea of Japan ( $1200 \text{ ng m}^{-3}$ ) [*Mochida et al.*, 2003b], the East China Sea ( $850 \text{ ng m}^{-3}$ ) [*Mochida et al.*, 2003b] and ( $325 \text{ ng m}^{-3}$ ) [*Fu et al.*, 2013b], California coast ( $424 \text{ ng m}^{-3}$ ) [*Fu et al.*, 2013b], and the Indian Ocean ( $301 \text{ ng m}^{-3}$ ) [*Fu et al.*, 2013b]. However, the average concentration of diacids from this study is comparable with those reported over the North Pacific ( $61 \text{ ng m}^{-3}$ ) [*Kawamura and Usukura*, 1993], WNP (87 and  $34 \text{ ng m}^{-3}$  in MBA and LBA, respectively) [*Miyazaki et al.*, 2010], and Atlantic Ocean ( $95 \text{ ng m}^{-3}$ ) [*Fu et al.*, 2013b].

### 3.2.2. Oxocarboxylic Acids

During the course of the study, concentrations of oxoacids show pronounced temporal variability, ranging from  $0.42$  to  $25 \text{ ng m}^{-3}$  with an average of  $\sim 3.2 \text{ ng m}^{-3}$ . Among the measured oxoacids, glyoxylic acid ( $\omega C_2$ ) was found to be the most abundant species followed by pyruvic acid (Pyr), 8-oxooctanoic acid ( $\omega C_8$ ), and 7-oxoheptanoic acid ( $\omega C_7$ ) (see Table 1). Figure 4 presents the latitudinal distributions of  $\omega$ -oxocarboxylic acids and  $\alpha$ -dicarbonyls in marine aerosols collected during the cruise. Relatively high concentrations were observed in MBA than LBA, being similar to that of major diacid species ( $C_2$ ,  $C_3$ , and  $C_4$ ) (Figure 3).

The 9-oxononanoic acid ( $\omega C_9$ ) has been detected in most of the aerosol samples studied in this cruise. However, its atmospheric concentration (average  $0.23 \text{ ng m}^{-3}$ ) is lower than that ( $37 \text{ ng m}^{-3}$ ) reported over the Antarctic aerosol during summer [*Kawamura et al.*, 1996b]. Previous study by *Kawamura and Gagosian* [1987] proposed that  $\omega C_9$  is a photochemical oxidation product of unsaturated fatty acids emitted from the surface ocean. Its further oxidation in the atmosphere leads to the formation of azelaic acid ( $C_9$  diacid). In addition, it has been suggested that other short-chain  $\omega$ -oxoacids are also produced in the marine atmosphere through photochemical oxidation of unsaturated fatty acids [*Kawamura et al.*, 1996a]. These intermediate compounds are further oxidized to produce low molecular weight diacids over the remote oceanic regions [*Kawamura et al.*, 1996a]. In this context, the observed linear correlations ( $P < 0.05$ , see Figure S3 in the supporting information) of  $\omega C_2$  versus  $C_2$  ( $R^2 = 0.30$ ),  $\omega C_3$  versus  $C_3$  ( $R^2 = 0.77$ ), and  $\omega C_4$  versus  $C_4$  ( $R^2 = 0.94$ ) suggest their source from biogenic unsaturated fatty acids. Based on the above observations together with high concentrations of azelaic acid in MBA samples, we infer that photochemical oxidation of biogenic unsaturated fatty acids could be a significant source of these molecular species in the MABL.

It is also possible that short-chain oxoacids such as glyoxylic and pyruvic acids ( $\omega C_2$  and Pyr), which are dominant oxoacids, could originate from the atmospheric oxidation of BVOCs such as isoprene. Several studies suggested that Pyr is produced in the atmosphere via the incloud oxidation of isoprene [*Carlton et al.*, 2006, 2009], a gaseous precursor emitted from the ocean surface during high biological activity [*Shaw et al.*, 2010]. Furthermore, laboratory studies demonstrated that incloud oxidation of Pyr also leads to the production of  $\omega C_2$  and oxalic acid [*Carlton et al.*, 2006]. Combining this knowledge with our results (higher abundance of  $\omega C_2$ , Pyr, and  $C_2$  in MBA), we propose that aqueous phase oxidation of isoprene in the MABL of the WNP is a significant contributor to atmospheric water-soluble organics. Relatively high



**Figure 4.** Latitudinal distribution of oxoacids (glyoxylic, 3-oxopropanoic, 4-oxobutanoic, 5-oxopentanoic, 7-oxoheptanoic, 8-oxooctanoic, 9-oxononanoic, and pyruvic acids:  $\omega C_2$ ,  $\omega C_3$ ,  $\omega C_4$ ,  $\omega C_5$ ,  $\omega C_7$ ,  $\omega C_8$ ,  $\omega C_9$ , and Pyr) and  $\alpha$ -dicarbonyls (glyoxal and methylglyoxal: Gly and MeGly) in marine aerosols sampled over the western North Pacific during August to September 2008. Temporal distributions of  $\omega C_2$ , Pyr, and MeGly are only used for comparison and obtained from *Bikkina et al.* [2014]. MBA and LBA refer to more and less biologically influenced aerosols that are sampled over the western North Pacific during high and low biological activities, respectively.

concentrations of isoprene-SOA tracers [*Bikkina et al.*, 2014] in the more biologically influenced aerosols further corroborate the isoprene oxidation pathway in contributing to atmospheric abundances of  $\omega C_2$ , Pyr, and  $C_2$ . This observation highlights a significant SOA formation from the isoprene oxidation pathway over the open ocean waters.

### 3.2.3. The $\alpha$ -Dicarbonyls

Although their concentrations are low, methylglyoxal (MeGly) and glyoxal (Gly) were detected in the marine aerosols. In contrast to diacids and oxoacids,  $\alpha$ -dicarbonyls show little temporal variability (Figure 4) with slightly higher concentrations in MBA than in LBA (see geometric concentration in Table 1). Since the range is too large for  $\alpha$ -dicarbonyls, comparison of geometric mean is more appropriate than arithmetic mean. Concentrations of total  $\alpha$ -dicarbonyls varied from 0.04 to 3.34  $\text{ng m}^{-3}$  with an average of 0.41  $\text{ng m}^{-3}$  (Table 1). The concentrations are comparable with those for the summed concentrations of supermicron and submicron aerosols collected over the North Pacific ( $0.51 \pm 0.22 \text{ ng m}^{-3}$  in MBA and  $0.66 \pm 0.20 \text{ ng m}^{-3}$  in LBA during summer) [*Miyazaki et al.*, 2010]. It has been suggested that over the remote oceanic regions, the atmospheric oxidation of biogenic VOCs emitted from the ocean surface (e.g., isoprene) can lead to the formation of MeGly and Gly [*Carlton et al.*, 2009]. Therefore, the presence of these compounds together with abundant glyoxylic acid suggests their possible marine source.

The covariability in the latitudinal distributions of MeGly and Gly together with significant linear relationship between them ( $R^2 > 0.5$ ,  $p < 0.05$ ; figure not shown here) suggests their common origin. Because  $\alpha$ -dicarbonyls are present largely in gas phase due to their high vapor pressure [Kawamura *et al.*, 2013a], their oxidation in the atmosphere can contribute significantly to SOA formation over the oceanic regions. Due to higher relative humidity (68–94%) over the WNP, MeGly further oxidizes in the MABL to produce  $\omega$ C<sub>2</sub> through aqueous phase oxidation. A notable linear relationship between MeGly and other isoprene oxidation products (viz., isoprene-SOA tracers, Pyr, and  $\omega$ C<sub>2</sub>) further supports isoprene contribution to SOA formation via its atmospheric oxidation in the MABL (see section 3.4 for more detailed explanation).

A recent laboratory experiment from Kawamura group to investigate the possible formation process of diacids and related compounds from isoprene ozonolysis has provided some new insights [Kawamura *et al.*, 2014]. One of the interesting results pertaining to this experiment is the formation of oxalic, malonic, and succinic acids together with  $\omega$ C<sub>2</sub>, MeGly, and Gly, and Pyr in aerosols sampled from the chamber. The mass ratios of MeGly to  $\omega$ C<sub>2</sub> and Gly to  $\omega$ C<sub>2</sub> in their experiment correspond to  $\sim 1.4$ – $2.6$  and  $\sim 0.3$ – $0.7$ , respectively. Comparisons of the results from isoprene/ozone laboratory experiment by Kawamura *et al.* [2014] with our study from the WNP (MeGly/ $\omega$ C<sub>2</sub>: 0.01–2.9; average 0.34; Gly/ $\omega$ C<sub>2</sub>: 0.03–2.36; average 0.36) are somewhat consistent.

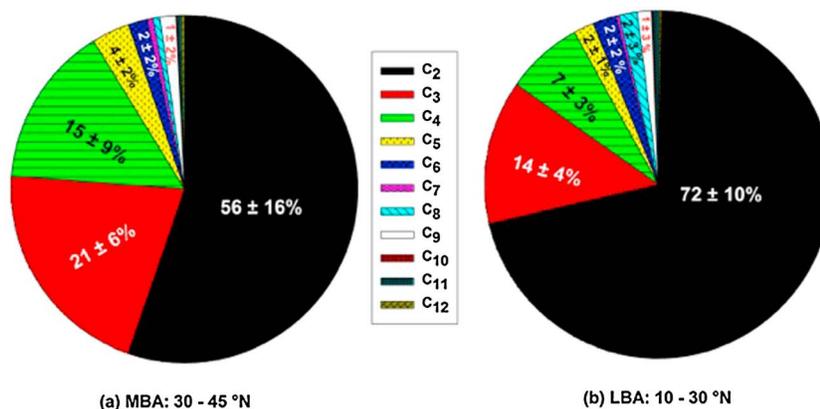
Although isoprene oxidation leads to the formation of semivolatile carbonyls such as Gly and MeGly, their partitioning to particulate phase shall depend on various factors such as aqueous phase chemistry, extent of photochemical oxidation processes, and meteorological factors as well as aerosol liquid water content (LWC). In comparison with the land sources, the isoprene oxidation pathway over the open ocean is not well understood and is an important area of future research. In this study, no gas phase measurements of these  $\alpha$ -dicarbonyls were made during the cruise in the WNP to further investigate their partitioning from gaseous to particulate phase through heterogeneous chemistry. Taken together, the consistent occurrence of high atmospheric abundances of isoprene-SOA tracers, MSA,  $\alpha$ -dicarbonyls,  $\omega$ C<sub>2</sub>, and Pyr in MBA and the lack of continental transport (as inferred from the AMBTs) and significant correlations altogether suggest that there is an aqueous phase oxidation of isoprene in the MABL over the WNP.

### 3.3. Average Chemical Composition and Their Relative Abundance

All the measured water-soluble organic species show a pronounced temporal variability during the cruise. Table 1 summarizes a brief statistical description (range, mean, standard deviation, and geometric mean) on the concentrations and relative abundances of water-soluble organic species in total diacids and related polar compounds. Among them, diacids (range: 5–153 ng m<sup>-3</sup>; average: 35 ng m<sup>-3</sup>) are found as most abundant followed by oxoacids (0.2–21 ng m<sup>-3</sup>; 2.7 ng m<sup>-3</sup>) and  $\alpha$ -dicarbonyls (0.3–3.0 ng m<sup>-3</sup>; 0.4 ng m<sup>-3</sup>). The mean molecular distribution of water-soluble organic species is depicted in Figure S4 in the supporting information. As mentioned earlier, oxalic acid (C<sub>2</sub>) is a dominant diacid species followed by malonic (C<sub>3</sub>) and succinic (C<sub>4</sub>) acids. It is noteworthy that concentrations of C<sub>2</sub> ( $25 \pm 15$  ng m<sup>-3</sup> for MBA and  $11 \pm 5$  ng m<sup>-3</sup> for LBA) are comparable to those reported over the WNP during summer by Miyazaki *et al.* [2010] ( $32 \pm 8$  ng m<sup>-3</sup> for MBA and  $14 \pm 5$  ng m<sup>-3</sup> for LBA; KH08-leg 1) and Kawamura and Usukura [1993] (24.9 ng m<sup>-3</sup> for sample No QFF 101), but lower than those documented during fall intermonsoon (22–429 ng m<sup>-3</sup>) [Sempéré and Kawamura, 2003], winter, and spring-intermonsoon cruises (139–173 ng m<sup>-3</sup>) [Fu *et al.*, 2013b]. Glyoxylic acid ( $\omega$ C<sub>2</sub>) is found as the fourth most abundant species followed by phthalic, terephthalic, adipic, and azelaic acids.

Pie diagrams are shown in Figure 5 for the fractional contributions of individual straight chain diacids to total mass of aliphatic diacids in two aerosol types (MBA and LBA). From this figure, we infer that the percentage contribution of low molecular weight diacids (LMW-diacids: C<sub>2</sub> + C<sub>3</sub> + C<sub>4</sub>) in the total mass concentration ( $\Sigma(C_2-C_{12})$ ) varies from 76 to 98% ( $92 \pm 6\%$ ) in MBA and 54 to 97% ( $92 \pm 11\%$ ) in LBA samples. A notable difference in the relative abundance of C<sub>2</sub> to mass concentrations of total diacids from C<sub>2</sub> to C<sub>10</sub> (i.e.,  $\Sigma C_2-C_{10}$ ) was found between MBA and LBA with higher values for later aerosol samples. In contrast, C<sub>3</sub> and C<sub>4</sub> show higher percentages in MBA than LBA.

Although mass concentrations are relatively high in MBA, their mass ratios (e.g., C<sub>2</sub>/C<sub>4</sub>) are higher in LBA (see Table 2). Surprisingly, no significant difference was observed between MBA and LBA for the mass ratios of C<sub>3</sub>/C<sub>4</sub>. Previous studies by Kawamura *et al.* [1996a] have suggested that oxalic acid can be



**Figure 5.** Pie diagrams, showing the percentage contribution of individual diacid to total aliphatic homologous diacids ( $\Sigma C_2-C_{12}$ ) in more and less biologically influenced aerosols (MBA: 30°N–45°N and LBA: 10°N–30°N) collected over the western North Pacific during August to September 2008.

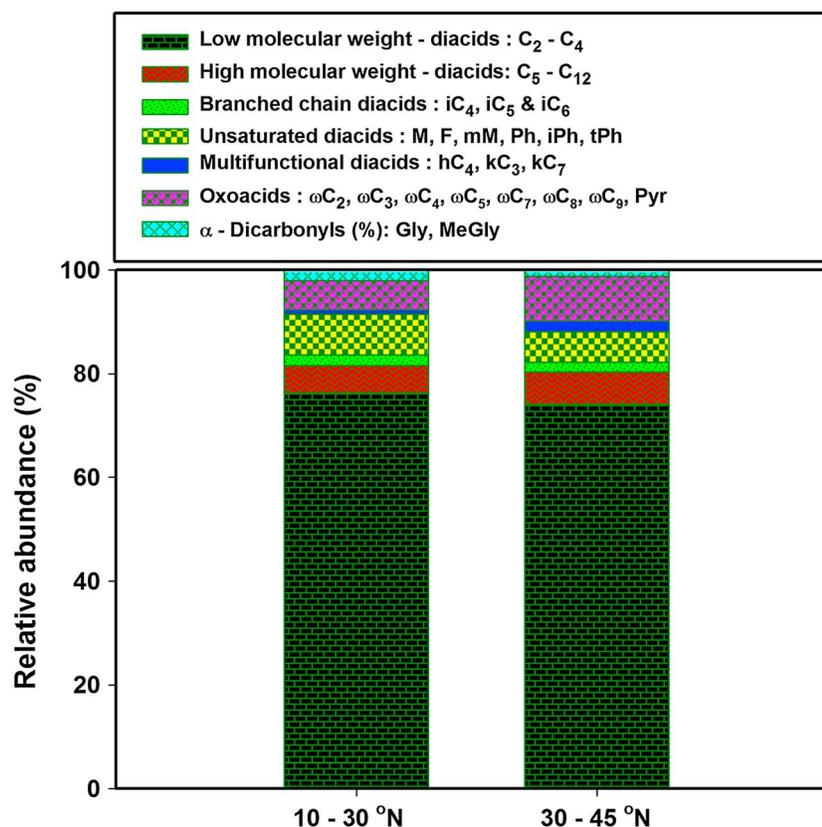
formed from the oxidation of its next higher homologues ( $C_3$  and  $C_4$  diacids). However, strong linear correlations among atmospheric concentrations of  $C_2$ ,  $C_3$ , and  $C_4$  perhaps signify the production of oxalic acid from malonic and succinic acids. This observation can be further supported by the linear relationship between  $C_2/C_4$  and relative abundances of  $C_2$  (see section 3.5), which gives a hint regarding its production from atmospheric oxidation of  $C_4$  diacid. In addition, similar analogy can be applied to the prevalent linear correlation between  $C_4/C_6$  and relative abundance of  $C_4$ . Very strong correlations among  $C_2$ ,  $C_3$ , and  $C_4$  together with their mass ratios of  $C_2/C_4$  and  $C_3/C_4$  altogether indicate the formation of oxalic acid from higher homologues. Based on these observations, the relative increase in  $C_2$ (%) from MBA to LBA could be explained by its production due to the degradation of  $C_3$  and  $C_4$ .

Atmospheric concentrations of diacids can be controlled by emissions of precursors, vertical mixing, formation processes, and their subsequent heterogeneous phase reactions. Therefore, it is important to assess their relative abundances and latitudinal variability, which could provide additional insights regarding these factors. Figure 6 presents the relative abundances of low molecular weight diacids (LMW-diacids:  $\Sigma(C_2-C_4)$ , high molecular weight diacids:  $\Sigma(C_5-C_{12})$ , unsaturated diacids:  $\Sigma(M, F, mM, Ph, iPh, \text{ and } tPh)$ , multifunctional diacids:  $\Sigma(hC_4, kC_3, \text{ and } kC_7)$ ,  $\omega$ -oxoacids ( $\Sigma(\omega C_2, \omega C_3, \omega C_4, \omega C_5, \omega C_7, \omega C_8, \text{ and } \omega C_9)$ , and  $\alpha$ -dicarbonyls (MeGly + Gly) in total diacids and related compounds in MBA and LBA. It is clear that a homologous series of straight chain diacids accounts for on average 77% (range: 31–90%) of total

**Table 2.** Mean and One Sigma of the Diagnostic Mass Ratios of Measured Water-Soluble Organics Along With Their Statistical Significance in More and Less Biologically Influenced Aerosols (MBA and LBA)

| Mass Ratio               | MBA: 30°N–45°N | LBA: 10°N–30°N | t Score, d.f., P Value <sup>a</sup> |
|--------------------------|----------------|----------------|-------------------------------------|
|                          | Avg ± SD       |                |                                     |
| $C_2/C_4$                | 6.0 ± 5.3      | 11.6 ± 4.5     | 3.7, 38, <0.05                      |
| $C_3/C_4$                | 1.9 ± 1.0      | 2.2 ± 0.9      | 1.0, 38, >0.05                      |
| $C_2/\omega C_2$         | 19.8 ± 17.3    | 62.3 ± 41.2    | 4.1, 37, <0.05                      |
| $C_2/Pyr$                | 60.9 ± 51.5    | 70.8 ± 76.4    | 0.5, 38, >0.05                      |
| $C_2/\Sigma(C_2-C_{12})$ | 0.55 ± 0.16    | 0.72 ± 0.10    | 4.1, 38, <0.05                      |
| $C_3/\Sigma(C_2-C_{12})$ | 0.21 ± 0.06    | 0.14 ± 0.04    | 4.6, 38, <0.05                      |
| $C_4/\Sigma(C_2-C_{12})$ | 0.16 ± 0.09    | 0.07 ± 0.03    | 4.1, 38, <0.05                      |
| $C_6/C_9$                | 1.8 ± 1.1      | 3.7 ± 6.0      | 1.3, 38, >0.05                      |
| $Ph/C_9$                 | 2.6 ± 1.3      | 8.7 ± 13.5     | 1.9, 38, >0.05                      |
| M/F                      | 2.2 ± 1.3      | 1.9 ± 1.2      | 0.6, 19, >0.05                      |
| $C_2/MeGly$              | 134 ± 99       | 186 ± 113      | 1.5, 37, >0.05                      |
| $C_2/Gly$                | 1.56 ± 107     | 240 ± 302      | 1.1, 37, >0.05                      |
| $Gly/MeGly$              | 1.9 ± 3.9      | 1.3 ± 0.9      | 0.6, 37, >0.05                      |

<sup>a</sup>d.f. = degrees of freedom; t score refers to two tailed t test at 95% confidence interval.



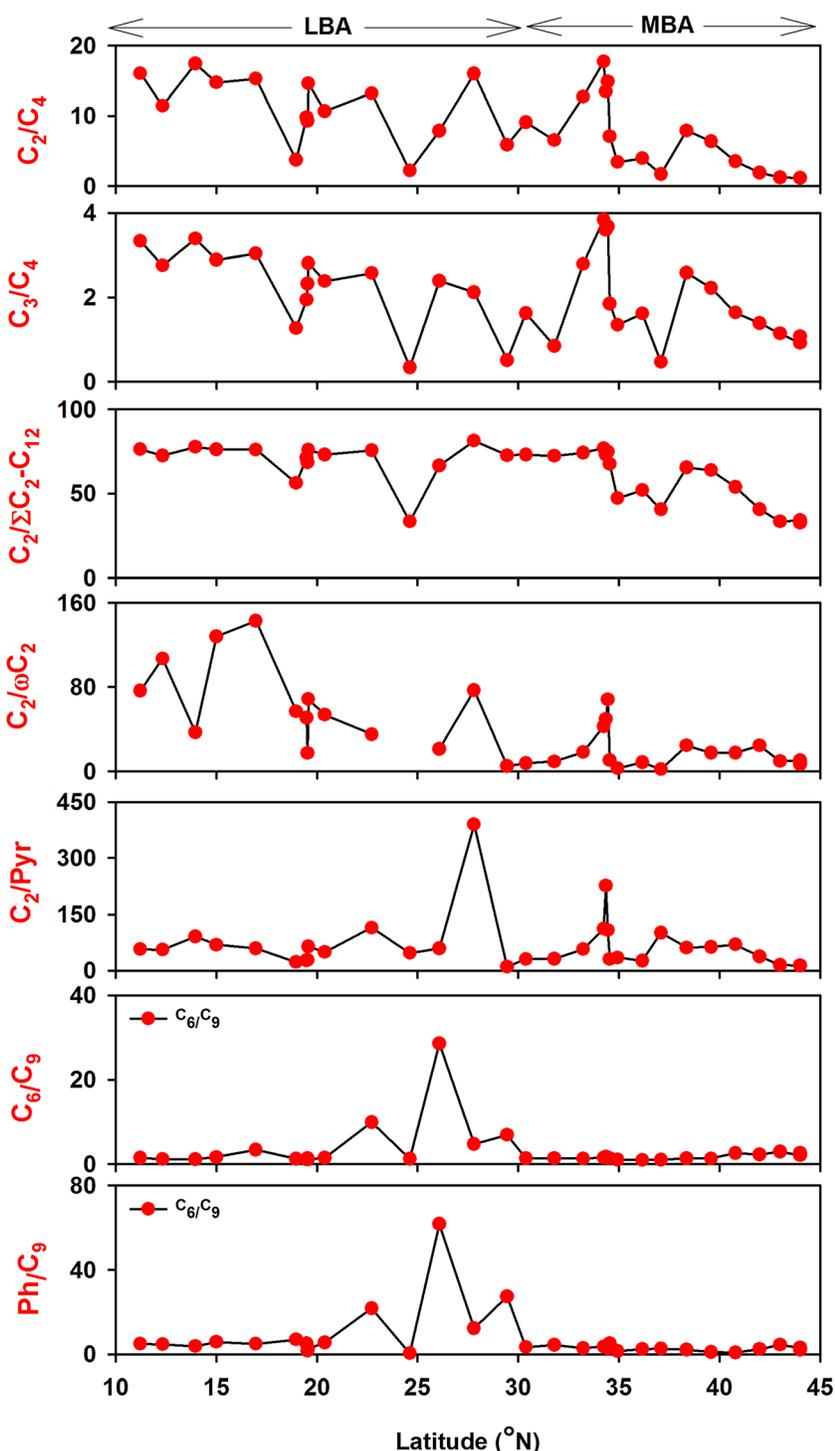
**Figure 6.** Latitudinal changes in relative abundances of individual compound class in the total diacids, oxoacids, and  $\alpha$ -dicarbonyls in more and less biologically influenced aerosols (MBA: 30°N–45°N and LBA: 10°N–30°N) collected from the western North Pacific during August to September 2008.

diacids and related compounds measured. The latitudinal differences in the relative abundances of  $\alpha$ -dicarbonyls show large variability, and a comparison of geometric mean concentration shows consistency with diacids and oxoacids.

No significant differences were observed for LMW- and HMW-diacids between 10°N–30°N and 30°N–45°N. The indistinguishable differences occurring in their relative abundances suggest their similar formation pathways in the MABL of the WNP. This probably indicates similar photochemical and aqueous phase oxidation of biogenic unsaturated fatty acids and isoprene. This observation is also corroborated by no significant differences in the relative abundances of total diacids, oxoacids, and  $\alpha$ -dicarbonyls to WSOC mass between MBA and LBA [Bikkina *et al.*, 2014].

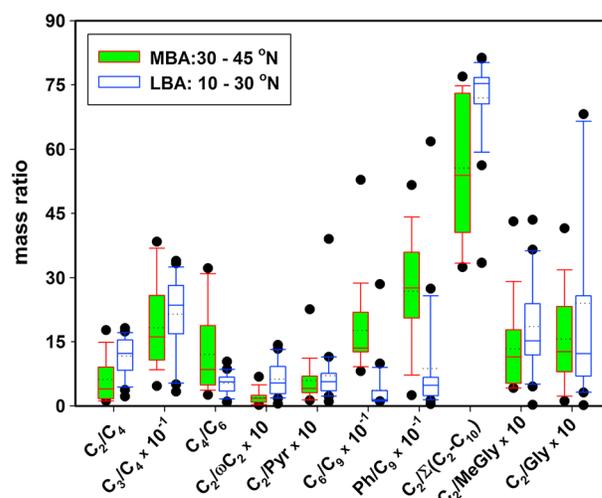
### 3.4. Diagnostic Mass Ratios

In order to understand the formation pathways of diacids and other related compounds in terms of their photochemical aging and variability in sources (e.g., azelaic acid or isoprene) and its emission strength over WNP during summer, we have investigated the latitudinal variability of diagnostic mass ratios of these water-soluble organic compounds (Figure 7). It has been suggested that the mass ratio  $C_3/C_4$  can provide some information on their production pathways and photochemical aging of organic aerosols [Ho *et al.*, 2006; Kawamura and Sakaguchi, 1999]. In this context, lower  $C_3/C_4$  ratios (0.25–0.44) have been reported for fossil fuel (in particular vehicular emissions) combustion sources [Kawamura and Kaplan, 1987]. In contrast, relatively high ratios (average: 3.9; range: 1–11) were documented for marine aerosols collected from the North Pacific including tropics [Kawamura and Sakaguchi, 1999]. In our samples,  $C_3/C_4$  mass ratio is greater than unity and almost constant during the entire sampling days (average:  $1.5 \pm 0.2$ ), suggesting a secondary production pathway of diacids in the remote WNP. In contrast,  $C_2/C_4$  ratio (1.1–14.4) shows an increasing trend from 40°N to 5°N (Figure 7), being similar to those reported in the North Pacific by



**Figure 7.** Latitudinal distribution of some of the diagnostic mass ratios (viz.,  $C_2/C_4$ ,  $C_3/C_4$ ,  $C_2/\Sigma C_2 - C_{12}$ ,  $C_2/\omega C_2$ ,  $C_6/C_9$ , and  $Ph/C_9$ ) in marine aerosols collected over western North Pacific during August to September 2008.

*Kawamura and Sakaguchi [1999].* This observation suggests that  $C_2$  could be abundantly formed by the photochemical degradation of  $C_4$  diacid. A concurrent trend (Figure 7) is also noteworthy for the increased contribution of  $C_2$  in total aliphatic diacids ( $C_2/(\Sigma C_2 - C_{12})$ ), supporting more photochemical aging of marine aerosols over the tropical (10°N–30°N) North Pacific compared to that of temperate region (30°N–45°N).



**Figure 8.** Box-whisker plot, showing the similarities or differences among diagnostic mass ratios of measured diacids and other related polar compounds for more and less biologically influenced aerosols collected over the western North Pacific during summer.

photochemical processes. No significant variability was observed for temporal ratios of adipic to azelaic ( $C_6/C_9$ ) and phthalic to azelaic acid ( $Ph/C_9$ ) between MBA and LBA (Figure 7) together with their lower atmospheric concentrations. These results suggest an important oceanic source rather than the continental contribution over the WNP.

Owing to large variability in the diagnostic mass ratios along the longitudinal transect, we have also examined their relative differences in the distributions between MBA and LBA. Figure 8 depicts the box-whisker plot showing the differences or similarities among different diagnostic mass ratios of measured water-soluble organic species between more and less biologically influenced aerosols (MBA and LBA). From Figure 8, it is clearly visible that mass ratios of  $C_2/C_4$ ,  $C_2/\omega C_2$ , and  $C_2/\Sigma(C_2-C_{10})$  show lower and higher values for MBA and LBA, respectively. In addition, the temporal variability of relative abundances of  $C_2$  diacids in sum of concentration of  $C_2$  to  $C_{10}$  diacids (i.e.,  $C_2/\Sigma(C_2-C_{10})$ ) shows similar temporal trend to the ambient measured temperature (Figure S6 in the supporting information) and downwind solar irradiation (downloaded from NOAA; figure not shown here). This observation suggests that the increase in relative abundances of  $C_2$  in  $\Sigma(C_2-C_{10})$  over LBA is due to enhanced photochemical process over  $10^\circ N-30^\circ N$  (i.e., aerosol samples collected close to the equator) compared to that over  $30^\circ N-45^\circ N$  (i.e., samples collected away from the equator). This is also reflected in mass ratio of oxalic to succinic and glyoxylic acids ( $C_2/C_4$  and  $C_2/\omega C_2$ ).

It is noteworthy that the mass ratios of malonic to succinic acid ( $C_3/C_4$ ) and oxalic to pyruvic acid ( $C_2/Pyr$ ) have not shown significant differences between MBA and LBA ( $P > 0.05$ ; see Table 2). Although the median mass ratio of  $C_3/C_4$  shows slightly higher value for LBA than MBA, their average values are consistent within the spread of the data (see Figure 8). Based on the observed linear correlations among oxalic, malonic, and succinic acids together with increase in and mere constant mass ratios of  $C_2/C_4$  and  $C_3/C_4$ , respectively, between MBA and LBA suggests the production of oxalic acid from succinic acid through malonic acid as intermediate. This inference is further supported by a significant positive linear relationship observed between  $C_2/C_4$  and  $C_2/\Sigma(C_2-C_{10})$ . Our field study provides a direct evidence for the hypothesis suggested by Kawamura and Sakaguchi [1999]. Recent laboratory experiments by Yang *et al.* [2008a] on photooxidation of succinic acid solution by OH radical results in the formation of malonic acid with malic acid (or hydroxy succinic acid,  $hC_4$ ) as an intermediate. Therefore, Yang *et al.* [2008a] observations also support the results from this study and that mechanism suggested by Kawamura and Sakaguchi [1999].

Since pyruvic acid (Pyr) is an incloud oxidation product of isoprene [Carlton *et al.*, 2006], the consistent mass ratios of oxalic to pyruvic acid (i.e.,  $C_2/Pyr$ ) between MBA and LBA can be interpreted as production of  $C_2$  diacid from isoprene oxidation. During the study period, the surface waters are characterized by higher biological activity. Previous studies have shown that isoprene could also be emitted from oceanic

Table 2 presents the statistically significant differences/similarities in the mass ratios of measured water-soluble organics between MBA and LBA. Significantly higher mass ratios of  $C_2/C_4$  and  $C_2/\omega C_2$  were observed in LBA than in MBA, suggesting an enhanced production of  $C_2$  over the tropical WNP. Likewise, the relative abundances of  $C_2$  are higher in LBA than in MBA, supporting the photochemical production of  $C_2$  in the tropical WNP. However, no significant difference was observed between MBA and LBA in the mass ratios of malonic to succinic acid (i.e.,  $C_3/C_4$ ). The prevailing intercorrelations among  $C_2$ ,  $C_3$ , and  $C_4$  together with increased (i.e.,  $C_2/\Sigma(C_2-C_{12})$ ) and decreased diagnostic mass ratios (i.e.,  $C_3/\Sigma(C_2-C_{12})$  and  $C_4/\Sigma(C_2-C_{12})$ ) suggest the formation of  $C_2$  from higher diacid homologues through

phytoplankton along with other BVOCs such as DMS [Shaw *et al.*, 2010]. Its subsequent intrusion into the MABL and atmospheric oxidation results in formation of various chemical species such as MeGly, Gly, Pyr, and isoprene-SOA tracers [Carlton *et al.*, 2009]. During the study period, the atmospheric abundances of isoprene-SOA tracers exhibit consistent higher and lower values to chlorophyll *a* concentration in seawater (see Figure S1 in the supporting information), suggesting the marine isoprene emissions to the MABL. It is important to note that pyruvic acid formation involves the isoprene oxidation through aqueous phase chemistry. If we consider aerosol liquid water content as a pseudo indirect proxy for aqueous phase chemistry, no significant differences were observed for this parameter between MBA and LBA (For more details, see section 3.6).

It has been suggested that gaseous phase oxidation of isoprene leads to the formation of semivolatile organic compounds, viz., glyoxal (Gly) and methylglyoxal (MeGly) [Carlton *et al.*, 2009]. Their partition into clouds or aerosol liquid water surfaces through diffusion results in the formation of pyruvic acid as these semivolatile organic compounds are highly reactive in aqueous solutions [Buxton *et al.*, 1997; Carlton *et al.*, 2009]. Therefore, we infer that isoprene oxidation to oxalic acid through pyruvic acid and methylglyoxal can explain the observed no significant differences of  $C_2/\text{Pyr}$ ,  $C_2/\text{MeGly}$ , and  $C_2/\text{Gly}$  between MBA and LBA. The aerosol samples used in this study for the assessment of diacids and other related polar compounds were also analyzed for diethyl ammonium ( $\text{DEA}^+$ ) [Miyazaki *et al.*, 2011], a specific tracer for secondary organic aerosol formed over the open oceans that are characterized by high biological activity [Facchini *et al.*, 2008a]. Relatively high atmospheric  $\text{DEA}^+$  in MBA suggests the significant contribution of SOA from marine origin.

Another piece of evidence for the oceanic organic precursors of LMW-diacids comes from the study of Miyazaki *et al.* [2011]. It has been suggested that sea-to-air emission of biogenic unsaturated fatty acids, phenolic compounds, and olefins can serve as an important source of atmospheric water-soluble organic species over the open ocean waters [Wang and Kawamura, 2006]. The photochemical oxidation of these precursor organic compounds upon their emission from the surface ocean to the MABL can lead to formation of LMW-diacids (from oxalic to succinic acids). As mentioned earlier, the photooxidation experiments of oleic acid by Matsunaga *et al.* [1999] and Tedetti *et al.* [2007] (publications from Kawamura's group) documented the formation of azelaic acid (which is being dominant among other diacids) and other diacids from oxalic to suberic acids. Likewise, the photooxidation experiments of azelaic acid solution by Yang *et al.* [2008a] have observed the formation of adipic acid as an intermediate secondary diacid which in turn subjected further photooxidation resulted its next lower homologues.

The mass ratio of  $C_6/C_9$  and  $\text{Ph}/C_9$  shows higher and lower mean and median concentrations for MBA and LBA, respectively. These distributions are consistent with the atmospheric concentrations of other chemical tracers of marine-derived SOA (viz., isoprene-SOA tracers, methylglyoxal, and pyruvic acid) and azelaic acid, respectively. As mentioned earlier, similar latitudinal variability of  $C_9$ ,  $C_6$ , and Ph suggests their common source (see Figure 3 and Figure S1 in the supporting information). Therefore, we attribute their origin from natural sources, possibly by the photochemical oxidation of biogenic unsaturated fatty acids and phenolic compounds (see section 3.2.1). Taken together, the similar temporal trends of  $C_6/C_9$  and  $\text{Ph}/C_9$  also indicate their natural sources.

Diagnostic mass ratios of diacids and related compounds from this study can be compared with those from other oceanic regions in Table 3. A remarkable consistency in the distribution of mass ratios of  $C_2/C_4$  and  $C_3/C_4$  (see Figure 7 and Figure S7 in the supporting information) over the North Pacific during all the cruises suggests that oxalic acid is formed by the photochemical degradation of higher molecular weight diacids in the air masses that are influenced by continental outflows (i.e., winter and spring intermonsoon) and in the pristine maritime air masses sampled during summer and fall seasons. It is important to note that the production of  $C_2$  from the higher diacids in the aged continental air mass transported from East Asia to the North Pacific during winter and spring intermonsoon has been documented by previous studies [Kawamura and Sakaguchi, 1999; Kundu *et al.*, 2010]. In contrast, the photochemical degradation of unsaturated fatty acids in the marine atmosphere results in higher homologues of diacids such as azelaic acid ( $C_9$ ), which further serve as precursors of LMW-diacids [Kawamura and Usukura, 1993].

Another notable characteristic includes higher mass ratios of oxalic acid to glyoxylic and pyruvic acids ( $C_2/\omega C_2$  and  $C_2/\text{Pyr}$ ) in the MABL during summer and fall (including our study with literature observations) cruises than those observed in winter (see Table 3 and Figure S7 in the supporting information, KH90)

**Table 3.** Comparison of Diagnostic Mass Ratios of Diacids and Related Compounds From the Western North Pacific<sup>a</sup>

| Region                          | Western North Pacific <sup>b</sup> | North Pacific <sup>c</sup> | North Pacific <sup>d</sup> | California Coast <sup>d</sup> | North Atlantic <sup>d</sup> | Indian Ocean <sup>d</sup> |
|---------------------------------|------------------------------------|----------------------------|----------------------------|-------------------------------|-----------------------------|---------------------------|
| Duration                        | Aug to Sept 2008                   | Aug 1989                   | Oct to Nov 1989            | Nov to Dec 1989               | Dec 1989                    | Feb 1990                  |
| Cruise                          | KH08-Leg2                          | KH89-T3, 4                 | KH89                       | KH89                          | KH89                        | KH89                      |
| Season                          | S                                  | S                          | F                          | F and W                       | W                           | W                         |
| C <sub>2</sub> /C <sub>4</sub>  | 1.1–18.2                           | 1.9–5.4                    | 2.5–8.5                    | 4.2–20.9                      | 5.1–7.4                     | 7.1                       |
| C <sub>3</sub> /C <sub>4</sub>  | 0.3–0.8                            | 0.9–2.3                    | 0.6–2.0                    | 1.8–5.8                       | 2.1–3.4                     | 2.0                       |
| C <sub>6</sub> /C <sub>9</sub>  | 0.8–9.9                            | 0.7–10.5                   | 0.9–4.5                    | 1.0–3.7                       | 1.9–2.9                     | 9.6                       |
| Ph/C <sub>9</sub>               | 0.3–27                             | 0.5–7.2                    | 0.5–2.4                    | 0.3–9.3                       | 0.5                         | 1.7                       |
| M/F                             | 0.2–1.9                            | 0.4–1.6                    | 0.4–1.5                    | 0.1–0.5                       | 0.4–0.5                     | 0.3                       |
| hC <sub>4</sub> /C <sub>4</sub> | 0.01–0.12                          | 0.06–1.5                   | 0.04–0.07                  | -                             | 0.4–0.7                     | 1.1                       |
| C <sub>2</sub> /ωC <sub>2</sub> | 2–143                              | 49–146                     | 15–66                      | 11–41                         | 11–14                       | 11                        |
| C <sub>2</sub> /Pyr             | 10–390                             | 3–15                       | 134–161                    | 22–112                        | 10–25                       | 29                        |
| C <sub>2</sub> /MeGly           | 2–435                              | 35–211                     | -                          | -                             | -                           | -                         |
| C <sub>2</sub> /Gly             | 2–682                              | 13–108                     | 43–97                      | 18–475                        | 26–87                       | 105                       |
| C <sub>2</sub> -C/WSOC (%)      | 1–17                               | -                          | -                          | -                             | -                           | -                         |
| ΣDCA-C/WSOC (%)                 | 4–52                               | -                          | -                          | -                             | -                           | -                         |

<sup>a</sup>This study with other literature-reported values. Here S, F, W, and SIM refer to summer, fall, winter, and spring-intermonsoon seasons, respectively, except that the fractional contribution of oxalic acid and total diacids (which are in amount of C percentage) all are expressed as weight ratios.

<sup>b</sup>This study.

<sup>c</sup>Kawamura and Usukura [1993].

<sup>d</sup>Fu et al. [2013a].

<sup>e</sup>Kawamura et al. [2010].

<sup>f</sup>Sempéré and Kawamura [2003].

<sup>g</sup>Miyazaki et al. [2010].

<sup>h</sup>Estimated by combining the supermicrometer and submicrometer sizes to obtain the total concentrations.

over the North Pacific. It has been suggested that aqueous phase oxidation of certain BVOCs such as isoprene in the MABL leads to the production of Pyr and ωC<sub>2</sub>, which further oxidize to result in C<sub>2</sub> [Bikkina et al., 2014]. A recent modeling study by Myriokefalitakis et al. [2011] suggested that the oceanic isoprene emissions and their contribution to marine SOA could be high over the open ocean waters of the WNP. Similar to our study, relatively high isoprene-SOA tracer concentrations were documented during a summer cruise in the western North Pacific by Hu et al. [2013]. Based on these observations, higher mass ratios of C<sub>2</sub>/ωC<sub>2</sub> and C<sub>2</sub>/Pyr in summer and fall than those in winter could be explained by the enhanced contribution of BVOCs emitted from the ocean surface and the subsequent aqueous phase production of C<sub>2</sub> in the MABL.

Based on 1 year observation of marine aerosols at Jeju Island (South Korea) in the WNP rim, Kundu et al. [2010] reported that the specific mass ratios (C<sub>2</sub>/Pyr, C<sub>2</sub>/ωC<sub>2</sub>, C<sub>2</sub>/MeGly, and C<sub>2</sub>/Gly) in summer are twofold to threefold higher than those in winter and spring. From this result, we can infer that the ambient photochemical activity during summer can be a factor for significant increase in these diagnostic ratios. Based on the significant correlations among isoprene-SOA tracers, pyruvic acid, glyoxylic acid, and glyoxal during the study period, Bikkina et al. [2014] strongly suggest the predominant oceanic control of BVOCs on the atmospheric distribution of oxalic and other diacids.

### 3.5. Formation Pathways of Diacids and Related Compounds

In order to investigate the possible sources of diacids and related polar compounds in the MABL, multiple linear regression analysis is performed among the measured chemical constituents. Figure 9 shows a Pearson's correlation matrix in which the lower diagonal triangle represents the scatterplot between some measured chemical species and the upper diagonal matrix corresponds to their coefficient of determination (i.e., R<sup>2</sup>). Significant (P < 0.05) correlations of succinic acid with oxalic and malonic acids indicate their photochemical degradation process in the marine aerosols. Likewise, significant correlations were noteworthy among MSA, isoprene-SOA tracers (i.e., methyltetrols + methylglyceric acid), methylglyoxal, pyruvic acid, and glyoxylic acid (ωC<sub>2</sub>). Based on the observed linear correlations and their high abundances in more biologically influenced aerosols, it is clear that oceanic biological activity is an important factor to control the atmospheric distributions of diacids and related compounds.

**Table 3.** (continued)

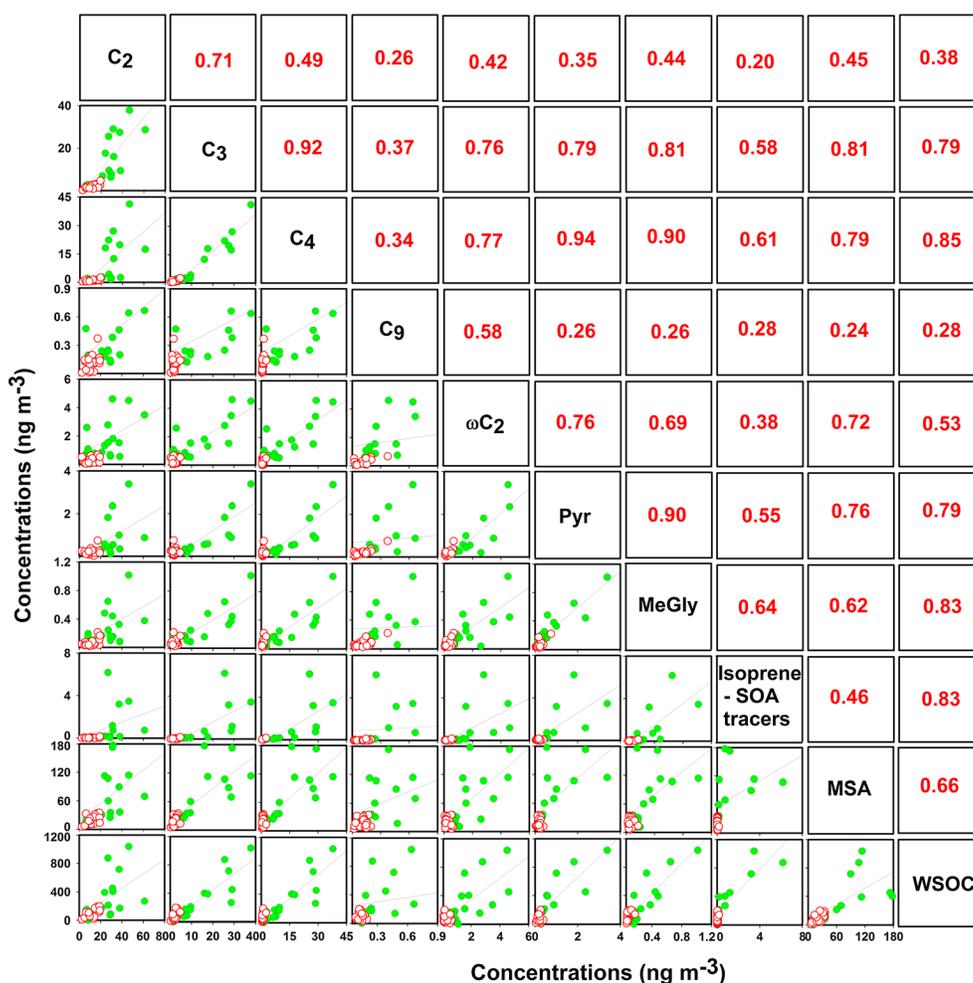
| South China Sea <sup>d</sup><br>Feb 1990 | Western North Pacific <sup>d</sup><br>Feb to Mar 1990 | North Pacific <sup>c</sup><br>Mar 1990 | Arctic Ocean <sup>e</sup><br>Aug 2009 | North Pacific <sup>f</sup><br>Sept 1992 | South Pacific <sup>f</sup><br>Sept to Oct 1992 | Western North Pacific <sup>g</sup><br>July to Aug 2008 |
|--|---|--|---------------------------------------|---|--|--|
| KH89                                     | KH89  | KH90                                   | MALINA                                | KH92                                    | KH92   | KH08-Leg1 <sup>h</sup>                                 |
| W  | W and SIM   | SIM                                    | S                                     | F                                       | F  | S  |
| 5.2–9.9                                  | 6.7–6.9   | 3.7                                    | 0.4–12.8                              | 5.5–23.8                                | 1.7–15.4                                       | 1.79   |
| 1.5–2.7                                  | 0.9–1.3   | 1.5                                    | 0.1–1.7                               | 2.0–4.4                                 | 1.0–3.6  | 1.31   |
| 3.0–6.5                                  | 3.0–3.7   | 2.8                                    | 0.4–2.7                               | 0.2–1.1                                 | 0.1–1.4  | 3.85   |
| 1.4–1.8                                  | 2.7–8.8   | 3.3                                    | 0.6–6.8                               | 0.5–3.0                                 | 0.4–1.7  | 5.04   |
| 0.5–1.4                                  | 0.9–1.0   | 1.0                                    | 0.02–0.2                              | 0.7–2.6                                 | 0.3–3.8  | 1.32   |
| 0.6–1.2                                  | 0.4–0.5   | 0.4                                    | 0.9–6.1                               | 0.05–0.2                                | 0.2–1.2  | 0.01   |
| 14–45                                    | 4–9   | 167                                    | 5–34                                  | 11–25                                   | 4.2–22   | 10.9   |
| 38–84                                    | 6–21  | 4                                      | 8–47                                  | 52–139                                  | 13–236   | 19.2   |
| -  | -   | 44                                     | 14–159                                | 86–459                                  | 28–181   | 75   |
| 120–168                                  | 14–36   | 22                                     | 10–140                                | 64–217                                  | 15–221   | 563  |
| -  | -   | -                                      | -                                     | 3–8                                     | 0.5–6  | 1.8  |
| -  | -   | -                                      | -                                     | 8–15                                    | 2–13   | 8.0  |

Another notable feature from Figure 9 is the presence of significant ( $P < 0.05$ ) correlations between isoprene oxidation products (isoprene-SOA tracers, MeGly, Pyr, and  $\omega C_2$ ) and malonic ( $C_3$ ) and succinic ( $C_4$ ) acids. Based on the laboratory experiment, *Nguyen et al.* [2010] suggested the possible formation of  $C_3$  and  $C_4$  diacids by the reaction of isoprene and ozone. However, it is also documented from the coastal U.S. sites that isoprene emission causes a significant enhancement in the marine SOA and  $O_3$  concentration [*Gantt et al.*, 2010]. It is noteworthy that relatively high columnar ozone concentration in the MABL of the WNP between  $30^\circ N$  and  $40^\circ N$  (Figure S5 in the supporting information) compared to that over  $10^\circ N$ – $30^\circ N$  could explain the higher concentrations of  $C_3$  and  $C_4$  diacids and their positive correlations with isoprene oxidation products (Figure 9).

During the course of this study, another striking observation pertains to a prominent negative correlation between the ambient temperature and relative abundances of  $C_3$ ,  $C_4$ , and  $C_5$  diacids in total diacids in the MABL (Figure 10). In contrast, relative abundance of  $C_2$  shows a significant positive correlation ( $R^2 = 0.44$ ;  $P < 0.05$ ; see Figure 10) with ambient temperature. Earlier study by *Sempéré and Kawamura* [2003] suggested that ambient temperature can be regarded as an indirect proxy for the photochemical activity. Their study also documented a negative linear relationship between ambient temperature and relative abundance of  $C_4$  in total diacids. Based on the linear dependence of relative abundances of  $C_2$ ,  $C_3$ ,  $C_4$ , and  $C_5$  diacids on ambient temperature (Figure 10), we consider that photochemical decomposition of higher diacids leads to the production of oxalic acid over the WNP.

More obvious linear trends are apparent for MBA than LBA due to insignificant variations in temperatures in the region between  $10^\circ N$  and  $30^\circ N$ . However, no such trends were observed between the relative humidity and relative abundances of diacids. We also found that significant positive correlations between relative abundance of  $C_2$  versus  $C_2/C_4$  and  $C_4$  versus  $C_4/C_6$  ratios (Figure 11), again suggesting a possible formation of oxalic acid through photochemical degradation of higher homologues of straight chain diacids. Although the ambient temperature varied from 14 to  $29^\circ C$  during the cruise, however, no significant differences were observed for this parameter between MBA and LBA. Similar temporal feature is also reflected in downward solar irradiance data obtained from National Centers for Environmental Prediction (NCEP) reanalysis meteorological fields. This observation indicates similar photochemical processes occurring in the MABL. In addition, a close resemblance in the temporal trend is also noteworthy between ambient temperature and relative abundance of oxalic acid in total aliphatic diacids (i.e.,  $C_2/\Sigma(C_2-C_{10})$ ; see Figure S6 in the supporting information). This observation can therefore be interpreted as production of oxalic acid through photochemical oxidation processes over the study region.

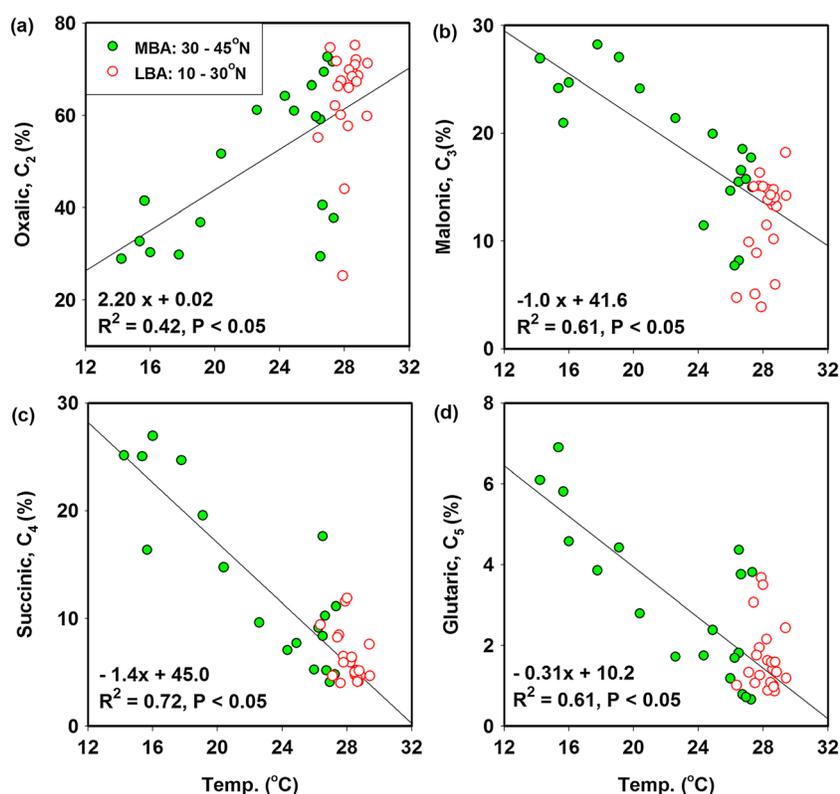
Moreover, low temperatures are in particular associated with the sampling days that are characterized by higher concentrations of measured water-soluble organic compounds (see Figure 2 and Figure S1 in the supporting information). Therefore, we believe that increase in precursor organic compounds (i.e., biogenic



**Figure 9.** Correlation matrix, showing scatterplots between the measured water-soluble organic species in the lower diagonal triangle, whereas Pearson's coefficient of determination ( $R^2$ ) is shown in the upper diagonal triangle for the bulk aerosols (the filled and open circles correspond to MBA and LBA, respectively). The data of isoprene-SOA tracers are from Bikkina *et al.* [2014].

unsaturated fatty acids and VOCs) from the ocean surface and their subsequent photochemical oxidation processes in the MABL can explain the observed high and low concentrations of measured diacids and related polar compounds in MBA and LBA, respectively. Since the precursor organic compounds are coemitted into the MABL, their similar photochemical oxidation process and aqueous phase reactions resulted in the formation of measured diacids and related polar compounds and, hence, can explain the observed high correlations among them. The similar formation pathways of measured chemical species can also be inferred from the diagnostic mass ratios of diacids in Table 2 (e.g.,  $C_3/C_4$ ,  $C_2/Pyr$ , and  $C_2/MeGly$ ).

Strong correlations were also observed among hydroxy succinic acid (malic acid,  $hC_4$ ), succinic ( $C_4$ ), and malonic ( $C_3$ ) acids ( $P$  value  $< 0.05$ ;  $R^2 = 0.77$  for  $hC_4$  versus  $C_3$  and  $R^2 = 0.85$  for  $hC_4$  versus  $C_4$ ; Figure 11). Kawamura and Sakaguchi [1999] suggested a possible formation of  $C_2$  and  $C_3$  from the photooxidation of  $C_4$  through  $hC_4$  as intermediate, based on the high-correlation coefficients observed among these species. The formation of malonic acid from succinic acid through malic acid intermediate has been observed in a laboratory study by Yang *et al.* [2008a] during photooxidation of  $C_4$  diacid which also supports the earlier hypothesis by Kawamura and Sakaguchi [1999]. Similarly, Kourtchev *et al.* [2009] reported a similar linear relationship of malic acid with succinic acid ( $R^2 = 0.85$ ) and oxalic acid ( $R^2 = 0.78$ ) in aerosols collected from a forested site in central Europe. Their studies have explained that the observed linear correlations among these diacid species are due to their photochemical production from biogenic unsaturated fatty acids.

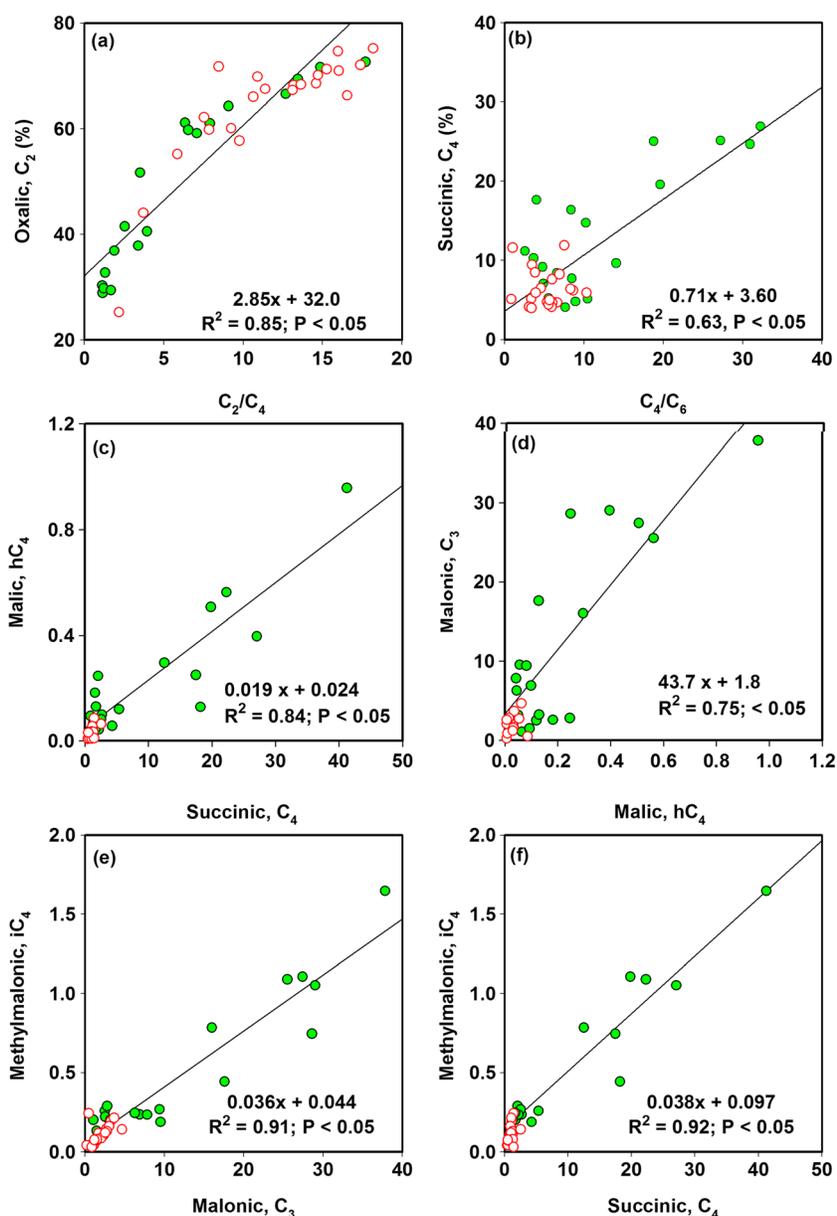


**Figure 10.** Linear regression analysis between measured ambient temperature and the relative abundance of (a) oxalic, (b) malonic, (c) succinic, and (d) glutaric acids in total diacid mass concentration in marine aerosols collected from the western North Pacific during August to September 2008.

The above-proposed mechanism could therefore explain the stringent correlations among  $C_3$ ,  $C_4$ , and  $hC_4$  in marine aerosols from the WNP. We also found a significant linear relationship of methylmalonic acid with  $C_3$  and  $C_4$  diacids. The branched chain diacids (methylmalonic acid) could be derived from the oxidation of isoprene in the MBAL upon the emission from sea surface. As explained earlier, linear trends are more apparent for MBA than LBA. Based on these considerations, we suggest that diacid and related compounds are produced by photochemical oxidation of biogenic unsaturated fatty acids and isoprene in the MABL as summarized in Figure 12.

Although low-correlation coefficient (but significant  $P < 0.05$ ) of lower molecular weight diacids with adipic acid and azelaic acid (Figure 9), similar temporal variability between them hints their photochemical oxidation of biogenic unsaturated fatty acids over the open ocean (Figure 3 and Figure S1 in the supporting information). Previous study by Kawamura and Sakaguchi [1999] had proposed that azelaic acid and its next lower homologues (from  $C_6$  to  $C_8$  diacids) are sources of low molecular weight diacids (from oxalic to succinic acids). During 1980s, the benchmark paper by Kawamura and Gagosian [1987] had shown the presence of  $\omega$ -oxocarboxylic acids and azelaic acid in remote marine aerosols and explained their origin from atmospheric oxidation of oleic acid. The oleic acid is a biogenic unsaturated fatty acid and a phytoplankton exudate [Marty *et al.*, 1979], which is enriched in sea surface microlayer ( $\sim 3$ –200 ppb [Marty *et al.*, 1979]). Subsequent laboratory studies by Matsunaga *et al.* [1999] had documented the formation of oxalic to azelaic acids during the oxidation of oleic acid in ozone system. In addition, several laboratory experiments confirmed the formation of azelaic acid and 9-oxononanoic acid as a result of ozonolysis of oleic acid [Zahardis and Petrucci, 2007, and references therein].

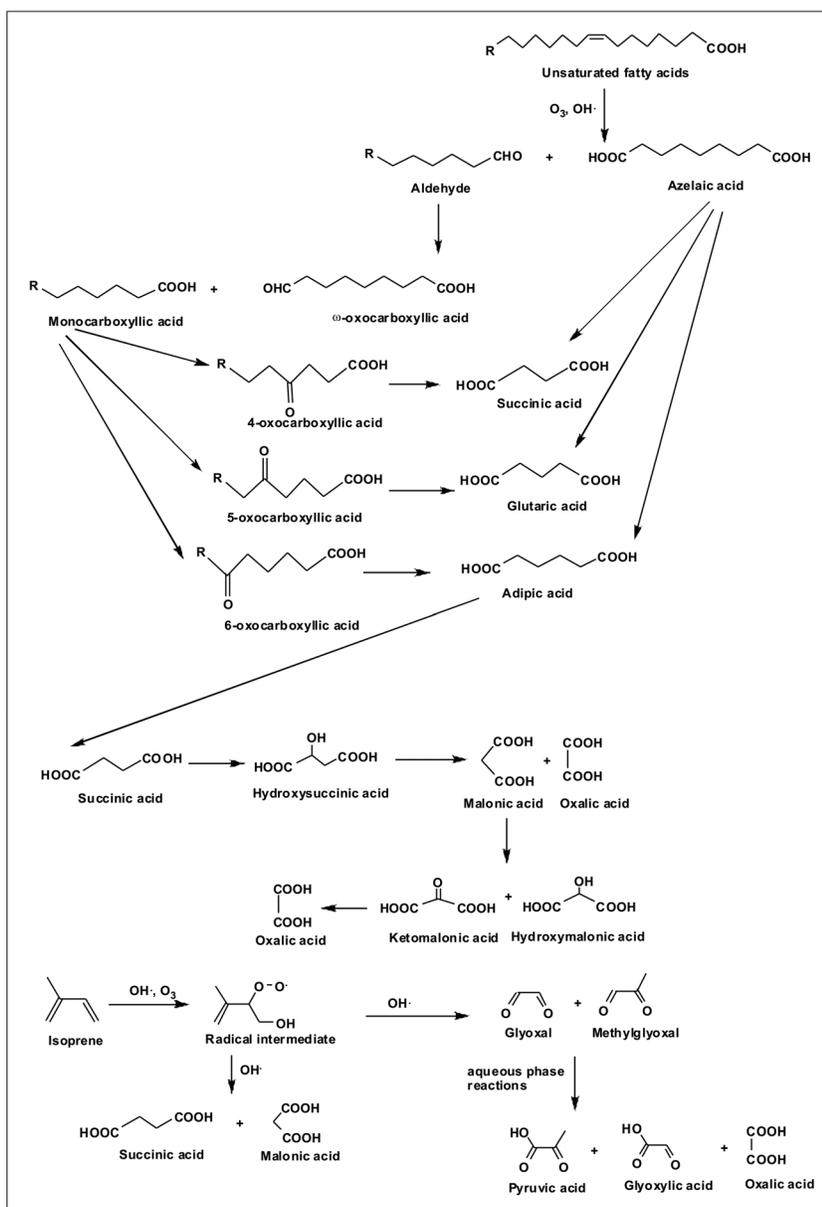
The hydroxyl radical-induced photooxidation experiment of oleic acid by Tedetti *et al.* [2007] showed the production of  $C_2$  to  $C_9$  diacids with azelaic acid being the dominant species followed by  $C_8$ ,  $C_7$ , and  $C_6$  diacids. However, they suggested that lower diacid homologues from oxalic to suberic acids are photochemical oxidation products formed from azelaic acid [Tedetti *et al.*, 2007]. More recent study by Yang



**Figure 11.** Scatterplots for (a) relative abundance of oxalic acid in total diacid mass versus  $C_2/C_4$  ratios, (b) relative abundance of succinic acid in total diacid mass versus  $C_4/C_6$  ratios, (c) malic versus succinic acids, (d) malonic versus malic acids, (e) methylmalonic versus malonic acids, and (f) methylmalonic versus succinic in aerosols collected over the western North Pacific during August to September 2008 (the filled and open circles represent the depicted parameters in MBA and LBA, respectively).

*et al.* [2008a] also demonstrated that photooxidation of azelaic acid results in the formation of oxalic to suberic acids, with succinic and glutaric acids as dominant intermediates, which are eventually converted to their lower homologues (viz., oxalic and malonic acids). In addition to the formation of lower diacids from azelaic acid, as mentioned above, photooxidation of  $\omega$ -oxocarboxylic acids also results in the formation of diacids.

The detailed mechanisms and laboratory results of *Yang et al.* [2008a] thus corroborate the hypotheses suggested by *Kawamura and Sakaguchi* [1999] for the formation pathways of diacids. In this regard, the observed similar temporal trends between LMW diacids, adipic acid, and azelaic acid during the study period hint their possible formation through atmospheric photochemical oxidation processes (Figure S1 in the supporting information). It is noteworthy that moderately significant correlations were observed between azelaic acid and LMW-diacids (Figure S8a in the supporting information) and the adipic acid (Figure S8b in the supporting information). However, no such correlation is observed between glutaric and



**Figure 12.** Schematic representation of formation pathways of diacids and other related water-soluble organic compounds in the marine atmosphere through photochemical oxidation of biogenic unsaturated fatty acids and isoprene over the western North Pacific. The hypothesized schematic production pathways of measured water-soluble organics were obtained from the literature [Kawamura *et al.*, 1996a].

azelaic acid, perhaps due to its further photochemical conversion to succinic acid and other LMW-diacids. As mentioned earlier, the secondary diacids formed from azelaic acid could eventually subject further photooxidation. This observation is also supported by Yang *et al.* [2008b] in the atmosphere and thus results in low molecular weight diacids. It is therefore expected to have low-correlation coefficient between individual LMW-diacids and  $C_9$  diacid, since their formation is from secondary diacids that are produced from the azelaic acid. In addition to the formation pathways of diacids from oxoacids as precursors, we have stemmed now these compounds formation from azelaic acid (see Figure 12).

### 3.6. Effect of Aerosol Liquid Water Content (LWC)

Recent studies by He *et al.* [2013] and Liu *et al.* [Junfeng Liu *et al.*, 2012a] reported various factors that can influence SOA formation in clouds. Furthermore, these studies suggested that LWC is an important

**Table 4.** Mean and One Sigma of the Relative Abundances of Diacids and Related Compounds in Water-Soluble and Total Organic Carbon (WSOC and OC) in Aerosols Collected From the Western North Pacific During August to September 2008

| Components                      | Relative Abundance (%)  |                          |
|---------------------------------|-------------------------|--------------------------|
|                                 | in WSOC                 | in OC                    |
| Oxalic, C <sub>2</sub>          | 0.8–16.7 (4.3 ± 3.3)    | 0.1–2.2 (0.6 ± 0.5)      |
| Malonic, C <sub>3</sub>         | 0.4–3.7 (1.4 ± 0.8)     | 0.01–0.36 (0.30 ± 0.33)  |
| Succinic, C <sub>4</sub>        | 0.2–2.6 (0.9 ± 0.6)     | 0.02–1.15 (0.23 ± 0.33)  |
| ΣC <sub>2</sub> –C <sub>4</sub> | 2–21 (7 ± 4)            | 0.2–4.6 (1.2 ± 1.1)      |
| ΣDiacids                        | 4–52 (14 ± 11)          | 0.5–6.3 (2.1 ± 1.5)      |
| ΣOxocarboxylic acids            | 0.2–2.3 (0.8 ± 0.5)     | 0.03–0.66 (0.16 ± 0.18)  |
| Σα-dicarbonyls                  | 0.02–0.51 (0.13 ± 0.11) | 0.003–0.06 (0.02 ± 0.01) |

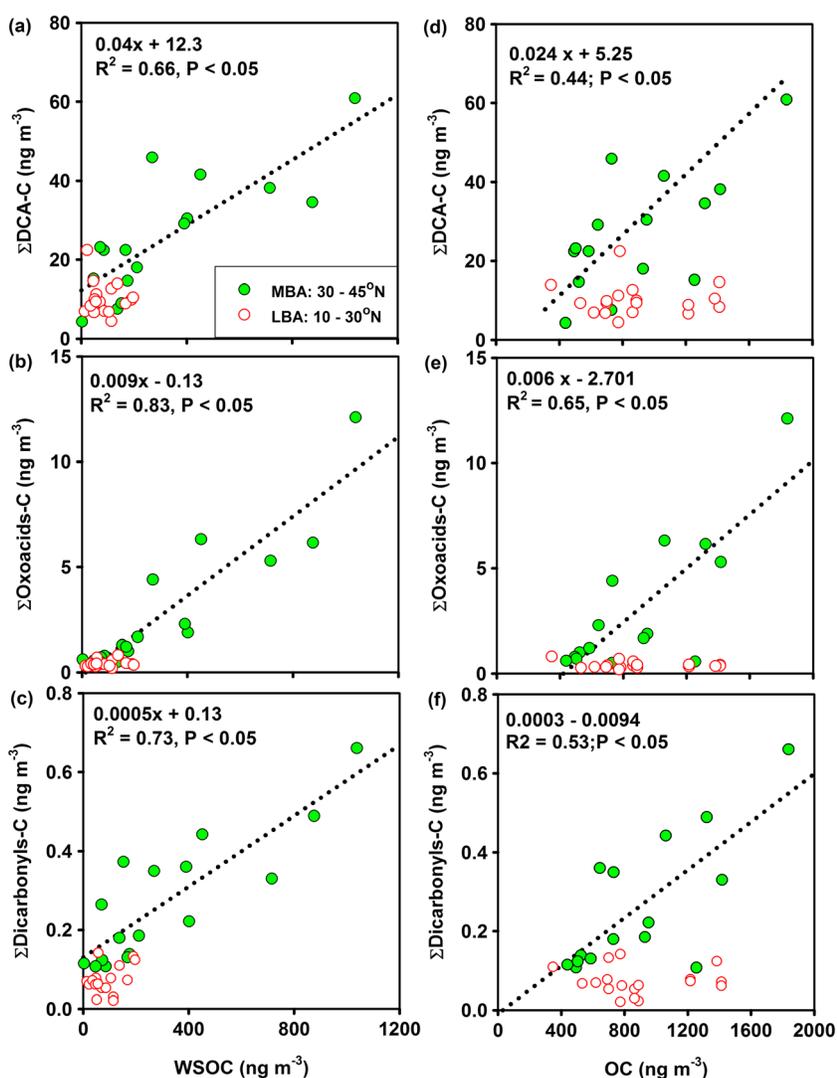
parameter that drives the incloud production of SOA. In this context, it is important to investigate whether the aerosol LWC could be a principal factor other than oceanic biological activity in marine SOA formation over the study region. Therefore, we have assessed the LWC using ISORROPIA-II for both types of aerosols (MBA and LBA). The estimated aerosol LWC has not shown significant differences ( $P$  value > 0.05) between MBA (range:  $(0.06\text{--}0.52) \times 10^{-4} \text{ g m}^{-3}$ ; average  $0.30 \pm 0.12 \times 10^{-4} \text{ g m}^{-3}$ ) and LBA ( $(0.03\text{--}0.84) \times 10^{-4} \text{ g m}^{-3}$ ;  $0.20 \pm 0.21 \times 10^{-4} \text{ g m}^{-3}$ ). We have also investigated the interrelationship between aerosol LWC and measured chemical constituents (e.g., WSOC, MSA, total diacids, and isoprene-SOA tracers) to infer its role in their formation processes (see Figure S9 in the supporting information).

It is noteworthy that no significant correlations were observed between aerosol LWC and other atmospheric water-soluble organics measured in this study, although correlations cannot be a direct evidence to ascertain its role in SOA formation. Interestingly, we found a good correlation between the LWC and estimated sea-salt content; the latter is estimated from the measured Na<sup>+</sup> in aerosols (sea salt =  $3.2 \times \text{Na}^+$ , where 3.2 is the conservative mass ratio of salinity to Na in seawater, data obtained from *Bikkina et al.* [2014]). Because the estimated LWC from ISORROPIA-II does not include organics, it should have considerable uncertainty. However, previous studies have assessed the aerosol LWC by including atmospheric water-soluble organics and using other thermodynamic equilibrium model such as extended aerosol inorganic ion model-II and found insignificant differences [*Jiumeng Liu et al.*, 2012b]. Based on the close agreement between measurements and thermodynamic models, *Fountoukis et al.* [2009, and references therein] suggested that aerosol LWC largely depends on inorganic salt concentrations. Furthermore, their study pointed that estimated aerosol LWC agrees well within the error of 15% among various inorganic models [*Fountoukis et al.*, 2009]. However, the predicted uncertainties on aerosol LWC could be as high as 20% when the contribution from atmospheric water-soluble organics is included in the thermodynamic models [*Aggarwal et al.*, 2007, and references therein].

It is noteworthy that the estimated sea-salt abundance has not shown significant differences between MBA and LBA [*Bikkina et al.*, 2014]. Based on these results, we infer that the predicted aerosol LWC cannot explain the observed atmospheric abundances of diacids during the study period. The high and low atmospheric abundances of WSOC, MSA, and isoprene-SOA tracers and diacids show a consistent pattern with surface Chl *a* concentrations (see Figure S1 in the supporting information). Although LWC is an important parameter for SOA-formation, no significant differences were observed in the LWC between MBA and LBA as stated above. If we consider that aerosol LWC is a pseudo proxy for assessing the extent of aqueous phase reactions in producing SOA, one can expect similar atmospheric abundances of measured water-soluble organics. Therefore, this observation has not allowed us to conclude its significance over the study region as a driving parameter for SOA formation over the productive open ocean waters. However, more studies are required to ascertain the controlling factor that governs the SOA formation over remote oceanic regions.

### 3.7. Contributions of Diacids and Related Compounds to WSOC and OC

The relative abundances of selected diacids and related compounds in water-soluble organic carbon (WSOC) and total organic carbon (OC) are presented in Table 4. On average, total diacids constitute  $\sim 14 \pm 11\%$  (range: 4–52%) of WSOC over the WNP during summer. Likewise, oxoacids and  $\alpha$ -dicarbonyls contribute to WSOC



**Figure 13.** Scatterplot between water-soluble organic carbon (WSOC) and total diacids, oxoacids, and  $\alpha$ -dicarbonyls in marine aerosols collected from the western North Pacific during Summer (August to September 2008).

from 0.2 to 2.3% ( $0.8 \pm 0.5\%$ ) and 0.02 to 0.5% ( $0.13 \pm 0.11\%$ ) in the MABL, respectively. We found a strong linear relationship of WSOC and OC with total diacids, oxoacids, and  $\alpha$ -dicarbonyls (Figure 13). Contributions of diacids, oxoacids, and  $\alpha$ -dicarbonyls to WSOC are rather constant between MBA and LBA samples [Bikkina et al., 2014], suggesting that their photochemical production pathways are similar (atmospheric oxidation of isoprene and biogenic unsaturated fatty acids) in the MABL of western North Pacific. In addition, a strong linear relationship of WSOC with MSA and C<sub>2</sub> suggests that important secondary formation of WSOC in the MABL (see Figure 9). Similar results were also observed during KH08-leg 1 cruise conducted in the WNP during July to August 2008 [Miyazaki et al., 2010].

Significant ( $P < 0.05$ ) linear correlations of particulate organic carbon (OC) with total diacids, oxoacids, and  $\alpha$ -dicarbonyls are evident only for MBA during the study period (Figure 13). Contributions of diacids to OC range from 0.5 to 6.3% with an average of 2.1%. Likewise, contributions of oxoacids and  $\alpha$ -dicarbonyls to OC vary from 0.03 to 0.7% and 0.003 to 0.06%, respectively. Interestingly, the percentages of diacids, oxoacids, and  $\alpha$ -dicarbonyls are higher in MBA than LBA (Table 4). The present observation emphasizes an important oceanic control on atmospheric distribution of these water-soluble organic species during high biological activity.

#### 4. Conclusions

Detailed molecular distributions of diacids and related compounds in aerosols collected over the North Pacific during a summer cruise (August to September 2008) provide insight on their formation processes. Their molecular distributions are characterized by the predominance of oxalic acid followed by malonic, succinic, and glyoxylic acids ( $C_2 > C_3 > C_4 > \omega C_2$ ). A close resemblance in the temporal abundances of  $C_9$  and LMW diacids together with the pronounced temperature dependence of relative abundances of  $C_2$ ,  $C_3$ ,  $C_4$ , and  $C_5$  in total diacids suggests the formation of lower diacids through the photochemical oxidation of higher diacids such as azelaic acid that is produced by the oxidation of unsaturated fatty acids emitted from the ocean surface. A notable difference in the mass ratios of oxalic to succinic acid ( $C_2/C_4$ ) and oxalic to glyoxylic acids ( $C_2/\omega C_2$ ) and no significant differences in malonic to succinic acid ( $C_3/C_4$ ) ratios between MBA and LBA along with their prevailing strong intercorrelations indicate the production of  $C_2$  from  $C_4$  diacid via the intermediate formation of  $C_3$ . This observation is also supported by the prominent linear relationship among succinic, malic, and malonic acids. In addition, significant linear correlations among isoprene-SOA tracers (i.e., 2-methylglyceric acid + methyltetrols), methylglyoxal, pyruvic, and glyoxylic acids together with their consistent higher and lower abundances in MBA and LBA, respectively, suggest that the formation of small diacids is also involved with aqueous phase oxidation of isoprene emitted from the ocean surface in the MABL over the western North Pacific.

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