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RESEARCH ARTICLE

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Key Points:

- Influence of continental sources over the North Pacific in winter/spring
- Marine sources dominate the atmospheric abundances of organics in summer/fall
- Seasonal cycles are well reflected in the diagnostic mass ratios

Supporting Information:

- Table S1, Data set S1, Movie S1, and Audio S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5
- Figure S6

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Seasonal and longitudinal distributions of atmospheric water-soluble dicarboxylic acids, oxocarboxylic acids, and α -dicarbonyls over the North Pacific

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Abstract In order to assess the seasonal variability of atmospheric abundances of dicarboxylic acids, oxocarboxylic acids, and α -dicarbonyls over the North Pacific and Sea of Japan, aerosol samples were collected along the longitudinal transects during six cruises between Canada and Japan. The back trajectory analyses indicate that aerosol samples collected in winter and spring are influenced by the East Asian outflow, whereas summer and fall samples are associated with the pristine maritime air masses. Molecular distributions of water-soluble organics in winter and spring samples show the predominance of oxalic acid (C_2) followed by succinic (C_4) and malonic acids (C_3). In contrast, summer and fall marine aerosols are characterized by the predominance of C_3 over C_4 . Concentrations of dicarboxylic acids were higher over the Sea of Japan than the North Pacific. With a lack of continental outflow, higher concentrations during early summer are ascribed to atmospheric oxidation of organic precursors associated with high biological activity in the North Pacific. This interpretation is further supported by the high abundances of azelaic acid, which is a photochemical oxidation product of biogenic unsaturated fatty acids, over the Bering Sea in early summer when surface waters are characterized by high biological productivity. We found higher ratios of oxalic acid to pyruvic and glyoxylic acids (C_2/Pyr and $C_2/\omega C_2$) and glyoxal and methylglyoxal (C_2/Gly and C_2/MeGly) in summer and fall than in winter and spring, suggesting a production of C_2 from the aqueous-phase oxidation of oceanic isoprene. In this study, dicarboxylic acids account for 0.7–38% of water-soluble organic carbon.

1. Introduction

Atmospheric organics constitute a significant fraction (20–90%) of fine particulate mass [Kanakidou *et al.*, 2005], which have a large impact on Earth's radiative balance directly by absorbing or scattering the sunlight and indirectly by acting as cloud condensation nuclei (CCN) [Novakov and Penner, 1993]. Despite their significant contribution to aerosol mass, the individually identified fractions of organic aerosols (OAs) are rather small (~10–14%) [Fu *et al.*, 2008; Roach *et al.*, 2010; Wang *et al.*, 2006]. However, the chemical characterization of continental OAs is more studied than that over the open ocean [Fu *et al.*, 2008, 2013; Mochida *et al.*, 2002]. OAs in the marine atmospheric boundary layer (MABL) can be derived from either long-range atmospheric transport of chemical constituents from the continents or sea-to-air efflux of biogenic compounds [Kawamura and Sakaguchi, 1999; Miyazaki *et al.*, 2011]. Among organic aerosol components, the water-soluble species have a greater significance due to their CCN activity and are also linked to the formation of secondary OAs [Bikkina *et al.*, 2014; Carlton *et al.*, 2009; Miyazaki *et al.*, 2011].

The water-soluble dicarboxylic acids, oxocarboxylic acids, and α -dicarbonyls are some of the most extensively studied OA components over the continents [Agarwal *et al.*, 2010; Aggarwal *et al.*, 2013; Ho *et al.*, 2007; Kawamura and Yasui, 2005; Miyazaki *et al.*, 2009; Pavuluri *et al.*, 2010; Wang *et al.*, 2012]. However, the studies on their chemical characterization over the open oceanic regions are mostly for the latitudinal distributions, and the studies on longitudinal distributions are very limited [Bikkina *et al.*, 2015, 2014; Fu *et al.*, 2013; Kawamura *et al.*, 2004; Kawamura and Sakaguchi, 1999; Kawamura and Usukura, 1993; Kunwar and Kawamura, 2014; Sempéré and Kawamura, 2003]. It has been suggested that atmospheric abundances of these water-soluble organic species can have significant influence on the regional radiative forcing through direct aerosol effect (via light scattering properties), as well as cloud or fog formation processes [Facchini *et al.*, 1999; Gierlus *et al.*, 2012; Matsumoto *et al.*, 1997]. However, these water-soluble organic species have been reported in various geographical locations such as urban, rural, remote continental

[Agarwal *et al.*, 2010; Hegde and Kawamura, 2012; Miyazaki *et al.*, 2009; Pavuluri *et al.*, 2010; Sempéré and Kawamura, 1994] and marine regions [Fu *et al.*, 2013; Kawamura and Sakaguchi, 1999; Kawamura and Usukura, 1993], and also in the polar regions [Kawamura *et al.*, 1996a, 2010, 2012, 1996b].

Owing to rather sparse observations from the open ocean, the sources and formation pathways of these atmospheric water-soluble organic species are not well understood. However, previous studies have documented that molecular distribution of dicarboxylic acids are often characterized by the predominance of low molecular weight compounds, i.e., oxalic acid followed by malonic and succinic acids [Fu *et al.*, 2013; Kawamura and Sakaguchi, 1999; Kawamura and Usukura, 1993]. The incomplete combustion of fossil fuels [Kawamura and Kaplan, 1987; Kerminen *et al.*, 2000, 1999; Legrand *et al.*, 2007], emission from the biomass/biofuel burning [Agarwal *et al.*, 2010; Narukawa *et al.*, 1999], and meat cooking [Rogge *et al.*, 1991] have been suggested as major primary sources of dicarboxylic acids over the polluted urban and rural regions. Further, dicarboxylic acids can be directly emitted from the terrestrial vegetation and be secondarily derived from the photochemical oxidation process [Kawamura *et al.*, 2005; Kawamura and Usukura, 1993; Kerminen *et al.*, 1999].

The major sources of these water-soluble dicarboxylic acids and related polar compounds in the MABL are the photochemical oxidation of biogenic unsaturated fatty acids, emitted from either ocean surface or terrestrial plants [Kawamura and Sakaguchi, 1999]. In addition, the aqueous-phase oxidation of oceanic biogenic volatile organic compounds (BVOCs), such as isoprene and monoterpenes, can also significantly contribute to the production of these atmospheric water-soluble organic species [Bikkina *et al.*, 2014; Miyazaki *et al.*, 2011]. However, the knowledge regarding the sources and formation pathways of atmospheric dicarboxylic acids, oxocarboxylic acids, and α -dicarbonyls are still limited in the literature. The present study is a step forward this direction to better understand the seasonal and longitudinal distributions of water-soluble organic species in the MABL and is carried out over the open ocean waters of the North Pacific and Sea of Japan.

2. Experiment

2.1. Site Description and Meteorology

The North Pacific Ocean has a considerable influence from the continental outflow from East Asia during winter (December–February) and spring (March–May), as inferred from the widespread occurrence of various gaseous [Blake *et al.*, 2003; Heald *et al.*, 2003] and particulate pollutants within the MABL [Arimoto *et al.*, 1996; Clarke *et al.*, 2004; Mochida *et al.*, 2007; Talbot *et al.*, 1997; Uematsu *et al.*, 2010]. The shallow atmospheric boundary layer height over Asia in winter and spring together with increase in ground level emissions causes a gradient in the East Asian outflow. However, the prevailing high-pressure zones over the North Pacific during summer (June–September), resulting in southeasterly winds from the ocean to land and, hence, restricting the passage of air masses from East Asia.

In comparison to winter and spring, the chemical characterization of organic aerosols over the North Pacific is rather limited in the literature in terms of sources and formation pathways of water-soluble dicarboxylic acids during summer. Nevertheless, recent studies have examined the role of primary emissions versus secondary organic aerosol formation mechanisms of marine aerosols over the North Pacific. These studies have suggested an influence from the direct emissions of biogenic unsaturated fatty acids and volatile organic compounds (VOCs) across the air-sea interface [Bikkina *et al.*, 2014; Bonsang *et al.*, 1992; Kawamura *et al.*, 2003; Kawamura and Usukura, 1993; Miyazaki *et al.*, 2012, 2011]. However, the fall (October–November) is a transition period for changing wind pattern from easterlies to westerlies and, thus, the North Pacific has a mild influence from the continental sources over the remote sites during this period.

2.2. Cruise Track and Aerosol Sampling

For this study, 50 bulk aerosol samples (total suspended particle (TSP)) were collected from the MABL of the Sea of Japan and North Pacific during six commercial cruises on board *M/S Skaugran* between Japan and Canada during different seasons (fall: 21–23 October 1995, late summer: 8–18 September 1996, winter: 27 December 1996 to 7 January 1997, spring: 6–15 April 1997, early summer: 27 May to 5 June 1997, and summer: 9–18 July 1997). The cruise tracks used for aerosol collection in the North Pacific are depicted in

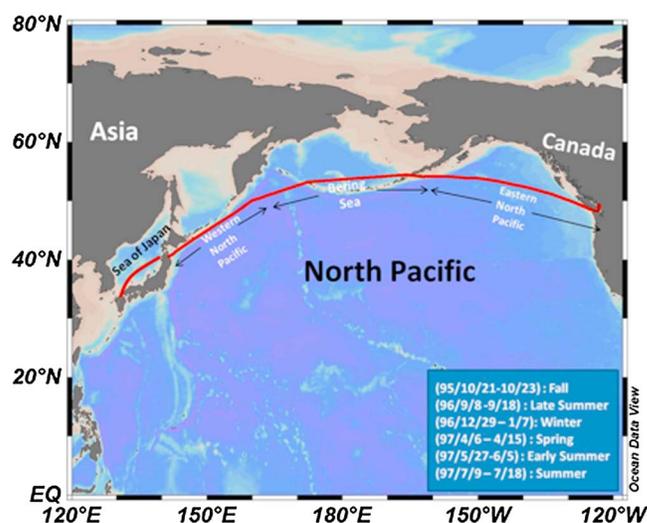


Figure 1. M/S *Skaugran* cruise tracks for aerosol sampling in the Sea of Japan and North Pacific during 1995–1997.

Figure 1. A brief description about the meteorological parameters during all cruises is made in Mochida *et al.* [2002]. For cruises conducted in winter and spring seasons, the prevailing westerlies dominate during the aerosol collection. In this study, we used only the samples collected during the westbound cruises, in which the ship bow is always against the westerlies.

The high-volume air sampler (Kimoto, Model-120F; flow rate: $1.0\text{ m}^3\text{ min}^{-1}$) was used for the collection of aerosols, which was set up on upper deck of M/S *Skaugran* (~20 m above sea level). In order to avoid the contamination from the ship smoke stack, the aerosol sampler was connected to a wind speed/sector sampling system and

operated only when a typical wind speed is greater than 2.0 m s^{-1} and the prevailing winds are from the bow side. Except for few samples, the filtered air volume is $\sim 1400\text{ m}^3$, and each aerosol filter is collected for $\sim 24\text{ h}$ (range: 3–24 h). For this study, aerosol samples were collected on precombusted (overnight at 450°C) quartz fiber filter substrates ($20 \times 25\text{ cm}$; Pallflex® 2500QAT-UP). After the collection, samples were placed in a precleaned (and precombusted) glass jar equipped with a Teflon-lined screw cap. Soon after the aerosol sampling, filters were stored in the deep freezer at -20°C until chemical analyses were carried out. The TSP load is ascertained gravimetrically by measuring the weight of filters prior to and after sample collection. The aerosol samples were analyzed for water-soluble dicarboxylic acids (referred hereafter as diacids), oxocarboxylic acids (oxoacids), and α -dicarbonyls, as well as water-soluble and total organic carbon. The analytical protocols used for the assay of diacids, oxoacids, and α -dicarbonyls are adapted from Kawamura and Ikushima [1993]. All the chemical analyses were completed by 1999. For the sake of completeness, brief analytical protocols are described as follows.

An aliquot of filter cut (approximately 10 cm^2) is extracted with organic-free deionized water (Milli-Q; specific resistivity: $>18.2\text{ M}\Omega\text{ cm}$) by ultrasonic agitation (10 min \times 3 times). These extracts are subsequently filtered and preconcentrated using rotary evaporator under vacuum followed by derivatization with 14% $\text{BF}_3/\text{n-butanol}$ at 100°C for $\sim 1\text{ h}$. During this process, diacids are converted to dibutyl esters, whereas aldehyde groups in α -dicarbonyls and ω -oxoacids are converted to dibutoxy acetals. After derivatization, these derivatives were back extracted with n-hexane and determined using a gas chromatograph (HP6890) equipped with a split/splitless injector, fused silica capillary column, and a flame ionization detector. Diacids and related compounds are determined by comparing the retention times of analyte peaks with those of authentic standards. Their identification was confirmed using gas chromatography–mass spectrometry. Another aliquot of aerosol filter is extracted with Milli-Q and analyzed for water-soluble organic carbon (WSOC) using a Shimadzu TOC-5000 analyzer. In addition, a portion of aerosol sample is analyzed for total carbon (TC) content using TC analyzer (model: Carlo Erba NA 1500 elemental analyzer). More details regarding measurement of these parameters are provided in our earlier publications [Fu *et al.*, 2013; Kawamura and Sakaguchi, 1999; Sempéré and Kawamura, 2003].

2.3. Quality Assurance

The extraction efficiency is determined by spiking authentic diacids on the quartz filters, and the recovery of major diacid species such as malonic, succinic, and adipic acids are better than 83%, except for oxalic acid whose recovery is 79%. Based on the replicate analysis of filter samples, the overall analytical error of major diacids is ascertained to be within 10%. Along with aerosol samples, filter blanks were also analyzed for

diacids and related compounds. No significant signals were detected for most of the measured water-soluble organics. Although some contaminations are detected for major diacids, their concentrations are 2–3 orders of magnitude lower than the analyte signals. All the reported concentrations were suitably corrected against blanks.

3. Results and Discussions

3.1. Air Mass Back Trajectories

To better assess the possible source regions of the measured atmospheric water-soluble organics over the North Pacific and Sea of Japan, air mass back trajectories (AMBTs) were examined for all cruises. Figure 2 depicts the AMBTs computed for all the six cruises conducted in the North Pacific and Sea of Japan. During the sampling periods, 7 day isentropic AMBTs were computed using a Hybrid Single-Particle Lagrangian Integrated Trajectory model (version 4) [Draxler and Rolph, 2014; Rolph, 2014] and using National Centers for Environmental Prediction (NCEP) reanalysis data (available from 1948 to present) from the NOAA air resource laboratory online Web application (<http://ready.arl.noaa.gov/hypub-bin/trajtype.pl?runtime=archive>) at three arrival heights of 100, 500, and 1000 m, which are indicated in Figure 2 with the red, blue, and green colors, respectively. From Figure 2, it is obvious that AMBTs for winter and spring cruises show the atmospheric transport from East Asia to the North Pacific. In contrast, the cruises conducted during summer and fall are mostly influenced by the prevailing easterlies, which are of maritime origin. Higher biological activity (i.e., phytoplankton bloom) is recognized during summer than winter and spring cruises (see chlorophyll *a* images obtained from Mochida *et al.* [2002] in Figure S1 in the supporting information).

3.2. Temporal Variability

Among the cruises conducted in the North Pacific, molecular distributions of water-soluble organics in the TSP samples collected in winter (27 December 1996 to 7 January 1997; $N=8$), spring (6–15 April 1997; $N=8$), and early summer (27 May 1997–5 June 1997; $N=10$), show the predominance of oxalic acid (C_2) followed by succinic (C_4) and malonic (C_3) acids. It is obvious that the concentrations are higher in spring and early summer than in winter (see Table 1). Phthalic acid (Ph) is the fourth most abundant water-soluble organic compound for the aerosols collected in these three cruises; however, its abundance is somewhat comparable to that of succinic acid. In contrast, water-soluble organics in the aerosols collected during late summer and fall cruises are dominated by C_2 followed by C_3 and C_4 . This pattern is also somewhat consistent with the previous study conducted over the Sea of Japan [Mochida *et al.*, 2003]. For all cruises conducted in the North Pacific, the molecular distributions of diacids, oxoacids, and α -dicarbonyls are shown in Figure 3.

Among all the cruises, higher abundances of measured water-soluble organics are noteworthy for aerosols collected over the Sea of Japan compared to those over the North Pacific (Table 1). The molecular distributions of these water-soluble organics in aerosols collected over the Sea of Japan (21–23 October 1995; $N=5$) are characterized by the predominance of C_2 diacid followed by C_3 and C_4 . Glyoxylic (ωC_2) and phthalic (Ph) acids are the next most abundant water-soluble organic species in the MABL of the Sea of Japan followed by glutaric (C_5) and adipic (C_6) acids. Overall, average molecular distribution of some of these organic compounds in the MABL of Sea of Japan is characterized as follows: $C_2 > C_3 > C_4 > \omega C_2 > Ph > C_5 > C_6$, as depicted in Figure 3.

3.3. Seasonal Variability

To better understand the spatial variability of atmospheric diacids and other related compounds, aerosol samples collected over the North Pacific along the cruise tracks shown in Figure 1 were divided into three oceanic regions: the western North Pacific (WNP: 140°E–160°E), Bering Sea (BS: 160°E–180°E, 180°W–160°W), and eastern North Pacific (ENP: 130°W–160°W), as described in Mochida *et al.* [2002]. Figure 4 depicts the bar graph, showing the seasonally averaged mass concentration of diacids among three oceanic regions (WNP, BS, and ENP). From Figure 4, relatively high concentrations of diacids were observed over the WNP compared to those over the BS and ENP. However, a comparable concentration of diacids is also noteworthy over the BS during the study period. Interestingly, relatively high concentration of azelaic acid is observed for aerosols collected over the Bering Sea in early summer when the oceanic basin is characterized by the occurrence of a phytoplankton bloom.

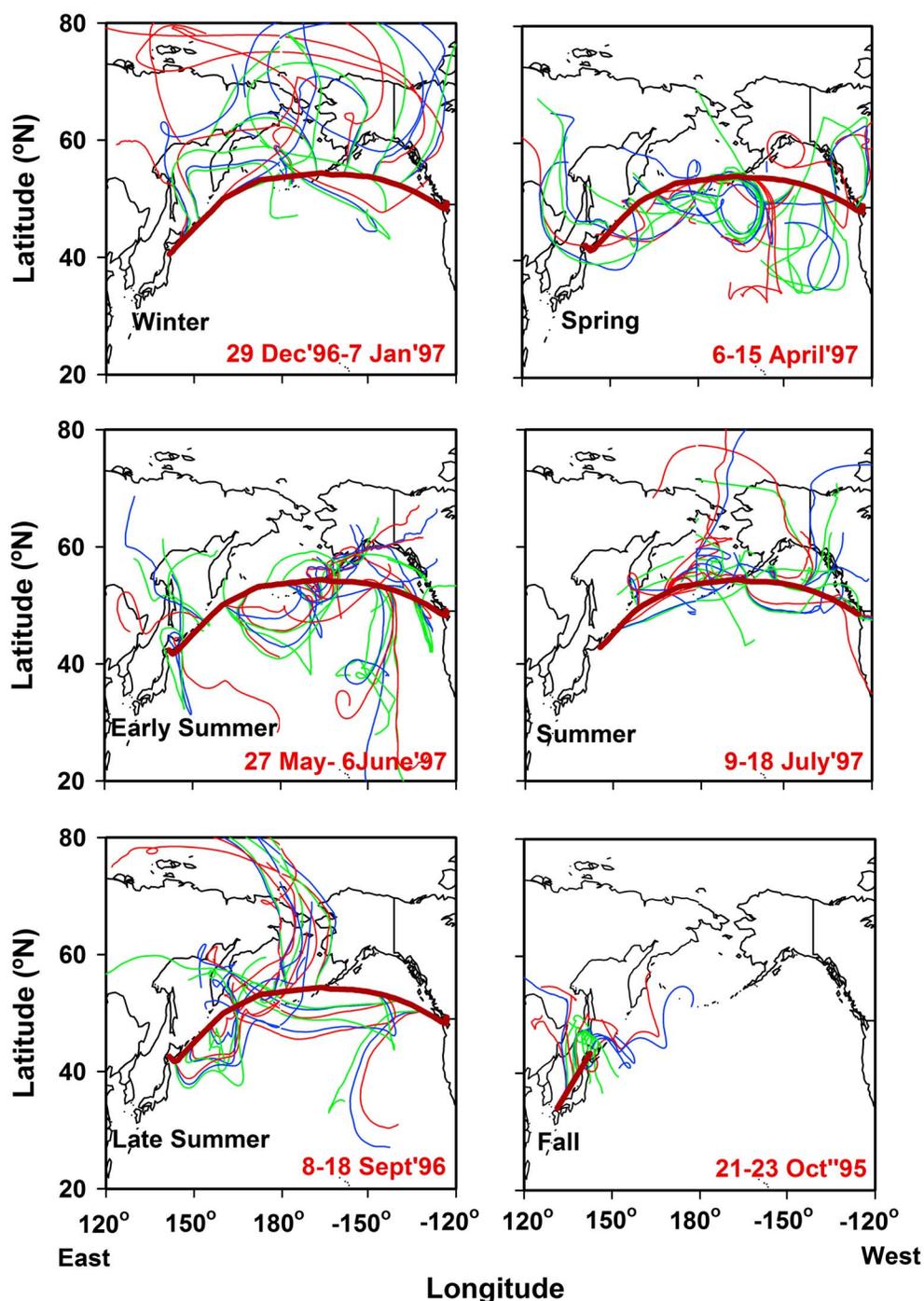


Figure 2. Air mass back trajectory clusters for the cruises conducted in the North Pacific and Sea of Japan during October 1995 to June 1997. The red, blue, and green correspond to back trajectories having an arrival height of 100 m, 500 m, and 1000 m for bulk aerosols collected along the cruise tracks in the North Pacific.

Previous studies postulated that azelaic acid (C_9 diacid) is a photochemical oxidation product of marine biogenic unsaturated fatty acids, which are directly emitted into the MABL from the productive oceanic regions along with sea-spray [Bikkina *et al.*, 2014; Kawamura and Sakaguchi, 1999; Kawamura and Usukura, 1993]. Furthermore, the photochemical oxidation of azelaic acid leads to the production of its next lower homologues, which eventually form low molecular weight diacids such as succinic, glutaric, and adipic acids [Kawamura *et al.*, 1996a, 1996b]. Therefore, the observed high and comparable concentrations of

Table 1. Statistical Description (Range, Mean, and Standard Deviation) of Mass Concentrations (ng m^{-3}) of Water-Soluble Dicarboxylic Acids, Oxocarboxylic Acids, and α -Dicarbonyls in the Marine Aerosols Collected During M/S Skaugran Cruises in the North Pacific and Sea of Japan (ND = Not Detected)^a

Constituent	#Winter		#Spring		#Early Summer		#Summer		#Late Summer		#Fall	
	December 1996	January 1997	April 1997	May-June 1997	July 1997	September 1996	October 1995					
Dicarboxylic acids												
Oxalic, C ₂	2.1–12.2 (6.8 ± 4.0)		9.2–172 (35.2 ± 56.3)	7.9–70.0 (34.0 ± 19.2)	4.1–36.9 (17.1 ± 9.5)	7.6–47.1 (20.6 ± 12.1)	81–260 (156 ± 75)					
Malonic, C ₃	0.2–1.4 (0.7 ± 0.5)		1.6–43.7 (8.2 ± 14.6)	3.5–26.3 (14.5 ± 7.9)	1.3–12.9 (7.9 ± 3.5)	2.6–19.8 (7.9 ± 5.2)	30.8–94.8 (56.0 ± 27.4)					
Succinic, C ₄	0.4–2.2 (1.2 ± 0.7)		1.9–60.7 (10.8 ± 20.3)	3.8–37.8 (16.3 ± 11.3)	1.0–14.1 (7.8 ± 3.8)	2.1–16.6 (6.2 ± 4.5)	22.3–73.8 (43.2 ± 21.9)					
Glutaric, C ₅	0.07–0.40 (0.27 ± 0.13)		0.4–13.7 (2.4 ± 4.6)	2.0–13.3 (6.8 ± 4.1)	0.5–5.5 (2.9 ± 1.3)	0.5–6.0 (2.2 ± 1.9)	3.9–12.9 (7.7 ± 3.9)					
Adipic, C ₆	0.12–0.65 (0.33 ± 0.21)		0.2–4.5 (1.0 ± 1.4)	0.8–4.4 (2.3 ± 1.3)	0.3–1.4 (0.9 ± 0.4)	0.2–2.3 (0.8 ± 0.7)	1.5–3.7 (2.6 ± 0.9)					
Pimelic, C ₇	ND		ND	ND–0.5 (0.2 ± 0.2)	ND–0.23 (0.09 ± 0.04)	ND–0.3 (0.1 ± 0.1)	0.3–0.8 (0.5 ± 0.2)					
Suberic, C ₈	ND–0.11 (0.09 ± 0.02)		ND–1.3 (0.5 ± 0.6)	0.3–1.4 (0.7 ± 0.4)	0.08–0.35 (0.23 ± 0.08)	0.07–0.62 (0.27 ± 0.18)	0.7–2.6 (1.3 ± 0.9)					
Azelaic, C ₉	ND–0.33 (0.17 ± 0.12)		ND–0.8 (0.3 ± 0.3)	0.3–2.1 (0.7 ± 0.5)	0.11–0.42 (0.26 ± 0.09)	0.10–0.70 (0.28 ± 0.17)	0.8–2.8 (1.6 ± 0.9)					
Sebacic, C ₁₀	ND		ND–0.3 (0.1 ± 0.1)	ND–0.4 (0.2 ± 0.2)	ND–0.07 (0.02 ± 0.03)	ND	ND					
Methylmalonic, iC ₄	ND		ND–4.1 (1.9 ± 2.0)	0.2–3.4 (1.1 ± 1.1)	ND–0.85 (0.38 ± 0.30)	0.1–1.2 (0.3 ± 0.3)	0.9–3.0 (1.8 ± 0.9)					
Methylsuccinic, iC ₅	ND		ND–4.8 (2.7 ± 2.9)	ND–1.6 (0.8 ± 0.5)	ND–0.42 (0.19 ± 0.13)	0.1–0.7 (0.3 ± 0.2)	0.9–4.0 (2.3 ± 1.3)					
Maleic, M	0.06–0.81 (0.29 ± 0.24)		0.2–5.7 (1.0 ± 1.9)	0.3–0.8 (0.5 ± 0.2)	0.12–0.60 (0.30 ± 0.15)	0.2–1.2 (0.5 ± 0.3)	1.3–3.2 (2.3 ± 0.8)					
Fumaric, F	ND–0.58 (0.52 ± 0.11)		ND–6.3 (2.3 ± 2.7)	0.4–1.8 (0.9 ± 0.4)	0.13–1.02 (0.47 ± 0.28)	0.3–1.6 (0.8 ± 0.4)	1.5–2.0 (1.8 ± 0.2)					
Methylmaleic, MeM	ND–0.32 (0.25 ± 0.07)		ND–3.1 (1.0 ± 1.5)	0.1–0.5 (0.3 ± 0.1)	ND–0.16 (0.07 ± 0.06)	0.1–0.6 (0.3 ± 0.2)	0.2–3.4 (2.1 ± 1.3)					
Phthalic, Ph	ND–8.8 (1.9 ± 3.1)		0.7–11.1 (3.0 ± 3.4)	0.4–1.7 (1.0 ± 0.4)	0.4–1.4 (0.7 ± 0.4)	0.3–3.4 (0.9 ± 0.9)	5.7–16.2 (9.4 ± 4.6)					
Oxomalonic, kC ₃	ND–0.52 (0.23 ± 0.21)		ND–10.5 (2.1 ± 4.1)	ND–1.1 (0.5 ± 0.3)	ND–0.75 (0.41 ± 0.26)	0.08–1.44 (0.42 ± 0.40)	1.2–3.9 (2.4 ± 1.2)					
4-oxopimelic, kC ₇	ND–0.20 (0.04 ± 0.08)		0.1–4.1 (0.9 ± 1.6)	0.7–6.9 (3.2 ± 2.1)	0.2–3.2 (1.6 ± 0.9)	0.17–2.56 (0.95 ± 0.84)	1.6–3.8 (2.5 ± 0.9)					
Malic, hC ₄	ND–0.39		0.2	ND–1.0 (0.4 ± 0.3)	ND–0.28 (0.15 ± 0.08)	0.07–0.95 (0.26 ± 0.25)	ND–0.7 (0.4 ± 0.3)					
Oxocarboxylic acid												
Pyruvic, Pyr	0.18–1.31 (0.55 ± 0.38)		0.4–6.5 (1.5 ± 2.1)	0.4–1.9 (1.1 ± 0.5)	0.22–0.83 (0.44 ± 0.19)	0.21–1.66 (0.62 ± 0.45)	2.5–6.4 (4.0 ± 1.7)					
Glyoxylic, ω C ₂	0.23–1.51 (0.87 ± 0.51)		0.8–16.2 (3.2 ± 5.3)	0.5–2.7 (1.5 ± 0.7)	0.41–1.22 (0.75 ± 0.24)	0.43–2.40 (1.14 ± 0.60)	5.6–15.9 (10.7 ± 4.2)					
3-Oxopropanoic, ω C ₃	ND–0.48 (0.17 ± 0.17)		0.1–3.5 (0.7 ± 1.2)	0.4–1.6 (1.1 ± 0.4)	0.04–0.71 (0.38 ± 0.22)	0.07–0.77 (0.35 ± 0.24)	1.5–4.4 (2.5 ± 1.3)					
4-Oxobutanoic, ω C ₄	ND–0.78 (0.23 ± 0.25)		0.1–5.6 (1.1 ± 1.9)	0.1–3.9 (1.6 ± 1.1)	0.16–1.39 (0.90 ± 0.46)	ND–0.32 (0.14 ± 0.12)	2.0–6.5 (4.0 ± 2.1)					
α -Dicarbonyls												
Glyoxal, Gly	0.19–0.83 (0.52 ± 0.22)		0.6–11.1 (2.1 ± 3.6)	0.4–1.8 (0.9 ± 0.4)	0.22–0.63 (0.46 ± 0.14)	0.23–1.0 (0.53 ± 0.26)	1.2–3.4 (2.5 ± 1.0)					
Methylglyoxal, MeGly	ND–0.15 (0.05 ± 0.05)		ND–1.9 (0.4 ± 0.6)	ND–0.3 (0.2 ± 0.1)	ND–0.25 (0.08 ± 0.08)	ND–0.37 (0.13 ± 0.11)	0.3–1.0 (0.7 ± 0.3)					

^aNote that samples with ND are not included in estimating the mean concentrations. # and * refer to data from the North Pacific and Sea of Japan, respectively.

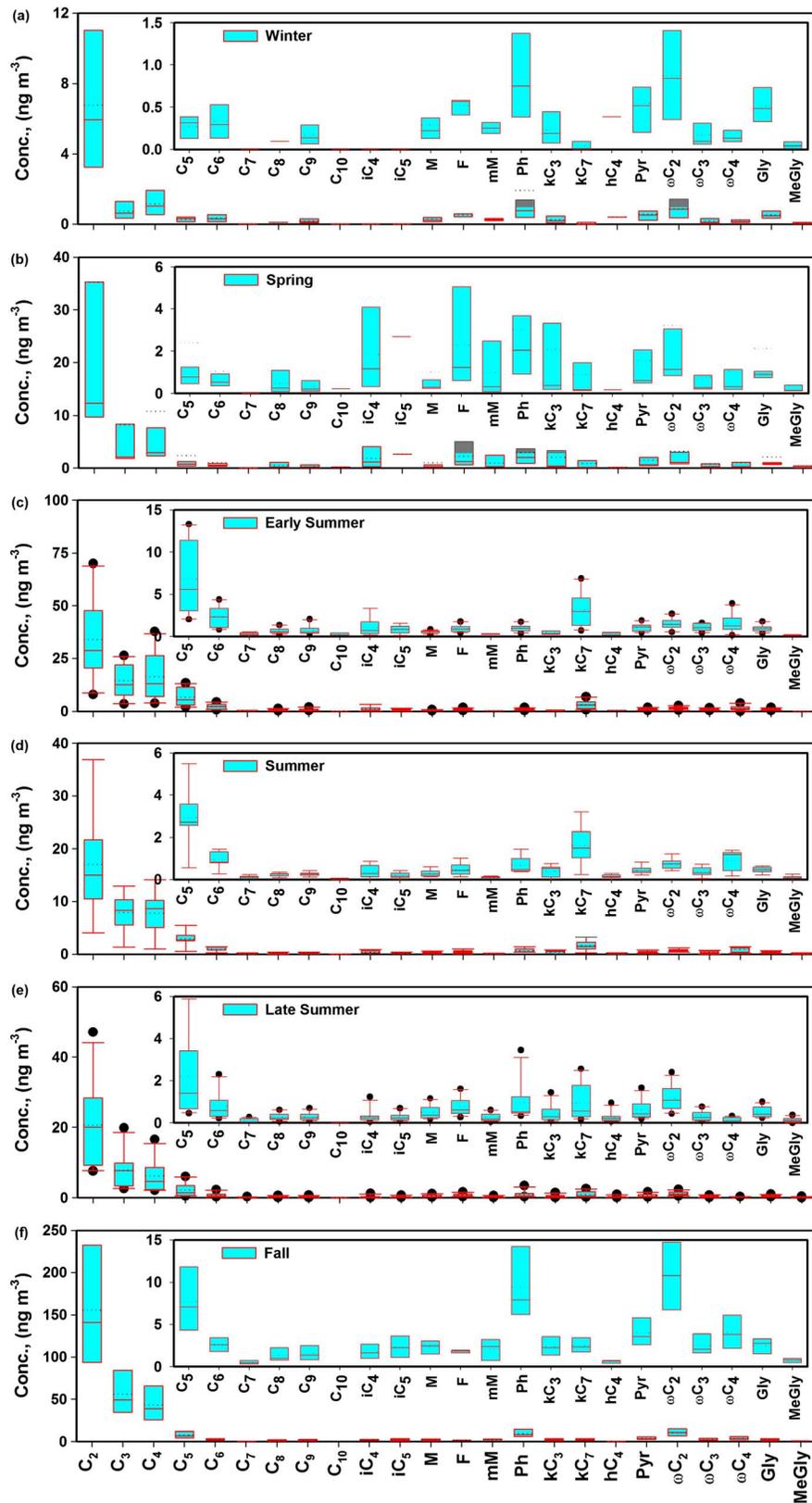


Figure 3. Molecular distributions of measured diacids, oxoacids, and α -dicarbonyls in the aerosols collected during the cruises conducted in (a) winter, (b) spring, (c) early summer, (d) summer, (e) late summer, and (f) fall over the Sea of Japan and North Pacific during 1995–1997.

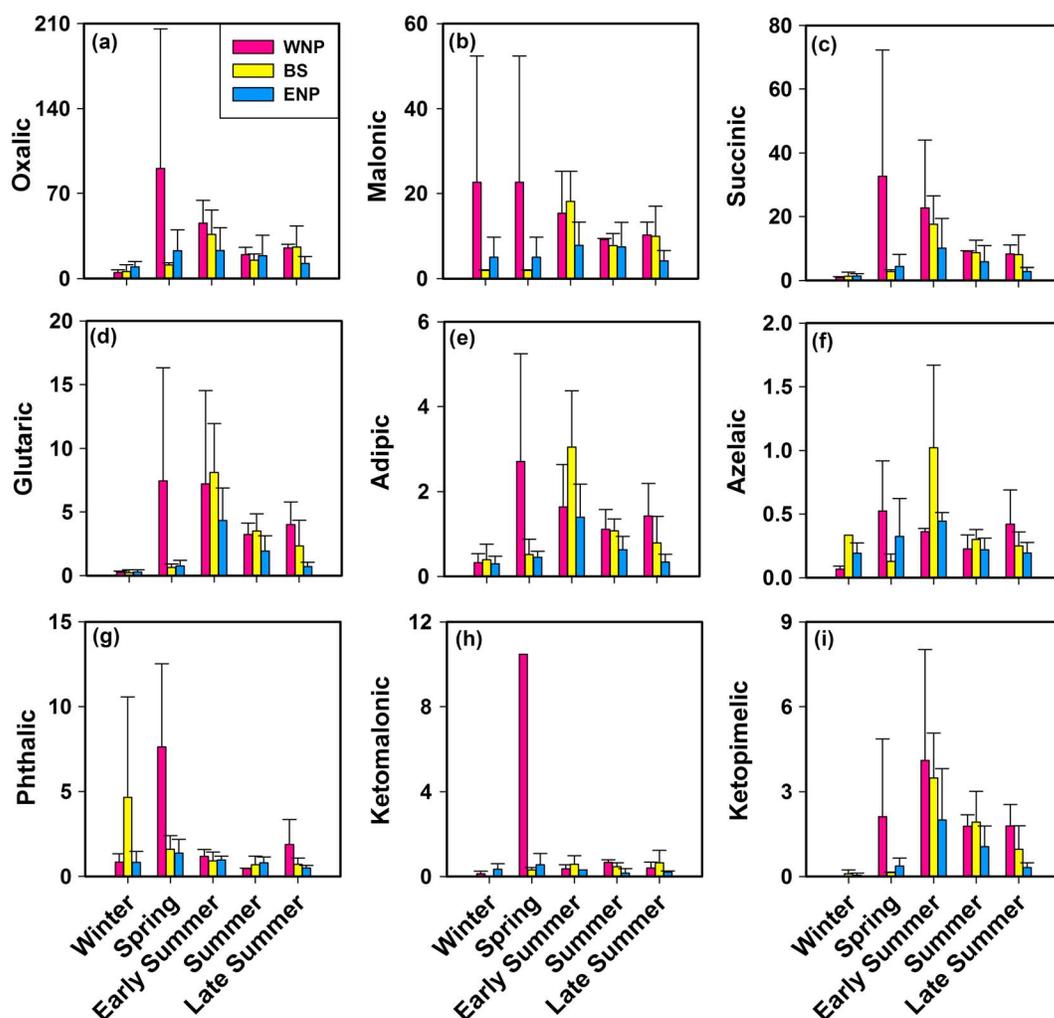


Figure 4. Mean seasonal variability of (a) oxalic, (b) malonic, (c) succinic, (d) glutaric, (e) adipic, (f) azelaic, (g) phthalic, (h) ketomalonic, and (i) ketopimelic acids in the aerosol samples collected over the North Pacific Ocean during 1995–1997.

diacids (C_2 to C_6 and C_9) over the BS and WNP in early summer (Figure 4), indicate the relative significance of oceanic source in pristine maritime air masses compared to that influenced by the continental air masses from East Asia during winter and spring. However, rather low concentrations of diacids are recognized for aerosols collected over the ENP, suggesting less continental influence of polluted air masses from East Asia than those from the WNP and BS. Overall, lower atmospheric abundances of diacids over the ENP than the WNP and BS may be resulted from a combination of its farther distance from the Asian outflow region during winter and spring, and lesser biological activity in the surface waters during summer.

Analogous to diacids, oxoacids and α -dicarbonyls also show higher atmospheric abundances over the western North Pacific compared to those over the Bering Sea and eastern North Pacific. The seasonally averaged mass concentrations of oxoacids and α -dicarbonyls among three oceanic regions (ENP, BS and WNP) are shown in Figure 5. Relatively high concentrations of Gly and MeGly over the WNP during the spring cruise are also consistent with those of dicarboxylic acids, which can be attributed to the long-range atmospheric transport of air masses from East Asia. It has been suggested that Gly and MeGly are derived from atmospheric oxidation of isoprene, a biogenic VOC emitted either from the terrestrial vegetation (i.e., continental origin) or from the marine phytoplankton (oceanic origin) [Sorooshian *et al.*, 2009]. In addition, Gly is also a photochemical oxidation product of aromatic hydrocarbons, which are produced from fossil-fuel combustion [Carlton *et al.*, 2007; Volkamer *et al.*, 2006, 2007]. Higher atmospheric abundances of Gly and MeGly in spring over the WNP than the BS and ENP can be explained by the proximity of former oceanic basin to the Asian outflow.

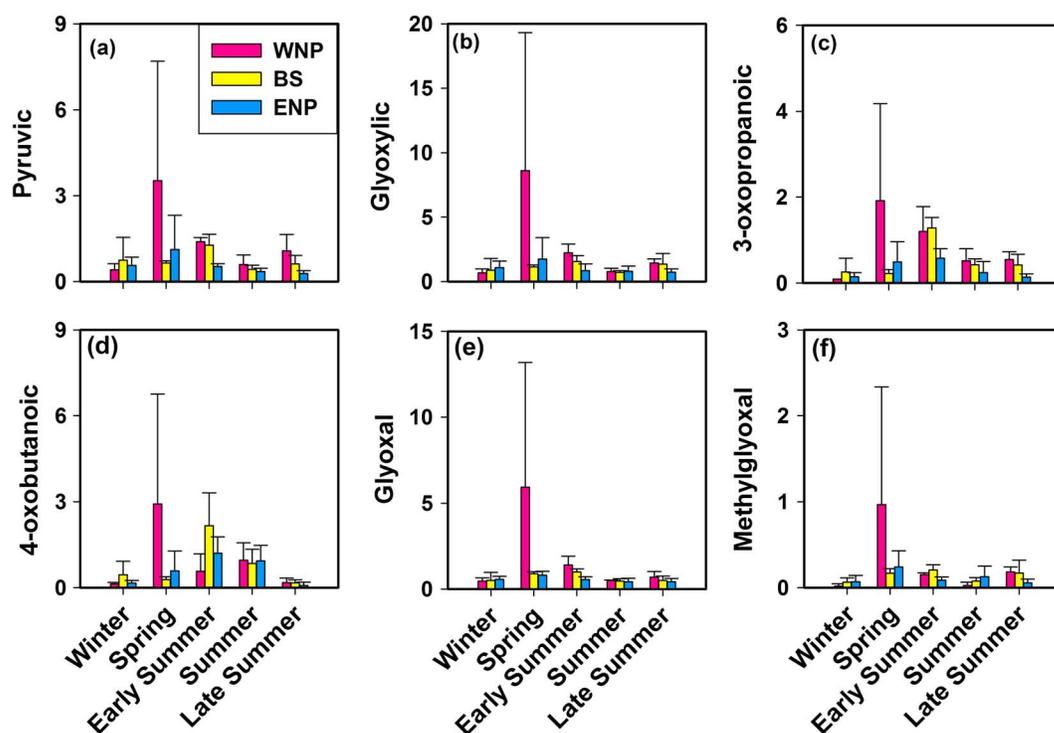


Figure 5. Mean seasonal variability of oxoacids: (a) pyruvic acid, (b) glyoxylic acid, (c) 3-oxopropanoic acid, (d) 4-oxobutanoic acid, (e) glyoxal, and (f) methylglyoxal in the aerosols collected over the North Pacific Ocean during 1995–1997.

However, recent studies have detected gaseous Gly in the MABL of remote tropical Pacific during Variability of the American Monsoon Systems Ocean-Cloud-Atmosphere-Land Study–Regional Experiment (VOCALS-REx) [Sinreich *et al.*, 2010]. Owing to short atmospheric lifetime of Gly (~2 h) and its highly water-soluble nature, they ruled out a possible transport from nearby continents. Instead, they attributed the presence of Gly to atmospheric oxidation of BVOCs (e.g., isoprene and acetylene), which are produced through photochemical degradation of dissolved organic matter in the surface waters [Sinreich *et al.*, 2010]. Therefore, the lower concentrations of α -dicarbonyls over the WNP during summer cruises (this study) might be a result of photochemical oxidation of oceanic isoprene. Interestingly, 3-oxopropanoic and 4-oxobutanoic acids also show high abundances over the Bering Sea during early summer, which may be derived from the photochemical oxidation of biogenic unsaturated fatty acids emitted from the ocean surface. In this regard, Mochida *et al.* [2002] have also documented an increase in the atmospheric concentrations of shorter-chain saturated fatty acids (from C₁₄ to C₁₉) in early summer during the same cruise.

3.4. Diagnostic Mass Ratios

Table 2 presents the diagnostic mass ratios (viz., C₂/C₄, C₃/C₄, C₂/ΣC₂-C₁₀, C₂/ωC₂, Ph/C₉, C₆/C₉, and M/F) calculated from the atmospheric concentrations of diacids, oxoacids, and α -dicarbonyls for all cruises conducted in the North Pacific and Sea of Japan. In the ambient atmosphere, photochemical oxidation of succinic acid (C₄) leads to the formation of oxalic (C₂) and malonic (C₃) acids. Several studies have used the C₂/C₄ and C₃/C₄ ratios as proxies for assessing the intensity of photochemical aging [Aggarwal and Kawamura, 2008; Kawamura and Sakaguchi, 1999; Kundu *et al.*, 2010]. We found that the mass ratios of C₂/C₄ in winter and spring cruises are higher than in summer and fall due to the type of aerosols collected over the North Pacific during former cruises, which are more aged and somewhat influenced by Asian outflow.

Figure S2 in the supporting information depicts the temporal trends in the mass concentration ratios of diacids and related compounds from winter cruise. A covariance of temporal trend is recognized for the combinations of C₂/Σ(C₂-C₁₀) versus C₂/C₄, C₃/C₄ versus C₄/C₆, C₆/C₉ versus Ph/C₉, and C₂/Pyr versus C₂/ωC₂. (Figure S2), and relative abundance of C₂ in total diacid mass (i.e., C₂/ΣDiacids) versus relative humidity (RH) (%) during winter cruise. These observations suggest the formation of oxalic acid during winter from its

Table 2. Diagnostic Mass Ratios of Atmospheric Water-Soluble Organics for the Cruises Conducted in the North Pacific and Sea of Japan^a

Mass Ratios	# Winter					# Spring		# Early Summer		# Summer		# Late Summer		# Fall	
	December 1996	January 1997	April 1997	May–June 1997	July 1997	July 1997	September 1996	October 1995							
C ₂ /C ₄	4.2–8.8 (6.1 ± 1.5)	2.0–6.3 (4.2 ± 1.5)	1.4–4.2 (2.4 ± 0.9)	1.4–4.0 (2.4 ± 0.9)	1.4–4.0 (2.4 ± 0.9)	1.4–4.0 (2.4 ± 0.9)	2.6–5.5 (3.7 ± 0.9)	3.5–3.7 (3.6 ± 0.1)							
C ₃ /C ₄	0.4–0.9 (0.6 ± 0.2)	0.4–1.2 (0.8 ± 0.3)	0.4–1.2 (0.8 ± 0.3)	0.6–1.4 (1.0 ± 0.3)	0.7–1.6 (1.1 ± 0.3)	0.7–1.6 (1.1 ± 0.3)	0.9–1.8 (1.3 ± 0.2)	1.3–1.4 (1.3 ± 0.1)							
iC ₄ /C ₄	na	ND–1.7 (0.6 ± 0.9)	ND–1.7 (0.6 ± 0.9)	0.02–0.13 (0.07 ± 0.05)	0.01–0.17 (0.06 ± 0.06)	0.01–0.17 (0.06 ± 0.06)	0.02–0.11 (0.05 ± 0.03)	0.039–0.044 (0.041 ± 0.02)							
C ₂ /ωC ₂	4.7–9.6 (8.2 ± 1.7)	8.1–17.4 (11.6 ± 3.1)	8.1–17.4 (11.6 ± 3.1)	15.8–30.5 (22.5 ± 5.7)	9.9–30.3 (21.6 ± 6.4)	9.9–30.3 (21.6 ± 6.4)	12.3–22.3 (17.7 ± 3.1)	12.9–16.3 (14.3 ± 1.5)							
C ₆ /C ₉	1.9–3.5 (2.4 ± 0.7)	1.1–5.6 (3.6 ± 1.7)	1.1–5.6 (3.6 ± 1.7)	2.1–6.2 (3.5 ± 1.4)	2.3–5.3 (3.6 ± 1.1)	2.3–5.3 (3.6 ± 1.1)	1.2–5.7 (2.8 ± 1.4)	1.3–3.0 (1.9 ± 0.8)							
Ph/C ₉	ND–26.4 (10.5 ± 9.7)	4.3–17.0 (10.9 ± 4.7)	4.3–17.0 (10.9 ± 4.7)	0.2–3.9 (1.9 ± 1.1)	1.3–5.8 (2.8 ± 1.6)	1.3–5.8 (2.8 ± 1.6)	1.3–21.5 (4.3 ± 5.7)	4.5–8.7 (6.6 ± 1.9)							
M/F	0.10–0.40 (0.28 ± 0.14)	0.3–0.9 (0.6 ± 0.3)	0.3–0.9 (0.6 ± 0.3)	0.5–1.1 (0.6 ± 0.2)	0.4–1.0 (0.7 ± 0.2)	0.4–1.0 (0.7 ± 0.2)	0.3–1.1 (0.6 ± 0.2)	0.8–1.6 (1.3 ± 0.4)							
C ₂ /Σ(C ₂ –C ₁₀)	0.65–0.78 (0.72 ± 0.05)	0.5–0.7 (0.6 ± 0.1)	0.5–0.7 (0.6 ± 0.1)	0.3–0.6 (0.5 ± 0.1)	0.4–0.6 (0.5 ± 0.1)	0.4–0.6 (0.5 ± 0.1)	0.5–0.7 (0.6 ± 0.1)	0.57–0.59 (0.58 ± 0.01)							
hC ₄ /C ₄	0.17	0.02	0.02	0.01–0.06 (0.03 ± 0.02)	0.01–0.12 (0.04 ± 0.04)	0.01–0.12 (0.04 ± 0.04)	0.02–0.09 (0.05 ± 0.03)	ND–0.02 (0.02 ± 0.01)							
C ₂ /Pyr	6.4–19.3 (13.8 ± 4.9)	15.6–31.5 (21.4 ± 6.6)	15.6–31.5 (21.4 ± 6.6)	18.1–69.5 (32.0 ± 14.9)	18.5–83.1 (39.2 ± 18.7)	18.5–83.1 (39.2 ± 18.7)	17–52 (38 ± 12)	33–45 (39 ± 5)							
C ₂ /Gly	9–16 (11 ± 2)	10–40 (18 ± 10)	10–40 (18 ± 10)	20–62 (35 ± 14)	19–58 (36 ± 14)	19–58 (36 ± 14)	21–69 (40 ± 16)	48–77 (62 ± 13)							
C ₂ /MeGly	69–150 (94 ± 33)	43–109 (85 ± 23)	43–109 (85 ± 23)	148–433 (270 ± 105)	61–456 (238 ± 124)	61–456 (238 ± 124)	105–298 (171 ± 59)	169–253 (212 ± 41)							
ΣDiacids-C/WSOC (%)	0.7–4.2 (2.3 ± 1.1)	3.0–38.2 (13.9 ± 13.2)	3.0–38.2 (13.9 ± 13.2)	3.0–12.2 (6.8 ± 3.3)	4.0–10.4 (6.9 ± 1.8)	4.0–10.4 (6.9 ± 1.8)	1.8–13.0 (4.7 ± 3.2)	-							
ΣOxoacids-C/WSOC (%)	0.1–0.6 (0.3 ± 0.2)	0.4–3.9 (1.4 ± 1.3)	0.4–3.9 (1.4 ± 1.3)	0.2–0.7 (0.5 ± 0.2)	0.3–0.6 (0.5 ± 0.1)	0.3–0.6 (0.5 ± 0.1)	0.1–0.8 (0.3 ± 0.2)	-							
Σα-dicarbonyls-C/WSOC (%)	0.06–0.32 (0.20 ± 0.10)	0.2–2.4 (0.9 ± 0.8)	0.2–2.4 (0.9 ± 0.8)	0.07–0.25 (0.14 ± 0.07)	0.10–0.20 (0.16 ± 0.04)	0.10–0.20 (0.16 ± 0.04)	0.04–0.37 (0.12 ± 0.09)	-							
ΣDiacids-C/TC (%)	0.2–1.5 (0.5 ± 0.4)	0.6–6.6 (2.6 ± 2.1)	0.6–6.6 (2.6 ± 2.1)	0.8–6.2 (3.1 ± 1.9)	0.9–3.6 (2.4 ± 0.8)	0.9–3.6 (2.4 ± 0.8)	0.4–3.0 (1.5 ± 0.8)	3.8–6.3 (4.6 ± 1.1)							
ΣOxoacids-C/TC (%)	0.03–0.2 (0.1 ± 0.1)	0.1–0.7 (0.3 ± 0.2)	0.1–0.7 (0.3 ± 0.2)	0.1–0.4 (0.2 ± 0.1)	0.1–0.3 (0.2 ± 0.1)	0.1–0.3 (0.2 ± 0.1)	0.03–0.2 (0.1 ± 0.1)	0.3–0.5 (0.4 ± 0.1)							
Σα-dicarbonyls-C/TC (%)	0.02–0.11 (0.05 ± 0.03)	0.1–0.4 (0.2 ± 0.1)	0.1–0.4 (0.2 ± 0.1)	0.02–0.11 (0.06 ± 0.03)	0.03–0.09 (0.05 ± 0.02)	0.03–0.09 (0.05 ± 0.02)	0.01–0.08 (0.04 ± 0.02)	0.06–0.11 (0.09 ± 0.02)							
MSA/mss-SO ₄ ²⁻	0.13–0.42 (0.22 ± 0.14)	0.05–0.10 (0.08 ± 0.02)	0.05–0.10 (0.08 ± 0.02)	0.10–1.33 (0.33 ± 0.32)	0.12–0.70 (0.39 ± 0.21)	0.12–0.70 (0.39 ± 0.21)	0.08–0.22 (0.16 ± 0.05)	0.01–0.04 (0.03 ± 0.01)							

^aNote that the number signs refer to cruises conducted in the North Pacific, whereas the asterisk refers to “Sea of Japan”; na = not available.

higher homologues (i.e., C₃, C₄, and C₆) and isoprene oxidation products (i.e., Pyr and ωC₂) [Carlton *et al.*, 2009, and references therein]. Similar covariances were also found in the temporal trends for spring, early summer, summer, and late summer cruises (see Figures S3, S4, S5, and S6 in the supporting information, respectively). Although a similarity is also apparent in the temporal trends between C₂/ΣDiacids (%) and ambient RH (%) for winter, spring, and summer, such pattern is not evident for early summer and late summer due to minor spread in the RH (%) values during the cruises. However, both the parameters have not shown statistically significant difference among early summer, summer, and late summer.

The mass ratios of C₃/C₄ are relatively low in winter and spring samples compared to those in summer and fall samples (see Table 2). This observation suggests that higher ambient temperatures and, thus, enhanced photochemical production in summer and fall than in winter and spring can explain the higher mass ratios of C₃/C₄ over the North Pacific. Analogous to C₃/C₄, the mass ratios of oxalic acid to glyoxylic acid and pyruvic acid (C₂/ωC₂ and C₂/Pyr; Table 2), oxalic acid to methylglyoxal (C₂/MeGly; Table 2) in marine aerosols collected during summer and fall cruises, show higher values than those in winter and spring. The longitudinal variability of some diagnostic mass ratios of measured atmospheric water-soluble organic acids (C₂/C₄, C₂/ωC₂, and C₂/MeGly) is depicted in Figure 6. This observation hints that production of C₂ diacid in the MABL through aqueous-phase oxidation of ωC₂, Pyr, and MeGly, which are the photochemical oxidation products of marine isoprene, is an important process over the remote oceanic regions.

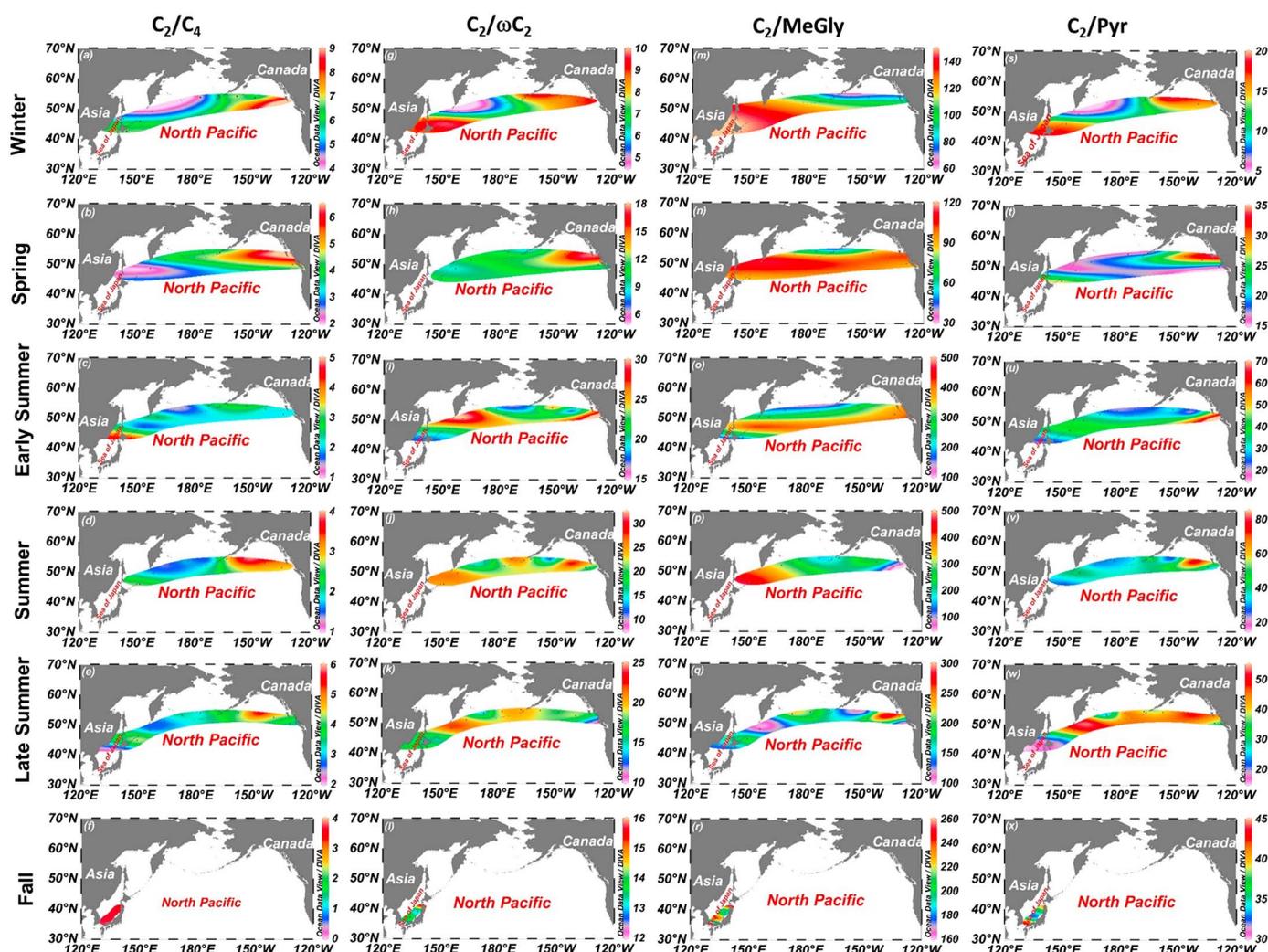


Figure 6. Longitudinal variability in the mass ratios of oxalic to succinic acid (C_2/C_4), oxalic to glyoxylic acid ($C_2/\omega C_2$), oxalic to pyruvic acid (C_2/Pyr), and oxalic acid to methylglyoxal ($C_2/MeGly$) in the aerosols collected from the North Pacific and Sea of Japan during 1995–1997.

It is difficult to ascribe the role of photochemical or heterogeneous reactions occurring in the MABL based on the chemical composition data. However, previous studies have suggested that atmospheric oxidation of gaseous isoprene leads to the formation of highly water-soluble and semivolatile α -dicarbonyls such as Gly and MeGly based on the laboratory experiment [Carlton *et al.*, 2007]. Soon after their production, they partition into cloud droplets and/or aerosol liquid water owing to their water solubility, followed by oxidation to ωC_2 and Pyr, which are further oxidized to less volatile oxalic acid [Carlton *et al.*, 2007]. Because the ambient RH levels are slightly higher (average $\sim 90\%$) in summer (although not significantly different than winter and spring), we believe that increase in mass ratios of C_2/Pyr , $C_2/\omega C_2$, C_2/Gly , and $C_2/MeGly$ in the MABL of North Pacific is due to aqueous-phase photochemical processes.

In this regard, the RH (%) data were examined to further understand the aqueous-phase reactions. No significant differences were observed for RH levels among all seasons (winter: $85 \pm 6\%$, spring: $87 \pm 9\%$, early summer: $91 \pm 6\%$, summer: $92 \pm 5\%$, and late summer: $89 \pm 4\%$). We have also estimated the liquid water content (LWC) of aerosols using a thermodynamic equilibrium model, ISORROPIA II [Fountoukis and Nenes, 2007]. In this study, ISORROPIA II is run as reverse problem in which aerosol composition and meteorological data are used to estimate the aerosol LWC. For the model, the ambient temperature and relative humidity obtained from NCEP reanalysis data and measured atmospheric abundances of water-soluble inorganic ions (Na^+ , SO_4^{2-} , NH_4^+ , NO_3^- , Cl^- , K^+ , Ca^{2+} , and Mg^{2+}) are chosen as input parameters

for the model. The estimated aerosol LWC is also consistent with RH (%) and has not shown significant variability among all cruises ($P > 0.05$, one-way analysis of variance (ANOVA) analysis; see Table S1 in the supporting information).

If we consider that RH levels and aerosol LWC are crucial for aqueous-phase chemical reactions within the MABL of the North Pacific, rather insignificant differences between winter/spring and summer/fall seasons alone cannot explain the increased mass concentrations of dicarboxylic acids and related polar compounds during summer cruises. It is interesting to note that ambient temperature during early summer and summer is relatively high compared to that of spring and winter (see Table S1 in the supporting information). Therefore, the photochemical oxidation process in the marine atmosphere can be an additional factor for the observed high concentrations of dicarboxylic acids in summer samples. However, it is likely that precursor compounds (e.g., unsaturated fatty acids) and BVOCs (e.g., isoprene and dimethyl sulphide: DMS) emitted from the ocean surface might also be an important factor for the increased atmospheric concentrations of measured water-soluble organic acids. This inference is supported by the higher atmospheric abundances of methanesulphonic acid (MSA), a proxy for marine-derived secondary organic aerosols (SOAs) from the oxidation of oceanic DMS [Bikkina *et al.*, 2014; Miyazaki *et al.*, 2011], together with concurrent increases in mass ratios of DMS oxidation products (i.e., MSA/non-sea-salt (nss)-SO₄²⁻) and isoprene oxidation products (C₂/Pyr, C₂/ωC₂, C₂/Gly, and C₂/MeGly) in summer than winter and spring in the North Pacific. The higher abundances of MSA in summer cruises (Table S1) are also consistent with satellite-derived chlorophyll *a* concentrations, whose images are given in Figure S1 in the supporting information for summer and fall cruises.

Previous study by Carlton *et al.* [2006] showed that gas-phase oxidation of isoprene leads to the formation of MeGly, which is water soluble. Its subsequent partition into cloud droplets and aerosol water leads to the production of Pyr. Furthermore, a laboratory experiment revealed that further aqueous-phase oxidation of Pyr results in the formation of oxalic acid [Carlton *et al.*, 2006]. Therefore, increases in C₂/Pyr and C₂/MeGly ratios in summer cruises (this study), during which higher biological activity is documented in the surface waters of the North Pacific (see Figure S1 in the supporting information [Mochida *et al.*, 2002]), demonstrate that BVOCs in the MABL and their aqueous-phase photochemical reactions can explain the observed increase of diacid concentrations.

Likewise, a laboratory experiment suggested that Gly oxidation in clouds (under the presence of acidic sulphate) with hydroxyl radical results in the formation of oxalic acid [Tan *et al.*, 2009]. More recently, Sinreich *et al.* [2010] documented higher concentrations of gaseous Gly over the open ocean waters of the North Pacific during fall season (20 October to 3 November 2008) as a part of VOCALS-REx, which is attributed to its formation from marine isoprene. Therefore, the higher biological activity in surface waters during summer cruises could lead to the enhanced atmospheric concentrations of precursor BVOCs such as DMS and isoprene via sea-to-air exchange. Previous studies have shown that DMS oxidation in the MABL leads to the formation of MSA and nss-SO₄²⁻, whereas isoprene oxidation leads to the formation of Gly, MeGly, Pyr, and ωC₂, which eventually result in oxalic acid (C₂) through aqueous phase photochemical reactions [Carlton *et al.*, 2009, and references therein].

In the pristine oceanic air masses sampled during summer cruises, we have observed significant increase in the mass concentrations of nss-SO₄²⁻ and MSA in the MABL. It is important to note that MSA concentrations are, in particular, higher in summer cruises (i.e., solely marine origin) than winter and spring (Table S1). In contrast, the continental air masses have higher nss-SO₄²⁻ abundances during winter (0.16–1.48 μg m⁻³; average 0.50 μg m⁻³) and spring (0.06–1.82 μg m⁻³; average 0.52 μg m⁻³) than in summer (0.15–0.23 μg m⁻³; average 0.12 μg m⁻³). Therefore, it is likely that coemission of both DMS and isoprene from the ocean surface during summer cruises can lead to increased concentrations of their oxidation products. In this context, the partition of Gly into cloud droplets, presence of acidic sulphate, and higher ambient temperature might have resulted in the increased mass ratio of C₂/Gly in summer cruises.

Our study is the first to report on atmospheric abundances of diacids and related compounds in aerosols sampled along the longitudinal transect across the Pacific Ocean in all seasons. Therefore, in order to understand the relative increase in C₂/Gly, C₂/Pyr, or other mass ratios in summer cruises in comparison to those in winter and spring season, we intended to compare our results with existing literature over this oceanic region. However, such chemical composition data are lacking in the literature from the North Pacific.

Table 3. Statistical Significance of Diagnostic Mass Ratios of Chemical Constituents in Aerosols Collected Over the North Pacific During 1996–1997

Diagnostic Ratios		C_2/C_4	C_3/C_4	$C_2/\omega C_2$	C_2/Pyr	C_2/MeGly	C_2/Gly	$C_2/\Sigma(C_2-C_{10})$
Winter	Spring	<0.05	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05
	Early summer	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	Summer	<0.05	<0.05	<0.05	<0.05	>0.05	<0.05	<0.05
	Late summer	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	Fall	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Spring	Winter	<0.05	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05
	Early summer	<0.05	>0.05	<0.05	>0.05	<0.05	<0.05	<0.05
	Summer	<0.05	>0.05	<0.05	<0.05	>0.05	<0.05	<0.05
	Late summer	>0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	Fall	>0.05	<0.05	>0.05	<0.05	<0.05	<0.05	>0.05
Early summer	Winter	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	Spring	<0.05	>0.05	<0.05	>0.05	<0.05	<0.05	<0.05
	Summer	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05
	Late summer	>0.05	<0.05	>0.05	>0.05	>0.05	>0.05	<0.05
	Fall	>0.05	<0.05	<0.05	>0.05	>0.05	<0.05	<0.05
Summer	Winter	<0.05	<0.05	<0.05	<0.05	>0.05	<0.05	<0.05
	Spring	<0.05	>0.05	<0.05	>0.05	>0.05	<0.05	<0.05
	Early summer	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05
	Late summer	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05	<0.05
	Fall	>0.05	>0.05	>0.05	>0.05	>0.05	<0.05	<0.05
Late summer	Winter	<0.05	<0.05	<0.05	<0.05	>0.05	<0.05	<0.05
	Spring	>0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	Early summer	>0.05	<0.05	>0.05	>0.05	>0.05	>0.05	<0.05
	Summer	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05	<0.05
	Fall	>0.05	>0.05	>0.05	>0.05	>0.05	<0.05	>0.05
Fall	Winter	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	Spring	>0.05	<0.05	>0.05	<0.05	<0.05	<0.05	>0.05
	Early summer	>0.05	<0.05	<0.05	>0.05	>0.05	<0.05	<0.05
	Summer	>0.05	>0.05	>0.05	>0.05	>0.05	<0.05	<0.05
	Late summer	>0.05	>0.05	>0.05	>0.05	>0.05	<0.05	>0.05
<i>F</i> statistic; <i>P</i> value at 95% confidence interval		<i>F</i> (5, 44) = 13.3; <0.05	<i>F</i> (5, 44) = 10.9; <0.05	<i>F</i> (5, 44) = 14.8; <0.05	<i>F</i> (5, 44) = 5.8; <0.05	<i>F</i> (5, 34) = 6.2; <0.05	<i>F</i> (5, 44) = 11.2; <0.05	<i>F</i> (5, 44) = 20.5; <0.05

Although some previous cruise data on diacids and related polar compounds were available [Fu *et al.*, 2013; Kawamura and Sakaguchi, 1999; Sempéré and Kawamura, 2003], they are mostly under the prevailing westerlies (i.e., under the influence of East Asian outflow). Therefore, we look for the Pacific Islands for which similar seasonal meteorological features are persisting. In this context, the long-term assessment of these characteristic mass ratios ($C_2/\omega C_2$, C_2/Pyr , and C_3/C_4) over the Gosan site, Jeju Island, (South Korea) by Kundu *et al.* [2010] reveals higher values during summer and fall. Similar to our study, the mass ratios of C_3/C_4 are higher in aerosol samples collected from Okinawa, the western North Pacific Rim, in August (i.e., summer) than winter months [Kunwar and Kawamura, 2014].

The apparent differences observed in the diagnostic mass ratios are also ascertained through one-way ANOVA analysis followed by posthoc's tests (see Table 3). The mass ratio of oxalic to succinic acid (i.e., C_2/C_4) in winter is significantly higher (Tables 2 and 3) than those documented for all other seasons. Likewise, C_2/C_4 ratio in spring is significantly lower than in winter but higher than in early summer and summer (Table 2), whereas it is comparable to those of late summer and fall samples. The decrease in C_2/C_4 ratio from winter to summer is consistent with the decrease of continental outflow from East Asia to the North Pacific. It has been suggested that C_2 , C_3 , and C_4 are produced from the photochemical oxidation (degradation) of their higher homologues [Kawamura and Sakaguchi, 1999; Yang *et al.*, 2008a, 2008b]. In this regard, previous studies have documented that C_2/C_4 can be used as a proxy for assessing aging of aerosols [Sorooshian *et al.*, 2007]. The higher C_2/C_4 values observed in winter and spring are consistent with those reported for Chinese cities (average 7.1) [Ho *et al.*, 2007], Sapporo (average 3.1) [Aggarwal and Kawamura, 2008], and South Korea (average 8.6) [Kundu *et al.*, 2010]. Although the fall season is a transition of winds from prevailing easterlies in summer to westerlies in winter and the Sea of Japan is very close to the Asian continent, the mass ratios of C_2/C_4 from this period can be compared with those for spring, which is also a transition period of wind patterns.

Since malonic acid (C_3) is a photochemical oxidation product of succinic acid (C_4) [Kawamura and Ikushima, 1993], C_3/C_4 ratio can be used to assess the extent of photochemical aging of aerosols [Aggarwal and Kawamura, 2008; Kunwar and Kawamura, 2014]. As mentioned above, C_3/C_4 ratio showed an increase from winter to summer (Table 2). We further examined the data to understand whether the apparent increase in C_3/C_4 ratio from winter to summer is statistically significant using one-way ANOVA analysis. We found that C_3/C_4 is significantly lower in winter than other seasons. Although C_3/C_4 ratio increased from winter to spring, the difference is not significant. Likewise, C_3/C_4 ratio in spring overlaps with those in early summer and summer (Table 3). Although C_3/C_4 ratio in early summer is consistent with those of winter, spring, and summer, it is significantly lower than those for late summer and fall. The C_3/C_4 values in summer cruise overlap with those in spring, early summer, late summer, and fall but significantly higher than winter samples. The ratios in late summer and fall samples are considerably higher than those for winter, spring, and early summer samples, being consistent with that reported for summer. Overall, the obvious increase in C_3/C_4 ratio from winter to summer indicates an enhanced photochemical aging of marine aerosols over the North Pacific and Sea of Japan, also being consistent with an increase in ambient temperature from winter/spring to summer/fall.

The statistical significance of other diagnostic mass ratios ($C_2/\omega C_2$, C_2/Pyr , C_2/MeGly , C_2/Gly , and $C_2/\Sigma(C_2-C_{10})$) among all seasons are shown in Table 3, where the ratios of winter cruise samples are consistent with those of spring samples. However, spring samples show distinctly lower values than those for other seasons (early summer, summer, late summer, and fall). Likewise, no significant differences were observed between winter and spring for all the above-mentioned mass ratios. For the mass ratio of $C_2/\omega C_2$, spring samples showed lower values than those for all the three summer cruises, which are comparable in magnitude to those obtained over the Sea of Japan during fall cruise.

As explained above, mass ratios of $C_2/\omega C_2$ in spring and fall samples are comparable owing to the fact that both sampling periods are in the transition of winds from westerlies to easterlies in spring and vice versa in fall. However, the $C_2/\omega C_2$ ratios in early summer cruise samples are consistent with those from summer and spring samples and are significantly higher than those for fall cruise. Likewise, the $C_2/\omega C_2$ values in summer, late summer, and fall cruises overlap each other but are significantly higher than those reported for winter and spring cruises. Except for few discrepancies as shown in Table 3, similar seasonal variability is observed for C_2/Pyr , C_2/Gly , and C_2/MeGly . The seasonal variability of relative abundance of C_2 in sum of total diacids (i.e., $C_2/\Sigma C_2-C_{10}$) is consistent with that of C_2/C_4 , which exhibits a decreasing trend from winter to summer samples.

It is important to note that the mass ratio of adipic to azelaic acid (C_6/C_9) is not significantly different among the cruises conducted over the North Pacific and Sea of Japan. Kawamura *et al.* [1996a] postulated that biogenic unsaturated fatty acids could lead to the formation of azelaic acid and other diacids (viz., adipic, glutaric, and succinic acids). Significant correlations ($P < 0.05$) between C_6 and C_9 in all cruises indicate their continuous production from photochemical oxidation of biogenic unsaturated fatty acids. We have also observed higher mass ratios of phthalic to azelaic acid ratios (Ph/C_9) during winter and spring than those of summer and fall cruise samples. It has been suggested that fossil-fuel combustion is a major source of Ph in ambient aerosols [Kawamura and Ikushima, 1993]. Therefore, the apparent increase in Ph/C_9 is implicit in the continental outflow sampled over the North Pacific during winter and spring cruises compared to the results of summer and fall seasons when pristine maritime air masses dominate in the North Pacific.

A comparison of certain diagnostic mass ratios of atmospheric abundances of diacids and related compounds ($C_2/\omega C_2$, C_2/MeGly , C_2/Pyr , and C_2/C_4) from this study with those documented over the North Pacific is presented in the Figure 7. The high mass ratios of $C_2/\omega C_2$ in summer (this study) are somewhat consistent with those documented over the WNP during similar time period (August–September 2008) by Bikkina *et al.* [2014] and other studies [Kawamura and Usukura, 1993; Sempéré and Kawamura, 2003]. In addition, the observed mass ratios of $C_2/\omega C_2$ from this study are also consistent with those documented over the remote Arctic Ocean during summer [Kawamura *et al.*, 2012]. Their study attributed the high ratios of $C_2/\omega C_2$ in the MABL to their production through aqueous-phase photochemical oxidation of isoprene, a BVOC emitted from the ocean surface during high biological activity.

As mentioned earlier, notably high concentrations of azelaic acid, a photochemical oxidation product of biogenic unsaturated fatty acid emitted from the ocean surface, in summer cruises from this study further

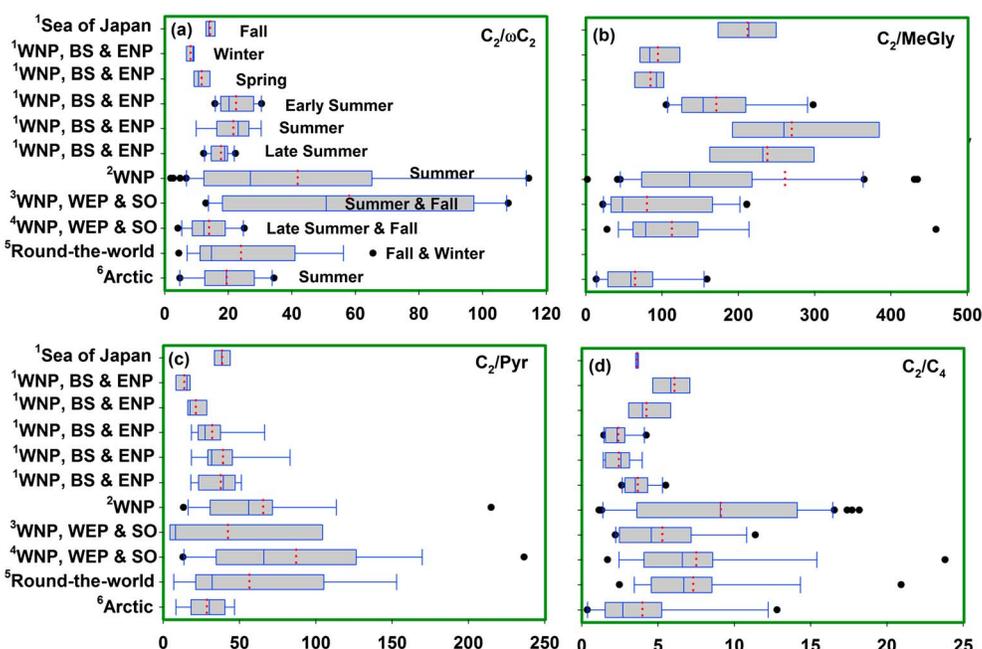


Figure 7. Box-whisker plots, showing the comparison of mass ratios of (a) oxalic to glyoxylic acids, (b) oxalic acid to methylglyoxal, (c) oxalic acid to pyruvic acid, and (d) oxalic to succinic acid, with other studies conducted from the North Pacific and other oceanic regions. Here the subscripts on sampling locations on y axis are as follows: 1 refers to “this study,” 2 refers to “Bikkina *et al.* [2014],” 3 refers to Kawamura and Usukura [1993], 4 refers to “Sempéré and Kawamura [2003],” 5 refers to “Fu *et al.* [2013],” and 6 refers to data from “Kawamura *et al.* [2012].” The boxes at lower and upper edges correspond to 25 and 75 percentile of the data, whereas the solid and dotted lines in the boxes refer to median and mean, respectively. The whiskers correspond to 5 and 95 percentile of the data, whereas the data correspond to less than 5 percentile, and more than 95 percentile are shown as outliers. Here WNP = western North Pacific, BS = Bering Sea, ENP = eastern North Pacific, WEP = western equatorial Pacific, and SO = Southern Ocean.

corroborate the high biological activity in the surface ocean. More recent study by Bikkina *et al.* [2014] suggested that azelaic acid and isoprene are significant sources of atmospheric diacids and related compounds over the open ocean waters of the North Pacific during a summer cruise. Therefore, the high mass ratios of $C_2/\omega C_2$ in summer and fall than winter and spring cruises could be explained by atmospheric oxidation of isoprene in the MABL. The temporal variability of other mass ratios such as C_2/MeGly and C_2/Pyr were also consistent with that of $C_2/\omega C_2$ for this study; the ratios show lower values in winter and spring compared to summer and fall seasons. As stated above, this trend is in contrast to that of C_2/C_4 ratios whose values were higher in winter and spring than in summer and fall. Several studies conducted over the North Pacific reveal an impact of continental outflow from East Asia during winter and spring [Fu *et al.*, 2013; Kawamura *et al.*, 2004; Kunwar and Kawamura, 2014; Sempéré and Kawamura, 2003].

Another remarkable feature of our data pertains to the relative abundances of oxalic acid (C_2) in total aliphatic diacids from C_2 to C_{10} (i.e., ΣC_2-C_{10}), showing higher values in winter and spring (~70%) than summer and fall cruises (~50%; see Table 2). This result can be explained by relatively more aged air masses by long-range transport over the North Pacific in winter and spring than the pristine maritime air masses during the summer and fall cruises. Figure 8 depicts pie diagrams, showing the seasonally averaged relative abundances of individual diacids for all cruises conducted in the North Pacific and Sea of Japan. From this figure, it is obvious that relative abundances of C_2 are somewhat higher in winter and spring than other seasons. In contrast, relative abundances of C_3 and C_4 are higher in summer and fall cruise samples. Kawamura *et al.* [2012] suggested that oxalic acid can undergo further photochemical oxidation over the Arctic Ocean. Therefore, we hypothesize that lower relative abundance of C_2 in the marine aerosols could also be possible during summer. However, the depletion of oxalic acid in the Arctic Ocean aerosols and its comparable concentration with C_4 diacid are in contrast to this study during summer, where C_2 is dominant followed by C_3 and C_4 .

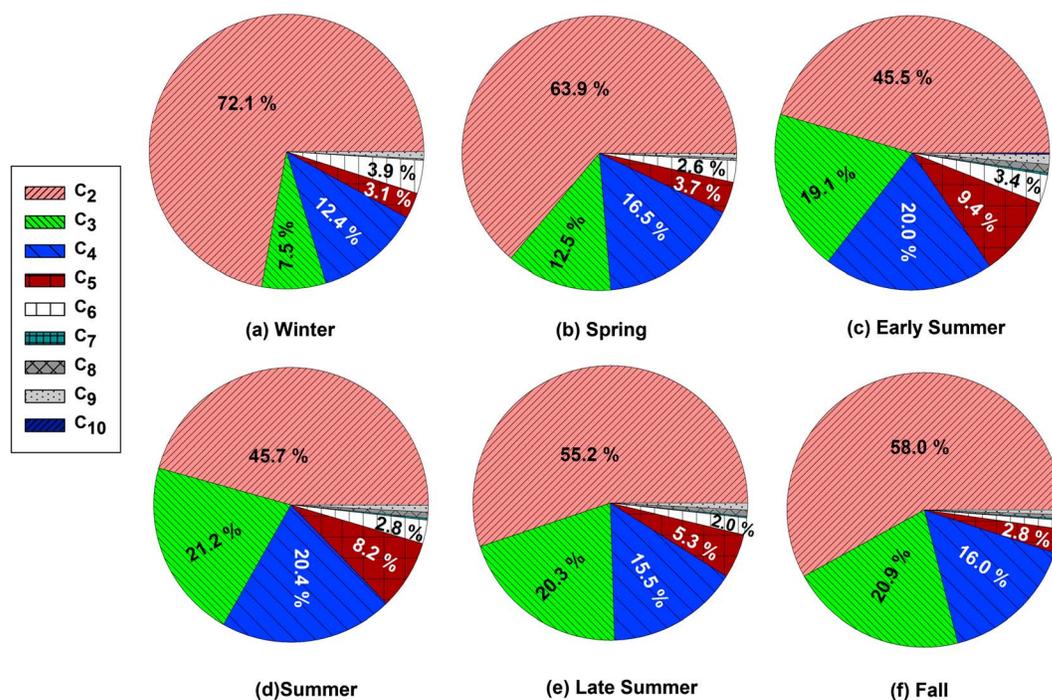


Figure 8. Pie charts showing the fractional abundances of individual aliphatic diacid in total diacids (ΣC_2-C_{10}) in aerosols collected from the Sea of Japan and North Pacific during *M/S Skaugran* cruises conducted for different seasons during 1994–1997: (a) winter, (b) spring, (c) early summer, (d) summer, (e) late summer, and (f) fall.

The higher relative abundances of C_2 diacid in winter and spring samples ($\sim 70\%$) may be linked to the impact of continental outflow from East Asia to the North Pacific. However, lower relative abundances of oxalic acid (45–60%) in pristine maritime air masses sampled during summer and fall cruises can have significant contribution from oceanic source. As mentioned earlier, the satellite image of chlorophyll *a* concentrations in the surface waters of the North Pacific during summer and fall shows enhanced biological activity (see Figure S1 in the supporting information, obtained from *Mochida et al.* [2002]). Interestingly, the measured atmospheric abundances of MSA during early summer (geomean: 73 ng m^{-3}) and summer (45 ng m^{-3}) are higher than those obtained in winter (39 ng m^{-3}) and spring (26 ng m^{-3}). MSA was not detected in few samples collected in winter ($N=2$) and spring ($N=4$) cruises; because of the range span over an order of magnitude, we used geometric mean concentrations. In contrast, MSA is detected in all the samples during early summer and summer.

In addition, we have observed a significant increase in mass ratios of $\text{MSA}/\text{nss-SO}_4^{2-}$ over the North Pacific during early summer (average 0.33) and summer (0.39) cruises compared to lower ratios in winter (0.18) and spring (0.08). It has been suggested that MSA and nss-SO_4^{2-} over the open ocean are produced by the atmospheric oxidation of dimethyl sulphide (DMS), a biogenic VOC emitted into the water column during phytoplankton bloom followed by the subsequent sea-to-air transport. Likewise, the marine productivity is also shown to influence the isoprene emissions into the surface water. Similar to DMS oxidation, isoprene oxidation in the MABL results in the formation of various water-soluble compounds such as Pyr, ωC_2 , Gly, and MeGly. This observation clearly indicates the influence of marine biological activity on SOA formation in summer than winter and spring. Concurrent increase in $\text{MSA}/\text{nss-SO}_4^{2-}$, C_2/Pyr , $C_2/\omega C_2$, C_2/Gly , and C_2/MeGly ratios (see Table 2) in summer months compared to winter and spring indicate a significant production of marine-derived SOA over the North Pacific.

Although C_3/C_4 ratio that is a proxy to assess the photochemical aging of air masses sampled from the MABL [*Kawamura and Sakaguchi*, 1999] is higher in summer and fall than in winter and spring (Table 2), the former samples are mostly influenced by oceanic source and the prevailing meteorology does not favor the continental transport. The more aged nature of aerosols sampled in winter and spring compared to summer and fall is also reflected in the molecular distribution. As mentioned earlier, the chemical composition data

Table 4. Correlation Matrices for the Chemical Constituents Measured in Aerosols Collected From the North Pacific and Sea of Japan During 1995–1997

Winter	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉	Ph	Pyr	ω C ₂	MeGly
C ₂	1.00									
C ₃	0.89	1.00								
C ₄	0.87	0.97	1.00							
C ₅	0.86	0.78	0.87	1.00						
C ₆	0.51	0.51	0.67	0.78	1.00					
C ₉	0.59	0.66	0.68	0.71	0.98	1.00				
Ph	0.48	0.66	0.71	0.57	0.78	0.98	1.00			
Pyr	0.71	0.80	0.89	0.82	0.90	0.95	0.92	1.00		
ω C ₂	0.93	0.91	0.96	0.93	0.77	0.79	0.68	0.90	1.00	
MeGly	0.56	0.80	0.73	0.37	0.08	0.22	0.40	0.43	0.55	1.00
Spring	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉	Ph	Pyr	ω C ₂	MeGly
C ₂	1.00									
C ₃	1.00	1.00								
C ₄	0.99	0.99	1.00							
C ₅	0.99	0.99	1.00	1.00						
C ₆	0.97	0.97	0.99	0.99	1.00					
C ₉	0.91	0.91	0.88	0.85	0.84	1.00				
Ph	0.93	0.93	0.96	0.96	0.98	0.86	1.00			
Pyr	0.99	0.99	0.97	0.96	0.94	0.95	0.92	1.00		
ω C ₂	1.00	1.00	1.00	0.99	0.97	0.91	0.95	0.99	1.00	
MeGly	1.00	1.00	0.99	0.98	0.95	0.90	0.91	0.98	1.00	1.00
Early summer	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉	Ph	Pyr	ω C ₂	MeGly
C ₂	1.00									
C ₃	0.72	1.00								
C ₄	0.85	0.88	1.00							
C ₅	0.45	0.89	0.81	1.00						
C ₆	0.04	0.66	0.38	0.80	1.00					
C ₉	−0.06	0.57	0.23	0.64	0.80	1.00				
Ph	−0.10	−0.29	−0.04	−0.09	−0.02	−0.48	1.00			
Pyr	0.80	0.73	0.66	0.43	0.21	0.14	−0.15	1.00		
ω C ₂	0.90	0.66	0.81	0.46	0.11	−0.12	0.17	0.87	1.00	
MeGly	0.67	0.64	0.41	0.23	0.14	0.23	−0.42	0.88	0.58	1.00
Summer	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉	Ph	Pyr	ω C ₂	MeGly
C ₂	1.00									
C ₃	0.90	1.00								
C ₄	0.70	0.88	1.00							
C ₅	0.42	0.68	0.87	1.00						
C ₆	0.37	0.55	0.75	0.92	1.00					
C ₉	0.50	0.65	0.72	0.89	0.78	1.00				
Ph	0.29	0.22	0.25	0.09	0.20	0.10	1.00			
Pyr	0.55	0.60	0.66	0.75	0.84	0.67	−0.01	1.00		
ω C ₂	0.94	0.80	0.62	0.39	0.44	0.50	0.50	0.56	1.00	
MeGly	0.41	0.47	0.19	0.25	0.14	0.52	0.29	0.14	0.44	1.00
Late summer	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉	Ph	Pyr	ω C ₂	MeGly
C ₂	1.00									
C ₃	0.96	1.00								
C ₄	0.96	0.97	1.00							
C ₅	0.77	0.87	0.88	1.00						
C ₆	0.72	0.85	0.82	0.98	1.00					
C ₉	0.51	0.67	0.57	0.80	0.89	1.00				
Ph	0.40	0.35	0.52	0.59	0.47	0.18	1.00			
Pyr	0.66	0.74	0.67	0.84	0.90	0.91	0.31	1.00		
ω C ₂	0.97	0.96	0.92	0.80	0.78	0.66	0.30	0.77	1.00	
MeGly	0.94	0.89	0.95	0.80	0.71	0.45	0.58	0.58	0.89	1.00

Table 4. (continued)

Fall	C ₂	C ₃	C ₄	C ₅	C ₆	C ₉	Ph	Pyr	ωC ₂	MeGly
C ₂	1.00									
C ₃	1.00	1.00								
C ₄	1.00	1.00	1.00							
C ₅	0.98	0.98	0.99	1.00						
C ₆	0.97	0.95	0.96	0.93	1.00					
C ₉	0.94	0.94	0.95	0.98	0.85	1.00				
Ph	0.99	0.99	0.99	0.96	0.92	0.92	1.00			
Pyr	0.98	0.98	0.98	1.00	0.90	0.99	0.97	1.00		
ωC ₂	0.97	0.96	0.97	0.97	0.99	0.91	0.92	0.94	1.00	
MeGly	0.90	0.87	0.88	0.89	0.97	0.81	0.82	0.84	0.97	1.00

for the North Pacific during winter and spring are characterized by the predominance of C₂ followed by C₄ and C₃. In contrast, the aerosol samples collected during summer and fall cruises show the order of C₂ > C₃ ≥ C₄. All these observations are consistent with the seasonal meteorological pattern, transport of organic aerosols from East Asia during strong westerly winds that occur in winter and spring, whereas pristine oceanic conditions exist during summer with easterlies.

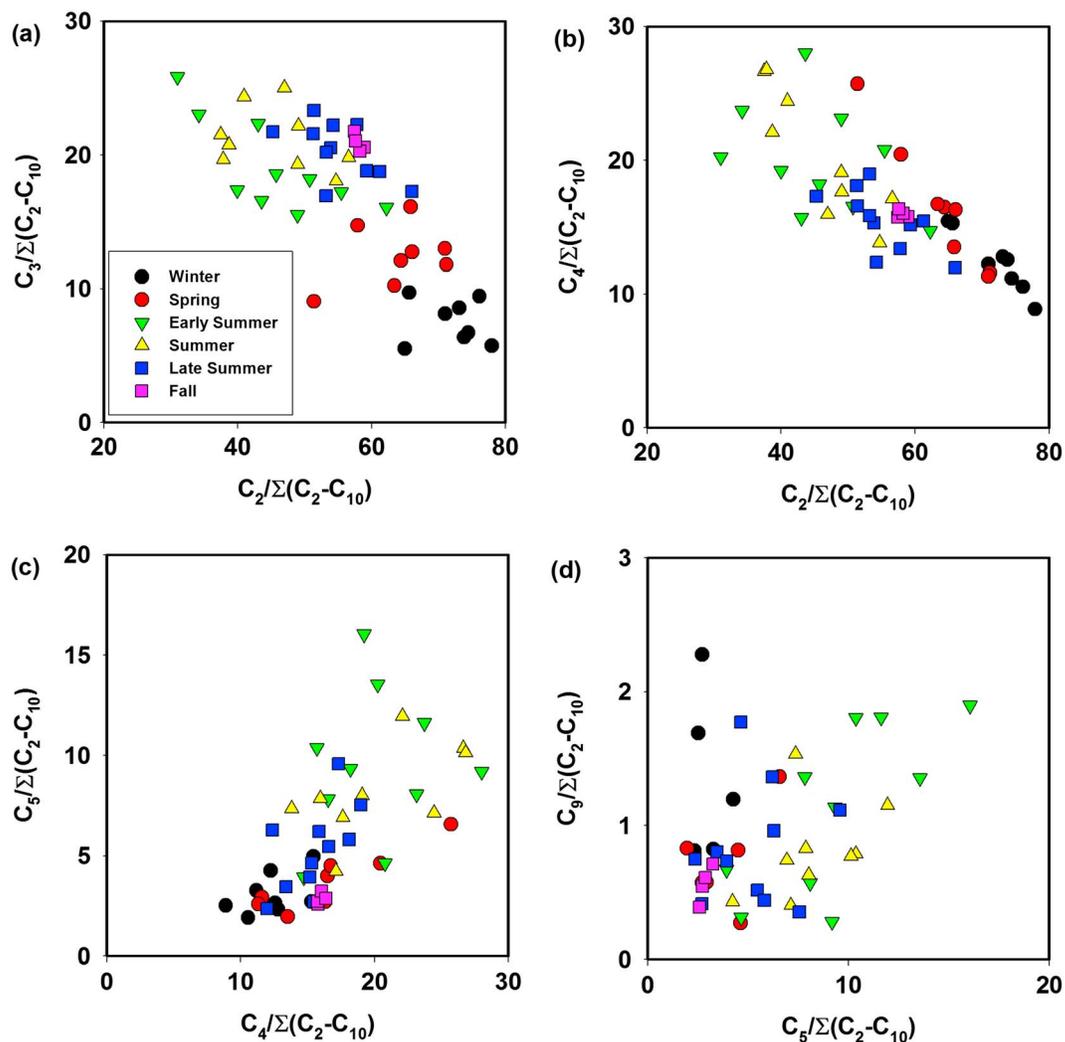


Figure 9. Scatterplots between the relative abundances of C₂ in their total aliphatic homologues (ΣC₂-C₁₀) with that of (a) malonic acid and (b) succinic acid. Likewise, scatterplots showing the relative abundances of C₅ in ΣC₂-C₁₀ with those of (c) C₄ and (d) C₉ diacids.

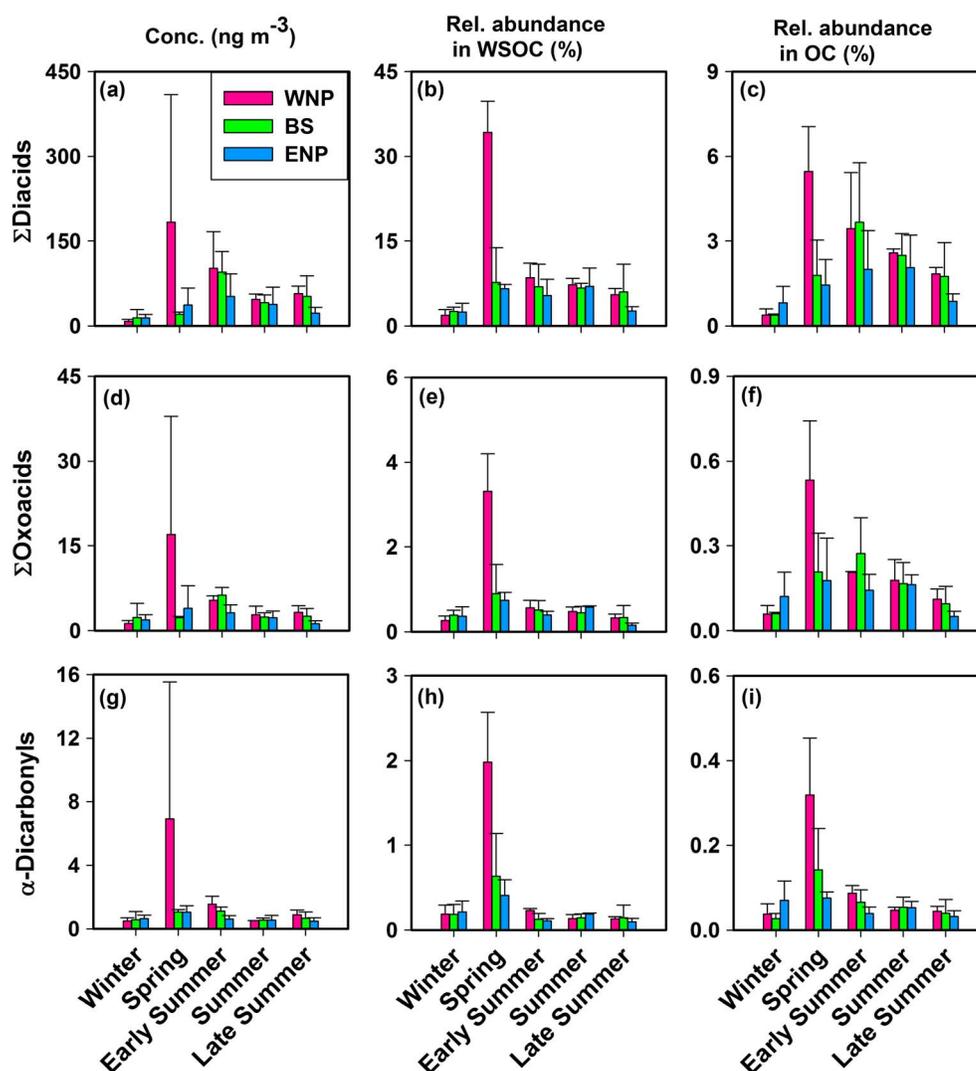


Figure 10. Bar graphs showing mean and standard deviation of total mass concentration of (a–c) diacids, (d–f) oxoacids, and (g–i) α -dicarbonyls and their relative abundances in WSOC and TC for the cruises conducted in the North Pacific.

3.5. Possible Sources and Formation Pathways

In order to infer possible sources of measured atmospheric water-soluble organic acids, multiple linear regression analyses have been carried out for selected chemical constituents. The correlation matrices for all cruises conducted in the North Pacific and Sea of Japan are given in Table 4. Significant correlations among C_2 , C_3 , and C_4 in all cruises suggest their common source. It is also noteworthy that moderate correlations are observed between C_6 and C_9 . It has been suggested that during the long-range atmospheric transport, photochemical oxidation of biogenic unsaturated fatty acids could lead to the formation of azelaic acid (C_9), which is further oxidized to result in shorter-chain homologues such as adipic, glutaric, and succinic acids [Kawamura *et al.*, 1996a; Kawamura and Sakaguchi, 1999; Kawamura *et al.*, 1996b]. Good correlations were also observed among pyruvic acid (Pyr), glyoxylic acid (ωC_2), and methylglyoxal (MeGly). It has been suggested that the biogenic volatile organic compounds emitted from the ocean surface (e.g., isoprene) lead to the formation of Pyr, ωC_2 , and MeGly in the MABL through aqueous-phase chemistry [Bikkina *et al.*, 2014; Carlton *et al.*, 2006; Ervens *et al.*, 2008].

In all cruises conducted over the open ocean waters of the North Pacific and Sea of Japan, relative abundances of C_2 in ΣC_2 - C_{10} exhibit negative correlations with those of C_3 and C_4 diacids (Figures 9a and 9b). This result suggests a possible formation of oxalic acid from malonic and succinic acids. However, it is important to note

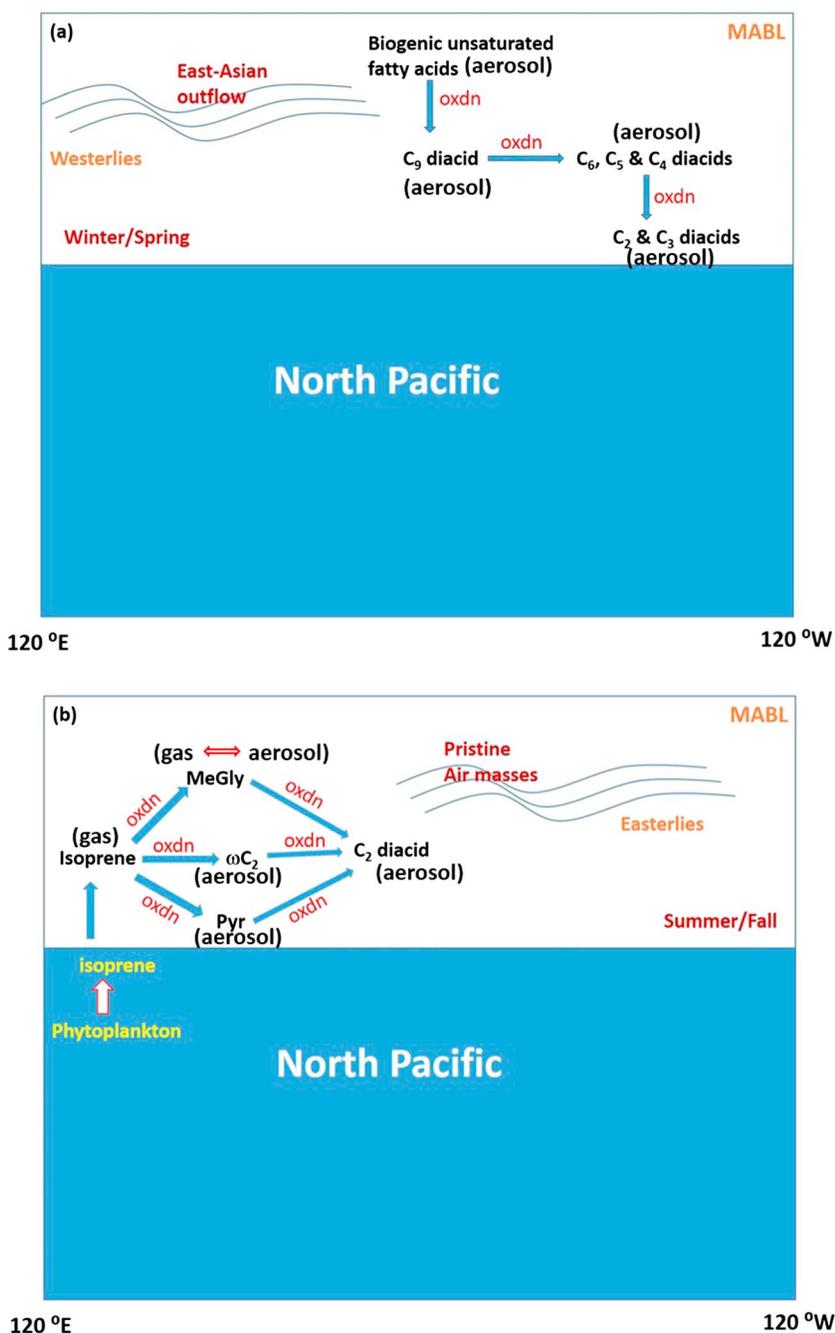


Figure 11. A schematic representation of prevailing atmospheric formation pathways of diacids in the marine atmospheric boundary layer (MABL) of the North Pacific during (a) winter and spring and (b) summer and fall.

that the relative abundance of C₄ in ΣC₂-C₁₀ shows a positive linear relation with glutaric acid (C₅ diacid; Figure 9c). In addition, a similar trend is obtained between the relative abundances of glutaric and azelaic acids (C₉; Figure 9d). It has also been suggested that C₉ diacid is further subjected to photochemical transformations in the MABL, leading to the formation of lower homologues such as adipic, glutaric, and succinic acids as stated above. Thus, the observed linear trends among the relative abundances of C₂, C₃, C₄, C₅, and C₉ hint the formation of oxalic acid. Based on the correlations, we hypothesize that photochemical and aqueous-phase oxidation of biogenic unsaturated fatty acids and isoprene could lead to the formation of water-soluble organic acids in the MABL of the North Pacific and Sea of Japan.

4. Contributions of Diacids to WSOC and TC

The percent contributions of total diacids to WSOC show lower values in winter (average $2.3 \pm 1.1\%$) and higher values in spring cruise samples ($14 \pm 13\%$), reaching as high as 38%. For remaining cruises conducted in the North Pacific and Sea of Japan, the relative contributions of total diacids to WSOC are in between 2.3% (winter) and 14% (spring) (Table 2). Similar pattern is also obtained for oxoacids and α -dicarbonyls, whose contributions to WSOC are higher in spring than other seasons (Table 2). By combining all the cruise data, we infer that the percent contribution of measured water-soluble diacids, oxoacids, and α -dicarbonyls in WSOC range from 0.7 to 38%, 0.1 to 3.9%, and 0.06 to 2.4%, respectively. Similarly, the percent contributions of these compounds to total carbon (TC) vary from 0.2 to 6.6%, 0.03 to 0.75%, and 0.02 to 0.4%, respectively, for the six cruises conducted in the North Pacific and Sea of Japan.

In order to assess the spatial and seasonal variability of relative abundances of organic acids and dicarbonyls in WSOC and TC, their seasonally averaged mean concentrations were compared among three oceanic regions (the WNP, BS, and ENP) and are presented in Figure 10. From this figure, higher concentrations of water-soluble organic acids and dicarbonyls are found in the WNP, and thus, their higher contributions to WSOC and TC are obtained in spring compared to other seasons. The atmospheric abundances over the WNP are also higher than those over the BS and ENP. However, as mentioned earlier, the mass concentrations of diacids, oxoacids, and α -dicarbonyls over the BS are comparable with the WNP and higher than those over the ENP during early summer cruise, due to the enhanced biological activity and thereby oceanic emissions of BVOCs and unsaturated fatty acids in the MABL.

5. Conclusions

In this study, we aim to assess the seasonal variability of atmospheric abundances of diacids, oxoacids, and α -dicarbonyls along the longitudinal transect of the cruises conducted in the North Pacific and Sea of Japan. In general, higher atmospheric loadings were observed for samples collected over the western North Pacific compared to those over the Bering Sea and eastern North Pacific. However, comparable atmospheric concentrations of diacids were found in the Bering Sea and western North Pacific during summer and fall seasons. The long-range atmospheric transport of pollutants to the MABL influences the abundances of diacids and related compounds over the open ocean waters of the North Pacific and Sea of Japan during winter and spring. However, the oceanic source dominates the distributions of these species in the MABL during summer and fall when the continental outflow is weakened. A schematic representation of these processes in the marine atmospheric boundary layer of the North Pacific and Sea of Japan is shown in Figure 11. Relatively high mass ratios of oxalic to glyoxylic acid and pyruvic acid, and oxalic acid to methylglyoxal over the North Pacific and Sea of Japan, suggest the production of C_2 diacid through aqueous-phase oxidation of short-chain water-soluble organic acids. Further, higher concentrations of azelaic acid, a photochemical oxidation product of biogenic unsaturated fatty acids emitted from the ocean, attest a significance of marine source over the Bering Sea during early summer.

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Erratum

In the originally published version of this article, page 5193, section 2.2, last paragraph, lines 4 and 5, and page 5199, line 3 from the bottom, were erroneous. The lines have since been corrected and this version may be considered the authoritative version of record.