

## Size distributions and chemical characterization of water-soluble organic aerosols over the western North Pacific in summer

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[1] Size-segregated aerosol samples were collected over the western North Pacific in summer 2008 to investigate marine biological contribution to organic aerosols. The samples were analyzed for organic carbon (OC), water-soluble organic carbon (WSOC), and water-soluble organic compounds including diacids (C<sub>2</sub>–C<sub>9</sub>), ω-oxocarboxylic acids, and α-dicarbonyls as well as methanesulfonic acid (MSA). The average concentrations of OC and oxalic acid (C<sub>2</sub>) were approximately two to three times larger in marine biologically more influenced aerosols, defined by the concentrations of MSA and azelaic acid (C<sub>9</sub>), than in less influenced aerosols. WSOC, which showed a statistically significant correlation with MSA, accounted for 15–21% of total mass of the components determined in the submicrometer range of biologically more influenced aerosols. These values are comparable to those of water-insoluble organic carbon (WIOC) (~14–23%), suggesting that organic aerosols in this region are enriched in secondary organic aerosols (SOA) linked to oceanic biological activity. In these aerosols, substantial fractions of C<sub>2</sub>–C<sub>4</sub> diacids were found in the submicrometer size range. Positive correlations of oxalic acid with C<sub>3</sub>–C<sub>5</sub> diacids and glyoxylic acid suggest that secondary production of oxalic acid occurs possibly in the aqueous aerosol phase via the oxidation of longer-chain diacids and glyoxylic acid in the oceanic region with higher biological productivity. We found similar concentration levels and size distributions of methylglyoxal between the two types of aerosols, suggesting that formation of oxalic acid via the oxidation of methylglyoxal from marine isoprene is insignificant in the study region.

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### 1. Introduction

[2] Marine aerosol contributes significantly to the Earth's radiative forcing and biogeochemical cycling of materials including carbon and nitrogen, impacting ecosystems and even regional air quality. Marine aerosols are composed of primary and secondary organic and inorganic components. An oceanic source of organic carbon (OC) aerosol has been recognized for many years, and significant concentrations of OC have been observed in several oceanic regions [Cavalli *et al.*, 2004; O'Dowd *et al.*, 2004; O'Dowd and de Leeuw, 2007; Spracklen *et al.*, 2008; Sciare *et al.*, 2009]. Primary emissions of biogenic organic matter by sea spray [e.g., O'Dowd *et al.*, 2004] have been suggested as possible mechanisms by which phytoplankton can modulate the chemical and physical properties of marine clouds. Laboratory experiments showed that bursting bubbles at the ocean surface produce significant numbers of submicrometer aero-

sols enriched with organics [Keene *et al.*, 2007]. In fact, a recent field study indicated that during periods of high biological activity and high wind speed, the organic component of marine aerosols exhibited considerable water uptake ability over the eastern Pacific Ocean [Sorooshian *et al.*, 2009], which could influence cloud microphysics. However, the role of organic compounds in remote marine aerosol remains largely uncertain, mainly due to the lack of comprehensive and quantitative measurements of their size-dependent chemical composition.

[3] The mechanisms responsible for secondary organic aerosol (SOA) formation in the marine atmosphere have not been fully clarified, although they are considered very important. Meskhidze and Nenes [2006] suggested that marine isoprene emissions could explain observed correlations between chlorophyll *a* and cloud droplet sizes observed by satellite. However, more recent studies have suggested that the abundance of marine atmospheric OC is much higher than can be explained by production from isoprene emissions alone [Spracklen *et al.*, 2008; Arnold *et al.*, 2009]. Laboratory and shipboard experiments by Yassaa *et al.* [2008] showed evidence of marine production of monoterpenes in areas of active phytoplankton bloom. Additionally, enrichment of OC

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having heteroatoms (halogens [Carpenter *et al.*, 2003], sulfur [Claeys *et al.*, 2010], and nitrogen [Miyazaki *et al.*, 2010]) in gas/particle phases in the marine atmosphere provides another indication of the potential biological sources for marine organic aerosols. Despite their importance, however, the global emission of oceanic OC aerosols is still highly uncertain.

[4] The North Pacific is influenced by Asian anthropogenic outflows, particularly in winter and spring, which transport anthropogenic gaseous species and particulate matter as well as dust particles to the remote marine atmosphere [e.g., Huebert *et al.*, 2003]. Previous studies on organic aerosols over this region have mostly been conducted on the continental outflows of terrestrial plants/soil [Matsumoto *et al.*, 2001; Kawamura *et al.*, 2003] and anthropogenic combustion products [e.g., Mochida *et al.*, 2003, 2007; Mader *et al.*, 2004; Simoneit *et al.*, 2004; Miyazaki *et al.*, 2007]. In contrast, in summer, large regions of the western North Pacific experience frequent intrusion of air from the south and southeast due to the persistent Pacific high pressure system. In addition, over the western North Pacific, massive phytoplankton blooms occur every spring [e.g., Kasai *et al.*, 1998] and last until summer. Consequently, the western North Pacific in summer is a suitable region for studying the effects of oceanic emissions on marine aerosols.

[5] We investigated the size-segregated chemical composition of marine aerosol samples collected over the remote western North Pacific during July–August 2008, coinciding with high biological activity periods in the study region. Here we show concentrations and size distributions of both bulk carbon and molecular compositions (dicarboxylic acids, ketocarboxylic acids, and  $\alpha$ -dicarbonyls) in water-soluble organic aerosols in the marine atmosphere. The objective of this study is to evaluate the contribution of marine biological sources to the organic aerosols over the western North Pacific. We aim to characterize chemical compositions and possible formation pathways of the water-soluble organics in remote marine aerosols during the period of high biological activity in this region.

## 2. Experiments

### 2.1. Aerosol Sampling

[6] Aerosol sampling was conducted from 29 July to 19 August 2008 on board the *R/V Hakuho Maru*. The sampling was carried out during the first half of cruise KH08-2 from Tokyo to Kushiro, Japan, over the western North Pacific [Miyazaki *et al.*, 2010]. Figure 1 shows the cruise track together with monthly averaged concentrations of chlorophyll *a* for August 2008 and typical 5-day back trajectories. The chlorophyll *a* concentrations were derived from SeaWiFS data, available at NASA's Goddard Space Flight Center/Distributed Active Archive Centers (<http://reason.gsfc.nasa.gov/OPS/Giovanni/ocean.aqua.shtml>). The trajectories were calculated for air masses starting from the middle points of each sampling at altitudes of 50, 100, and 200 m. For the calculation, we used the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (<http://www.arl.noaa.gov/ready/hysplit4.html>, NOAA Air Resources Laboratory, Silver Spring, MD, USA). During summer in the western North Pacific, frequent intrusion of air from the south and southeast occurs due to the prevailing

high-pressure condition over the Pacific, as suggested by the back trajectories (Figures 1b and 1c).

[7] A cascade impactor was used to collect ambient aerosols in nine size fractions, according to the following 50% equivalent aerodynamic cutoff diameters: 0.39, 0.58, 1.0, 1.9, 3.0, 4.3, 6.4, and 10.0  $\mu\text{m}$  [Miyazaki *et al.*, 2010]. The ambient samples were collected on precombusted (450°C, 3 h) quartz filters. The impactor was set on the deck above the bridge of the ship. Marine air was drawn at a flow rate of 7.2  $\text{m}^3 \text{h}^{-1}$  for 48–72 h per sample without temperature and humidity control. Possible contamination from the ship exhaust was avoided by shutting off the sampling pump when air came from the beam and/or when the wind speed was low ( $<5 \text{ m s}^{-1}$ ). This resulted in an effective pumping time of about 82% of the sampling period. In total, seven sets of the collected samples are used for the present analysis.

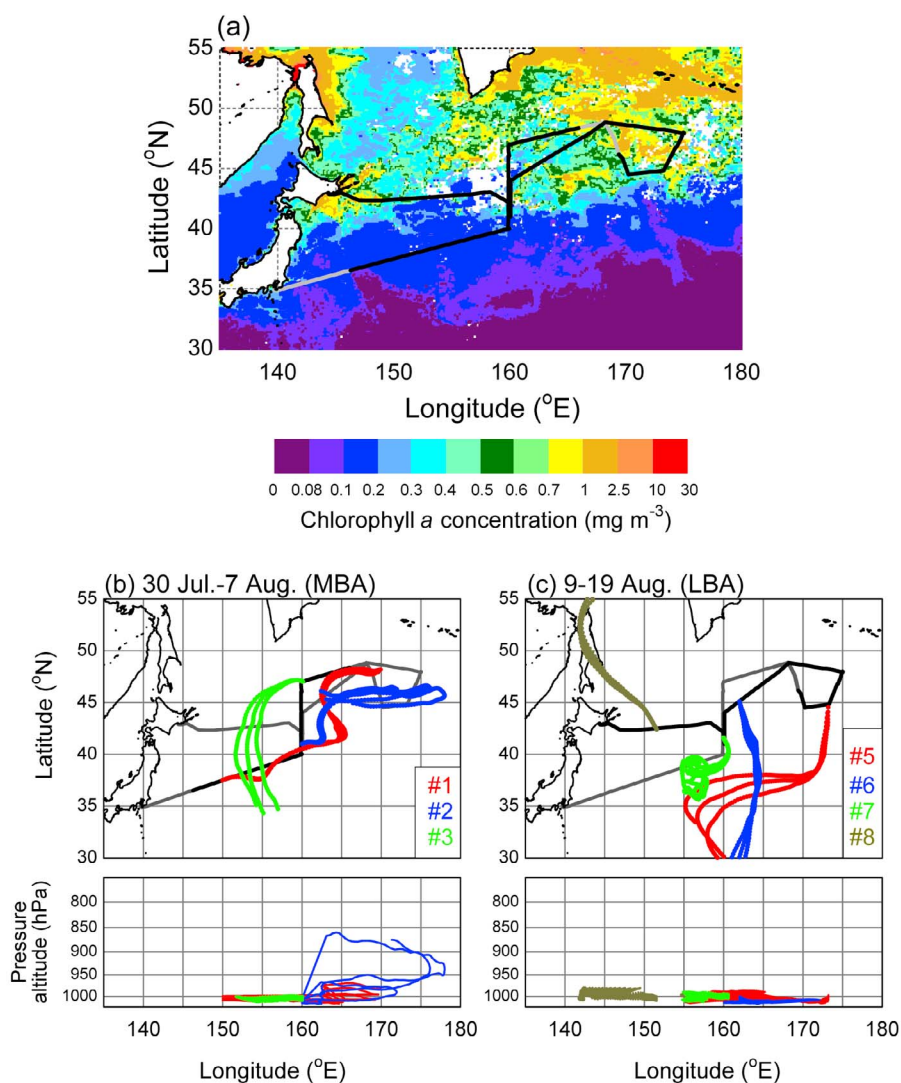
### 2.2. Organic and Elemental Carbon

[8] OC and elemental carbon (EC) were measured using a Sunset Lab OC/EC analyzer (Sunset Laboratory, Inc., Tigard, OR, USA) [Birch and Cary, 1996]. In this study, we used a temperature protocol [e.g., Miyazaki *et al.*, 2009] based on that proposed by the National Institute for Occupational Safety and Health (NIOSH). Possible interferences for the OC measurements were assessed by the measurement of field blanks. The OC concentration of field blanks equivalent to that for ambient aerosols accounted for 18% of the average OC concentrations of the real samples. The blank variability for OC in all stages is  $\pm 15 \text{ ngC cm}^{-2}$ . The OC data presented here were all corrected against field blanks. The analytical errors were tested by analyzing different sections of the same filter sample three times. The coefficient of deviation was less than 7% for OC and 3% for EC. Overall random uncertainty of the average OC concentration in each stage is estimated to be less than 19% by calculating error propagation. We did not use a carbon denuder during the sampling. In this case, the positive artifact such as adsorption of gaseous species to filters may be more significant in the lowest stage (i.e., backup filters). However, this uncertainty does not significantly affect the discussion and conclusions in this study as discussed in section 3.

### 2.3. WSOC, Methanesulfonic Acid, and Inorganic Species

[9] A filter cut of 1.54  $\text{cm}^2$  was extracted with ultrapure Milli-Q water using an ultrasonic bath (10 min  $\times$  3 times). The total extracts (10 ml) were then filtrated with a disc filter (Millex-GV, 0.22  $\mu\text{m}$ ; Millipore, Billerica, MA, USA). Dissolved OC in the extracts was then determined by a total organic carbon (TOC) analyzer (model 810; Sievers Corp., Boulder, CO, USA) [Miyazaki *et al.*, 2006]. Analyses were duplicated for several filter samples, and a good reproducibility was obtained with a mean deviation of  $1.0 \pm 0.5\%$  between the measurements. Using the measured mass concentrations of OC and WSOC, water-insoluble OC (WIOC) was defined as  $\text{WIOC} = \text{OC} - \text{WSOC}$ . The overall uncertainties of the average WSOC and WIOC concentrations are estimated to be 16% and 24%, respectively.

[10] The water extracts from the samples were also filtrated with a membrane disc filter. Major anions, including methanesulfonic acid (MSA), and cations were determined with Metrohm ion chromatographs (model 761 compact IC;



**Figure 1.** (a) A map of the *R/V Hakuho* cruise track in the western North Pacific, together with monthly averaged concentrations of chlorophyll *a*, for August 2008 derived from SeaWiFS data (available at NASA Goddard Space Flight Center/Distributed Active Archive Centers). Also shown are typical 5-day backward trajectories calculated from the middle points of each sampling during (b) 30 July–7 August and (c) 9–19 August 2008.

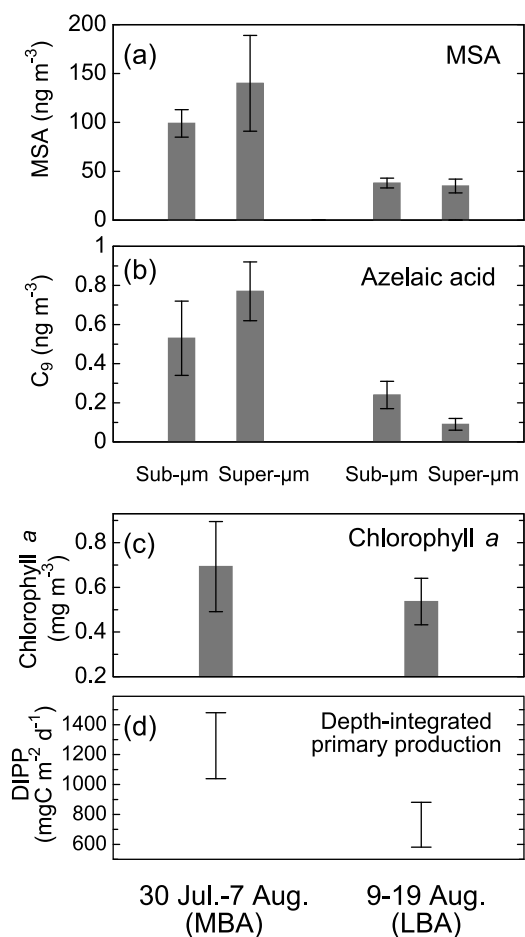
Metrohm, Herisau, Switzerland). Anions were measured using a SI-90 4E Shodex, Showa Denko, Tokyo, Japan column equipped with a suppressor having an eluent of 1.8 mM  $\text{Na}_2\text{CO}_3$  + 1.7 mM  $\text{NaHCO}_3$ . For cation analysis, we used a Metrosep C2-150 (Metrohm) column with 4 mM tartaric acid + 1 mM dipicolinic acid as an eluent. The random errors range from 1 to 3% for the major anions and cations. The overall uncertainty in the determination of ionic species is estimated to be 4%.

#### 2.4. Diacids and Related Water-Soluble Compounds

[11] The filter samples were analyzed for dicarboxylic acids, ketoacids, and  $\alpha$ -dicarbonyls using the method of Kawamura and Ikushima [1993] and Kawamura [1993]. A part of the quartz-fiber filter was cut into pieces and soaked in 5 ml of Milli-Q water. Then water-soluble species were extracted with pure water (5 ml  $\times$  3 times) under ultra-

sonication. After filtration with quartz wool, the extracts were combined in a 50-ml flask and concentrated to almost dryness, followed by addition of 14%  $\text{BF}_3/n$ -butanol. The extracts and reagents were then heated at 100°C for 1 h to convert the carboxyl groups to butyl esters and aldehyde groups to dibutoxy acetals. The derived butyl esters and acetals were extracted with *n*-hexane. They were then concentrated and dissolved in 50  $\mu\text{l}$  of *n*-hexane. The butyl esters and acetals were determined by capillary gas chromatography (GC6890N; Agilent Technologies, Santa Clara, CA, USA) with a flame ionization detector. Each compound was identified on the basis of the retention times of GC peaks compared to those of authentic standards and mass spectra obtained by GC/mass spectrometry.

[12] Recoveries of authentic standards spiked on a pre-combusted quartz-fiber filter were 78% and 83% for oxalic and malonic acids, respectively, and greater than 95% for



**Figure 2.** Average concentrations of (a) MSA, (b) azelaic acid in aerosols, and (c) chlorophyll *a* in seawater during 30 July–7 August and 9–19 August. Bars in Figures 2a–2c represent standard deviation. (d) Ranges of depth-integrated primary production in seawater during the two periods.

succinic and adipic acids. The variations due to analytical errors were tested by analyzing different sections of the same filter sample repeatedly, and the coefficient of deviation was found to be less than 8% for major diacids. The levels of field blanks were generally less than 17% of mass concentrations for the major species. The concentrations of diacids and related compounds presented here were corrected for the field blanks.

### 3. Results and Discussion

#### 3.1. Marine Biological Tracers and Air Mass Classification

[13] In our previous study [Miyazaki *et al.*, 2010], methanesulfonic acid (MSA) and azelaic acid (C<sub>9</sub>) were used as biological tracers to evaluate the marine biological activity and its contribution to the aerosols obtained during the study period. MSA is produced by the atmospheric oxidation of dimethylsulfide (DMS), which is released as a gas from marine microbial processes. It thus can be used as an indicator of secondary aerosols of marine biological origin. Azelaic acid is also used as a biogenic tracer and is derived from the photooxidation of unsaturated fatty acids

that are produced by marine phytoplankton and emitted to the atmosphere via the marine microlayer [Kawamura and Gagosian, 1987; Mochida *et al.*, 2002].

[14] Figures 2a and 2b show average concentrations of MSA and azelaic acid during two sampling periods. Three sample sets collected during the period 30 July–7 August showed increased concentrations of MSA and azelaic acid, both in the submicrometer and supermicrometer size ranges. The average MSA/non-sea salt (nss)-SO<sub>4</sub><sup>2-</sup> ratio was  $0.35 \pm 0.11$  in these samples. This ratio is similar to a marine biogenic MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio ( $\sim 0.33$ ) from a high latitudinal site [e.g., Savoie *et al.*, 2002], but higher than those ( $\sim 0.1$ – $0.2$ ) reported for marine aerosols at unpolluted mid-latitude sites and in the tropics [e.g., Ayers and Gras, 1991]. Moreover, the azelaic acid concentration summed for all size ranges during this period (average  $1.30 \pm 0.24$  ng m<sup>-3</sup>) is approximately twice as large as the value ( $0.57$  ng m<sup>-3</sup>) for remote marine aerosols collected over the western North Pacific to equatorial Pacific (35°N–15°S) [Kawamura and Sakaguchi, 1999]. Therefore, these aerosol samples appear to have been more influenced by marine biological activity. In fact, Miyazaki *et al.* [2010] reported that marine-derived carbon accounted for  $\sim 46$ – $72\%$  of total carbon in these aerosols on the basis of the measurements of stable carbon isotopic ratios for the same sample sets.

[15] Notably, the relative abundance of azelaic acid is higher in the supermicrometer size range than in the submicrometer range in these samples. This result can be attributed to the oxidation of unsaturated fatty acids (e.g., oleic acid), which are released to the air from the ocean with sea salts and predominantly reside in the supermicrometer range; oxidation of unsaturated fatty acids has been suggested to be an important pathway in the formation of azelaic acid [Kawamura and Gagosian, 1987; Mochida *et al.*, 2007]. In contrast, concentrations of MSA and azelaic acid in the aerosol samples collected during 9–19 August are three to four times lower than those obtained during 30 July–7 August, suggesting that they were biologically less influenced than the former samples. It should be noted that local wind speeds were similar during the periods of 30 July–7 August ( $5.9 \pm 3.3$  m s<sup>-1</sup>) and 9–19 August ( $6.4 \pm 4.6$  m s<sup>-1</sup>), suggesting that dynamic effects by local wind (e.g., occurrence of sea spray) did not significantly contribute to the observed difference in the two sample sets.

[16] On the basis of the MSA and azelaic acid concentrations discussed above, we classified aerosol samples into two broad categories: biologically more influenced aerosols (MBA), composed of three sample sets taken during 30 July–7 August, and biologically less influenced aerosols (LBA), composed of four sample sets taken during 9–19 August. Although the number of data sets is limited, each category is represented by a data set of approximately 10 days, which is longer than the time scale of several days in synoptic scale meteorology. In several previous studies, satellite-derived chlorophyll *a* concentrations were compared to measured OC concentrations to estimate the emission of oceanic OC in a global chemical transport model. However, many SeaWiFS data are missing over the high productivity region due to cloud cover (see Figure 1a) because the North Pacific (>40°N) is characterized by a frequent occurrence of sea fog from June to August [Wang, 1985]. In fact, meteorological data obtained every minute onboard the ship

**Table 1.** Concentrations in the Different Size Ranges for Biologically More Influenced Aerosols (MBA) and Less Influenced Aerosols (LBA) Sampled on Board the R/V Hakuho<sup>a</sup>

Sample Number (Period)	MBA		LBA	
	#1 (30 July–1 Aug.), #2 (1–4 Aug.), #3 (4–7 Aug.)		#5 (9–12 Aug.), #6 (12–15 Aug.), #7 (15–17 Aug.), #8 (17–19 Aug.)	
Compounds	Sub- $\mu\text{m}$	Super- $\mu\text{m}$	Sub- $\mu\text{m}$	Super- $\mu\text{m}$
MSA <sup>b</sup>	99 ± 14	140 ± 49	38 ± 5	35 ± 7
WSOC	337 ± 68	541 ± 235	236 ± 34	269 ± 104
WIOC	295 ± 82	446 ± 183	158 ± 39	284 ± 72
nssSO <sub>4</sub> <sup>2-</sup> <sup>b</sup>	553 ± 123	234 ± 205	630 ± 252	148 ± 102
NH <sub>4</sub> <sup>+</sup> <sup>b</sup>	48 ± 7	15 ± 14	96 ± 37	8 ± 7
Na <sup>+</sup> <sup>b</sup>	335 ± 200	697 ± 185	229 ± 79	636 ± 362
NO <sub>3</sub> <sup>-</sup> <sup>b</sup>	5 ± 5	59 ± 38	10 ± 13	107 ± 71
EC <sup>b</sup>	21 ± 6	7 ± 5	43 ± 8	11 ± 9
<i>Diacids</i>				
Oxalic acid, C <sub>2</sub>	35.20 ± 11.82	32.34 ± 8.07	15.27 ± 10.47	14.28 ± 5.09
Malonic acid, C <sub>3</sub>	26.93 ± 12.57	22.75 ± 8.18	7.54 ± 2.99	8.68 ± 2.53
Succinic acid, C <sub>4</sub>	20.65 ± 8.21	17.18 ± 7.15	5.86 ± 2.94	5.98 ± 1.61
Glutaric acid, C <sub>5</sub>	6.97 ± 0.69	6.11 ± 3.30	2.71 ± 1.89	2.53 ± 1.33
Adipic acid, C <sub>6</sub>	2.04 ± 0.03	1.97 ± 0.71	1.06 ± 0.20	1.44 ± 0.14
Pimelic acid, C <sub>7</sub>	0.75 ± 0.34	0.74 ± 0.42	0.41 ± 0.33	0.62 ± 0.30
Suberic acid, C <sub>8</sub>	0.05 ± 0.04	0.05 ± 0.01	N.D. <sup>c</sup>	N.D. <sup>c</sup>
Azelaic acid, C <sub>9</sub> <sup>b</sup>	0.53 ± 0.19	0.77 ± 0.15	0.24 ± 0.07	0.09 ± 0.03
Maleic acid	0.81 ± 0.05	1.26 ± 0.90	0.23 ± 0.05	0.42 ± 0.10
Fumaric acid	0.64 ± 0.33	0.93 ± 0.90	0.21 ± 0.08	0.29 ± 0.03
Methylmaleic acid	0.63 ± 0.33	0.12 ± 0.07	0.28 ± 0.06	0.37 ± 0.18
Phthalic acid	2.44 ± 0.10	2.67 ± 0.98	0.66 ± 0.07	0.80 ± 0.14
Malic acid, hC <sub>4</sub>	0.17 ± 0.10	0.13 ± 0.07	0.03 ± 0.03	0.05 ± 0.04
Subtotal	97.81 ± 19.13	87.02 ± 14.05	34.50 ± 11.44	35.55 ± 6.07
<i>Ketoacids</i>				
Glyoxylic acid	4.26 ± 1.92	3.11 ± 1.87	3.33 ± 0.78	2.44 ± 0.87
Pyruvic acid	0.41 ± 0.19	1.35 ± 0.70	0.40 ± 0.10	0.58 ± 0.26
3-Oxopropanoic acid	0.75 ± 0.19	0.67 ± 0.31	0.32 ± 0.14	0.23 ± 0.08
4-Oxobutanoic acid	0.47 ± 0.35	0.57 ± 0.25	0.38 ± 0.19	0.29 ± 0.24
9-Oxononanoic acid	0.04 ± 0.02	0.04 ± 0.06	0.07 ± 0.03	0.24 ± 0.23
Subtotal	5.93 ± 1.95	5.74 ± 2.04	4.50 ± 0.99	3.78 ± 0.97
<i><math>\alpha</math>-Dicarbonyls</i>				
Glyoxal	0.03 ± 0.01	0.03 ± 0.01	0.12 ± 0.03	N.D. <sup>c</sup>
Methylglyoxal	0.20 ± 0.14	0.25 ± 0.17	0.22 ± 0.14	0.32 ± 0.14
Subtotal	0.23 ± 0.14	0.28 ± 0.17	0.34 ± 0.14	0.32 ± 0.14

<sup>a</sup>Values are averages given in ng m<sup>-3</sup> with  $\pm 1$  standard deviation.

<sup>b</sup>Values are from Miyazaki *et al.* [2010].

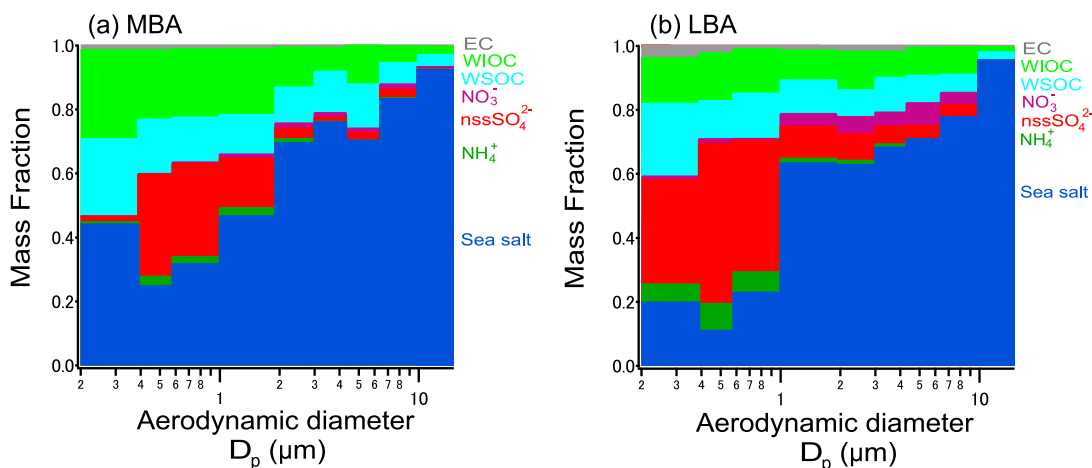
<sup>c</sup>N.D. indicates that the concentration was not detectable.

showed that relative humidity reached  $\sim 100\%$  during 15% of the MBA period (average  $92.4 \pm 6.6\%$ ) and during 19% of the LBA period (average  $93.9 \pm 6.2\%$ ). The results support the frequent occurrence of fog/clouds around the sampling location during the study period.

[17] Chlorophyll *a* concentrations in seawater obtained by in situ measurements during the MBA period ( $0.69 \pm 0.20$  mg m<sup>-3</sup>) are slightly higher than those during the LBA period ( $0.54 \pm 0.10$  mg m<sup>-3</sup>) (Figure 2c) (K. Suzuki, personal communication, 2009). Figure 2d presents depth-integrated primary production in seawater, which was derived from the measured surface chlorophyll *a* concentration, sea surface temperature, and photosynthetic available radiation [Isada *et al.*, 2010]. The primary production ( $\sim 1,040$ – $1,480$  mgC m<sup>-2</sup> d<sup>-1</sup>) during the MBA period is significantly higher than that ( $\sim 580$ – $880$  mgC m<sup>-2</sup> d<sup>-1</sup>) during the LBA period [Y. Nosaka, unpublished data]. Back trajectories suggest that sampled air masses with MBA were transported within the marine boundary layer (MBL) and frequently encountered oceanic regions with high productivity upwind of the sam-

pling locations (Figures 1a and 1b). The transport of LBA within the MBL was also suggested, although most of the LBA originated from low-productivity oceanic regions south of the sampling points (Figures 1a and 1c). The back trajectories, together with in situ measurements of productivity, are consistent with the larger abundance of MSA and azelaic acid in MBA.

[18] It should be noted that the background marine aerosol composition can be influenced by aged ship emissions [e.g., Capaldo *et al.*, 1999]. However, the low concentrations of both EC and NO<sub>3</sub><sup>-</sup> in our samples (Table 1) suggest less significant contribution from anthropogenic sources including ship emissions to MBA. The average bulk EC concentrations agree with the ranges of EC reported for clean marine aerosols in the North Atlantic [Cooke *et al.*, 1997]. The low concentrations of the anthropogenic tracers are consistent with the trajectory (Figure 1b) and stable carbon isotope ratios reported in our previous study [Miyazaki *et al.*, 2010].



**Figure 3.** Average chemical components of biologically (a) more and (b) less influenced aerosols in each size interval. Note that WSOC and WIOC are presented in carbon mass and do not represent the mass of organic matter.

### 3.2. Size Dependence of Aerosol Chemical Components

[19] Figure 3 illustrates the chemical composition of marine aerosols as a function of particle size for MBA and LBA. OC and  $\text{nss-SO}_4^{2-}$  are the main components of the submicrometer size fractions in both MBA and LBA. In the supermicrometer range, sea salt is the dominant component of both MBA and LBA, as is typically observed in marine aerosols. In MBA, contributions of OC to the total mass of the identified components ranged from 35% to 52% in the submicrometer range, whereas they ranged from 6% to 33% in the supermicrometer range. The OC fractions in the submicrometer range of MBA (35–52%) are higher than those in LBA (27–37%). The higher contribution of OC found in MBA can be attributed to the larger influence of biologically more active conditions compared to LBA.

[20] On average, the fraction of WSOC to the total mass of the identified components in the submicrometer range of MBA (~21%) is higher than that found in LBA (~15%). The relative contributions of WIOC (~23% in MBA and ~14% in LBA) were similar to those of WSOC in the submicrometer ranges. Previous studies have also reported an increased organic fraction in smaller sizes of marine aerosols [e.g., O'Dowd *et al.*, 2004; Rinaldi *et al.*, 2009]. O'Dowd *et al.* [2004] showed that during bloom periods in the North Atlantic, the organic fraction contributed ~63% of the submicrometer aerosol mass, wherein ~45% was WIOC and ~18% was WSOC. Interestingly, our results show comparable fractions of WSOC and WIOC.

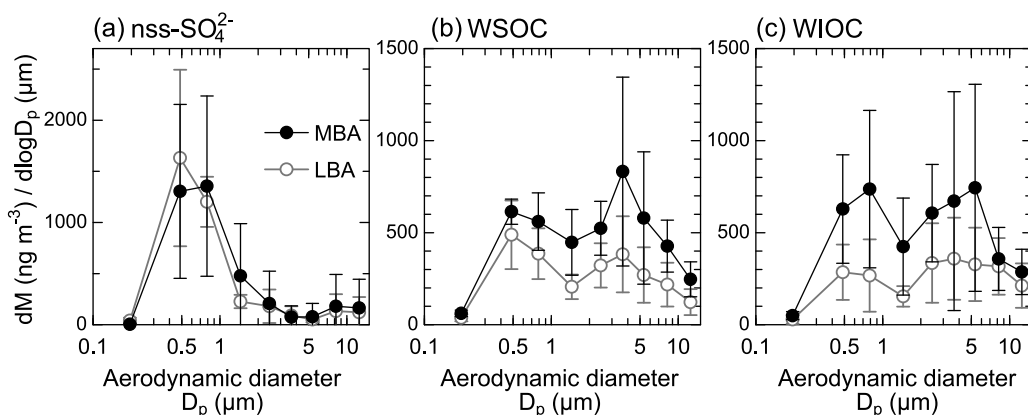
[21] Note that here WSOC and WIOC are presented in carbon mass. Previous studies over the North Atlantic have used carbon-to-mass conversion factors of 1.8 and 1.4 derived from functional group analysis using proton nuclear magnetic resonance ( $^1\text{H NMR}$ ) [Decesari *et al.*, 2007]. These factors have been used to obtain mass concentrations of water-soluble organic matter (WSOM) and water-insoluble organic matter (WIOM), respectively (i.e.,  $\text{WSOM} = 1.8 \times \text{WSOC}$ ,  $\text{WIOM} = 1.4 \times \text{WIOC}$ ). Assuming that WSOM and WIOM can be estimated in this study by using these factors, OM (= WSOM + WIOM) accounts for 56% and 39% in the submicrometer ranges of MBA and LBA, respectively. In

particular, WSOM contributes as much as 30% in the submicrometer MBA mass, whereas WIOM accounts for 26% in the same category. These results suggest that submicrometer aerosols in this oceanic region in summer are enriched in water-soluble organic matter associated with oceanic biological activity. This point is further discussed in the following sections.

### 3.3. Concentrations and Size Distributions of Sulfate and Organics

[22] Figure 4 shows the average size distributions of  $\text{nss-SO}_4^{2-}$ , WSOC, and WIOC for MBA and LBA. The size distributions of  $\text{nss-SO}_4^{2-}$  exhibit a peak in the submicrometer range with aerodynamic diameters between 0.39 and 1.0  $\mu\text{m}$  for both MBA and LBA (Figure 4a). On average, the bulk concentrations of  $\text{nss-SO}_4^{2-}$  in MBA ( $787 \pm 239 \text{ ng m}^{-3}$ ) and LBA ( $778 \pm 272 \text{ ng m}^{-3}$ ) are similar. In contrast, WSOC and WIOC both exhibit bimodal size distributions with peaks in the submicrometer and supermicrometer ranges. The average concentration of WSOC in MBA ( $878 \pm 245 \text{ ngC m}^{-3}$ ) is larger than that in LBA ( $505 \pm 109 \text{ ngC m}^{-3}$ ). The bulk concentrations of WSOC are comparable to those of  $\text{nss-SO}_4^{2-}$  (Table 1). It is of interest to note that the WSOC concentrations are substantially larger than those reported for bulk aerosols over the North Atlantic (~420  $\text{ngC m}^{-3}$ ) [Cavalli *et al.*, 2004] and in the Austral Ocean (<100  $\text{ngC m}^{-3}$ ) [Sciare *et al.*, 2009], although both were obtained during the period of high biological activity.

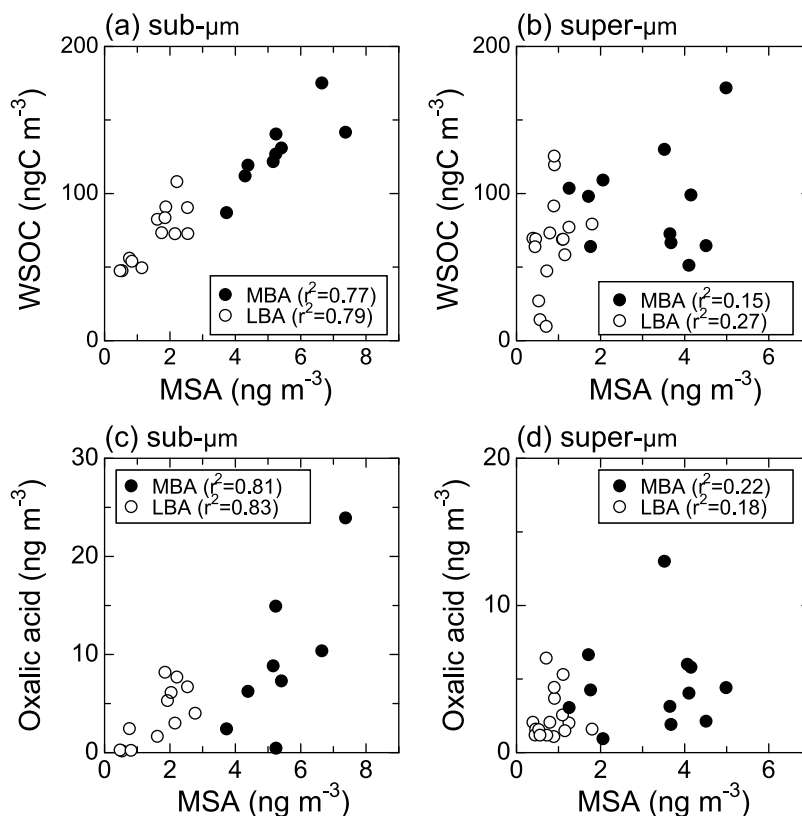
[23] In MBA, MSA/WSOC carbon mass ratios were  $3.8 \pm 0.1\%$  and  $3.7 \pm 0.8\%$  in the submicrometer and supermicrometer size ranges, respectively (Table 2). These ratios are higher than those for LBA ( $1.2 \pm 1.1\%$  and  $2.3 \pm 0.5\%$  in the submicrometer and supermicrometer size ranges, respectively). The WSOC and MSA concentrations showed a statistically significant correlation in the submicrometer size range of MBA ( $r^2 = 0.77$ ,  $P < 0.01$ ), but not in the supermicrometer size range ( $r^2 = 0.15$ ) (Figures 5a and 5b). Because the production of MSA from DMS is also strongly linked to photochemical activity, this result suggests an important secondary production of WSOC originated from



**Figure 4.** Average size distributions for the concentrations of (a)  $\text{nss-SO}_4^{2-}$ , (b) WSOC, and (c) WIOC in MBA and LBA. Particle sizes shown are mean aerodynamic diameters of each stage. Bars represent  $\pm 1$  standard deviation.

marine biological sources, being similar to the case of MSA in the submicrometer size range. Assuming a typical average OH concentration of  $1 \times 10^6 \text{ cm}^{-3}$  over the 5-day trajectory, a lifetime of DMS is roughly estimated to be  $\sim 1$  day with respect to oxidation by OH in the MBL [Andreae et al., 2003; Kloster et al., 2006]. Similarly, we assume that it takes a few hours to  $\sim 1$ –2 days for WSOC formation from biogenic VOCs [e.g., Limbeck et al., 2003]. Under these assumptions, the strong correlation between the WSOC and MSA concentrations in the submicrometer range (Figure 5a) suggests

similar formation processes that are likely completed within  $\sim 5$  days. It is noted that Russell et al. [2010] recently observed that an ocean-derived composition in the submicrometer range of primary organic aerosol is dominated by carbohydrate-like compounds containing organic hydroxyl groups (i.e., water-soluble organics) over the North Atlantic and Arctic Oceans. In our samples, however, no significant correlation between WSOC and  $\text{Na}^+$  ( $r^2 = 0.03$ ) was found in the submicrometer range. This result also suggests that a majority of WSOC is derived from secondary production.



**Figure 5.** Scatterplots between WSOC and MSA concentrations in each size-segregated aerosol within the (a) submicrometer and (b) supermicrometer size ranges. Also shown are scatterplots between oxalic acid ( $\text{C}_2$ ) and MSA concentrations in the (c) submicrometer and (d) supermicrometer size ranges.

**Table 2.** Percentage of OC That Is Water Soluble (WSOC) and Percentages of the WSOC That Are Accounted for by Carbon in the Measured MBA and LBA

Percentage (%) in Carbon Mass	MBA		LBA	
	Sub- $\mu\text{m}$	Super- $\mu\text{m}$	Sub- $\mu\text{m}$	Super- $\mu\text{m}$
WSOC/OC	46.4 $\pm$ 3.7	55.3 $\pm$ 5.9	52.1 $\pm$ 7.0	47.1 $\pm$ 6.3
MSA/WSOC	3.8 $\pm$ 0.1	3.7 $\pm$ 0.8	1.2 $\pm$ 1.1	2.3 $\pm$ 0.5
Oxalic acid (C <sub>2</sub> )/WSOC	2.2 $\pm$ 1.7	1.4 $\pm$ 0.8	1.2 $\pm$ 0.9	1.3 $\pm$ 2.1
Diacids/WSOC	10.2 $\pm$ 9.3	5.7 $\pm$ 2.1	5.0 $\pm$ 4.9	4.6 $\pm$ 1.8

[24] The difference in the WIOC concentrations between MBA and LBA was more significant than those of nss-SO<sub>4</sub><sup>2-</sup> and WSOC, particularly in the submicrometer range (Figure 4c). The average concentrations of WIOC in the submicrometer MBA (295  $\pm$  82 ng m<sup>-3</sup>) are about twice those in the LBA (158  $\pm$  39 ng m<sup>-3</sup>) (Table 1). As described in section 3.1, the average local wind speeds were similar between the MBA and LBA periods, suggesting that dynamic effects by local wind did not significantly contribute to the observed difference in the WIOC concentrations. Rather, the larger concentrations of WIOC in MBA may be mainly attributable to hydrophobic properties of organic matter that accumulates in the surface film of the ocean with high biological productivity and is preferentially transferred into the atmosphere through bubble-bursting processes [Blanchard, 1964; Gershey, 1983; Oppo *et al.*, 1999]. In fact, WIOC is positively correlated with Na<sup>+</sup> ( $r^2 = 0.52$ ) in the submicrometer range, supporting the primary formation of WIOC. In previous studies, some evidence points out the occurrence of WIOC including mainly lipidic species in marine aerosols, for which marine biological origin has been suggested [Gogou *et al.*, 1998; Mochida *et al.*, 2002]. Simoneit *et al.* [2004] reported that 1–45% of the total identified organic compound mass (<16% of OC) were marine-derived fatty acids (<C<sub>20</sub>) in the aerosols collected over the mid- to western Pacific.

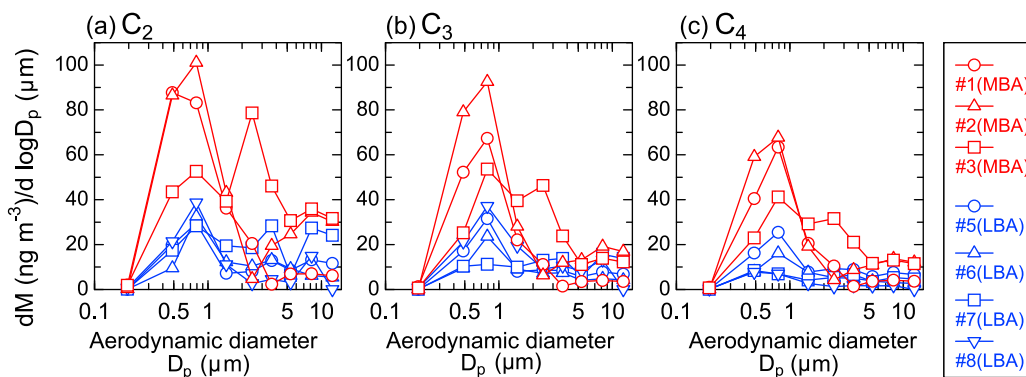
[25] Ceburnis *et al.* [2008] measured gradient flux of the marine aerosol component and found the upward fluxes indicative of sea-surface (primary) formation for sea salt and WIOC. They also found the downward flux characteristics of secondary formation products, i.e., nss-SO<sub>4</sub><sup>2-</sup> and WSOC. Along with the results of Ceburnis *et al.* [2008], recent experiments have shown that WIOC and/or sea salt are the major components of sea spray in the North Atlantic

[Facchini *et al.*, 2008a], the southern Indian Ocean [Claeys *et al.*, 2010], and the Austral Ocean [Sciare *et al.*, 2009]. In contrast, our samples showed that the mass fraction of WSOC was comparable to that of WIOC in both MBA and LBA, which can be attributed to larger abundance of marine SOA in our study region.

[26] As described above, sea salt (i.e., Na<sup>+</sup>) was dominant in the supermicrometer ranges of both MBA and LBA. However, primary emission of WSOC with sea salts in supermicrometer particles may be less significant because the peak diameter of WSOC (3.0–4.3  $\mu\text{m}$ ) is smaller than that of Na<sup>+</sup> (6.4–10  $\mu\text{m}$ ) (data not shown as a figure). Possible pathways for the formation of WSOC in the supermicrometer size range may include condensation of volatile organic compounds (VOC) originating from marine biological sources onto preexisting sea salt particles, coagulation of submicrometer particles on supermicrometer particles, and photochemical formation within clouds/fog. Uptake of VOC by dust particles seems unlikely, because the average Ca<sup>2+</sup> concentrations were notably low (<6 ng m<sup>-3</sup>) in our aerosol samples.

### 3.4. Concentrations and Size Distributions of Diacids

[27] Figure 6 shows the size distributions of oxalic acid (C<sub>2</sub>), malonic acid (C<sub>3</sub>), and succinic acid (C<sub>4</sub>) in each sample of MBA and LBA. Average concentrations of C<sub>2</sub>–C<sub>9</sub> saturated and unsaturated diacids and C<sub>2</sub>–C<sub>4</sub> oxoacids in the submicrometer and supermicrometer size ranges are summarized in Table 2. The average mass concentration of the sum of C<sub>2</sub>–C<sub>4</sub> diacids in the submicrometer range of MBA (82.8  $\pm$  19.1 ng m<sup>-3</sup>) is about three times larger than that of LBA (28.7  $\pm$  9.1 ng m<sup>-3</sup>). In all the samples, oxalic acid is the most abundant diacid, followed by malonic and succinic acids. Generally, oxalic acid is more abundant in the sub-

**Figure 6.** Size distributions of the concentrations of (a) oxalic acid (C<sub>2</sub>), (b) malonic acid (C<sub>3</sub>), and (c) succinic acid (C<sub>4</sub>) in each sample of MBA (red) and LBA (blue).



micrometer size ranges of MBA. Substantial fractions of malonic and succinic acids in the submicrometer range are also found in MBA. The enrichment of oxalic acid in the submicrometer range of MBA indicates a preferential net production of oxalic acid via the oxidation of precursor gases and/or particles emitted from the oceanic region with higher biological productivity.

[28] In the submicrometer size range, the average contribution of oxalic acid to WSOC in MBA was  $2.2 \pm 1.7\%$ , which is higher than that in LBA ( $1.2 \pm 0.9\%$ ) (Table 2). Total diacids showed average contribution of  $10.2 \pm 9.3\%$  to WSOC in MBA, which is twice higher than that in LBA ( $5.0 \pm 4.9\%$ ). Interestingly, about 14% of the submicrometer WSOC in MBA could be attributed to MSA and C<sub>2</sub>–C<sub>9</sub> diacids, with MSA and oxalic acid contributing similar fractions. Moreover, the oxalic acid and MSA concentrations showed a significant correlation for the submicrometer size range of MBA ( $r^2 = 0.81$ ) and LBA ( $r^2 = 0.83$ ) as shown in Figure 5c. These results suggest that larger secondary production of diacids occurs in the submicrometer particles that are biologically more influenced.

[29] The C<sub>2</sub>–C<sub>4</sub> diacids and other water-soluble organic species may mainly be produced through photochemical oxidation of their precursors originated from marine sources in the North Pacific. The precursors may be supplied predominantly by sea-to-air emissions of biogenic organic compounds, such as unsaturated fatty acids, olefins, and phenolic compounds [e.g., Wang *et al.*, 2006]. They may be subsequently oxidized to result in more water-soluble organics in MBA as suggested by the higher ratios of both oxalic acid/WSOC and MSA/WSOC. Our finding, that is, the secondary organic aerosols of marine biological origin account for a large fraction of the submicrometer WSOC in this region, is supported by the presence of diethylammonium (DEA<sup>+</sup>), which was detected in the submicrometer size range of MBA in the same samples [Miyazaki *et al.*, 2010]. DEA<sup>+</sup> has been suggested to be derived from an oceanic biological source and is produced by the reaction of gaseous amines with sulfuric acid or acidic sulfates [Facchini *et al.*, 2008b].

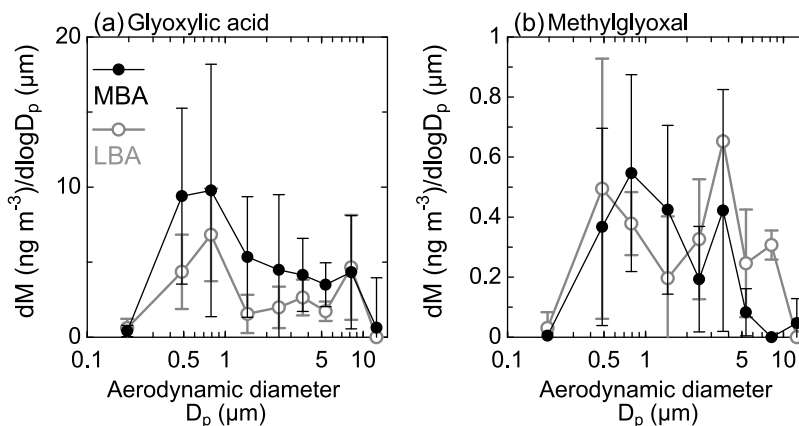
[30] It is noted that the size distributions of C<sub>2</sub>–C<sub>4</sub> diacids in MBA (Figure 6) are in general similar to those of nss-SO<sub>4</sub><sup>2-</sup> (Figure 4a), although C<sub>2</sub>–C<sub>4</sub> diacids showed relatively large concentrations in the supermicrometer size range. The oxalic acid and nss-SO<sub>4</sub><sup>2-</sup> concentrations showed a positive correlation in the submicrometer size range of MBA ( $r^2 = 0.87$ ) (data not shown as a figure), suggesting a similar production process. Previous studies have noted similarity in size distributions of these two species, suggesting a common source [e.g., Yao *et al.*, 2003; Crahan *et al.*, 2004]. A correlation between oxalic acid and nss-SO<sub>4</sub><sup>2-</sup> and its slope of linear regression line have been used to investigate production processes of oxalic acid mainly via aqueous phase reactions [e.g., Yu *et al.*, 2005]. The slope of a linear regression line between oxalic acid and nss-SO<sub>4</sub><sup>2-</sup> in each size-segregated sample of MBA (0.037) is 76% higher than that of LBA (0.021). The difference in the slopes, together with larger concentrations of oxalic acid in the submicrometer size range of MBA, suggests more efficient net production of oxalic acid in biologically more influenced aerosols.

[31] Substantial fractions of diacids and ketoacids were also found in the supermicrometer size ranges of MBA and LBA. Malonic and succinic acids were often more abundant in the supermicrometer size ranges than in the submicrometer size ranges of LBA (Table 1). Poor correlations between oxalic acid and MSA ( $r^2 = 0.18$ – $0.22$ ) (Figure 5d) suggest that formation processes of diacid in the supermicrometer size range of MBA and LBA may be different from those in the submicrometer size range. Condensation of VOC of marine biological origin onto preexisting sea salt particles and subsequent oxidation, coagulation of submicrometer particles, and photochemical formation within cloud/fog droplets may be possible formation pathways for diacids and ketoacids in the supermicrometer range. Large abundance of diacids in the larger size range of marine aerosols was also reported by Ricard *et al.* [2002], who found that C<sub>4</sub> and C<sub>5</sub> diacids in northern Finland were rich in coarse particles in air masses of marine origin. Mochida *et al.* [2007] showed similar fractions of major diacids in the supermicrometer range in the western Pacific, which is likely associated with sea salt and/or dust particles. Primary emission of diacids as supermicrometer sea salts particles should be unlikely, because no significant correlation was found between diacids and Na<sup>+</sup> ( $r^2 < 0.10$ ).

### 3.5. Potential Processes for the Net Production of Oxalic Acid and WSOC

[32] As described in section 3.1, sea fog frequently occurred in the study region during the entire period. Organics can partition into gases, aerosols, and cloud/fog droplets and undergo aqueous phase oxidation to produce low-volatility organic species such as organic acids and oligomers [Warneck, 2003; Ervens *et al.*, 2004; Altieri *et al.*, 2006; Sorooshian *et al.*, 2006, 2007]. One plausible explanation for the increased concentrations and fractions of oxalic acid in the submicrometer size range of MBA is the aqueous phase formation of oxalic acid by the oxidations of precursors derived from marine biological sources. In aqueous phase, oxalic acid is known to be formed by OH oxidation of longer-chain dicarboxylic acids and glyoxylic acid. In addition, various loss processes of oxalic acid could affect the concentrations and fractions of oxalic acid. Oxalic acid is lost by its oxidation to CO<sub>2</sub> [e.g., Warneck, 2003]. Zuo and Holgné [1992] suggested that photolysis of iron(III)/iron(II)-oxalato complexes can be an important sink of oxalic acid in the aqueous phase in the atmosphere. Ervens *et al.* [2003] used a photochemical box model and showed that photolysis of the iron-dioxalato-complex is much more effective than oxidation of oxalic acid by OH. Evaporation of oxalic acid can be negligible because the vapor pressure of oxalic acid is sufficiently low ( $<10^{-4}$  mm Hg) [Saxena and Hildemann, 1996].

[33] Oxalic acid is well correlated with C<sub>3</sub>–C<sub>5</sub> diacids ( $r^2 = 0.62$ – $0.83$ ) in the submicrometer size range of MBA. Kawamura and Ikushima [1993] proposed that malic acid (hC<sub>4</sub>), hydroxylated dicarboxylic acid, can be formed by hydration of maleic acid and/or hydroxylation of succinic acid and is further oxidized to produce oxalic acid. Since no direct emissions have been identified for malic acid, the change in the relative abundances of succinic acid and malic acid may indicate the progress in photochemical aging of aerosols, probably in the aqueous phase. Indeed, the



**Figure 7.** Average size distributions of the concentrations of (a) glyoxylic acid and (b) methylglyoxal in MBA and LBA.

average malic acid ( $\text{hC}_4$ )/succinic acid ( $\text{C}_4$ ) ratio in MBA ( $8.23 \times 10^{-3}$ ) is higher than that in LBA ( $5.11 \times 10^{-3}$ ). Together with the correlation between oxalic acid and  $\text{C}_3$ – $\text{C}_5$  diacids, these results provide evidence for aqueous phase secondary production of oxalic acid in the submicrometer MBA via decay of longer-chain dicarboxylic acids. The results also imply that the chemical aging of water-insoluble organics (e.g., unsaturated fatty acids and olefins) primarily emitted from the ocean surface and the subsequent production of more water-soluble organics may be important for the SOA formation in this oceanic region with higher biological productivity. In fact, *Mochida et al.* [2002] showed enhanced concentrations of fatty acids ( $\text{C}_{14}$ – $\text{C}_{19}$ ) likely emitted with sea-salt particles over the northern North Pacific in spring and summer, when marine biological activity was high.

[34] Another possible pathway for the production of oxalic acid is the oxidation of glyoxylic acid, which is formed by the OH oxidation of glyoxal, methylglyoxal, glycolic acid, and hydroxyl acetaldehyde [*Ervens et al.*, 2004; *Lim et al.*, 2005]. In particular, methylglyoxal is a well-known oxidation product of aromatics [*Andino et al.*, 1996] and isoprene [*Talbot et al.*, 1995]. *Lim et al.* [2005] have proposed that methylglyoxal yields low-volatility organic acids including oxalic acid through oxidation to glyoxylic acid via intermediate steps involving pyruvic and acetic acid. Furthermore, there is experimental evidence that oxalic acid and higher-molecular-weight oligomers are produced from methylglyoxal oxidation through cloud processing [*Hastings et al.*, 2005; *Altieri et al.*, 2006, 2008].

[35] Figure 7 presents the size distributions of glyoxylic acid and methylglyoxal in MBA and LBA. Both compounds showed peaks in submicrometer and supermicrometer size ranges. Oxalic acid and glyoxylic acid showed a positive correlation in both MBA ( $r^2 = 0.72$ ) and LBA ( $r^2 = 0.79$ ), suggesting a secondary formation of oxalic acid from glyoxylic acid, possibly in the aqueous phase of aerosols. In fact, *Sorooshian et al.* [2007] conducted aircraft measurements and found that relative abundance of glyoxylic acid in total organic acids detected is higher in cloud droplets than in aerosols collected below clouds. Their result suggests the formation of glyoxylic acid in an early stage of liquid phase

reaction. It should be noted that no significant difference was found between MBA and LBA for the mass concentrations and size distributions of methylglyoxal (Figure 7b). The average concentrations of methylglyoxal in MBA and LBA are  $0.45 \pm 0.22 \text{ ng m}^{-3}$  and  $0.54 \pm 0.20 \text{ ng m}^{-3}$ , respectively. In our samples, the average concentrations of methylglyoxal are much larger than those of glyoxal (Table 1), with the glyoxal concentrations being extremely low in most of the samples. The predominance of methylglyoxal was also observed in the western Pacific [*Wang et al.*, 2006]. Methylglyoxal can be produced by the oxidation of isoprene in the marine atmosphere [*Lim et al.*, 2005], and the larger concentration of methylglyoxal compared to glyoxal in aerosols can be attributed to the large production from isoprene [*Fu et al.*, 2008].

[36] Because influences of anthropogenic emissions on aerosols (e.g., aromatics, ethane) are likely insignificant in MBA as discussed in section 3.1, glyoxylic acid in our samples appeared to be mainly formed by the oxidation of isoprene from marine biological sources. In fact, *Matsunaga et al.* [2002] measured concentrations of isoprene in the marine air and surface seawater in the western North Pacific during early summer to estimate the isoprene sea-to-air fluxes of 32–300  $\text{nmol m}^{-2} \text{ d}^{-2}$ . Concentrations of pyruvic acid, an important intermediate in the oxidation of methylglyoxal [*Lim et al.*, 2005; *Carlton et al.*, 2006], are also comparable in the submicrometer size ranges of MBA ( $0.41 \pm 0.19 \text{ ng m}^{-3}$ ) and LBA ( $0.40 \pm 0.10 \text{ ng m}^{-3}$ ) (Table 1). These results suggest that, given that methylglyoxal in the present study were mostly derived from the oxidation of biogenic isoprene [*Fu et al.*, 2008], isoprene alone could not explain the observed difference in the levels of oxalic acid via the formation of methylglyoxal as intermediate in MBA and LBA.

[37] This implication is in agreement with recent studies, which suggest that the abundance of marine atmospheric OC is much higher than that explained by the production from oceanic isoprene emissions [*Spracklen et al.*, 2008; *Arnold et al.*, 2009]. Although it is not documented, we cannot exclude a possibility that oligomers are formed from the oxidation of methylglyoxal, thus contributing to WSOC. Other possible reaction pathways to form glyoxylic acid in

marine aerosols include the oxidation of glycolic acid and hydroxyl acetaldehyde. However, their importance remains elusive and thus requires further research.

#### 4. Conclusions

[38] We carried out size-segregated aerosol measurements over the remote western North Pacific in summer to better understand the marine biological contribution to organic aerosols. The average concentrations of organic carbon (OC) and oxalic acid are twice as large in marine biologically more influenced aerosols as in less influenced aerosols. Water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WIOC) exhibit bimodal size distribution, with peaks in submicrometer and supermicrometer size ranges. WSOC accounted for ~15–21% of total mass of the components determined in the submicrometer size range of biologically more influenced aerosols. This fraction is comparable to that of WIOC (~14–23%), which may be produced by bubble-bursting processes at the ocean surface. Moreover, WSOC showed a significant correlation with MSA in the submicrometer size range of these aerosols. These results suggest that organic aerosols in this remote oceanic region are enriched with secondary organic aerosols (SOA) that are linked to oceanic biological activity. The enrichment of marine biological SOA is also supported by the larger concentrations of diethylammonium in biologically more influenced aerosols found in the same sample sets in our previous study [Miyazaki et al., 2010].

[39] We found substantial fractions of oxalic acid and other low-molecular-weight organic acids in the submicrometer size range of biologically more influenced aerosols. MSA and diacids (C<sub>2</sub>–C<sub>6</sub>) accounted for approximately 14% of the submicrometer WSOC mass in biologically more influenced aerosols, with MSA and oxalic acid providing similar fractions. This result indicates a preferential net production of oxalic acid from organic precursors emitted from the oceanic region with higher biological productivity. Positive correlations of oxalic acid with C<sub>3</sub>–C<sub>5</sub> diacids and glyoxylic acid suggest that secondary production of oxalic acid occurs possibly in the aqueous aerosol phase via the oxidation of longer-chain diacids and glyoxylic acid. In contrast, no significant difference was observed between the two types of aerosols for mass concentrations and size distributions of methylglyoxal, which is likely produced by the oxidation of isoprene emitted from marine biological sources. This implies that isoprene from marine biological sources did not significantly contribute to the observed difference in the levels of oxalic acid via the formation of methylglyoxal over the region. The present work requires more studies to better understand the high abundance of WSOC produced from marine biological sources in remote marine regions using various approaches including global modeling.

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