HOKKAIDO UNIVERSITY

Title	High abundances of oxalic, azelaic, and glyoxylic acids and methylglyoxal in the open ocean with high biological activity: Implication for secondary OA formation from isoprene
Author(s)	Bikkina, Srinivas; Kawamura, Kimitaka; Miyazaki, Yuzo; Fu, Pingqing
Citation	Geophysical Research Letters, 41(10), 3649-3657 https://doi.org/10.1002/2014GL059913
Issue Date	2014-05-28
Doc URL	http://hdl.handle.net/2115/57474
Rights	Copyright 2014 American Geophysical Union.
Type	article
File Information	grl51689.pdf

High abundances of oxalic, azelaic, and glyoxylic acids and methylglyoxal in the open ocean with high biological activity: Implication for secondary OA formation from isoprene

Srinivas Bikkina[1], Kimitaka Kawamura[1], Yuzo Miyazaki[1], and Pingqing Fu[1,2]

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan, [2]Now at LAPC, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China

Abstract Atmospheric dicarboxylic acids (DCA) are a ubiquitous water-soluble component of secondary organic aerosols (SOA), which can act as cloud condensation nuclei (CCN), affecting the Earth's climate. Despite the high abundances of oxalic acid and related compounds in the marine aerosols, there is no consensus on what controls their distributions over the open ocean. Marine biological productivity could play a role in the production of DCA, but there is no substantial evidence to support this hypothesis. Here we present latitudinal distributions of DCA, oxoacids and α-dicarbonyls in the marine aerosols from the remote Pacific. Their concentrations were found several times higher in more biologically influenced aerosols (MBA) than less biologically influenced aerosols. We propose isoprene and unsaturated fatty acids as sources of DCA as inferred from significantly higher abundances of isoprene-SOA tracers and azelaic acid in MBA. These results have implications toward the reassessment of climate forcing feedbacks of marine-derived SOA.

1. Introduction

Oceans can significantly contribute to global aerosol burden and thus have been considered to influence the Earth's albedo and climate [*Meskhidze and Nenes*, 2006; *O'Dowd et al.*, 1997, 2004]. However, knowledge of chemical composition of marine aerosols that originated from primary emissions (e.g., sea salt or organic matter) and/or secondary formation is still limited [*Gantt and Meskhidze*, 2013; *Langmann et al.*, 2008; *O'Dowd and de Leeuw*, 2007]. More recent studies have focused on the formation of secondary organic aerosols (SOAs), which are essentially produced by the oxidation of biogenic volatile organic compounds (BVOCs) and subsequent gas-to-particle conversion [*Facchini et al.*, 2008a; *Myriokefalitakis et al.*, 2010; *Rinaldi et al.*, 2010]. Several studies have shown that SOAs are mostly composed of water-soluble organic species; therefore, SOAs are characterized by high abundance of water-soluble organic carbon (WSOC) [*Claeys et al.*, 2004a; *Kondo et al.*, 2007; *Miyazaki et al.*, 2010, 2011; *Mochida et al.*, 2011]. *Myriokefalitakis et al.* [2011] reported in-cloud oxalate formation in the global troposphere using 3-D model and discussed abundant oxalic acid over the open ocean.

Dicarboxylic acids (DCA) and related compounds with the predominance of oxalic acid are major components of atmospheric organic aerosols and thus significantly contribute to total aerosol carbon (up to 15%) over the oceanic regions [*Kawamura and Sakaguchi*, 1999]. Over the continent, their primary (fossil-fuel combustion and biomass burning emissions) and secondary sources (photochemical production and transformation of anthropogenic and biogenic VOCs) are well characterized and supported by extensive observations [*Agarwal et al.*, 2010; *Kawamura et al.*, 1996; *Kawamura and Yasui*, 2005; *Mkoma et al.*, 2013]. It has also been suggested that their distribution in the remote marine environment is primarily driven by either long-range transport of pollutants [*Fu et al.*, 2013a; *Kawamura and Sakaguchi*, 1999] or in situ production from the oxidation of BVOCs emitted from the ocean surface [*Claeys et al.*, 2004b; *Miyazaki et al.*, 2010]. The source strength over the coast is characterized by higher contribution of pollutants by continental outflow compared to that of pelagic ocean.

Based on previous observations from the island stations and oceanic cruises [*Fu et al.*, 2013a; *Kawamura and Usukura*, 1993; *Kawamura and Sakaguchi*, 1999; *Kawamura et al.*, 2004; *Miyazaki et al.*, 2010; *Mochida et al.*,
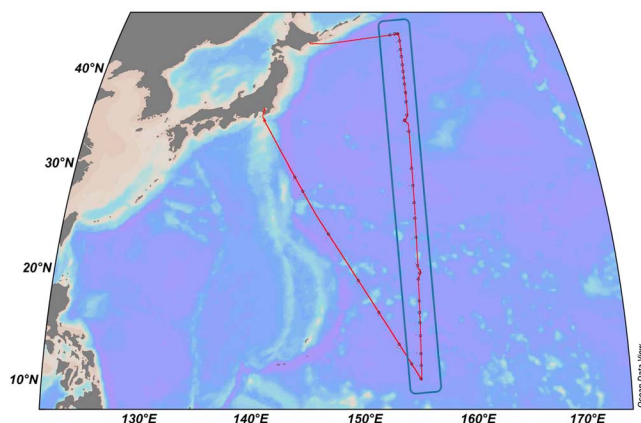
Figure 1. Locations of aerosol samples collected along the cruise track of KH08 in the western North Pacific during summer (August–September 2008), when the impact from continental outflow is rather weak. The latitudinal samples in the square were used in this study. The blue color means pelagic ocean whereas brown color means coastal/shallow waters.

2003; *Sempéré and Kawamura*, 2003], phytoplankton activity in the surface ocean has been suggested to control the distribution of atmospheric diacids. However, there are no field-based measurements of DCA to verify this hypothesis on the role of marine biota in controlling the atmospheric distribution of DCA over the oceanic regions.

The objective of this study is to understand what controls the atmospheric abundances of dicarboxylic acids, oxoacids, and α-dicarbonyls over the open ocean. Here we conducted analyses of DCA and related compounds in remote marine aerosols collected from the western North Pacific (NP) during summer when ocean biological productivity is high and the impact of continental outflow is low. We compare the concentrations of diacids and related compounds between high and low biological productivity regions and discuss possible formation processes of DCA from isoprene and phytoplankton-derived unsaturated fatty acids.

2. Methods

In this study, bulk aerosols were collected over the open ocean waters of the western subarctic and subtropical NP along the latitudinal transection of 10–45°N (see Figure 1) using a high-volume air sampler with a wind speed/sector control [*Kawamura and Sakaguchi*, 1999]. The sampler was set up on the upper deck of a research vessel, R/V *Hakuho-maru* (cruise: KH08-2). All the samples were collected on precombusted (450°C for 3 h) quartz filters (Pallflex, 2500 QAT-UP) during 24 August to 13 September 2008. The sample air volume in general varied from 500 m^3 to 800 m^3.

Samples were analyzed for dicarboxylic acids, oxoacids, and α-dicarbonyls using the protocols described in our earlier publications [*Kawamura*, 1993; *Kawamura and Ikushima*, 1993]. Briefly, an aliquot of filter is extracted with ultrapure deionized water, followed by derivatization with 14% BF_3 in *n*-Butanol to convert diacids to butyl esters. The aldehyde groups of ω-oxoacids and α-dicarbonyls, and keto group of pyruvic acid are derivatized to dibutoxy acetals. After the derivatization, esters and acetals are back extracted in *n*-Hexane and determined using gas chromatography–flame ionization detector. Peak identification is performed using authentic standards and examining the mass spectra with gas chromatography–mass spectrometry. The recoveries of spiked standards on quartz filters are better than 80% for oxalic acid (C_2) and 85% for other diacids (C_3, C_4, C_5, and C_6). The overall analytical uncertainties in the diacid measurement are within 5% based on replicate analyses of authentic standards and real samples. Aerosol samples were also analyzed for isoprene-SOA tracers (methylglyceric acid and 2-methyltetrols) using the protocol described elsewhere [*Fu et al.*, 2013b]. The results of water-soluble inorganic ions and methanesulfonic acid (MSA), organic carbon (OC) and water-soluble organic carbon (WSOC) are previously described [*Miyazaki et al.*, 2011] and presented here as a supporting information.

3. Results and Discussion

3.1. Oceanic Control on Atmospheric Abundances of Water-Soluble Organic Species

During the course of this study (August–September, 2008), phytoplankton bloom was observed in the subarctic western NP. A notable difference in the surface chlorophyll a concentration was observed along the latitudinal transect between 10–30°N (range: 0.01–0.3 mg m^{-3}) and 30–45°N (0.3–30 mg m^{-3}) [*Miyazaki et al.*, 2011]. Thus, the samples collected along the latitudinal transact of the cruise (Figure 1) have been categorized as more biologically influenced aerosols (hereafter referred as MBA: 30–45°N) and less

Table 1. Statistically Significant Differences/Similarities for the Atmospheric Abundances (in ng m^{-3}) of Diacids and Other Chemical Species, Diagnostic Carbon Mass Ratios Between More and Less Biologically Influenced Aerosols (MBA and LBA) Collected Along the Latitudinal Transection in the Western North Pacific During August–September 2008 (for Cruise Track, See Figure 1)

Compound	MBA: 30–45°N ($n = 15$)	LBA: 10–30°N ($n = 13$)	Ratio (f) = MBA/LBA	Two-Tailed t Score, df, P Value*
	Ave, $\pm$ SD (Min–Max)			
Oxalic acid, C_2	26.1 $\pm$ 15.9 (6.3–61.2)	10.3 $\pm$ 4.8 (2.5–18.8)	2.5 $\pm$ 0.3	3.5, 26, < 0.05
Malonic acid, C_3	13.3 $\pm$ 12.5 (1.1–37.8)	2.1 $\pm$ 0.9 (0.2–3.7)	6.3 $\pm$ 0.2	3.2, 26, < 0.05
Succinic acid, C_4	9.9 $\pm$ 12.6 (0.9–41.2)	0.9 $\pm$ 0.3 (0.4–1.4)	11.6 $\pm$ 0.1	2.6, 26, < 0.05
Glutaric acid, C_5	2.0 $\pm$ 2.4 (0.2–7.0)	0.2 $\pm$ 0.1 (0.05–0.4)	10.0 $\pm$ 0.1	2.6, 26, < 0.05
Adipic acid, C_6	0.6 $\pm$ 0.5 (0.2–1.7)	0.2 $\pm$ 0.1 (0.05–0.3)	3.0 $\pm$ 0.3	3.4, 26, < 0.05
Azelaic acid, C_9	0.35 $\pm$ 0.23 (0.13–0.85)	0.09 $\pm$ 0.06 (0.02–0.20)	3.9 $\pm$ 0.2	3.9, 26, < 0.05
Glyoxylic acid, ωC_2	1.82 $\pm$ 1.42 (0.56–4.61)	0.24 $\pm$ 0.19 (0.06–0.62)	7.6 $\pm$ 0.1	4.0, 26, < 0.05
Glyoxal (Gly)	0.22 $\pm$ 0.15 (0.07–0.62)	0.07 $\pm$ 0.06 (0.00–0.19)	3.1 $\pm$ 0.3	3.5, 26, < 0.05
Methylglyoxal (MeGly)	0.28 $\pm$ 0.26 (0.04–1.02)	0.06 $\pm$ 0.02 (0.03–0.09)	4.7 $\pm$ 0.2	3.0, 26, < 0.05
ΣDCA	58 $\pm$ 45 (13–153)	15 $\pm$ 6 (5–26)	3.9 $\pm$ 0.2	3.4, 26, < 0.05
ΣOxoacids	5.3 $\pm$ 5.8 (1.1–21.2)	0.7 $\pm$ 0.3 (0.3–1.3)	7.6 $\pm$ 0.2	2.9, 26, < 0.05
Σα-Dicarbonyls	0.50 $\pm$ 0.32 (0.20–1.28)	0.12 $\pm$ 0.07 (0.04–0.26)	4.2 $\pm$ 0.2	4.1, 26, < 0.05
Σ[Isoprene-SOA tracers][a]	3.0 $\pm$ 2.2 (0.7–6.2)	0.05 $\pm$ 0.05 (0.01–0.08)	60 $\pm$ 74	2.1, 23, < 0.05
ΣDCA-C/WSOC (%)	9.1 $\pm$ 4.7 (3.9–17.3)	9.2 $\pm$ 6.1 (2.6–26.3)	1.0 $\pm$ 0.9	0.04, 25, > 0.05
ΣOxoacids-C/WSOC (%)	0.92 $\pm$ 0.34 (0.37–1.64)	0.77 $\pm$ 0.60 (0.18–2.33)	1.2 $\pm$ 0.7	0.8, 25, > 0.05
Σα-Dicarbonyls-C/WSOC (%)	0.14 $\pm$ 0.09 (0.05–0.38)	0.15 $\pm$ 0.14 (0.02–0.52)	0.9 $\pm$ 1.2	0.2, 25, > 0.05

*The statistical significant differences/similarities between MBA and LBA at 95% CI.
[a]Samples with high isoprene-SOA concentrations are only averaged in MBA and the remaining concentrations were included in LBA as their temporal distributions show initially high concentrations and remain flat thereafter.

biologically influenced aerosols (LBA: 10–30°N) [*Miyazaki et al.*, 2011]. In addition, higher MSA concentrations were observed in MBA than in LBA (Figure S1). Due to the formation of MSA by the oxidation of dimethyl sulphide (DMS, a biogenic gas) and subsequent gas-to-particle conversion, it was used as a potential proxy for assessing the contribution of BVOCs from the ocean surface to SOA [*Miyazaki et al.*, 2011].

The molecular distribution of diacids was characterized by the predominance of oxalic acid (C_2) followed by malonic (C_3) and succinic (C_4) acids, whose atmospheric abundances were 3 to 12 times higher in MBA than in LBA (see Table 1). Glyoxylic acid (ωC_2) was found as a dominant oxoacid, whose concentrations are 8 times higher in MBA than in LBA. Likewise, concentrations of glyoxal (Gly) and methylglyoxal (MeGly) are 3 to 5 times higher in MBA than in LBA. These compounds are produced by the photochemical oxidation of isoprene and other VOCs in the atmosphere [*Carlton et al.*, 2006, 2009]. Laboratory oxidation of isoprene with ozone reported the production of malonic, succinic, and malic acids [*Nguyen et al.*, 2010]. These diacids may be further oxidized to result in oxalic acid [*Kawamura and Sakaguchi*, 1999]. Azelaic acid (C_9), a specific photochemical oxidation product of biogenic unsaturated fatty acids emitted from the ocean surface [*Kawamura and Sakaguchi*, 1999], also exhibited a fourfold increase in MBA.

Figure 2 shows increased concentrations of selected diacids (C_2 and C_9), oxoacids (ωC_2 and pyruvic acid), and α-dicarbonyl (MeGly) in MBA compared to LBA along the latitudinal transact of the cruise, together with isoprene-SOA tracers (methylglyceric acid and 2-methyltetrols). It is noteworthy that temporal variability of C_2 and C_9 diacids shows a phase match that suggests the production of C_2 via oxidation of higher homologues of diacids in the marine atmospheric boundary layer (MABL). Likewise, covariance of isoprene-SOA, MeGly, and pyruvic acid (Pyr), suggests the formation of these species via the oxidation of isoprene [*Carlton et al.*, 2006]. In addition, significant correlations ($P < 0.05$; see Figure S2) among these species (isoprene-SOA tracers, Pyr, and MeGly) in the MABL, further attests their common origin (i.e., isoprene oxidation products). We found that the abundances of all measured diacids, oxoacids, α-dicarbonyls, and isoprene-SOA tracers increased during phytoplankton bloom, suggesting a coupling between the ocean biological activity and atmospheric concentrations of water-soluble organics.

Earlier study by *Kieber and Mopper* [1987] showed that photochemical and biological formation processes are responsible for the observed high concentrations of glyoxylate and pyruvate in the surface ocean, respectively. *Zhou and Mopper* [1997] reported that photochemical reactions in the surface ocean and sea
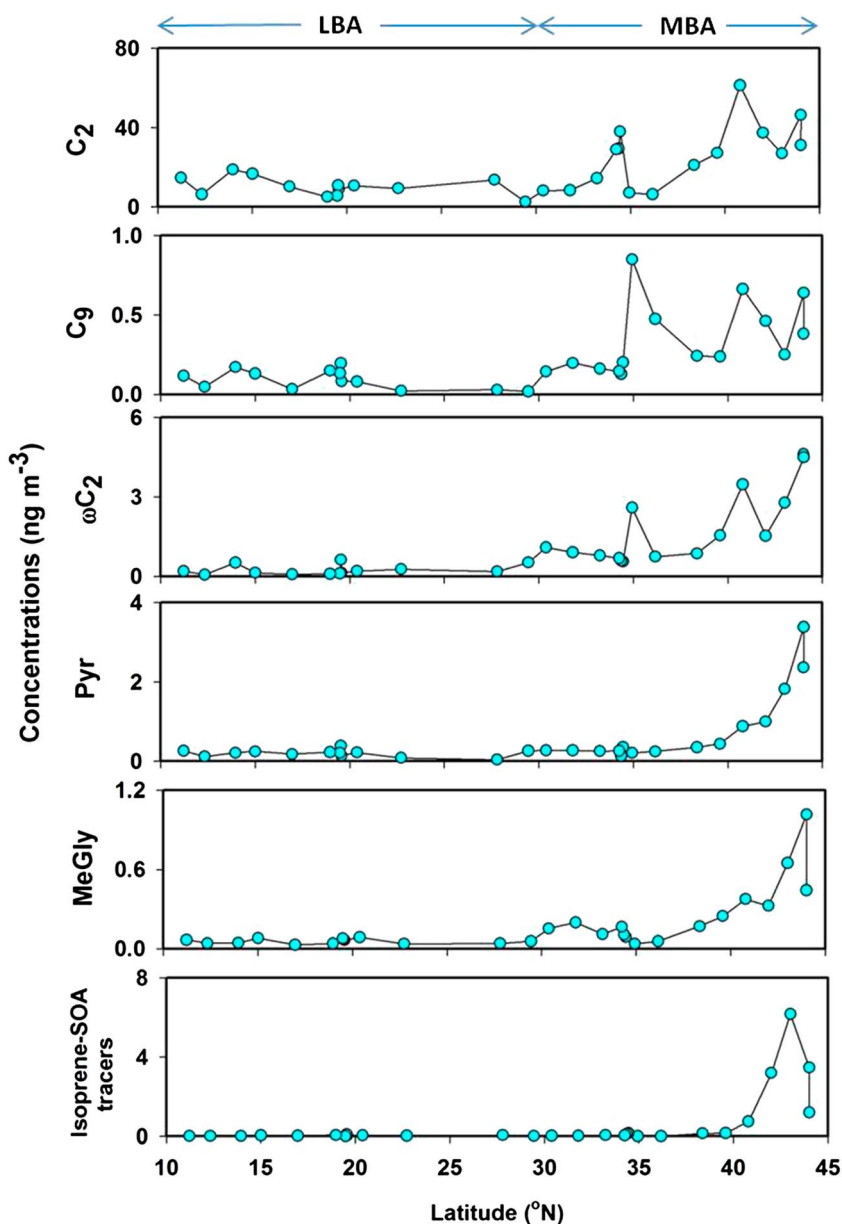
Figure 2. Latitudinal distributions of atmospheric concentrations of selected dicarboxylic acids (oxalic acid: C_2 and azelaic acid: C_9), oxoacids (glyoxylic acid: ωC_2 and pyruvic acid: Pyr), α-dicarbonyls (methylglyoxal: MeGly), and isoprene-SOA tracers in aerosols collected from the western North Pacific during August–September 2008.

surface microlayer lead to the formation of α-dicarbonyls. Another study by *Steinberg and Bada* [1984] also observed the significantly high concentrations of pyruvic and glyoxylic acids in the surface waters of the eastern North Pacific. Therefore, the sea-to-air emission of these species in the MABL could also contribute to their atmospheric abundances by bubble bursting process. However, *Tedetti et al.* [2006] reported the predominance of glyoxylic acid over oxalic acid in the Mediterranean Sea surface water, being in contrast to the predominance of oxalic acid in marine aerosols [*Fu et al.*, 2013a; *Kawamura and Sakaguchi*, 1999; *Sempéré and Kawamura*, 2003].

Interestingly, no significant differences were observed between MBA and LBA for the atmospheric abundances of sea salts and water-insoluble organic carbon (WIOC). Based on the laboratory studies, the primary organic aerosols emitted with the sea spray in a more biologically active ocean are suggested to be primarily comprised of water-insoluble organic matter (up to 77 ± 5%) that contain phytoplankton-derived

detritus such as lipopolysaccharides [*Facchini et al.*, 2008b]. In this study, the concentration of WIOC, on average, account for $71 \pm 20\%$ and $91 \pm 7\%$ of OC in MBA and LBA, respectively, being consistent with the high WIOC fraction in OC during high biological activity in the surface ocean [*Facchini et al.*, 2008b; *O'Dowd et al.*, 2004; *O'Dowd and de Leeuw*, 2007]. Therefore, it can be argued that the primary contribution of WSOC might have been invariant for both types of aerosols (MBA and LBA) owing to the similar production pathway, i.e., bubble bursting process that injects sea salt, water-soluble, and insoluble organics into the MABL [*O'Dowd and de Leeuw*, 2007, and references therein].

It is noteworthy that WSOC concentrations are 4 times higher in the MBA than in LBA. Moreover, the higher WSOC/OC ratios in MBA ($28.9 \pm 19.7\%$) than in LBA ($9.5 \pm 6.9\%$) cannot solely be explained by the contribution of primary oceanic emissions. In this study, the concentrations of diacids and other related water-soluble organic compounds account for ~ 6 to 35% of the WSOC mass (see Table 1). Based on these observations, we suggest that sea-to-air emission of diacids and related compounds is not the main source of these organics in marine aerosols. We emphasize the enhanced atmospheric abundances of isoprene-SOA tracers (sixtyfold), diacids (fourfold), oxoacids (eightfold), and α-dicarbonyls (fourfold) in MBA than in LBA, suggesting a significant secondary formation of these compounds via the photochemical oxidation in the MABL (Table 1, Figure 2, and Figure S3). Another evidence for the secondary formation processes was also inferred based on the prevalent strong positive correlations ($R^2 = 0.46$–0.81) between MSA and other water-soluble organic species (i.e., C_2, C_3, and C_4 diacids, ωC_2, Pyr, and MeGly; Figure S4).

In our cruise, we found that relative humidity is slightly higher in the region of 30–45°N (MBA: 75–95%; ave. $82 \pm 6\%$) than 10–30°N (LBA: 68–82%; ave. $75 \pm 4\%$). Higher relative humidity can enhance the aqueous phase oxidation of isoprene and its intermediate products, which leads to the formation of diacids and related compounds in the MABL [*Carlton et al.*, 2009]. Therefore, the high atmospheric abundances of isoprene-SOA tracers, diacids, oxoacids, and α-dicarbonyls in MBA together with high relative humidity suggest that aqueous phase reactions may play an important role in the increased production of these species. *Youn et al.* [2013] documented a significant formation of SOAs via the aqueous phase oxidation of BVOCs under enhanced moisture conditions, in which WSOC/OC ratio increased by twofold during monsoon season compared to the rest of the year. Based on the above discussions, we infer that isoprene and unsaturated fatty acids emitted from the ocean surface can serve as pivotal source of atmospheric DCAs and related compounds in the pristine remote atmosphere over high-productivity ocean.

### 3.2. Source Apportionment: Biogenic Versus Anthropogenic Origin

Miyazaki et al. [2011] suggested the predominant oceanic source for marine organic aerosols rather than the continental sources based on the air mass back trajectories and chemical constituents of marine aerosols. This idea is further corroborated by very low concentrations of anthropogenic terephthalic (ave. 0.6 ± 0.4 ng m^{-3}) and phthalic acids (0.5 ± 0.3 ng m^{-3}) in the MABL, which are 30–40 times lower than those reported for continental aerosols in Japan [*Agarwal et al.*, 2010]. In addition, nondetectable levels of elemental carbon were found in most of the samples, suggesting a minor contribution from continental sources over the open ocean waters in the western NP during the study period.

Although measured concentrations of water-soluble organic species (e.g., MSA, DCA, oxoacids, and α-dicarbonyls) are higher in MBA than in LBA (Figure 3a), no significant difference ($P > 0.05$; Table 1) was observed in their contributions to WSOC between MBA and LBA (Figure 3b). This observation emphasizes that there is a similar formation pathway of diacids and related water-soluble organic compounds in the MABL (via photochemical transformation/in-cloud processing). Interestingly, contributions of DCA, oxoacids, and α-dicarbonyls to OC showed higher values in MBA than in LBA (Figure 3c). These results demonstrate that water-soluble organic acids and related compounds are more enriched in organic aerosols as a result of photochemical transformations of organic precursors emitted from the ocean.

3.3. Contribution of Oceanic Isoprene to SOA

As mentioned earlier, isoprene and monoterpenes can be emitted from the ocean during biologically active period. Based on the laboratory study, their contributions to SOA mass were estimated to be ~2% for isoprene and ~32% for monoterpenes [*Lee et al.*, 2006]. Using these values and measured concentrations of isoprene-SOA tracers, *Hu et al.* [2013] estimated the sea-to-air fluxes of isoprene to be 13 to 38 μg m^{-2} d^{-1} during nonbloom (background) conditions and suggested a possible increase in the isoprene emissions
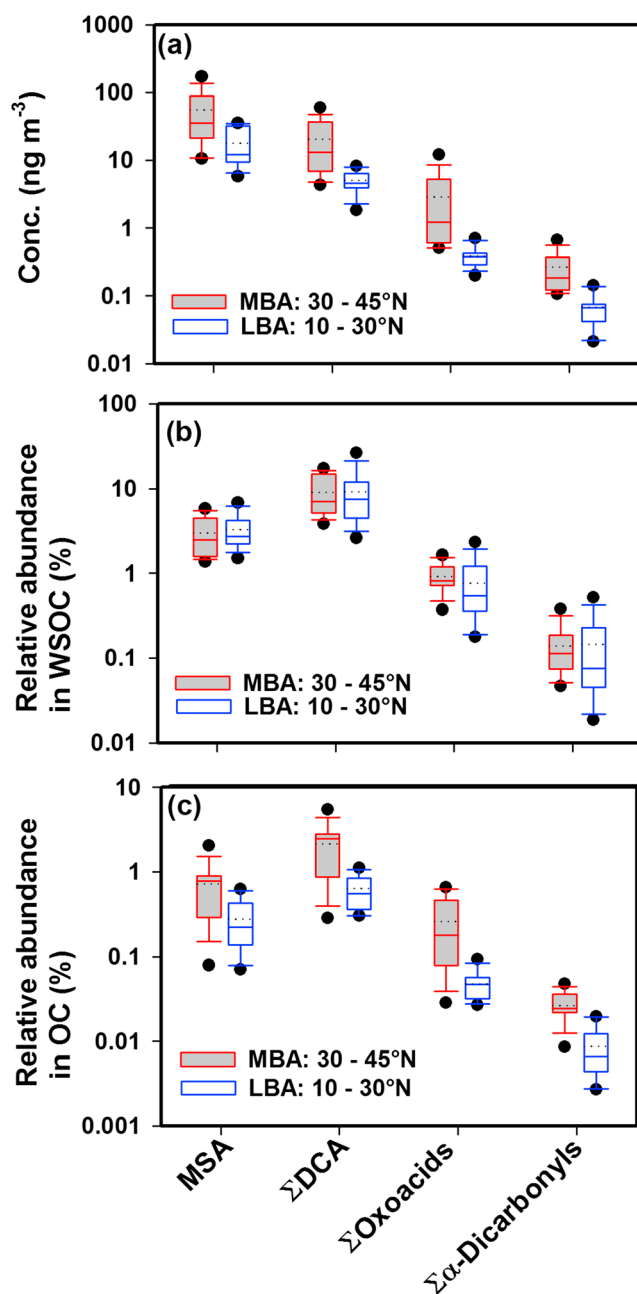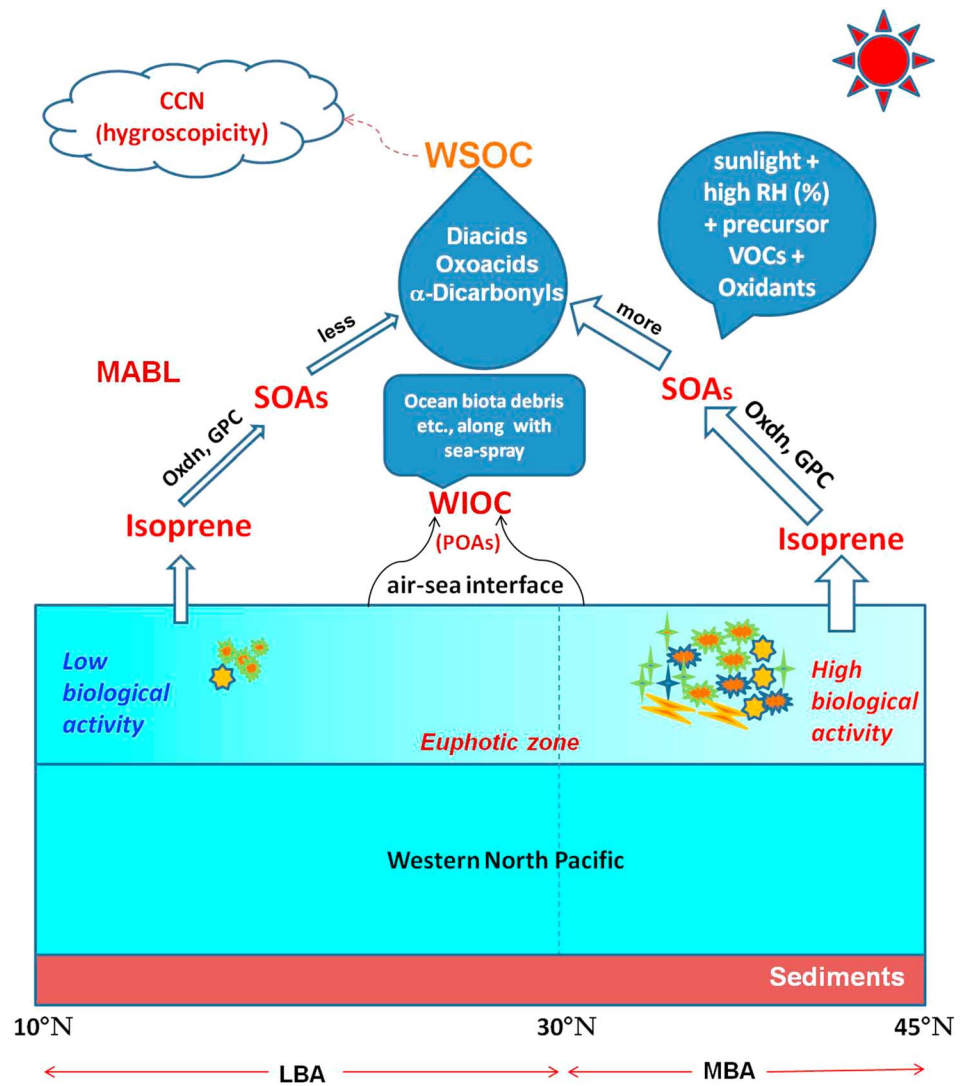
Figure 3. Box whisker plot, showing (a) atmospheric concentrations of methanesulfonic acid (MSA), total diacids (ΣDCA), oxoacids (ΣOxoacids), and α-dicarbonyls (Σα − Dicarbonyls) and their contributions to (b) water-soluble organic carbon (WSOC) and (c) total organic carbon (OC) in marine aerosols collected over the western North Pacific during August–September 2008. MBA and LBA refer to more and less biologically influenced aerosols, respectively.

during phytoplankton blooms. In this context, recent model estimates of global oceanic emissions of VOCs also suggested a relatively high concentration of isoprene in the surface waters (e.g., the western NP) during high biological productivity period and, thus, its emission flux to the MABL could significantly contribute to SOA formation in the open oceans [*Myriokefalitakis et al.*, 2010].

In order to ascertain the enhanced contribution of BVOCs to the MABL during high biological activity period, we measured isoprene-SOA tracers and found that their concentrations (ΣIsoprene-SOA tracers) are significantly higher in MBA (ave. 3.0 ± 2.2 ng m^{-3}; only samples with higher concentrations were considered for the average; median: 3.2 ng m^{-3}) than in LBA (0.05 ± 0.05 ng m^{-3}; median: 0.04 ng m^{-3}), being consistent with other parameters (i.e., Chl a, MSA, WSOC, diacids, and related compounds). Although the average concentrations of isoprene-SOA tracers are 30–40 times higher in MBA than in LBA, the maximum value observed during phytoplankton bloom is 6.2 ng m^{-3}, which is significantly higher than those of LBA (0.01–0.08 ng m^{-3}; Table 1).

As a pseudo first-order approximation, we used this maximum concentration to estimate the sea-to-air fluxes of isoprene during bloom conditions over the western NP. The concentration of isoprene-SOA in the MABL of the western NP during the high productivity period is ~ 98 ng m^{-3}, which is estimated based on *Hu et al.* [2013]; isoprene-SOA = [ΣIsoprene-SOA tracer conc.]/$f_{\text{tracer/SOA}}$, where $f_{\text{tracer/SOA}}$ (0.063) is the conversion factor for aerosol tracer concentration to SOA mass. Interestingly, this value is close to the higher end of oxalic acid concentrations (~ 60 ng m^{-3}; Figure 2), indicating that isoprene-SOA can explain the observed levels of oxalic acid. This value also corresponds to isoprene sea-to-air flux of ~ 422–1230 μg m^{-2} d^{-1} (see supporting information), which is 2 orders of magnitude higher than those estimated for the background isoprene SOA tracer concentrations by *Hu et al.* [2013]. Our isoprene-SOA concentration and corresponding sea-to-air flux of isoprene are similar to those reported in the coastal regions of Antarctica (Prydz Bay) during high biological activity period characterized by high concentrations

Figure 4. Conceptual model for productivity-driven SOA formation in the marine atmospheric boundary layer (MABL) via oxidation of isoprene emitted from the ocean surface and its control on atmospheric abundances of water-soluble dicarboxylic acids in the marine aerosols. Here GPC, WIOC, and CCN refer to gas-to-particle conversion, water-insoluble organic carbon, and cloud condensation nuclei, respectively.

of Chl a (~30 mg m^{-3}) and high-isoprene sea-to-air efflux (~ 18–1200 μg m^{-2} d^{-1}), which were estimated by isoprene-SOA tracers [*Hu et al.*, 2013].

3.4. Conceptual Model: Productivity-Driven Distribution of DCA in the MABL

Some dialkenes such as isoprene and monoterpenes [*Bonsang et al.*, 1992; *Gantt et al.*, 2010; *McKay et al.*, 1996; *Meskhidze and Nenes*, 2006; *Shaw et al.*, 2003, 2010; *Yassaa et al.*, 2008] and carbonyl compounds such as glyoxal [*Sinreich et al.*, 2010; *Zhou and Mopper*, 1997] are produced in the surface ocean by biological activity combined with many complex processes (i.e., bacterial degradation of organic matter, photochemical processes, redox reactions, etc.). During Subarctic Ecosystem Response to Iron Enrichment Study, sea-to-air emission of isoprene has been documented to increase by *Moore and Wang* [2006]. Likewise, during Southern Ocean iron Fertilization Experiment, a factor of 4 increase was reported for the concentrations of isoprene in the fertilized patch [*Wingenter et al.*, 2004]. The intrusion of isoprene into the MABL through air-sea interface and subsequent oxidation in the atmosphere can result in the formation of diacids and related compounds that are more water soluble than the precursor. Owing to their hygroscopic nature, the particles containing these SOA components can act as cloud condensation nuclei (CCN) in the MABL.

Figure 4 depicts the conceptual model, which deals with productivity-driven atmospheric distribution of water-soluble organic species, in particular, dicarboxylic acids over the open oceans. Contribution of WSOC to OC drastically increases from low to high biological activity regions, showing its control on the abundances of water-soluble diacids and related compounds in the MABL. However, as mentioned above, WIOC did not show any significant difference between MBA and LBA, being consistent with the results of sea salt (see Table S1). This result indicates that WIOC is a primary emission product that contributes as high as ~70% and 90% of OC over the high- and low-productivity oceans, respectively (Table S1).

During the same cruise, high CCN activity has been documented by *Mochida et al.* [2011]. Earlier studies also documented an enhanced CCN activity over the open ocean waters during high biological activity [*Korhonen et al.*, 2008; *Meskhidze and Nenes,* 2006, 2010; *Sorooshian et al.*, 2009; *Sorooshian and Duong*, 2010; *Vallina et al.*, 2006]. Although we do not have the size distribution data of diacids in the present cruise, previous study has shown that the size-segregated molecular distribution of oxalic acid and other low molecular weight diacids are enriched in the fine mode particles [*Miyazaki et al.*, 2010]. Based on the higher abundances of MSA and diacids in MBA together with $nss\text{-}SO_4^{2-}$ (0.3 to 10.4 $\mu g\ m^{-3}$), we suggest that these water-soluble organics as well as $nss\text{-}SO_4^{2-}$ might enhance the hygroscopic growth of the ambient aerosols over the open ocean waters characterized by high biological activity, acting as CCN. However, the role of atmospheric water-soluble organics in CCN activity remains largely uncertain and is still a major source of uncertainty in estimating their indirect radiative forcing.

Overall, we infer that marine biogenic emissions of isoprene followed by photochemical oxidation significantly control the abundances of water-soluble diacids, oxoacids, and α-dicarbonyls in the MABL, although the formation mechanism of oxalic and other small diacids is still not well known. These observations highlight an important role of oceanic isoprene as a source of SOA in the open ocean, suggesting a need to incorporate these outcomes into the coupled ocean-atmosphere feedback models.

References

Agarwal, S., et al. (2010), Size distributions of dicarboxylic acids, ketoacids, alpha-dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in atmospheric particles over Northern Japan: Implication for long-range transport of Siberian biomass burning and East Asian polluted aerosols, *Atmos. Chem. Phys.*, *10*(13), 5839–5858.

Bonsang, B., C. Polle, and G. Lambert (1992), Evidence for marine production of isoprene, *Geophys. Res. Lett.*, *19*, 1129–1132, doi:10.1029/92GL00083.

Carlton, A. G., B. J. Turpin, H.-J. Lim, K. E. Altieri, and S. Seitzinger (2006), Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, *Geophys. Res. Lett.*, *33*, L06822, doi:10.1029/2005GL025374.

Carlton, A., C. Wiedinmyer, and J. H. Kroll (2009), A review of secondary organic aerosol (SOA) formation from isoprene, *Atmos. Chem. Phys.*, *9*(14), 4987–5005.

Claeys, M., et al. (2004a), Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, *303*(5661), 1173–1176.

Claeys, M., W. Wang, A. C. Ion, I. Kourtchev, A. Gelencsér, and W. Maenhaut (2004b), Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, *Atmos. Environ.*, *38*(25), 4093–4098.

Facchini, M. C., et al. (2008a), Important source of marine secondary organic aerosol from biogenic amines, *Environ. Sci. Technol.*, *42*(24), 9116–9121.

Facchini, M. C., et al. (2008b), Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, *Geophys. Res. Lett.*, *35*, L17814, doi:10.1029/2008GL034210.

Fu, P., K. Kawamura, K. Usukura, and K. Miura (2013a), Dicarboxylic acids, ketocarboxylic acids and glyoxal in the marine aerosols collected during a round-the-world cruise, *Mar. Chem.*, *148*, 22–32.

Fu, P. Q., K. Kawamura, J. Chen, B. Charrière, and R. Sempéré (2013b), Organic molecular composition of marine aerosols over the Arctic Ocean in summer: Contributions of primary emission and secondary aerosol formation, *Biogeosciences*, *10*(2), 653–667.

Gantt, B., and N. Meskhidze (2013), The physical and chemical characteristics of marine primary organic aerosol: A review, *Atmos. Chem. Phys.*, *13*(8), 3979–3996.

Gantt, B., N. Meskhidze, Y. Zhang, and J. Xu (2010), The effect of marine isoprene emissions on secondary organic aerosol and ozone formation in the coastal United States, *Atmos. Environ.*, *44*(1), 115–121.

Hu, Q.-H., Z.-Q. Xie, X.-M. Wang, H. Kang, Q.-F. He, and P. Zhang (2013), Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic, *Sci. Rep.*, *3*, doi:10.1038/srep02280.

Kawamura, K. (1993), Identification of C2-C10 omega-oxocarboxylic acids, pyruvic acid, and C2-C3 alpha-dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC/MS, *Anal. Chem.*, *65*(23), 3505–3511.

Kawamura, K., and F. Sakaguchi (1999), Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, *104*(D3), 3501–3509.

Kawamura, K., H. Kasukabe, and L. A. Barrie (1996), Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos. Environ.*, *30*, 1709–1722.

Kawamura, K., and K. Ikushima (1993), Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, *27*(10), 2227–2235.

Kawamura, K., and K. Usukura (1993), Distributions of low molecular weight dicarboxylic acids in the North Pacific aerosol samples, *J. Oceanogr.*, *49*(3), 271–283.

Kawamura, K., and O. Yasui (2005), Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, *39*(10), 1945–1960.

Kawamura, K., M. Kobayashi, N. Tsubonuma, M. Mochida, T. Watanabe, and M. Lee (2004), Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in *Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan, The Geochemical Society*, edited by R. J. Hill et al., pp. 243–265, Elsevier, New York.

Kieber, D. J., and K. Mopper (1987), Photochemical formation of glyoxylic and pyruvic acids in seawater, *Mar. Chem.*, *21*(2), 135–149.

Kondo, Y., et al. (2007), Oxygenated and water-soluble organic aerosols in Tokyo, *J. Geophys. Res.*, *112*, D01203, doi:10.1029/2006JD007056.

Korhonen, H., et al. (2008), Influence of oceanic dimethyl sulfide emissions on cloud condensation nuclei concentrations and seasonality over the remote Southern Hemisphere oceans: A global model study, *J. Geophys. Res.*, *113*, D15204, doi:10.1029/2007JD009718.

Langmann, B., C. Scannell, and C. O'Dowd (2008), New directions: Organic matter contribution to marine aerosols and cloud condensation nuclei, *Atmos. Environ.*, *42*(33), 7821–7822.

Lee, A., A. H. Goldstein, M. D. Keywood, S. Gao, V. Varutbangkul, R. Bahreini, N. L. Ng, R. C. Flagan, and J. H. Seinfeld (2006), Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, *J. Geophys. Res.*, *111*, D07302, doi:10.1029/2005JD006437.

McKay, W., M. F. Turner, B. M. R. Jones, and C. M. Halliwell (1996), Emissions of hydrocarbons from marine phytoplankton—Some results from controlled laboratory experiments, *Atmos. Environ.*, *30*(14), 2583–2593.

Meskhidze, N., and A. Nenes (2006), Phytoplankton and cloudiness in the Southern Ocean, *Science*, *314*, 1419–1423.

Meskhidze, N., and A. Nenes (2010), Effects of ocean ecosystem on marine aerosol-cloud interaction, *Adv. Meteorol.*, *2010*, 239808, doi:10.1155/2010/239808.

Miyazaki, Y., K. Kawamura, and M. Sawano (2010), Size distributions and chemical characterization of water-soluble organic aerosols over the western North Pacific in summer, *J. Geophys. Res.*, *115*, D23210, doi:10.1029/22010JD014439.

Miyazaki, Y., K. Kawamura, J. Jung, H. Furutani, and M. Uematsu (2011), Latitudinal distributions of organic nitrogen and organic carbon in marine aerosols over the western North Pacific, *Atmos. Chem. Phys.*, *11*(7), 3037–3049.

Mkoma, S. L., K. Kawamura, and P. Q. Fu (2013), Contributions of biomass/biofuel burning to organic aerosols and particulate matter in Tanzania, East Africa, based on analyses of ionic species, organic and elemental carbon, levoglucosan and mannosan, *Atmos. Chem. Phys.*, *13*(20), 10,325–10,338.

Mochida, M., A. Kawabata, K. Kawamura, H. Hatsushika, and K. Yamazaki (2003), Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific, *J. Geophys. Res.*, *108*(D6), 4193, doi:10.1029/2002JD002355.

Mochida, M., C. Nishita-Hara, H. Furutani, Y. Miyazaki, J. Jung, K. Kawamura, and M. Uematsu (2011), Hygroscopicity and cloud condensation nucleus activity of marine aerosol particles over the western North Pacific, *J. Geophys. Res.*, *116*, D06204, doi:10.1029/2010JD014759.

Moore, R. M., and L. Wang (2006), The influence of iron fertilization on the fluxes of methyl halides and isoprene from ocean to atmosphere in the SERIES experiment, *Deep Sea Res., Part II*, *53*(20–22), 2398–2409.

Myriokefalitakis, S., et al. (2010), Global modeling of the oceanic source of organic aerosols, *Adv. Meteorol.*, *2010*, 939171, doi:10.1155/2010/939171.

Myriokefalitakis, S., K. Tsigaridis, N. Mihalopoulos, J. Sciare, A. Nenes, K. Kawamura, A. Segers, and M. Kanakidou (2011), In-cloud oxalate formation in the global troposphere: A 3-D modeling study, *Atmos. Chem. Phys.*, *11*(12), 5761–5782.

Nguyen, T. B., A. P. Bateman, D. L. Bones, S. A. Nizkorodov, J. Laskin, and A. Laskin (2010), High-resolution mass spectrometry analysis of secondary organic aerosol generated by ozonolysis of isoprene, *Atmos. Environ.*, *44*(8), 1032–1042.

O'Dowd, C. D., and G. de Leeuw (2007), Marine aerosol production: A review of the current knowledge, *Roy. Soc. London Philos. Trans. Ser. A*, *365*, 1753–1774.

O'Dowd, C. D., M. H. Smith, I. E. Consterdine, and J. A. Lowe (1997), Marine aerosol, sea-salt, and the marine sulphur cycle: A short review, *Atmos. Environ.*, *31*(1), 73–80.

O'Dowd, C. D., M. C. Facchini, F. Cavalli, D. Ceburnis, M. Mircea, S. Decesari, S. Fuzzi, Y. J. Yoon, and J.-P. Putaud (2004), Biogenically driven organic contribution to marine aerosol, *Nature*, *431*(7009), 676–680.

Rinaldi, M., S. Decesari, E. Finessi, L. Giulianelli, C. Carbone, S. Fuzzi, C. D. O'Dowd, D. Ceburnis, and M. C. Facchini (2010), Primary and secondary organic marine aerosol and oceanic biological activity: Recent results and new perspectives for future studies, *Adv. Meteorol.*, *2010*, 310682, doi:10.1155/2010/310682.

Sempéré, R., and K. Kawamura (2003), Trans-hemispheric contribution of C2–C10 α, ω-dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions, *Global Biogeochem. Cycles*, *17*(2), 1069, doi:10.1029/2002GB001980.

Shaw, S. L., S. W. Chisholm, and R. G. Prinna (2003), Isoprene production by Prochlorococcus, a marine cyanobacterium, and other phytoplankton, *Mar. Chem.*, *80*(4), 227–245.

Shaw, S. L., B. Gantt, and N. Meskhidze (2010), Production and emissions of marine isoprene and monoterpenes: A review, *Adv. Meteorol.*, *2010*, 408696, doi:10.1155/2010/408696.

Sinreich, R., S. Coburn, B. Dix, and R. Volkamer (2010), Ship-based detection of glyoxal over the remote tropical Pacific Ocean, *Atmos. Chem. Phys.*, *10*(23), 11,359–11,371.

Sorooshian, A., and H. T. Duong (2010), Ocean emission effects on aerosol-cloud interactions: Insights from two case studies, *Adv. Meteorol.*, *2010*, doi:10.1155/2010/301395.

Sorooshian, A., et al. (2009), On the link between ocean biota emissions, aerosol, and maritime clouds: Airborne, ground, and satellite measurements off the coast of California, *Global Biogeochem. Cycles*, *23*, GB4007, doi:10.1029/2009GB003464.

Steinberg, S. M., and J. L. Bada (1984), Oxalic, glyoxalic and pyruvic acids in eastern Pacific Ocean waters, *J. Mar. Res.*, *42*(3), 697–708.

Tedetti, M., K. Kawamura, B. Charrière, N. Chevalier, and R. Sempéré (2006), Determination of low molecular weight dicarboxylic and ketocarboxylic acids in seawater samples, *Anal. Chem.*, *78*(17), 6012–6018.

Vallina, S. M., et al. (2006), What controls CCN seasonality in the Southern Ocean? A statistical analysis based on satellite-derived chlorophyll and CCN and model-estimated OH radical and rainfall, *Global Biogeochem. Cycles*, *20*, GB1014, doi:10.1029/2005GB002597.

Wingenter, O. W., K. B. Haase, P. Strutton, G. Friederich, S. Meinardi, D. R. Blake, and F. Sherwood Rowland (2004), Changing concentrations of CO, CH4, C5H8, CH3Br, CH3I, and dimethyl sulfide during the Southern Ocean Iron Enrichment Experiments, *Proc. Natl. Acad. Sci. U.S.A.*, *101*(23), 8537–8541.

Yassaa, N., I. Peeken, E. Zöllner, K. Bluhm, S. Arnold, D. Spracklen, and J. Williams (2008), Evidence for marine production of monoterpenes, *Environ. Chem.*, *5*(6), 391–401.

Youn, J.-S., Z. Wang, A. Wonaschütz, A. Arellano, E. A. Betterton, and A. Sorooshian (2013), Evidence of aqueous secondary organic aerosol formation from biogenic emissions in the North American Sonoran Desert, *Geophys. Res. Lett.*, *40*, 3468–3472, doi:10.1002/grl.50644.

Zhou, X., and K. Mopper (1997), Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air-sea exchange, *Mar. Chem.*, *56*(3), 201–213.