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RESEARCH ARTICLE
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Key Points:
- Maximum concentrations of hydroxy fatty acids in winter and spring
- Springtime Asian dust over Gosan and Chichijima shows characteristic predominance of β-hydroxy C_{12} fatty acid
- A remarkable similarity of ω-hydroxy C_{16} fatty acid between Gosan (coastal island) and Chichijima (remote marine island) for all seasons

Supporting Information:
- Supporting Information S1
- Figure S1
- Figure S2
- Figure S3

Correspondence to:
K. Kawamura,
kkawamura@isc.chubu.ac.jp

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Tracing atmospheric transport of soil microorganisms and higher plant waxes in the East Asian outflow to the North Pacific Rim by using hydroxy fatty acids: Year-round observations at Gosan, Jeju Island

Poonam Tyagi[1,2], Kimitaka Kawamura[2,3], Tadashi Kariya[1,2], Srinivas Bikkina[2,4], Pingqing Fu[5], and Meehye Lee[6]

[1]Graduate School of Environmental Sciences, Hokkaido University, Sapporo, Japan, [2]Institute of Low Temperature Sciences, Hokkaido University, Sapporo, Japan, [3]Now at Chubu Institute for Advanced Studies, Chubu University, Kasugai, Japan, [4]Now at Department of Environmental Science and Analytical Chemistry (ACES), Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden, [5]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China, [6]Department of Earth and Environmental Sciences, Korea University, Seoul, South Korea

Abstract Atmospheric transport of soil microorganisms and higher plant waxes in East Asia significantly influences the aerosol composition over the North Pacific. This study investigates the year-round atmospheric abundances of hydroxy fatty acids (FAs), tracers of soil microorganisms (β-isomers), and plant waxes (α- and ω-isomers), in total suspended particles collected at Gosan, Jeju Island, during April 2001 to March 2002. These hydroxy FAs showed a pronounced seasonality, higher concentrations in winter/spring and lower concentrations in summer/autumn, which are consistent with other tracers of soil microbes (trehalose), resuspended dust (nss-Ca^{2+}), and stable carbon isotopic composition ($\delta^{13}C$) of total carbon. The molecular distributions of β-hydroxy FAs (predominance of C_{12} and C_{16} in winter/spring and summer/autumn, respectively) are consistent with those from a remote island (Chichijima) in the North Pacific and Asian dust standards (CJ-1 and CJ-2). This observation together with back trajectories over Gosan reveal that desert sources in China during winter and arid regions of Mongolia and Russian Far East during spring are the major contributors of soil microbes over the North Pacific. Predominance of ω-isomers (83%) over β-hydroxy FAs (16%) revealed a major contribution of terrestrial lipids from higher plant waxes over soil microbes in the East Asian outflow.

1. Introduction

Atmospheric transport of mineral dust to the open ocean has a considerable influence on the biogeochemical cycles of the dissolved carbon pool through the supply of various inorganic and organic constituents [*Schulz et al.*, 2012; *Jickells and Moore*, 2015]. It is also a major source of terrestrial lipid compounds to pelagic sediments. Hydroxy fatty acids (FAs) are one of the major constituents in the lipid fractions of a variety of organisms that include bacteria [*Wilkinson*, 1988], algae [*Blokker et al.*, 1999], and higher plants [*Pollard et al.*, 2008; *Molina et al.*, 2006]. Previous studies have used hydroxy fatty acids (FAs) in lacustrine, marine, and lake sediments [*Volkman et al.*, 1980; *Cardoso and Eglinton*, 1983; *Kawamura and Ishiwatari*, 1984; *Wakeham*, 1999] to understand the transport and distribution of lipids from microalgae, soil microbes, and plant waxes over the recent past. In addition, some studies also document their occurrence in soils [*Zelles*, 1999, and references therein], snow [*Tyagi et al.*, 2015b; *Tyagi et al.*, 2016b], dust [*Saraf et al.*, 1997; *Milton et al.*, 2000], and atmospheric aerosols [*Lee et al.*, 2004; *Tyagi et al.*, 2015a]. However, there remains an urgent need to understand and evaluate hydroxy FAs as potential tracers of changing wind patterns, sources, and source strengths of soil microbes and plant waxes in the Anthropocene.

Hydroxy FAs are often categorized into different source groups based on their carbon chain lengths and positions of the hydroxyl (OH) group. In particular, aliphatic homologues of α-, β-, and ω-monohydroxy FAs serve as tracers of soil microbes and terrestrial higher plants in ambient aerosols [*Kawamura*, 1995; *Kawamura et al.*, 2003; *Lee et al.*, 2004]. Wind-driven abrasion of leaf surface lipids and resuspension of soil particles both

contribute to the atmospheric abundances of hydroxy FAs [*Rogge et al.*, 1993]. Among the terrestrial (land-derived) lipid biomarkers, aliphatic short-chain β-hydroxy FAs (typically C_{10}–C_{20}) mostly originate from the structural constituents of soil microorganisms such as bacteria, fungi, yeasts, and protozoa [*Ratledge and Wilkinson*, 1988; *Lee et al.*, 2004, 2007]. However, certain cyanobacteria spp. also contribute to the atmospheric abundances of β-hydroxy FAs over the open ocean [*Wakeham et al.*, 2003]. In particular, β-hydroxy FAs from C_{10} to C_{18} are the important structural constituents of the lipid A fraction of lipopolysaccharides (LPSs) of the soil Gram-negative bacteria (GNB) [*Wilkinson*, 1988; *Maitra et al.*, 1986; *Paba et al.*, 2013].

Long-chain ω-hydroxy FAs (from C_{16} to C_{34}) and α- and β-hydroxy FAs ($>C_{20}$) are abundant in epicuticular plant waxes [*Simoneit*, 1989; *Rogge et al.*, 1993]. However, microalgae/algal detritus [*Cranwell*, 1981], cyanobacteria [*Matsumoto and Nagashima*, 1984; *Matsumoto et al.*, 1984], and sea grasses [*Volkman et al.*, 1999] also contribute to short-chain homologues of α- and ω-hydroxy FAs. Moreover, short-chain α-hydroxy FAs are formed as intermediates in the photochemical oxidation pathways by which long-chain fatty acids from higher plants are degraded during atmospheric transport [*Volkman et al.*, 1998; *Wakeham*, 1999]. All these observations suggest a limited usage of α-hydroxy FAs as proxies for plant and microbial metabolites in environmental samples. However, their presence in continental outflows hints at their contributions from terrestrial lipid biomarkers (i.e., either soil microbes/plant waxes or their oxidation products during transport). Therefore, α-, β-, and ω-hydroxy FAs can certainly be used as tracers of soil microbes and plant metabolites in airborne particulate matter.

The East Asian outflow significantly influences the aerosol chemical composition over the western North Pacific during winter and spring. To assess the impact of this continental outflow, previous studies established a long-term aerosol characterization station at the Gosan site in Jeju Island, South Korea [*Seinfeld et al.*, 2004, and references therein]. Gosan receives mineral dust in winter/spring from arid areas such as the Gobi and Taklamakan Deserts in China, Mongolia, and Russia [*Duce et al.*, 1980]. Asian dust serves as a carrier for soil microorganisms in East Asia to the North Pacific [*Tyagi et al.*, 2015a]. Previous studies revealed seasonal occurrences of East Asian outflow based on the chemical composition of various inorganic and organic tracer compounds in Gosan aerosols [*Kawamura et al.*, 2004; *Wang et al.*, 2009; *Yamamoto et al.*, 2013; *Kundu and Kawamura*, 2014]. However, we find no similar attempts to assess the atmospheric abundances and molecular distribution of lipid biomarkers that are specific to soil microbes and plant waxes. Therefore, we studied aerosol samples collected from Gosan as part of the ACE-Asia (Aerosol Characterization Experiment) campaign [*Huebert et al.*, 2003; *Seinfeld et al.*, 2004] to assess along-range atmospheric transport of bacteria and plant metabolites by using α-, β-, and ω-hydroxy FAs. The aim of this study is to ascertain the seasonal and temporal variations of hydroxy FAs to gain insights into the relative influence of continental versus oceanic sources of lipids in the East Asian outflow. We also compared their molecular distributions in aerosols over Gosan with those documented for a remote island (Chichijima) in the western North Pacific [*Tyagi et al.*, 2015a] to understand transport-induced changes in their composition.

2. Experimental Methods

2.1. Site Description and Sample Collection

The Gosan site is located at the top of a 71 m cliff on the southwestern edge of Jeju Island, South Korea (Figure 1). Jeju Island (33.36°N, 126.53°E; area of 1845 km^2; population 0.55 million) is distal to Mainland China, Korea, and Kyushu Island of Japan and is located at the boundary of the Yellow Sea and the East China Sea. Because of its remoteness and location at the southwestern side of Jeju Island, Gosan is not much influenced by anthropogenic activities. Gosan is dominated by westerly winds from winter (December–February) to spring (March–May), mainly coming from the Asian continent. On the other hand, easterly winds blow from the Pacific Ocean over Gosan during summer (June–August) and autumn (September–November). Gosan has been used as a super site for the study of chemical compositions of air masses in the representative background of Northeast Asia not only during ACE-Asia [*Huebert et al.*, 2003; *Seinfeld et al.*, 2004] but also for other field campaigns such as Pacific Exploratory Mission West A and B [*Hoell et al.*, 1996]. This is mainly because of its location on the pathway of atmospheric transport of particulate matter from the Asian continent to the North Pacific.

Aerosol samples were collected at the Gosan site on a daily/few days' basis from April 2001 to March 2002 [*Kawamura et al.*, 2004]. We used precombusted (450°C, 6 h) quartz fiber filters (PALLFLEX® 2500QAT-UP, 20 cm × 25 cm) to collect aerosol samples with a high volume air sampler (Kimoto AS-810, flow rate

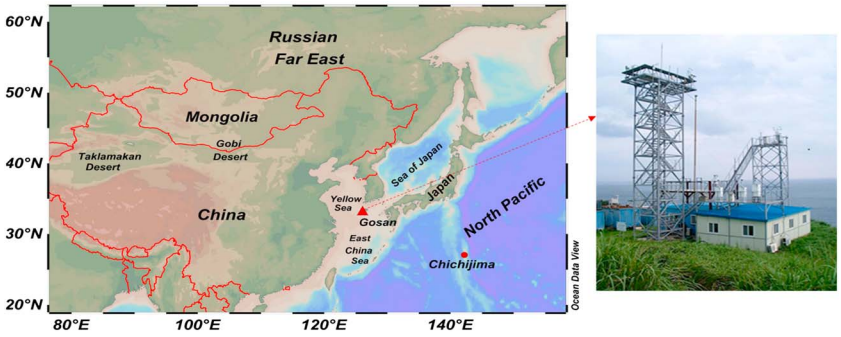

Figure 1. Geographical map, showing the location of sampling site (Gosan) in Jeju Island, surrounded by China in the east, by South Korea in the north, and by the western North Pacific in the east.

50 m^3 h^{-1}). We installed the air sampler on the top of a ~15 m high tower during April 2001 and then, after May 2001, moved it to the rooftop of a trailer house (~3 m above ground level, agl). We kept the aerosol filters in a clean glass jar with a Teflon-lined screw cap before and after sampling. We took precautions in order to avoid contamination while collecting aerosol and blank filter samples. After collection, all the filter samples were stored in a dark cold room at −20°C until analysis.

In a fashion similar to other aerosol samples, we also analyzed two certified reference materials, namely, Chinese loess (CJ-1) and simulated Asian dust (CJ-2), to better assess the source regions for hydroxy FAs in particulate matter. The CJ-1 refers to dust sample from the Malan loess horizon (1.8–2.5 m deep) near Huiningin Gansu Province, with a particle size range of 10–400 μm (mode diameter ~49 μm). The CJ-2 is a surface (0–6 cm) loess sample from the southeast part of the Tengger Desert in the Ningxia Hui autonomous region of China with a particle size of <100 μm (mode diameter ~26 μm). A detailed description of the chemical compositions of CJ-1 and CJ-2 samples is given in *Nishikawa et al.* [2000].

We also compared the results from Gosan super site with those obtained from a remote oceanic Island, Chichijima (27°04′N, 142°13′E), located in the western North Pacific. Chichijima is also an important site to track a long-range transport of mineral dust and associated waxy lipids (e.g., hydroxy FAs) from East Asia during winter and spring [*Chen et al.*, 2013; *Yamamoto et al.*, 2011; *Mochida et al.*, 2003]. Dust outbreaks from East Asia are very common during late winter and spring, originating from arid and semiarid regions in northern China, Mongolia, and central Asia under high surface wind conditions. Aerosol samples ($N = 69$) were collected on a biweekly basis from April 1990 to November 1993 at the Ogasawara downrange station of the Japan Aerospace Exploration Agency (elevation: 254 m above sea level) on Chichijima. More details regarding site description, aerosol collection, and hydroxy FAs analyses in Chichijima aerosols can be seen in *Tyagi et al.* [2015a].

2.2. Sample Analysis and Derivatization

We analyzed 48 bulk aerosol samples by using the extraction procedure initially developed by *Kawamura et al.* [2003] and thoroughly discussed in several subsequent papers [*Kariya*, 2007; *Yamamoto et al.*, 2013; *Tyagi et al.*, 2015a]. Briefly, each filter aliquot was extracted with 0.1 M KOH/methanol solution (10 mL × 3) by using DIONEX ASE200 at 100°C and 1000 psi for 5 min, followed by subsequent ultrasonication with dichloromethane (DCM) (10 mL × 3). We combined these extracts and concentrated them down to 1 mL by using a rotary evaporator under vacuum. The extracts were divided into neutral and acidic fractions after adding 6 M HCl, and then carboxylic acids were extracted with DCM. By adding 14% BF_3/methanol (SUPELCO™) to the acidic fraction, carboxylic acids were converted to their methyl esters at 100°C. These derivatives were separated into monocarboxylic acid, dicarboxylic acid, and hydroxy fatty acid (FA) ester fractions by using a silica gel (deactivated with 1% H_2O) column chromatography. The hydroxy FA fractions were stored at −20°C in darkness until analysis.

Prior to GC/MS injection, the hydroxy FA fraction was derivatized with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (SUPELCO™ Analytical) at 80°C for 1 h to convert hydroxyl groups to trimethylsilyl (TMS) ethers. After reaction, 50 μL of *n*-hexane solution containing 1.43 ng μL^{-1} of internal standard (C_{13} *n*-alkane/tridecane, Wako) was added to dilute the derivatives. We used a gas chromatograph (Agilent Technologies, Model 7890 GC) equipped with a split/splitless injector and HP-5 fused silica capillary column (25 m

Table 1. Statistical Summary of Concentrations of α-, β-, and ω-Hydroxy FAs in ng m^{-3} in TSP Samples Collected Over Gosan, Jeju Island, During April 2001 to March 2002[a]

	Ave ± SE	Range (Median)	Ave ± SE	Range (Median)	Ave ± SE	Range (Median)
Compounds	α-Hydroxy FAs (C_{21}–C_{34})		β-Hydroxy FAs (C_7–C_{20})		ω-Hydroxy FAs (C_7–C_{32})	
C_7			0.09 ± 0.01	0.01–0.21 (0.09)	0.28 ± 0.11	0.02–1.04 (0.18)
C_8			0.21 ± 0.03	0.02–0.88 (0.19)	0.17 ± 0.06	0.00–2.63 (0.1)
C_9			0.18 ± 0.02	0.02–0.61 (0.16)	0.18 ± 0.02	0.01–0.50 (0.15)
C_{10}			0.29 ± 0.06	0.01–2.26 (0.18)	0.15 ± 0.02	0.01–0.54 (0.12)
C_{11}			0.1 ± 0.01	0.00–0.41 (0.07)	0.23 ± 0.03	0.01–0.71 (0.15)
C_{12}			0.86 ± 0.4	0.00–15.6 (0.12)	0.6 ± 0.07	0.01–2.67 (0.48)
C_{13}			0.07 ± 0.01	0.00–0.25 (0.05)	0.1 ± 0.01	0.00–0.33 (0.09)
C_{14}			0.16 ± 0.03	0.01–0.84 (0.12)	0.46 ± 0.05	0.04–1.8 (0.37)
C_{15}			0.06 ± 0.01	0.00–0.18 (0.04)	0.21 ± 0.02	0.02–0.68 (0.19)
C_{16}			0.17 ± 0.02	0.01–0.65 (0.14)	3.59 ± 0.53	0.06–17.1 (2.62)
C_{17}			0.04 ± 0.01	0.00–0.15 (0.03)	0.22 ± 0.06	0.00–2.38 (0.15)
C_{18}			0.12 ± 0.02	0.00–0.50 (0.09)	0.71 ± 0.31	0.01–13.6 (0.3)
C_{19}			0.03 ± 0.00	0.00–0.11 (0.02)	0.17 ± 0.02	0.00–0.62 (0.14)
C_{20}			0.07 ± 0.01	0.01–0.27 (0.05)	0.63 ± 0.14	0.01–4.46 (0.33)
C_{21}	0.04 ± 0.01	0.00–0.10 (0.03)			0.41 ± 0.1	0.03–3.39 (0.19)
C_{22}	0.07 ± 0.01	0.01–0.24 (0.07)			2.83 ± 0.95	0.02–37 (0.79)
C_{23}	0.04 ± 0.01	0.00–0.16 (0.03)			0.19 ± 0.03	0.01–1.01 (0.12)
C_{24}	0.08 ± 0.01	0.00–0.27 (0.05)			1.97 ± 0.62	0.02–25.2 (0.75)
C_{25}	0.04 ± 0.01	0.00–0.13 (0.04)			0.19 ± 0.03	0.00–0.98 (0.13)
C_{26}	0.06 ± 0.01	0.00–0.24 (0.04)			0.81 ± 0.16	0.02–4.36 (0.44)
C_{27}	0.04 ± 0.01	0.00–0.12 (0.03)			0.14 ± 0.02	0.00–0.55 (0.11)
C_{28}	0.06 ± 0.01	0.00–0.21 (0.05)			0.42 ± 0.07	0.01–1.74 (0.23)
C_{29}	0.04 ± 0.01	0.00–0.10 (0.02)			0.11 ± 0.02	0.00–0.35 (0.08)
C_{30}	0.07 ± 0.01	0.01–0.22 (0.05)			0.15 ± 0.02	0.02–0.45 (0.12)
C_{31}	0.02 ± 0.00	0.00–0.06 (0.02)			0.1 ± 0.05	0.06–0.15 (0.1)
C_{32}	0.05 ± 0.01	0.00–0.16 (0.04)			0.12 ± 0.03	0.05–0.23 (0.09)
C_{33}	0.01 ± 0.00	0.00–0.03 (0.01)				
C_{34}	0.03 ± 0.01	0.00–0.07 (0.03)			0.07 ± 0.00	0.00–0.07 (0.07)
Total	0.41 ± 0.09	0.00–1.92 (0.2)	2.29 ± 0.53	0.04–20.1 (1.6)	13.6 ± 2.4	0.4–77.9 (8.5)

[a]Ave, average; SE, standard error = $\sigma/N^{1/2}$, where σ refers to the standard deviation of total number (N) of samples.

long × 0.2 mm internal diameter and 0.5 μm film thickness) connected in line with a mass spectrometer (Hewlett-Packard Model 5975 C inert XL EI/CI mass-selective detector, MSD with Triple-Axis Detector). The mass spectrometer was operated in an electron impact mode (70 eV).

We used helium as a carrier gas at a flow rate of 1 mL min^{-1}, and the GC oven temperature was programmed to start at 50°C (2 min) to 120°C (15°C min^{-1}), then to 305°C (15 min) at 5°C min^{-1}. We processed the data by using Chemstation software. Identification of hydroxy FAs was performed by comparing retention times and mass spectra with those of TMS derivatives of authentic α-hydroxy n-C_{12} and n-C_{16} FAs; β-hydroxy n-C_{12}, n-C_{14}, n-C_{15}, and n-C_{16} FAs; and ω-hydroxy n-C_{16}, n-C_{20}, and n-C_{22} FAs, which were also used as external standards. The recoveries of authentic β- and ω-hydroxy FAs standards were better than 72%, and duplicate analysis of the aerosol sample KOS 111 (refers to the sample code for the total suspended particle (TSP) collected during 21–23 March 2002) showed that analytical error was less than 19% for fatty acids [*Kariya*, 2007].

3. Results and Discussion

3.1. Molecular Distributions

We observed a strong even-to-odd carbon number predominance in the molecular distributions of α-, β-, and ω-hydroxy FAs (Table 1). A notable feature of these molecular distributions is the occurrence of only high (HMW: C_{21}–C_{34}; Figure 2) and low (LMW: C_7–C_{20}; Figure 3) molecular weight α- and β-hydroxy FAs, respectively. However, we detected both LMW and HMW ω-hydroxy FAs (Figure 4) during the study period. Furthermore, we compared the molecular distributions from Gosan with those documented from Chichijima [*Tyagi et al.*, 2015a]. Because all homologues possess similar chemical properties, it is reasonable to describe lipid biomarkers by their varying carbon chain length. Accordingly, we refer to the homologues of

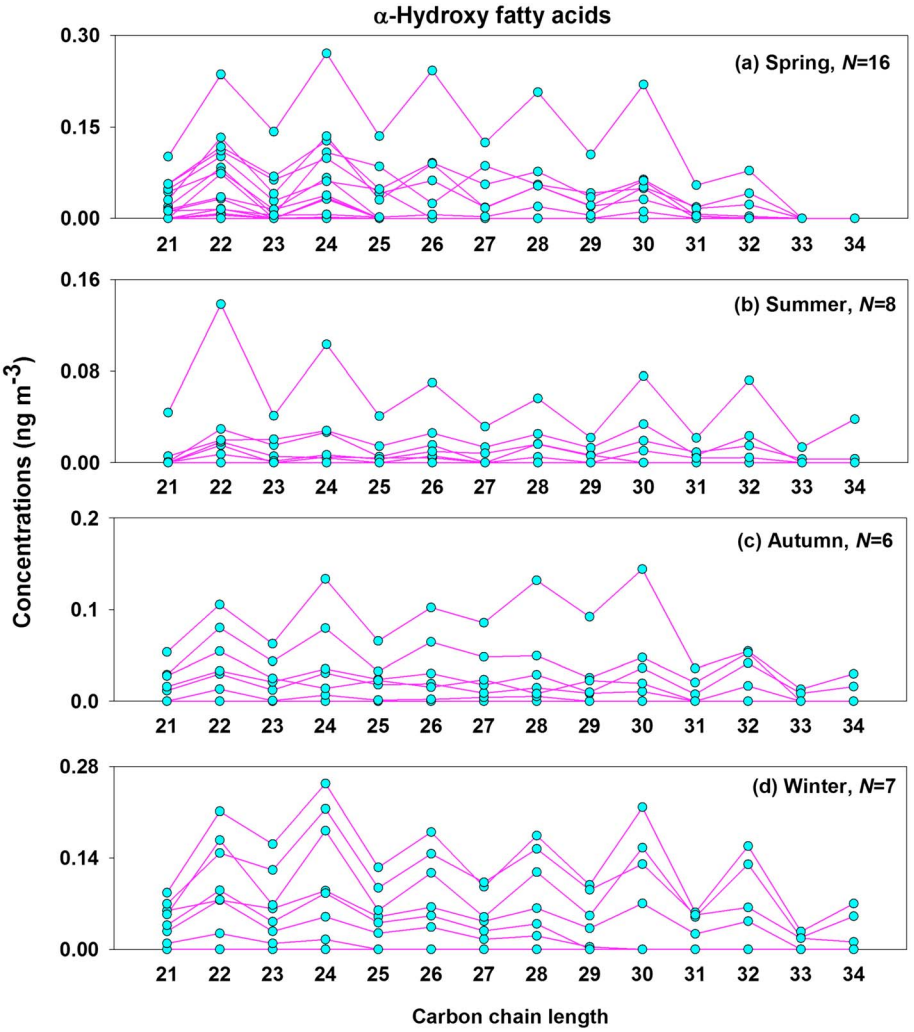

Figure 2. Molecular distributions of α-hydroxy FAs (C_{21}–C_{34}) in aerosols collected over Gosan during 2001–2002.

α, β-, and ω-hydroxy FAs by their carbon chain length number (e.g., ω-hydroxy C_{24} FA refers to ω-hydroxy FA containing carbon chain length of 24) while discussing their molecular distributions.

3.1.1. α-Hydroxy FAs

We detected α-hydroxy FAs only in Gosan aerosols (Figure 2) but not in those collected over Chichijima [*Tyagi et al.*, 2015a]. The molecular distributions of α-hydroxy FAs are characterized by a predominance of C_{22} (α-hydroxydocosanoic acid) and C_{24} (α-hydroxytetracosanoic acid). Moreover, this pattern is similar for all the seasons. Occurrence of HMW α-hydroxy C_{21}–C_{34} FAs at Gosan during winter and spring may indicate their origin from photochemical or microbial oxidation of higher plant waxes during long-range atmospheric transport [*Kawamura et al.*, 2003; *Ho et al.*, 2007; *Cranwell*, 1981]. In contrast, HMW α-hydroxy FAs ($>C_{20}$) may originate from marine sources (e.g., algae and seagrasses) over Gosan during summer and autumn [*Volkman et al.*, 1980; *De Leeuw et al.*, 1995]. For instance, α-hydroxy C_{22}–C_{30} FAs were detected in green microalgae from genus *Choricystis*, and those from C_{26} to C_{30} were identified in class *Eustigmatophyceae* [*Volkman et al.*, 1998; *Zhang et al.*, 2014]. Therefore, transport of marine derived algal decomposition products emitted from the ocean surface could also explain the atmospheric abundances of α-hydroxy FAs at Gosan during summer and autumn (for which back trajectories showed marine origin, see Figure S1 in the supporting information).

3.1.2. β-Hydroxy FAs

A comparison of molecular distributions of β-hydroxy FAs over Gosan with those from Chichijima [*Tyagi et al.*, 2015a] revealed their common source and transport pattern (Figure 3), especially for spring samples. We

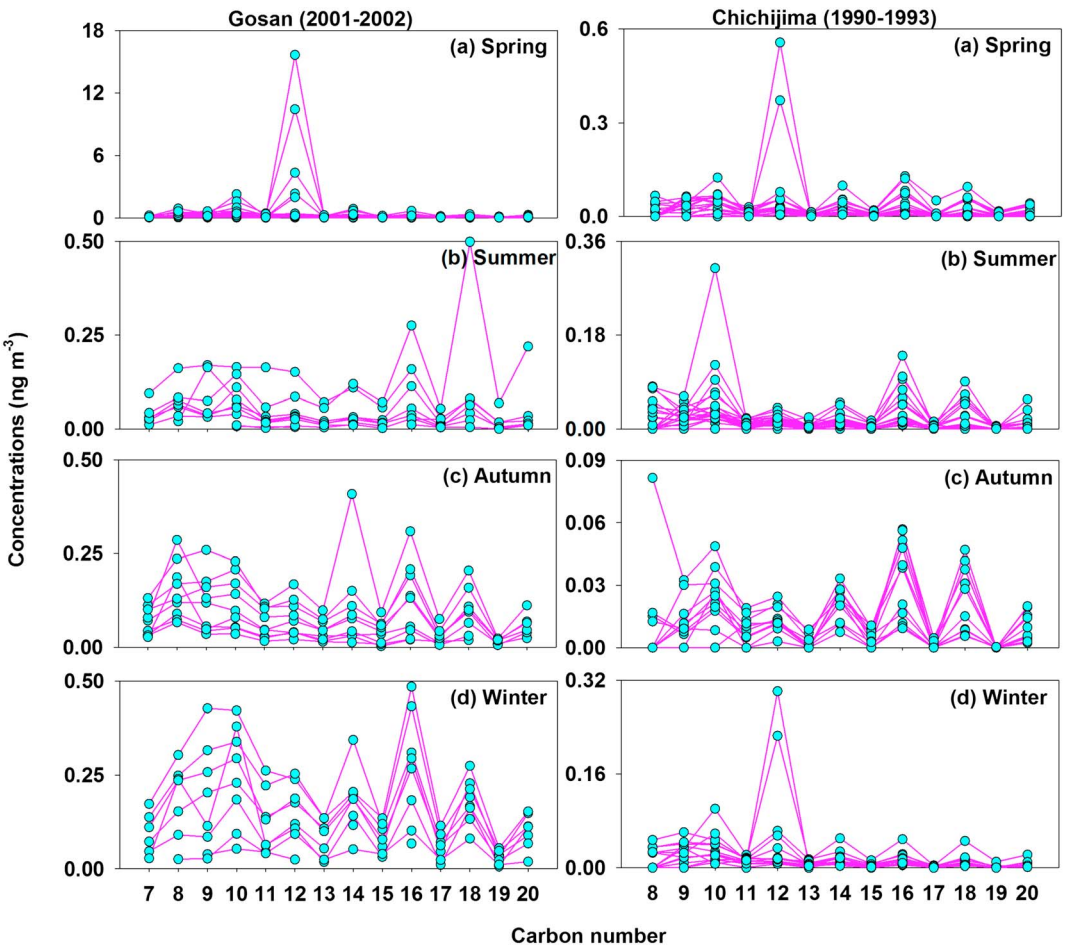

Figure 3. Molecular distributions of β-hydroxy FAs in aerosols collected over Gosan during 2001–2002 (this study) and Chichijima during 1990–1993 [*Tyagi et al.*, 2015a]. Albeit sampling period varied between Gosan and Chichijima, both receptor sites are influenced by similar wind regimes.

observe a characteristic predominance and relatively high concentrations of β-hydroxy C_{12} FA (β-hydroxydodecanoic acid) over Gosan compared to those reported from Chichijima. Based on the high abundances of water-soluble calcium in aerosols, a proxy of mineral dust [*Simoneit et al.*, 2004; *Grigholm et al.*, 2015], we ascertained that both Gosan and Chichijima are significantly influenced by the Asian dust outbreak events during the spring season. Likewise, we observe a similarity in the molecular distributions of β-hydroxy FAs between summer and autumn at both the receptor sites, characterized by the predominance of β-hydroxy C_{16} (β-hydroxypalmitic acid) followed by C_{10} (β-hydroxydecanoic acid) or C_{18} (β-hydroxystearic acid).

Overall temporal shift in the molecular distributions of β-hydroxy FAs between spring and summer/autumn is mostly due to differences in the contributing source type (i.e., soil bacteria and marine dissolved organic matter, respectively). For instance, organic compounds emitted from the North Pacific significantly influence the aerosol composition over Gosan in summer and autumn as evident from increased atmospheric abundances of azelaic acid and methanesulfonic acid (i.e., photochemical oxidation products of oleic acid and dimethylsulfide, respectively, emitted from the ocean surface) [*Kundu and Kawamura*, 2014]. Therefore, marine sources could contribute to β-hydroxy FAs over Gosan and Chichijima during summer/autumn. *Wakeham et al.* [2003] documented the predominance of β-hydroxy C_{14} (β-hydroxymyristic acid) or C_{16} FA in dissolved or particulate organic matter from the equatorial Pacific and the North Sea, attributing their origin to the LPS of marine GNB. However, the subtropical gyre of the North Pacific during late summer is characterized by widespread (~350,000 km^2) and long lasting occurrence (~4 months) of *Trichodesmium* blooms (a marine GNB) [*Wilson*, 2003]. Because the easterlies dominate over Chichijima and Gosan during summer/autumn,

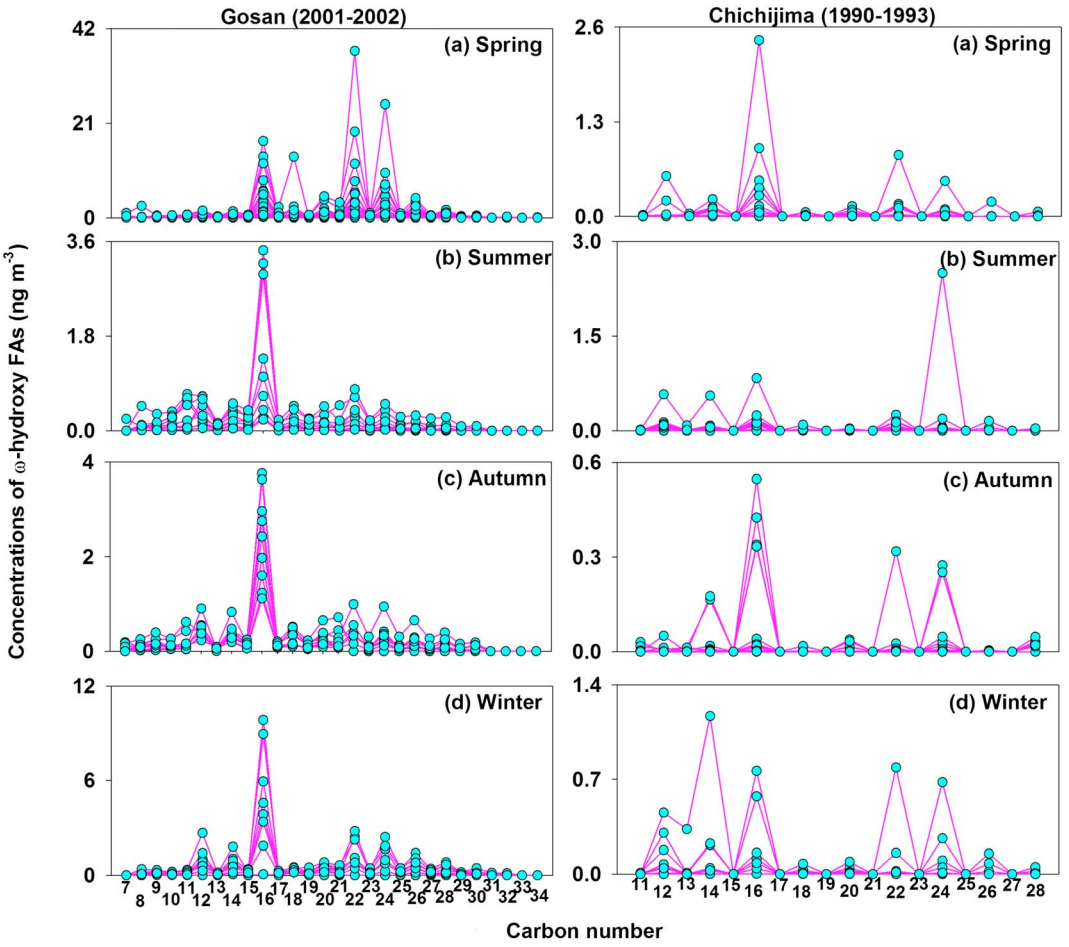

Figure 4. Molecular distributions of ω-hydroxy FAs in aerosols collected over Gosan during 2001–2002 (this study) and Chichijima during 1990–1993 [*Tyagi et al.*, 2015a]. Albeit sampling period varied between Gosan and Chichijima, both receptor sites are influenced by similar wind regimes.

the observed molecular distributions of β-hydroxy FAs with C_{16} predominance in aerosols could be due to their contribution from oceanic source.

We also observed some similarity in the molecular distributions between Gosan and Chichijima for the winter season with characteristic higher abundances of C_{10} followed by C_{12} and C_{14} or C_{16}. Two sampling days with rather high concentrations of β-hydroxy C_{12} FA from Chichijima (i.e., beyond 95% CI) are not included for this interpretation. The impact of local anthropogenic/natural sources (e.g., urban dust/loess deposits) from China (Figure S1) over Gosan (due to its proximity) could be a likely factor for the observed discrepancies in the molecular distributions. However, the overall molecular distributions of β-hydroxy FAs at Chichijima (including all data points) in winter were consistent with those in spring, showing increased atmospheric abundances during the latter season. This correspondence could be due to their common source of soil microbes (also supported by the similar air mass back trajectory (AMBT) cluster, see section 3.4) and enhanced mobilization of mineral dust in spring [*Uematsu et al.*, 1992] through high altitudinal long-range atmospheric transport.

3.1.3. ω-Hydroxy FAs

The molecular distributions of ω-hydroxy FAs over both Gosan and Chichijima in spring and winter are characterized by the predominance of C_{16} and/or C_{22} (hydroxydocosanoic acid) followed by C_{24} (hydroxytetracosanoic acid). This suggests their common sources of lipids from higher plant waxes. However, significant differences were noteworthy in summer between Gosan and Chichijima with respect to the predominance of ω-hydroxy FAs (C_{16} and C_{24}, respectively). The observed shifts in the even carbon predominance at Chichijima in summer (AMBTs showed an oceanic origin [*Tyagi et al.*, 2015a]) cannot be explained by the

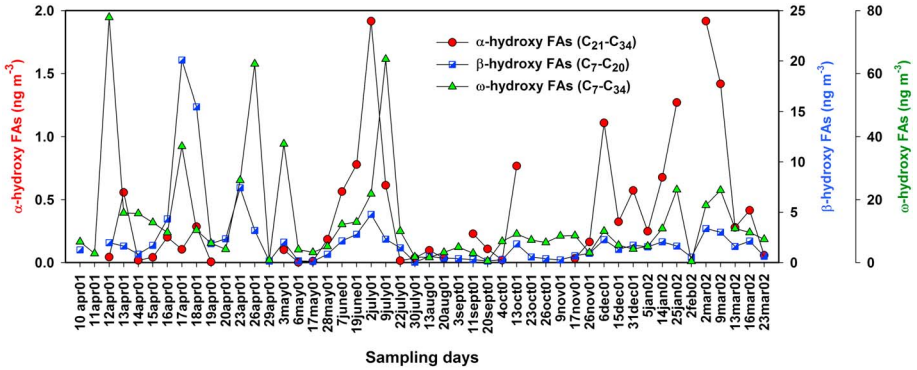

Figure 5. Temporal variability of total mass concentrations of α-, β-, and ω-hydroxy FAs in TSP collected during April 2001 to March 2002 over Gosan, Jeju Island, as a part of ACE-Asia campaign. The carbon number with subscript indicates the chain length of the respective hydroxy FAs.

impact of East Asian outflow. However, contribution from local sources (island-based minor emissions from vascular plants) could result in such shifts in the molecular distribution of ω-hydroxy FAs.

Relatively high concentrations of ω-hydroxy FAs over Gosan compared to those from Chichijima (Figure 4) could be attributed to the proximity of the former sampling site to continental sources (e.g., terrestrial higher plant emissions). At Gosan, we found highest concentrations of ω-hydroxy FAs in spring, followed by winter and autumn. However, the concentrations were found to be lowest in summer over Gosan when the air mass transport is mainly from the western North Pacific. Alternately, atmospheric abundances of ω-hydroxy FAs over Chichijima in summer are comparable to those observed in spring followed by winter and autumn. A remarkable similarity in the predominance of ω-hydroxy C_{16} FA (hydroxypalmitic acid) is noteworthy for all seasons over Gosan, suggesting a linkage of its proximity to continental sources of higher plants.

3.2. Temporal and Seasonal Variabilities

The mass concentrations of total α-, β-, and ω-hydroxy FAs showed pronounced temporal (*in between samples*) and seasonal (*in between seasons*) variabilities over Gosan during the study period (April 2001 to March 2002; Table 1 and Figure 5). ω-Hydroxy FAs (proxy for plant waxes) dominate total hydroxy FAs throughout the sampling period and peaked during spring followed by winter. α-Hydroxy FAs peaked irregularly but with relatively high concentrations in winter and early spring (March–April). Interestingly, in late June and early July samples, we observed moderately higher loading of ω- and α-hydroxy FAs. The temporal variability of β-hydroxy FAs showed sporadic increase only in spring season, which is characterized by frequent dust storms. The occurrence of relatively high concentrations of β-hydroxy FAs in spring indicates their contribution from East Asian deserts.

The seasonal trends of hydroxy FAs over Gosan typically reflect their variability in the sources/source regions as well as their emissions in the East Asian outflow. This seasonality can be better understood by examining the pollution rose diagrams (generated by using "*openair package*" [*Carslaw and Ropkins*, 2012; *Carslaw*, 2015]), where concentrations of hydroxy FAs are combined with meteorological parameters (Figure 6). The pollution rose diagrams reveal a systematic change in hydroxy FA concentrations over Gosan according to the seasonal variability in wind direction. Over Gosan, winds mostly blow from NW and NE in winter, spring, and autumn, representing the impact of the East Asian outflow in which we observed higher concentrations of hydroxy FAs. A sudden change in prevailing winds from NW and/or NE to SW over Gosan (i.e., transport mostly from the South/East China Sea and North Pacific) during summer months could explain the observed lowest concentrations of α-, β-, and ω-hydroxy FAs.

β- and ω-Hydroxy FAs (i.e., tracers of soil microbes and higher plant waxes, respectively) showed higher concentrations in spring and winter than summer and autumn seasons. In particular, significant differences are noteworthy (approximately fivefold higher) between spring and summer for β- and ω-hydroxy FAs (Figure 6). Such large differences, mostly associated with change in wind direction between spring and summer, clearly emphasize the relative significance (or emission strength) of continental versus oceanic sources of hydroxy FAs over Gosan. Similar to our findings, *Yamamoto et al.* [2013] also documented higher

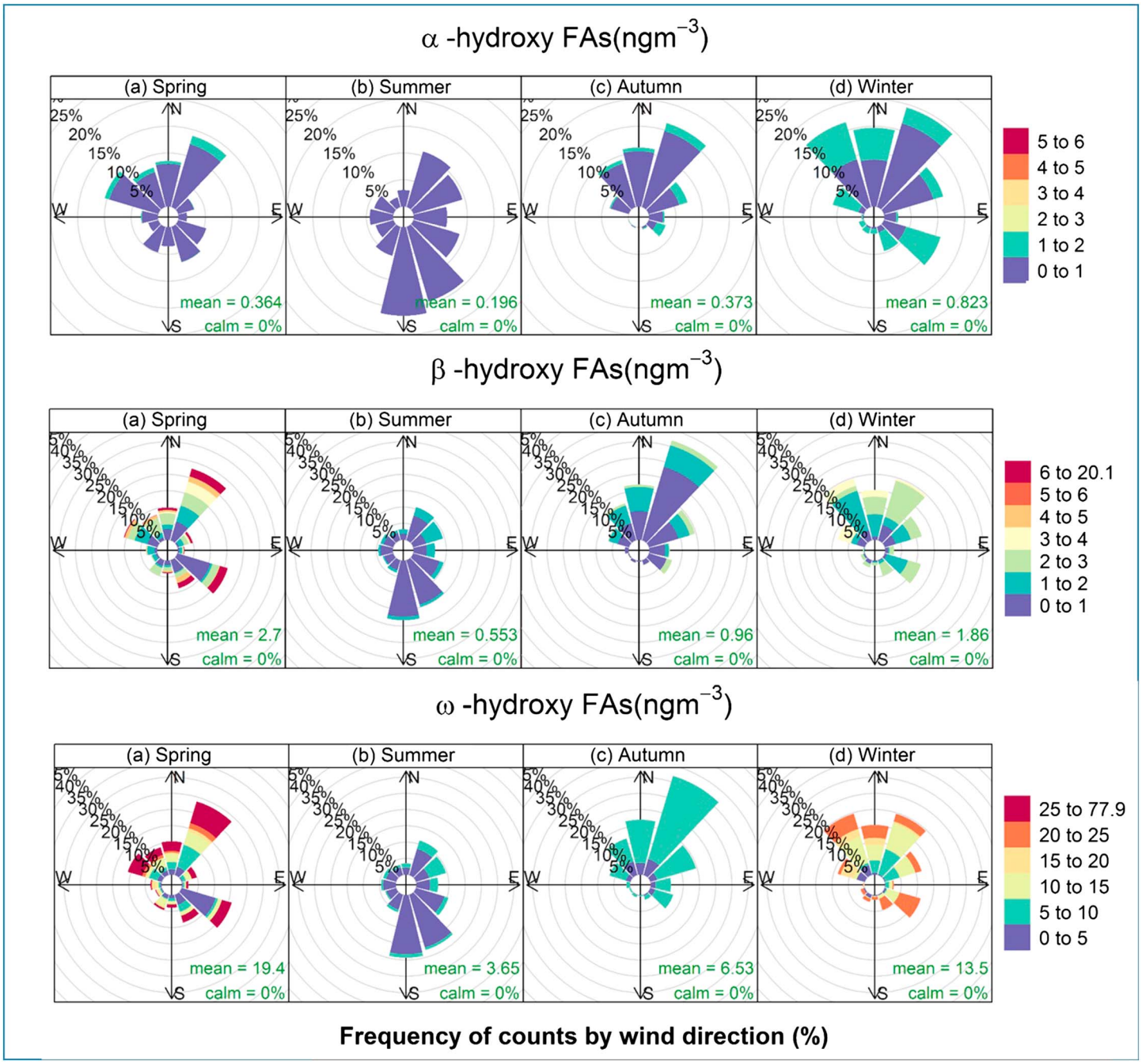

Figure 6. Pollution rose diagram (source: "*openair package*"), showing the seasonal variability of atmospheric abundances of α-, β-, and ω-hydroxy FAs (OH FAs) with the wind direction over Gosan during the study period (April 2001 to March 2002).

abundances of even carbon numbered C_{22}–C_{28} *n*-fatty acids (i.e., from terrestrial plants) in spring followed by winter/autumn over Gosan that were mostly associated with transport from northeast Asia. On the other hand, their lower concentrations over Gosan in summer are linked to air masses from Southeast Asia or Pacific [*Yamamoto et al.*, 2013]. Therefore, we infer that seasonal variability of hydroxy FAs over Gosan clearly reflects the relative dominance of soil microbes and higher plant waxes in the East Asian outflow.

The predominance of α-hydroxy FAs in winter, unlike β- and ω-hydroxy FAs that showed spring maximum, clearly indicates a different source (Figure 6). Gosan is mostly influenced by anthropogenic pollution sources (e.g., wood/crop-residue burning) in East Asia during the winter [*Kim et al.*, 2007; *Fu et al.*, 2012].

Table 2. One-Way ANOVA and Posthoc Test Results for Assessing the Differences/Similarities Among Seasonal Mean Hydroxy FA Concentrations

Differences Between Seasonal Mean		α-Hydroxy FAs	β-Hydroxy FAs	ω-Hydroxy FAs
Spring	Summer	>0.1	<0.1	<0.1
	Autumn	>0.1	>0.1	<0.1
	Winter	>0.1	<0.1	>0.1
Summer	Autumn	>0.1	>0.1	>0.1
	Winter	<0.1	<0.1	<0.1
	Spring	>0.1	<0.1	<0.1
Autumn	Winter	>0.1	>0.1	>0.1
	Spring	>0.1	>0.1	<0.1
	Summer	>0.1	>0.1	>0.1
Winter	Spring	>0.1	>0.1	>0.1
	Summer	<0.1	<0.1	<0.1
	Autumn	>0.1	>0.1	>0.1
F-statistic; *P* value at 90% CI		$F(3, 33) = 2.9$; <0.1	[a] $F(3,24) = 5.2$; < 0.1	[a] $F(3,29.2) = 6.7$; <0.1

[a] Brown-Forsythe *F*-statistic is used instead of regular one-way ANOVA output.

For instance, by combining the air mass trajectories with source-specific organic tracer compounds (e.g., sugars), previous studies documented the impact of biomass burning emissions in Siberia and Mongolia on the aerosol composition over Gosan and Chichijima during winter [*Fu et al.*, 2012; *Chen et al.*, 2013]. Likewise, high concentrations of α-hydroxy FAs were also found in fresh snow samples (in winter) collected from Sapporo, northern Japan [*Tyagi et al.*, 2015b] and in biomass burning-derived aerosols from Mount Tai in the North China Plain [*Tyagi et al.*, 2016a]. Furthermore, these α-hydroxy FAs can have contributions from epicuticular waxes and from the α-oxidation of monocarboxylic acids during atmospheric transport [*Fulco*, 1967; *Volkman*, 2005]. Therefore, we attribute the observed high concentrations of α-hydroxy FAs (Figure 6) in winter season over Gosan to the contribution from anthropogenic sources/plant waxes in the East Asian outflow.

We also examined the overall seasonal distributions of total α-, β-, and ω-hydroxy FAs by using box-whisker plots to understand their consistency with regard to source emissions (i.e., more homogeneous or skewed distribution, which is related to a single source or multiple sources/source regions). We observed a more skewed distribution of β-hydroxy FAs in spring than in other seasons (Figure S2). Several studies documented a frequent occurrence of dust storms from the Asian deserts during spring [*Seinfeld et al.*, 2004; *Darmenova et al.*, 2005]. Because β-hydroxy FAs are specific to soil microbes (GNB), their distribution with relatively high concentrations in spring is attributed to contribution from loess deposits and desert dust in the East Asian outflow. We also observed such a skewed distribution for ω-hydroxy FAs in winter and spring with large number of samples exceeding the median values (50 percentile; Figure S2). However, the distributions are near symmetric for summer and autumn seasons. This observation indicates more heterogeneity in the sources and emissions of β- and ω-hydroxy FAs in the East Asian outflow than those from more stable oceanic sources in summer and autumn.

Overall, the total hydroxy FA mass ($\Sigma\alpha$- + β- + ω-isomers) showed the highest average concentration in spring (24.2 ng m^{-3}) followed by winter (15.5 ng m^{-3}), autumn (7.9 ng m^{-3}), and summer (5.3 ng m^{-3}). These results are consistent with the seasonal trend documented from Chichijima, although their concentrations are lower (winter: 0.83 ng m^{-3}; spring: 0.81 ng m^{-3}; summer: 0.67 ng m^{-3}; autumn: 0.31 ng m^{-3}) in the western North Pacific [*Tyagi et al.*, 2015a]. This is most likely due to the proximity of continental sources (biogenic/anthropogenic emissions) to Gosan, whereas the dilution effect is more significant during long-range transport of Asian aerosols over Chichijima. To ascertain whether the observed differences in seasonal mean concentrations of hydroxy FAs are statistically significant or not, we performed one-way analysis of variance (ANOVA).

Due to the unequal number of aerosol samples (*N*) for four seasons (spring: 22; summer: 9; autumn: 9; winter: 8), we used one-way ANOVA with a 90% confidence interval (i.e., we consider $p < 0.1$ as less significant results). The summary of one-way ANOVA results, to ascertain whether there exists at least one inequality or difference among seasonal mean concentrations of hydroxy FAs, is provided in Table 2 together with the analysis of posthoc test (i.e., to assess or identify which group's means are similar or different). We performed the nonparametric median test for α-hydroxy FAs, which revealed that only ~38% and 25% of data have

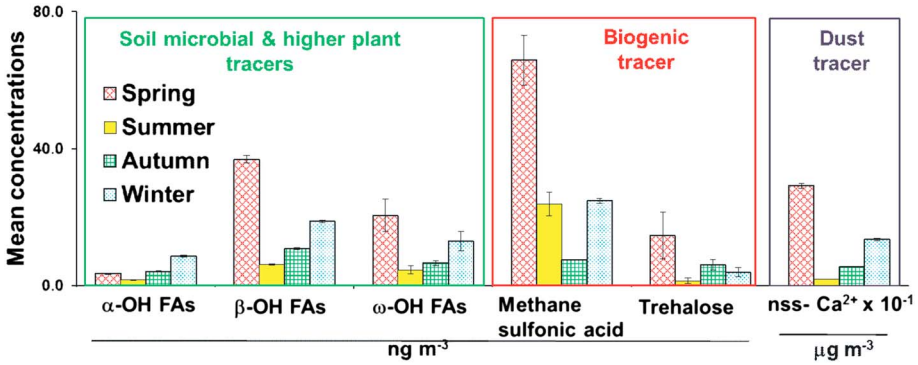

Figure 7. Seasonal variability of mean concentrations of water-soluble nonsea-salt (nss)-Ca^{2+}, methanesulfonic acid (MSA), trehalose, and hydroxy FAs (α-, β-, and ω-isomers) in TSP collected at Gosan during April 2001 to March 2002. The data of trehalose are from *Fu et al.* [2012].

shown higher concentrations than median values for the respective seasons. However, overall median values among the groups do not exhibit significant differences for α-hydroxy FAs.

Because the Levene's statistic is significant ($p = 0.016$; assumption of normality or homogeneity of variances to perform ANOVA was violated), we used both Welch and Brown Forsyth's *F*-statistics to examine the seasonal mean differences. These tests suggest that significant differences exist between seasonal means of β-hydroxy FAs (Welch: $F(3,21.1) = 4.9$; $p < 0.05$ and Brown-Forsythe: $F(3,24.3) = 5.2$; $p < 0.05$). Subsequent posthoc tests revealed that concentrations in winter and spring are significantly different (higher) than those observed in summer. Interestingly, no such differences are observed between autumn and other seasons. Overall, these results suggest the impact of East Asian outflow over Gosan during winter and spring, while summer and, to some extent, autumn seasons, are influenced instead by the oceanic air masses. Hence, the summer and autumn results exhibit lower concentrations of β-hydroxy FAs. We also conducted a nonparametric median test that reveals significant differences between seasonal median concentrations. More specifically, ~70% and 63% of data points in spring and winter, respectively, showed higher concentrations of β-hydroxy FAs than median values of the respective season. However, only ~11% and 21% of samples collected during summer and autumn, respectively, have higher concentrations of β-hydroxy FAs than the median value of respective season.

In case of ω-hydroxy FAs, the Levene's test for homogeneity of variances is also violated. Therefore, we used Welch's *F*-statistic ($F(3,19.6) = 5.3$; $p < 0.05$) or Brown-Forsythe *F*-statistic ($F(3,29.2) = 6.7$; $p < 0.05$), which shows significant differences between seasonal means for ω-hydroxy FAs at Gosan. The subsequent posthoc test showed that winter and spring have higher mean values than observed for summer. Although the mean concentration of ω-hydroxy FAs in spring is higher than in autumn, it is comparable to that in winter. Likewise, we could not observe significant differences between autumn and summer. The nonparametric median test also shows significant differences between seasonal median values for ω-hydroxy FAs ($p < 0.05$). In addition, the relative contribution of samples collected in winter (~75%) and spring (~64%) had higher ω-hydroxy FAs than median values. On the other hand, only ~22% of the data in summer and autumn showed higher ω-hydroxy FAs concentrations than the median values of the respective seasons. This seasonal feature is similar to the observed distributions of β-hydroxy FAs at Gosan.

A comparison of seasonal variability between hydroxy FAs and other chemical tracers in TSP [*Kawamura et al.*, 2004; *Fu et al.*, 2012] was also made to further ascertain the relation to their contribution from microbial lipids associated with mineral dust transport in the East Asian outflow (Figure 7). Several studies have used water-soluble nonsea-salt Ca^{2+} (nss-Ca^{2+}) in ambient aerosols to trace the transport of mineral dust [*Arimoto et al.*, 2004; *Srinivas and Sarin*, 2012]. Likewise, methanesulfonic acid (MSA) in the East Asian outflow originates from biomass burning/biogenic emissions [*Boreddy and Kawamura*, 2015]. Likewise, trehalose (a tracer for fungal spores associated with soil organic matter) has been documented over Chichijima during winter and spring [*Chen et al.*, 2013]. We observed a remarkable consistency between these chemical tracers and hydroxy FAs, which show high concentrations in winter/spring and low concentrations summer/autumn (Figure 7). Therefore, concurrent increases in soil organic matter (source of GNB-specific β-hydroxy FAs) and biogenic emissions (ω- and α-hydroxy FAs) in the East Asian outflow during winter and spring are responsible for the observed seasonal variability of hydroxy FAs over Gosan.

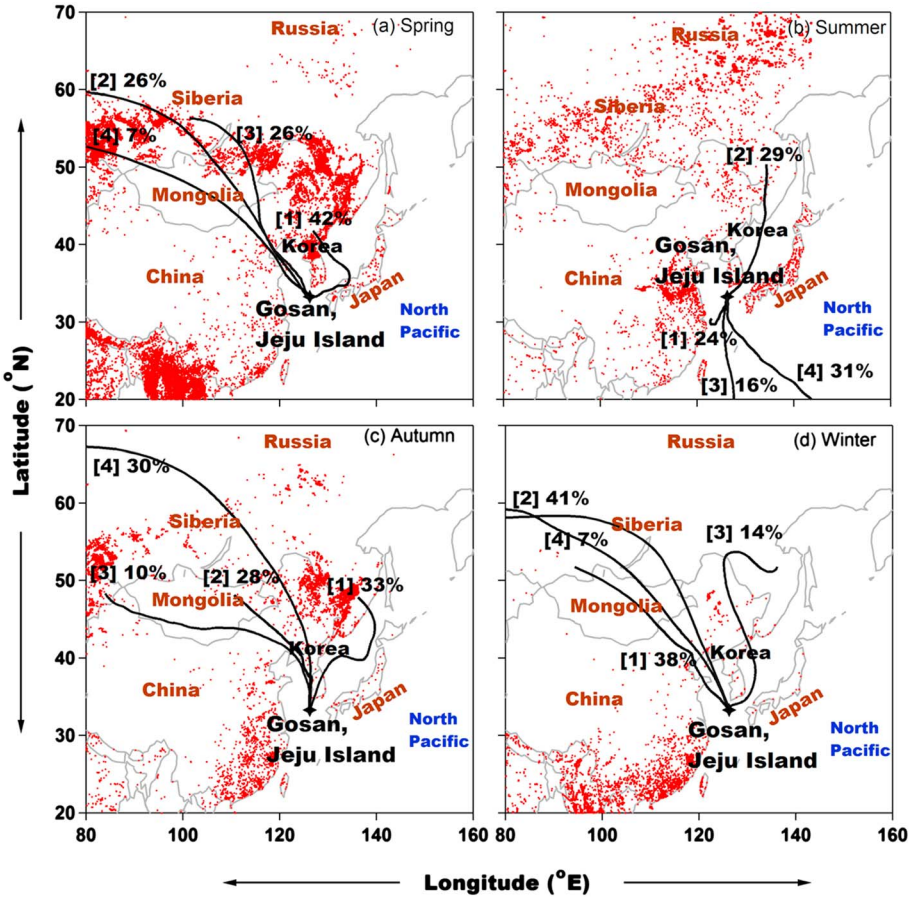

Figure 8. Mean trajectory paths, obtained by the clustering of air mass back trajectories (AMBTs) over Gosan, Jeju Island, at an arrival height of 100 m agl. during the period of April 2001 to March 2002. The red dots in the map represent the MODIS satellite-derived fire count data for the sampling days. Individual AMBTs, computed for the arrival height of 100, 500, and 1000 m, were shown in Figure S1.

3.3. Air Mass Back Trajectory Analyses

Air mass back trajectories (AMBTs) provide information on potential source regions of hydroxy FAs in TSP at Gosan. Seven-day isentropic AMBTs were computed at air mass arrival heights of 100, 500, and 1000 m agl (Figure S1) by using a hybrid single particle Lagrangian integrated trajectory model (Hybrid Single-Particle Lagrangian Integrated Trajectory, version 4 [*Draxler and Rolph*, 2009; *Stein et al.*, 2015]) and archived meteorological data sets from the National Oceanic and Atmospheric Administration air resources laboratory (http://ready.arl.noaa.gov/HYSPLIT.php). AMBTs were clustered according to seasons (winter: December 2001 to February 2002; spring: April–May 2001 and March 2002; summer: June–August 2001; autumn: September–November 2001) to ascertain the relative contribution of various geographical sources to atmospheric hydroxy FAs over Gosan. In addition, we superimposed the fire count data from the Moderate Resolution Imaging Spectroradiometer (MODIS) satellite on the mean trajectory cluster paths to evaluate the effects of biomass burning in East Asia on the atmospheric abundances of hydroxy FAs at Gosan (Figure 8).

In general, AMBTs for winter and spring samples showed their origin from Siberia, Mongolia and, to some extent, China (Figure S1). Alternately, AMBTs in summer mostly originated from the western North Pacific due to prevailing westerlies. In autumn, AMBTs showed mixed origins (i.e., from oceanic and continental air masses) over Gosan. The cluster analysis reveals that in spring, air masses that originated from Korea contribute 40% of aerosol compositions at Gosan, while air mass transport from Siberia and Mongolia accounts for 52% (clusters 2 and 3) and 7% (cluster 4), respectively (Figure 8). Despite being influenced by similar geographical source regions, the relative contribution of hydroxy FAs over Gosan varied significantly between spring and winter.

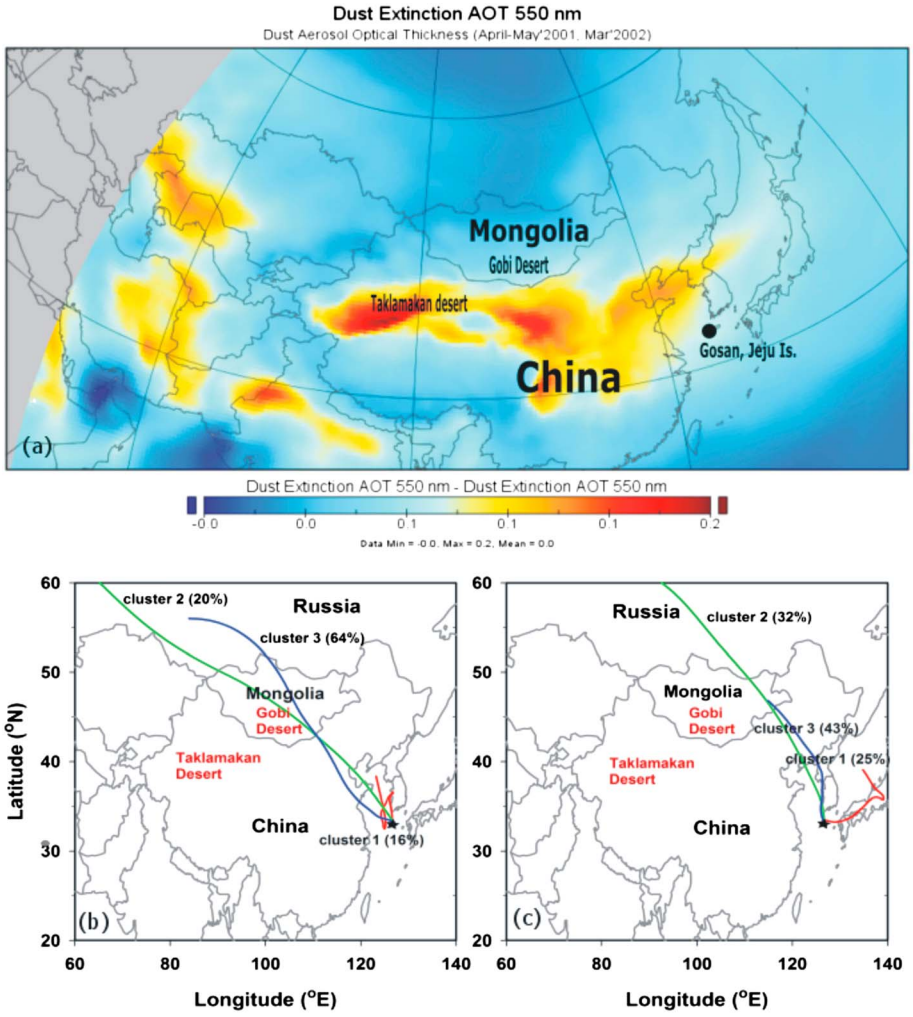

Figure 9. Map showing (a) occurrence of Asian dust events during March–April 2001 and March 2002 and cluster analyses of (b) carbonate-rich desert dust and (c) Chinese loess deposits in East Asia (individual back trajectory clusters were provided as Figure S3).

In winter, air masses from China and Korea contributed ~38% and 14%, respectively, while those from Siberia and Mongolia accounted for ~41% and 7%, respectively, to the TSP composition over Gosan (Figure 8). Interestingly, major source regions in autumn are somewhat similar to those in winter with minor contributions from oceanic air masses (cluster 1, ~30%) from the Sea of Japan. On the other hand, oceanic air masses transported across the Sea of Japan, North Pacific, Yellow Sea, and East China Sea over Gosan in summer accounted for 29% (cluster 2), 31% (cluster 4), 16% (cluster 3), and 24% (cluster 1), respectively (Figure 8). Overall, cluster analysis provides information on the relative significance of dust/biomass combustion source regions in the East Asian outflow that could be linked with temporal and seasonal variabilities of hydroxy FAs over Gosan. The large spread in AMBT cluster (Figure S1) during spring season is consistent with the observed temporal variability in the mass concentrations of β-hydroxy FAs (range: 0.12–20.1 ng m^{-3}; median: 2.0 ng m^{-3}; Figure 3) as well as ω-hydroxy FAs (0.8–79 ng m^{-3}; 12 ng m^{-3}). This observation suggests greater heterogeneity or temporal variability in the sources/source regions of hydroxy FAs (i.e., soil microbes and plant waxes) during spring.

As mentioned earlier, the AMBT clustering reveals transport from China, Mongolia, and Siberia to Gosan in winter and spring (Figure 8). Recent studies have documented the impact of mineral dust from East Asian Deserts on the Yellow Sea and South China through long-range atmospheric transport during the spring [*Tan et al.*, 2012]. Likewise, several studies have documented the impact of

biomass burning emissions in China and Siberia to the aerosol composition over the North Pacific [*Ding et al.*, 2013; *Verma et al.*, 2015; *Zhu et al.*, 2015] and the Japanese Islands [*Pavuluri et al.*, 2013] during winter and spring, as assessed by the analyses of ^{14}C and biogenic organic tracers in aerosols. Therefore, a large temporal variability of β- and ω-hydroxy FAs over Gosan during spring can be explained by different contributions from Mongolian desert dust and higher plant waxes from Siberia.

We observed low atmospheric abundances of hydroxy FAs in summer and autumn mostly due to the contribution from oceanic biological sources (algae/phytoplankton detritus in the surface waters). In support of this possibility, *Tsuda et al.* [2015] documented the occurrence of phytoplankton blooms in the seas around the Japanese Islands. Therefore, marine derived organic matter emitted with sea spray could contribute to ambient hydroxy FAs over Gosan in autumn. Several studies suggested that marine cyanobacteria and dissolved organic matter in the surface water contain short-chain homologues of β- and ω-hydroxy FAs [*Wakeham et al.*, 2003]. In addition, phytoplankton blooms occur during late spring to early summer in the Sea of Japan [*Kwak et al.*, 2013], Yellow Sea and East China Sea [*Yamaguchi et al.*, 2012], and North Pacific [*Miyazaki et al.*, 2011]. Therefore, emission of sea spray containing marine algal excreta, dead phytoplankton, and dissolved organic matter from these marginal seas could be a major source of hydroxy FAs over Gosan during summer months.

3.4. Hydroxy FAs as Bacterial Tracers

Dust storms in East Asia during spring are a conspicuous seasonal phenomenon that occur as a result of low precipitation, freshly tilled agricultural soils, and high wind speeds associated with cold frontal systems [*Seinfeld et al.*, 2004]. Each year, these episodic Asian dust events cause elevated dust loadings in the marine atmospheric boundary layer of the North Pacific [*Uematsu et al.*, 2003]. The dust outbreaks from East Asia during 5–20 April 2001 were recorded as one of the largest Asian dust events [*Huebert et al.*, 2003; *Seinfeld et al.*, 2004]. In support of the influence of Asian dust storms and associated transport of airborne soil microbes over Gosan, we examined the satellite-derived dust optical thickness at 550 nm (Figure 9a) during the study period (April–May 2001 and March 2002). These observations were consistent with the results of our AMBT analyses that indicate the importance of long-range atmospheric transport of dust from the East Asian deserts to Gosan during spring.

We observed high concentrations of TSP for all the Asian dust events sampled during April–May 2001 and March 2002 [*Fu et al.*, 2012]. In particular, exceptionally high loadings were observed for three specific sampling periods (170–444 $\mu g\ m^{-3}$ during 10–14 April 2001; 192 $\mu g\ m^{-3}$ during 25–6 April 2001; 883 $\mu g\ m^{-3}$ during 21–23 March 2002; Table 3). Similar to our study, *Huebert et al.* [2003] also observed the strong influence of dust storms from Gobi and Taklamakan Deserts during 11–13 April 2001 and 25–26 April 2001 on the chemical composition of aerosols over Gosan. We observed high loadings of total hydroxy FAs for these Asian dust events related to heterogeneous distributions of soil microbes within dust source regions in East Asia, although they are not synchronized.

We divided the entire spring samples from Gosan into two categories, "carbonate-rich dust and loess deposit-influenced air masses," based on the differences in stable carbon isotopic composition of TSP with and without acidification ($\Delta\delta^{13}C$ [*Kawamura et al.*, 2004]). The carbonate-rich dust samples (e.g., 10–17 April 2001 and 21–23 March 2002) are characterized by significant depletion in ^{13}C upon exposure of these aerosol filter punches to concentrated HCl fumes. On the other hand, no such difference (i.e., less than 0.5‰) was evident for the remaining Asian dust events sampled over Gosan (Table 3). However, all these samples are characterized by high atmospheric abundances of β- and ω-hydroxy FAs. Therefore, we performed a cluster analysis to ascertain whether any shifts exist in their potential dust source regions (Figures 9b, 9c, and S3).

The carbonate-rich Asian dust sampled during April–May 2001 and March 2002 mostly originated from the Gobi, Tenegger, and Taklamakan Deserts with a minor contribution from arid soils in the Chinese Loess Plateau (Figures 9 and S3). In contrast, other Asian dust samples from Gosan had contributions mostly from Chinese loess and deserts in Russian Far East. *Zhang et al.* [2003] document that mineral dust accounts for 12% of the East Asian Deserts compared to 6–7% in Chinese loess deposits. Therefore, observed temporal variability in the atmospheric abundances of hydroxy FAs (i.e., tracers of

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Table 3. Mass Concentrations of Measured Total α-, β-, and ω-Hydroxy FAs Along With Other Chemical Tracers Such As TSP Load, Nonsea-Salt (nss) Ca^{2+} and SO_4^{2-} and Stable Carbon Isotopic Composition of Aerosols (With and Without Acidification) in Aerosols Sampled Over Gosan During Spring Season (April 2001 to May 2001 and March 2002)[a]

Sampling Date	$\Sigma\alpha$-Hydroxy FAs	$\Sigma\beta$-Hydroxy FAs	$\Sigma\omega$-Hydroxy FAs	$\Sigma(\alpha+\beta+\omega)$-Hydroxy FAs	TSP	nss-Ca^{2+}	nss-SO_4^{2-}	$\delta^{13}C_{w/oHCl}$	$\delta^{13}C_{HCl}$	$\Delta\delta^{13}C$	Provenance
	Ng m^{-3}				μg m^{-3}			Incl. Carbonates	Carbonates Removed		
10–11/4/2001			2.9	2.9	442	8.1	15.9	−20.4	−22.5	2.14	Taklamakan and Gobi
11–12/4/2001	0.04	2.0	77.9	79.9	270	5.5	7.2	−19.4	−22.5	3.09	Taklamakan and Gobi
12–13/4/2001	0.56	1.6	15.8	18.0	171	5.0	7.1	−20.2	−17.9	−2.24	Taklamakan and Gobi
13–14/4/2001	0.02	0.8	15.6	16.4	270	9.0	16.0	−22.7	−24.2	1.50	Taklamakan and Gobi
14–15/4/2001	0.04	1.7	12.7	14.5	84	1.0	6.5	−22.3	−23.0	0.64	Taklamakan and Gobi
15–16/4/2001	0.20	4.3	9.5	14.1	87	1.3	4.4	−23.7	−26.3	2.60	Taklamakan and Gobi
16−17/4/2001	0.10	20.1	37.0	57.1	102	1.7	7.1	−25.3	−26.1	0.71	Taklamakan and Gobi
21–23/3/2002	0.61	2.3	64.5	67.5	883	12.8	13.8	−15.7	−21.3	5.57	Taklamakan and Gobi
9–10/4/2001		1.3	6.6	7.9	113	0.4	12.7	−24.4	−24.1	−0.35	Chinese loess
17–18/4/2001	0.29	15.5	10.3	26.1	106	1.9	9.0	−25.1	−25.2	0.13	Chinese loess
18–19/4/2001	0.01	1.9	6.1	8.0	94	2.1	9.0	−23.2	−23.6	0.41	Chinese loess
19–20/4/2001		2.4	4.2	6.6	166	4.9	16.0	−25.2	−25.6	0.39	Chinese loess
22–23/4/2001		7.4	26.2	33.6	110	0.9	4.6	−25.2	−25.0	−0.15	Chinese loess
25–26/4/2001		3.2	63.1	66.3	192			−24.1	−23.8	−0.24	Chinese loess
28–29/4/2001		0.1	0.8	0.9	43	0.0	4.0	−25.7	−24.3	−1.46	Chinese loess
1–3/5/2001	0.10	2.0	37.7	39.9	69	0.3	10.5	−24.0	−24.1	0.06	Chinese loess
4–6/5/2001	0.00	0.2	4.1	4.3	57	0.3	6.4	−24.6	−24.7	0.10	Chinese loess
14–17/5/2001	0.01	0.1	3.2	3.4	124	1.5	9.1	−23.3	−23.2	−0.10	Chinese loess
24–28/5/2001	0.18	0.8	5.1	6.1	71	0.5	15.0	−23.8	−23.5	−0.28	Chinese loess
6–9/3/2002	0.56	2.1	12.1	14.8	143	1.9	8.8	−23.1	−23.4	0.31	Chinese loess
11–13/3/2002	0.78	2.8	12.9	16.5	44	0.4	2.9	−24.5	−24.9	0.32	Chinese loess
15–16/3/2002	1.92	4.8	21.8	28.5	153	1.7	17.5	−23.6	−23.5	−0.11	Chinese loess

[a]Here, $\Delta\delta^{13}C$ refers to difference between $\delta^{13}C_{w/oHCl}$ and $\delta^{13}C_{HCl}$.

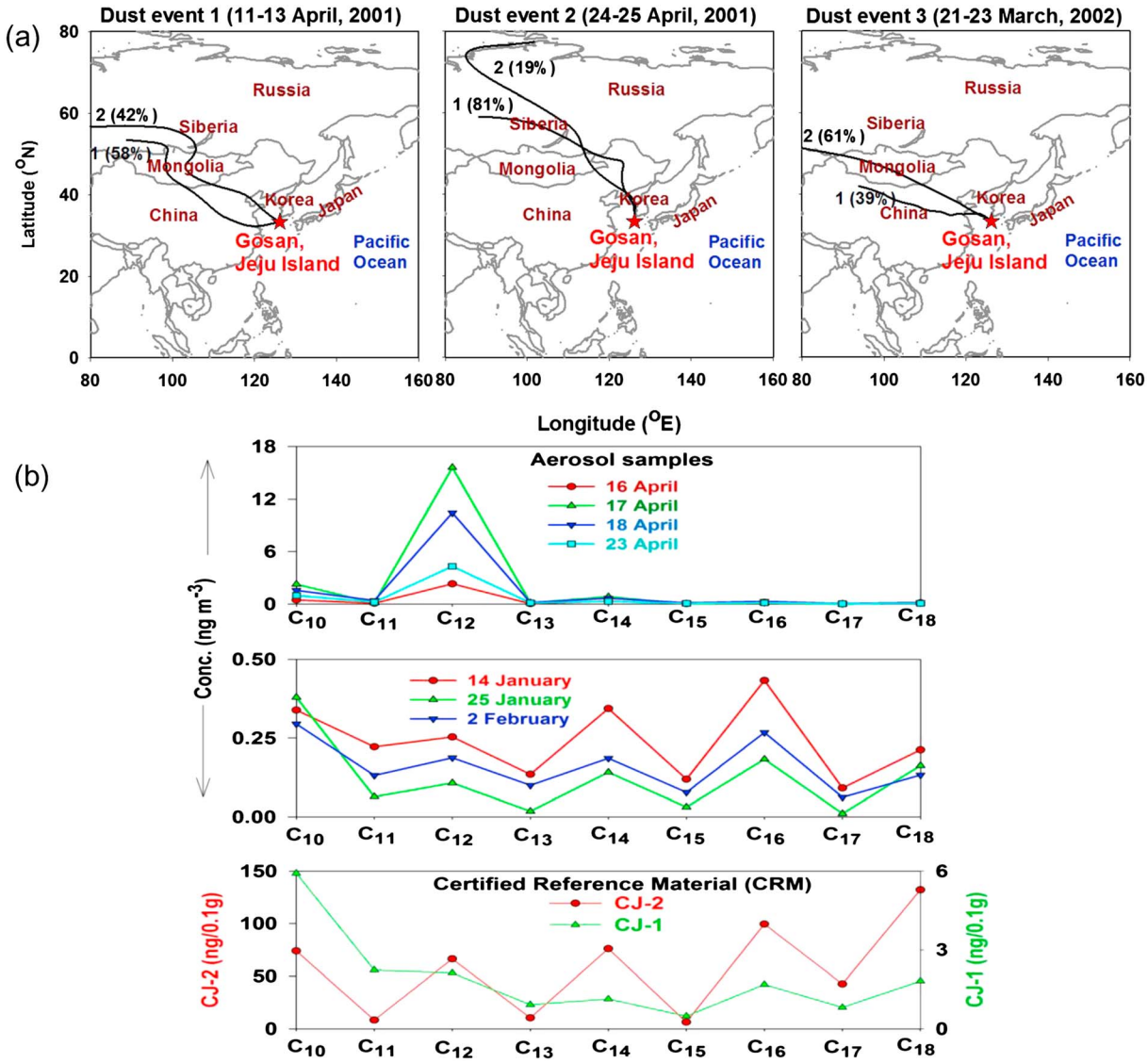

Figure 10. (a) Mean AMBT pathways of identified clusters for three specific dust events and (b) molecular distributions of β-hydroxy FAs during three dust events and in certified reference materials (CJ-1 and CJ-2).

soil microbes and/or plant waxes) over Gosan for these two types of Asian dust could be in direct connection with heterogeneity in the mineral dust. Significant contributions of air masses originating from south Japan during 10–11 April 2001, where the "Miyakejima" volcanic eruption was observed, could be responsible for high TSP loading (444 μg m^{-3}), but they are instead characterized by a low concentration of total hydroxy FAs (2 ng m^{-3}; no detectable signal for β-hydroxy FAs) for this sampling day. This observation also highlights that when the impact of East Asian outflow is at a minimum during spring, contribution of hydroxy FAs from other sources (oceanic sources and/or local emissions) are negligible over Gosan. Three other dust samples over Gosan (11–13 April 2001, 24–25 April 2001, and 21–23 March 2002) are characterized by higher loading of TSP (Table 3) and β-hydroxy FAs (tracer for soil GNB/other microbes), nss-Ca^{2+} (soil dust), and trehalose (soil fungal spores). Therefore, β-hydroxy FAs over Gosan during spring are mostly derived from soil microorganisms residing over/in dust particles.

We observed similar molecular distributions of β-hydroxy FAs ($C_8 > C_{10} > C_{12} \approx C_{14}$) for these three dust events and their AMBTs, suggesting contributions from the Mongolian Desert (Figure 10a). Furthermore,

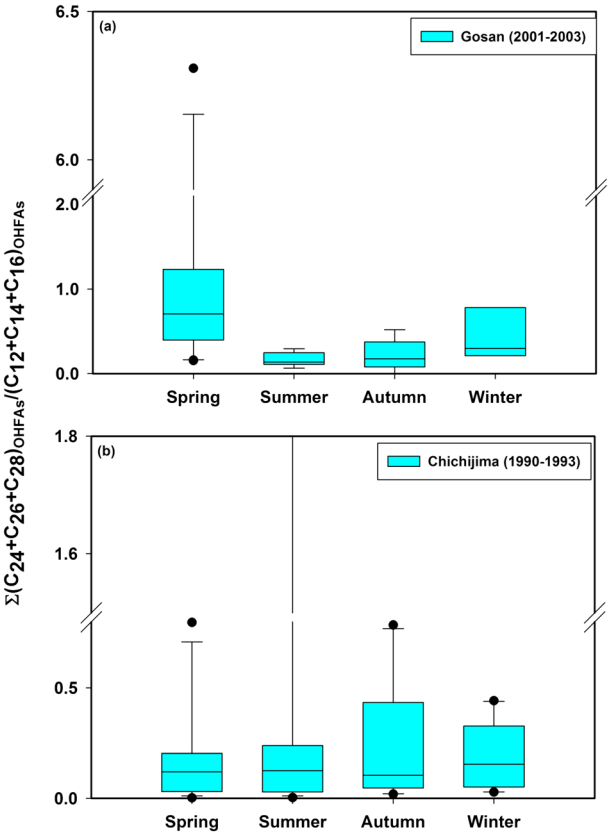

Figure 11. Box-whisker plots, showing the concentration ratio (R_{OHFAs}) of sum of C_{24}, C_{26}, and C_{28} hydroxy FAs to sum of C_{12}, C_{14}, and C_{16} hydroxy FAs at (a) Gosan (this study) and (b) Chichijima [*Tyagi et al.*, 2015a].

we found no similarity in the molecular distributions of β-hydroxy FAs between these three dust event samples and CJ-1 (Chinese loess) and CJ-2 (Asian mineral dust, China) samples (Figure 10b). This result excludes a possible contribution of soil microbes (or GNB) from Chinese loess deposits to the springtime dust events. However, we observed molecular distributions of β-hydroxy FAs in the winter season similar to the two certified reference material samples (CJ-1 and CJ-2), suggesting their probable source as Chinese loess sediments. This argument is further corroborated by a recent study of *Maki et al.* [2014], which suggests that airborne bacterial communities over Japan are highly affected by Asian dust events from the Chinese loess during winter. Therefore, atmospheric abundances and molecular distributions of β-hydroxy FAs over Gosan during the spring season can be explained by a significant contribution of soil microbes from the Mongolian Gobi Desert rather than Chinese loess.

3.5. Relative Significance of Continental Versus Marine Sources

Waterson and Canuel [2008] used the concentration ratio of terrigenous-to-aquatic fatty acids, a concept that was initially introduced by *Bourbonniere and Meyers* [1996], to examine the relative contribution of continental (higher plant waxes/soil microbes) versus oceanic sources (algal/phytoplankton derived organic matter) to sediments. We used a similar approach based on hydroxy FAs over Gosan to deconvolute the relative significance of soil microbes vis-à-vis higher plant waxes in the East Asian outflow. In general, long-chain homologues of hydroxy FAs (e.g., C_{24}, C_{26}, and C_{28}) are mostly derived from the epicuticular waxes of higher plants [*Waterson and Canuel*, 2008; *Tyagi et al.*, 2015a], whereas short-chain homologues are from soil microbes [*Tyagi et al.*, 2015a] and marine (i.e., algae/phytoplankton) derived organic matter [*Wakeham*, 1999; *Wakeham et al.*, 2003]. Therefore, we defined a parameter "R_{OHFAs}," which is a concentration ratio of the sum of C_{24}, C_{26}, and C_{28} hydroxy FAs to the sum of C_{12}, C_{14}, and C_{16} hydroxy FAs and can be mathematically represented as follows:

$$R_{OHFAs} = [C_{24} + C_{26} + C_{28}]/[C_{12} + C_{14} + C_{16}]$$

R_{OHFAs} follows a seasonal trend at Gosan with higher ratios in spring (median: 0.57) and winter (0.30) and lower ratios in summer (0.16) and autumn (0.17) (Figure 11a). A comparison of R_{OHFAs} from Gosan with those from Chichijima (Figure 11b) indicates a predominance of continental sources over the Gosan site, whereas mostly marine sources contribute to atmospheric hydroxy FAs at Chichijima site. No such seasonality is apparent for R_{OHFAs} at Chichijima because it is a pelagic oceanic island, where marine derived organic matter dominates hydroxy FAs in summer/autumn aerosols. Although influenced by continental pollutants, oceanic sources overwhelm the contribution of the East Asian outflow over Chichijima even in spring and winter. On the other hand, R_{OHFAs} at Gosan in spring and winter indicate a dominant emission from vascular plants (e.g., lipid waxes) over soil microbes in the East Asian outflow.

4. Conclusions

We documented the year-round atmospheric abundances of α-, β-, and ω-hydroxy FAs, which are chemical markers of soil microorganisms and plant waxes, in TSP collected over Gosan, Jeju Island, in the western North Pacific Rim during April 2001 to March 2002. These hydroxy FAs showed pronounced temporal and seasonal variabilities. In particular, concentrations of hydroxy FAs were highest in spring followed by winter, whereas they were lowest in summer and autumn. The seasonal variability of β-hydroxy FAs is consistent with other tracers of soil microbes (trehalose), resuspended dust (nss-Ca^{2+}), and stable carbon isotopic composition ($\delta^{13}C$) of total carbon. In addition, the seasonal variabilities and molecular distributions of β-hydroxy FAs (with characteristic C_{12} predominance) over Gosan are also consistent with those collected from remote island Chichijima in the western North Pacific. This observation together with AMBTs in spring season clearly indicates their source as "*Asian dust*." We compared the molecular distributions of β-hydroxy FAs in TSP from this study with those measured in Asian mineral dust standards (CJ-1 and CJ-2). This comparison reveals that loess deposits in China during winter and mineral dust from arid regions in Mongolia (Gobi Desert) and China (e.g., Taklamakan and Tengger Deserts) during spring are the major contributors of soil microbes over Gosan. The contribution from higher plant waxes dominates over soil microbes in the East Asian outflow, as inferred from the predominance of ω-hydroxy FAs in total hydroxy FAs. This study clearly demonstrates that airborne bacteria and higher plant waxes can either adhere to dust particles or form aggregates with them and therefore be subjected to a long-range atmospheric transport with influences on the downwind oceanic waters through changes in the marine microbial community structure.

Additional information based on culturing of aerosols from Gosan and Chichijima is needed to enhance our understanding of what dominant types of airborne soil bacteria persist in the East Asian outflow that eventually influences microbial diversity in the downwind surface waters. Because the samples investigated for hydroxy FAs in this study are from ACE-Asia campaign in 2001–2002, we could not perform the culture-based identification and/or DNA sequencing of possible microbial species. Therefore, our future perspective deals with characterization of soil microbes from freshly collected aerosols using both laboratory analyses: molecular markers and culture techniques. These results could help in identification of bacterial species and plant waxes and thus provide valuable information regarding their role in the East Asian outflow as well as in the biogeochemistry of surface waters of the North Pacific.

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