Hydroxy Fatty Acids in Remote Marine Aerosols over the Pacific Ocean: Impact of Biological Activity and Wind Speed

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ABSTRACT: Current parametrization of cloud–aerosol interactions of nascent sea-spray aerosols (SSA) in the climate models is hampered by our limited understanding of the constituents of organic aerosols. We investigated here the mass concentrations, molecular distributions, and relative abundances of hydroxy fatty acids (FAs), ubiquitous lipid compounds in the SSA collected over the western Pacific Ocean (35°N–40°S). Detectable levels of methanesulfonic acid (an oxidation product of dimethyl sulfide) and high enrichment factors of Mg2+ and Ca2+ relative to Na+ emphasize the impact of the marine biological activity on the organic fraction of SSA. The molecular distributions of β-hydroxy FAs with characteristic “odd-C” predominance (C9 > C10 and C11 > C12) among short-chain homologues (<C14) reveal their formation from the photochemical oxidation of marine-derived organic matter. Molecular distributions and the carbon preference index of n-fatty acids and n-alkanes in the SSA also indicate their oceanic origin. A rapid decrease in the mass ratio of low molecular weight FAs to sea-salts with wind speed indicates the significant variability of organic compounds with production pathways of SSA (fine film-drops versus coarse jet-droplets). On the basis of the multitracer approach, this study underscores the background oceanic influence on the abundances of microbial lipids over the remote Pacific Ocean.

KEYWORDS: hydroxy fatty acids, latitudinal distribution, western Pacific cruise, higher plant waxes, marine microbes

1. INTRODUCTION

Hydroxy fatty acids (or hydroxy FAs) and n-fatty acids (or n-alkanoic acids) are the pivotal lipid constituents of marine aerosols. These compounds have a profound influence on various atmospheric processes including the effect on surface tension, hygroscopicity, and cloud condensation nuclei (CCN) activity of sea spray aerosols (SSA). Hydroxy FAs and n-fatty acids can either originate from terrestrial inputs (e.g., higher plant waxes, soil microbes) or from the surface ocean (e.g., cellular lipids of phytoplankton/heterotrophic bacteria). Many studies have examined the molecular distributions and relative abundances of these lipids in the continental outflows, for example, the E. Asian outflow to the W. North Pacific. These studies have unveiled that changes in the meteorology, sources, and emission-strength (e.g., biomass burning, forest fires, plant waxes, and episodic dust events) significantly affect the atmospheric abundances of hydroxy FAs and n-fatty acids. However, the lack of such details on these lipids originating from the oceanic microbial sources, calls for more measurements.

At the air–sea interface, the bubble-bursting process ejects the jet and film droplets, and both evaporate to form SSA. However, the surface seawater and sea–surface microlayer (SSML) contain high levels of organic surfactants such as hydroxy FAs, n-fatty acids, proteins, and saccharides. These surfactants originate from the dissolved/particulate organic matter. Because of the amphipathic nature of fatty acids (i.e., with both hydrophobic (CH3(CH2)n-) and hydrophilic (–COOH) nature), these compounds float to the...
surface and became enriched in the SSML. Hence, the nascent SSA are often coated with fatty acids/hydroxy FAs. Furthermore, fatty acid concentrations are 10-fold higher than those of other lipids (e.g., n-fatty alcohols, and n-alkanes) in the SSA. The relative enrichment of these n-fatty acids in the SSA than bulk seawater is likely to be an important factor for the CCN activation. Likewise, the lipopolysaccharide (LPS) of Gram-negative bacteria (GNB) in seawater (e.g., *Escherichia coli*, *Aeromonas hydrophila* and *Stenotrophomonas maltophilia*) also contains β-hydroxy FAs, and hence, contributes to marine aerosols. GNB cannot retain the crystal violet stain used in the gram-staining method of bacterial differentiation. Because of the high abundance of GNB originating from seawater, the marine bacterial aerosol has global ecological significance and also influence the cloud nucleation process and atmospheric chemistry.

We can determine the sources of hydroxy FAs/fatty acids in marine aerosols using the relative abundances of high versus low molecular weight (HMW vs LMW) homologues, even/odd-C predominance in the molecular distributions and their carbon preference index (CPI). The homologues of hydroxy FAs/fatty acids have similar chemical properties and can be represented as “Cₙ”, where n is the number of C atoms. While higher plant waxes (e.g., cutin and suberin) contribute to HMW-fatty acids and ω-hydroxy FAs (>C₂₀), LMW-fatty acids and β-hydroxy FAs (≤C₂₀) are specific to soil-GNB and marine-GNB/heterotrophic bacteria. Despite the source variability (terrestrial vs marine), the molecular distributions of hydroxy FAs/fatty acids show strong even-C predominance due to their synthesis through biological pathways. Likewise, the CPIhydroxy FAs, which is an abundance ratio of even/odd homologues, is also a useful proxy to identify their sources (i.e., higher plants or marine phytoplankton). Numerous researches have used these tracers to understand the possible sources of hydroxy FAs/n-fatty acids in marine aerosols.

Chichijima, a remote island in the western North Pacific, aerosols have higher concentrations of C₁₁−C₁₄ n-fatty acids and C₁₃−C₁₄ hydroxy FAs in winter/spring than other seasons because of the input from terrestrial higher plant waxes. In contrast, LMW-fatty acids and hydroxy FAs (C₅−C₁₀) are more abundant in summer over Chichijima because of the influence from marine-derived organic matter. Mochida et al. documented a positive correlation between LMW-fatty acids and sea salts along with a significant increase in the LMW-fatty acid/sea-salt ratio in spring/summer during high chlorophyll levels in the N. Pacific. Furthermore, LMW-fatty acids occur in supermicrometer mode (i.e., association with sea salts) and HMW-fatty acids in the submicrometer mode (i.e., from biomass burning emission). All these observations are from the coastal ocean and along the longitudinal cruise tracks in the N. Pacific. However, no such information was available for better constraining the sea-to-air emission of fatty acids and related compounds from the open ocean waters of the Pacific. Therefore, our study here focuses on the hydroxy FAs/fatty acids in marine aerosols over the western Pacific Ocean during KH92-4 expedition, covering the latitudes from 35°N to 40°S. The aim of this study is to assess the governing factors of atmospheric abundances, molecular distributions, and relative abundances of hydroxy FAs/fatty acids over the western Pacific during September and October.

2. EXPERIMENTAL METHODS

2.1. Aerosol Sampling and Determination of Water-Soluble Inorganic Species. Total suspended particulate (TSP) samples were collected during the cruise KH92-4 (16 September–24 October 1992) in the western Pacific Ocean (Figure S1). A high-volume air sampler (Shibata HVC 1000; flow rate of 1.0 m³ min⁻¹) was set up on the upper deck of the *R/V Hakuko Maru* (~14 m above sea surface). Each sample was collected for ~24–48 h with a precombusted (450 °C for 6 h) quartz fiber filter (PALLFLEX, 20 × 25 cm). To ensure the clean sample collection, we used a wind speed/speed controlled (±45° and ≥5 ms⁻¹) sampling system connected to a high-volume air sampler. The purpose of using this system is to avoid a potential contamination from the ship exhausts. However, this system does not detect a potential contamination from other ships, although there were no ships nearby the research vessel (*R/V Hakuko Maru*) because the cruise was operated on the remote open ocean. All meteorological parameters were obtained from the onboard weather station of the ship. The cruise track and surface wind conditions (>7 ms⁻¹) at the time of sampling are shown in Figure S1. After sampling, all the filters were stored in a precleaned glass bottle individually with a Teflon-lined screw cap at ~20 °C until analysis. Details of cruise track and aerosol sampling are reported in Sempéré and Kawamura. A fraction of TSP sample was extracted in ultrapure deionized water by sonication and analyzed for water-soluble anions and cations by an ion chromatography as described in Suzuki et al.

2.2. Extraction and Measurement of Hydroxy FAs. Briefly, a fraction of the aerosol filter was extracted with 0.1 M KOH/methanol solution (10 mL × 3) under reflux, followed by subsequent ultrasonication with dichloromethane (DCM) (10 mL × 3). We combined methanol extracts with DCM extracts to obtain a better recovery for nonpolar lipids such as n-alkanes. The combined extract was concentrated to ca. 1 mL using a rotary evaporator under vacuum and then divided into neutral and acidic fractions according to the method described in Kawamura. From the acidic fraction, carboxylic acids were extracted with DCM. By adding 0.5 mL of 14% BF₃/methanol (Supelco) to the acidic fraction, carboxylic acids were converted to methyl esters at 100 °C. Excess derivatizing agent and hydrofluoric acid were removed by adding 10 mL of water and n-hexane/DCM (10:1). These derivatives were separated into (1) monocarboxylic acid, (2) dicarboxylic acid, and (3) hydroxy fatty acid ester fractions using a silica gel (deactivated with 1% H₂O) column chromatography.

The hydroxy FA fractions were stored at ~20 °C in darkness until analysis. Prior to GC/MS injection, hydroxy FAs were derivatized with N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) (Supelco Analytical) at 80 °C for 1 h to convert hydroxyl groups to trimethylsilyl (TMS) ethers. After the reaction, 50 μL of an n-hexane solution containing 1.43 ng μL⁻¹ of internal standard (C₁₃ n-alkane/tridecane, Wako) was added to dilute the derivatives. We used a mass spectrometer (Hewlett-Packard model 5975 C inert XL EI/CI mass-selective detector, MSD with triple-axis detector) interfaced to a gas chromatograph (Agilent Technologies, model 7890 GC) for compound identification and quantification. For the quantification of hydroxy FAs, HP-5 fused silica capillary column (Agilent; 25 m long × 0.20 mm i.d. × 0.5 μm film thickness) was used with the GC oven temperature-programmed from 50 °C (2 min) to 120 °C at 15 °C min⁻¹ then to 305 °C (15 min)
The recoveries of authentic hydroxy FAs and processed in a similar fashion as that of real blanks were also analyzed for hydroxy FAs (e.g., in methanol, ff solvents are toxic for bacteria being dominant in the deep-sea sediment, ice core, snow/snow pit, and aerosol samples.

More detailed description of the analytical procedures of these lipid biomarkers was reported in several of our previous publications.

2.3. Quality Assurance. The identification of hydroxy FAs was performed by comparing retention time and mass spectra with those of TMS derivatives of authentic methyl esters of α-hydroxy n-C12 and n-C16 FAs; β-hydroxy n-C12, n-C14, n-C15, and n-C16 FAs; and αω-hydroxy n-C16, n-C20, and n-C22 FAs, which were also used as external standards. The precombusted blank quartz filters were spiked with known concentrations of hydroxy FAs and processed in a similar fashion as that of real samples. The recoveries of authentic β- and αω-hydroxy FAs standards were better than 60% and 70%, respectively. Procedural field blanks were also analyzed for hydroxy FAs and no signals were detected on the mass spectrometer of the target compounds. We previously showed, using the same analytical protocol adopted here, that molecular distributions of β- and αω-hydroxy FAs in certified reference materials of Asian dust and Chinese loess matches with the TSP collected in 2001 over Gosan, Jeju Island during the influence of dust outbreaks from East Asia. Moreover, the reported lipid compounds are well-known proxies for the paleoclimate studies. The extraction protocol includes various fractions and after derivatization, these aliquots were well preserved at −20 °C. Sample extraction and BF3/methanol derivatization procedures were performed in 1993, but TMS derivatization of hydroxyl groups and subsequent GC–MS measurements were performed in 2015. Because the extracted samples were kept in a 1.5 mL glass vial with a Teflon-lined screw cap in a dark freezer room at −20 °C, chemical breakdown/oxidation of lipid compounds is very unlikely. In fact, based on the unpublished data sets from our group, we ascertained that the storage induced artifacts were not detected, as inferred from the repeated analyses of organic compounds (e.g., dicarboxylic acids) in 1991 Alert aerosols in 2010 using the same filter sample stored at −20 °C (i.e., reproducible within 10%). Therefore, it is unlikely to consider that the interpretations of the sources and molecular distributions of hydroxy FAs investigated in this study are affected by the storage artifacts of aerosol extracts.

3. RESULTS AND DISCUSSION

3.1. Air Mass Back Trajectories and Wind Speed Dependence of SSA. To identify the sources/origin of aerosol particles collected during the cruise, 10-day isentropic air mass back-trajectories (AMBTs) were computed for every 12 h at arrival heights of 100, 500, and 1000 m (Figure S2) using a hybrid single particle lagrangian integrated trajectory model (HYSEPLiT, version 4). By combining the origin of AMBTs with the abundances of levoglucosan (i.e., a biomass burning tracer), we classified the TSP into "continental" and...
levoglucosan can be degraded during transport and, hence, undermine the influence of continental impact to TSP collected here, the composition and relationships of major water-soluble inorganic ions are consistent with the seawater source. Only the TSP samples collected near Japan, Papua New Guinea, and Australia (N = 7) have shown slightly higher abundances of levoglucosan (i.e., > 1 ng m$^{-3}$; data obtained from Kunwar et al., manuscript in preparation), which are referred here as “continental” and the rest is referred to “marine”. Therefore, the “continental” samples are likely to have contributions of hydroxy FAs from terrestrial biogenic sources. For all other samples, the AMBTs originated mostly from the Southern Ocean.

As the AMBTs for most of the samples showed marine origin (Table 1), sea-salts and associated organic compounds can contribute to aerosol total carbon (TC) during the cruise. We found the predominance of Cl$^-$ and Na$^+$ among other ions and their significant correlations with Mg$^{2+}$, K$^+$, and Ca$^{2+}$ (Table S1), which are derived from sea-salts. Notably, the slope of the linear regression between Cl$^-$ and Na$^+$ is $\sim$1.8 ($\approx$[Cl$^-$/Na$^+]\text{seawater}$; $R^2 = 0.93$; Figure 1a), further suggesting a lack of heterogeneous processing of sea-salt by the atmospheric acidic species (HNO$_3$ and H$_2$SO$_4$) that are usually abundant in continental outflows. However, we observed rather low concentrations of Cl$^-$ in three TSP samples due to high SO$_4^{2-}$ contribution from nearby volcanoes and, therefore, excluded those from the linear regression. We also found a significant linear relation between average surface wind speed during TSP collection and the sea-salt load (i.e., Na$^+$ aero × [Salinity/Na$^+$]$\text{seawater}$; Figure 1b). Several other studies have also observed a similar relationship over the remote
oceans.41–43 These observations highlight the wind-speed-driven sea-salt contribution in marine aerosols.

3.2. Organic Matter Association with SSA. Biological activity in the sunlit surface waters (e.g., phytoplankton bloom) affects the composition of organic mass in the SSA.44–47 This effect can be traced by the enrichment factors of aerosol-Mg2+ and Ca2+(EF_{Mg2+/Ca2+} \approx (X/Na^+)_{seawater}/(X/Na^+)_{seawater}; here X = Mg2+ or Ca2+) due to their association with biogenic carbonaceous particles in seawater (e.g., gel type substances, phytoplankton exudates, and phytodetritus).44–47 EF_{Mg2+} (~1.2 ± 0.2) and EF_{Ca2+} (~1.8 ± 0.8) in the TSP during KH92-4 (Figure 1c) are comparable with those reported in the literature.44–47 Keene et al.36 observed a median and maximum EF_{Ca2+}, ∼1.2 and 4 in the nascent SSA. Salter et al.44 detected high EF_{Ca2+}, (>1–10) for the submicrometer SSA from the N. Atlantic seawater. Likewise, fine mode SSA from the natural seawater during a mesocosm are coated with organic compounds enriched in Mg.45 In seawater, Ca\(^{2+}\) and Mg\(^{2+}\) have a tendency to deprotonate and react with COOH moieties of surface-active fatty acids and hydroxy FAs.48–50 Gaston et al.47 observed organically bound Mg\(^{2+}\) and Ca\(^{2+}\) particles in SSA, particularly when wind speeds were ≥10 ms\(^{-1}\), over different oceanic regions characterized by an increase in chlorophyll-a and DMS levels due to high biological activity.

Wang et al.51 observed an enrichment of aliphatic rich lipids (e.g., fatty acids), amino acids, proteins, and saccharides in the SSA compared to those in surface seawater and SSMU during a phytoplankton bloom. Jayarathne et al.52 documented a selective enrichment of saccharides relative to Na\(^+\) in both sea spray and sea salt aerosols compared to that in the SSMU during a phytoplankton bloom. Therefore, observed EF_{Mg2+/Ca2+} during the KH92-4 cruise signify the role of ocean biological activity in the western Pacific in controlling the composition of organic mass associated with sea-spray/sea salt emissions. Due to a lack of measurements on in situ productivity during the KH92-4 cruise (September–October 1992), we used satellite-based chlorophyll-a data from 1998–2001 as a surrogate (Figure S3) to support the influence of biological activity in seawater.

3.3. Latitudinal Variability. We detected the presence of methanesulfonic acid (MSA), an oxidation product of dimethyl sulfide (DMS) originating from phytoplankton exudates,53–55 but with no latitudinal variability (Figure 1d). The nonsea-salt SO\(_4^{2-}\)/MSA ratios between −20°S and −40°S (56 ± 25) are lower than other TSP samples (Figure 1e). These ratios perhaps represent the marine biogenic signature, which are consistent with those reported over the Atlantic Ocean (37 ± 16).56 Sea-to-air emission of isoprene during phytoplankton bloom could lead to the formation of glyoxylic acid (ωC\(_2\)) in deliquescent marine aerosols.57 Therefore, we compared the latitudinal distributions of MSA and ωC\(_2\) (Figure S4), which are gas- and aqueous phase oxidation products of DMS58 and isoprene,59 respectively. No similarity was found for the latitudinal distributions, perhaps due to relative stability of MSA over ωC\(_2\), which further oxidizes to form more stable oxalic acid in marine aerosols.60

The impact of marine-derived organic matter on TSP is also evident by the lower relative abundance of water-soluble organic carbon (WSOC) in TC (median, 37%; mean, 40%; Figure 1f) compared to that in the East Asian outflow to the western North Pacific (48%61). Marine-derived organic matter is characterized by lower WSOC/TC (∼35%,62 ∼39%,63 ∼20%64) in remote marine aerosols due to the contribution from colloidal aggregates of phytodetritus/bacteria.19,65 These findings are in accordance with those of O’Dowd et al.,55 emphasizing the predominance of water-insoluble organic matter (here hydroxy FAs) in remote marine aerosols. However, Miyazaki et al.62 have recently documented a somewhat higher percentage contribution of WSOC/TC (~60%) over the productive open ocean waters of the western Pacific. We also found slightly higher values of up to 55% in samples collected near Australia, where surrogate chlorophyll-a maps showed phytoplankton blooms during September and October (Figure S3). Overall, the relative influence of continental versus marine sources on TSP collected here are diverse and difficult to interpret.

We detected the homologous series of C\(_9\)–C\(_{20}\) β-hydroxy FAs in some samples (Table S2) and C\(_9\)–C\(_{22}\) ω-hydroxy FAs in merely three TSP samples collected near Japan, Papa New Guinea, and Australia (Table S3). The LMW β-hydroxy FAs are specific to LPS of marine GNB/heterotrophic bacteria10 and/or soil GNB.5 The long-range transport of Asian dust (i.e., a carrier of soil GNB) to the western North Pacific is dominant during late spring–early summer but not in autumn (i.e., September–October).3,5,6,8 On a similar note, terrestrial plant waxes and soils contribute to HMW ω-hydroxy FAs, but LMW homologues (e.g., C\(_{16}\)) originate from both continental and marine emissions.3,4 On the basis of the predominance of C\(_{16}\) and C\(_{22}\) ω-hydroxy FAs in remote marine aerosols and deepsea sediments, Kawamura suggested their contribution from both oceanic and terrestrial sources. Hence, if ω-hydroxy FAs in TSP are from higher plant waxes, we would expect a significant contribution of both HMW and LMW homologues (i.e., evident only for 3 TSP). However, we observed only the C\(_{16}\) ω-hydroxy FAs in another six samples among which one TSP sample also contained C\(_{10}\) and C\(_{14}\) ω-hydroxy FAs. Overall, these results emphasize the significance of LMW β- and ω-hydroxy FAs derived from marine organic matter in the marine atmospheric boundary layer (MABL) (see Table S4 for a statistical summary).

To evaluate the relative source strength of marine/continental sources, we examined the pollution Roses (i.e., using "openair" package in R) of total β- and ω-hydroxy FAs according to their wind direction/speed (Figure S5). The pollution Roses of β- and ω-hydroxy FAs, consistent with those of n-fatty acids and n-alkanes, revealed influence from SW/SE direction (i.e., Pacific/Southern Ocean), which are associated with high wind speeds (av. 7.1 m s\(^{-1}\)). These high wind speeds could result in increased emissions of surface-active compounds (e.g., fatty acids, hydroxy FAs) associated with SSA.65–68 In particular, LMW β-hydroxy FAs have been detected in the ultrafiltered dissolved organic matter (UDOM) from the surface waters of the Pacific Ocean, Gulf of Mexico, and North Sea;10 contributed mainly from the LPS of microbial lipids (i.e., marine GNB species). Therefore, the presence of LMW hydroxy FAs signifies the importance of marine-derived organic matter (i.e., phytoplankton/microbial detritus, dissolved organic matter, etc.).

We could not observe any significant latitudinal variability for both total mass loadings of β- and ω-hydroxy FAs (Figure 1g,h). However, the TSP sample collected around 32°N shows high loadings of β- and ω-hydroxy FAs compared to the sample collected around 28°N (Table 1), which could be explained by a strong influence from East Asian outflow (including Japanese islands) for the 32°N sample versus 28°N.
sample. The total mass concentrations of β-hydroxy FAs showed no significant differences (unpaired two-tailed t-score: 1.16; df = 13; \( P > 0.05 \)) between “continental” and “marine” type samples. In seawater, concentrations of hydroxy FAs are rather low compared to those of \( n \)-fatty acids. This is due to the specific origin of hydroxy FAs from the membrane lipids (i.e., LPS) of marine GNB/heterotrophic bacteria compared to LMW-fatty acids and mono/polysaturated fatty acids in bulk dissolved/particulate organic matter fractions.10,69,70

Therefore, we observed a strong latitudinal variability for LMW \( n \)-fatty acids (C\(_8\)–C\(_{20}\)) but not for hydroxy FAs. However, unsaturated fatty acids are less abundant than \( n \)-fatty acids in seawater due to their rapid photooxidation to result in \( \omega \)-oxocarboxylic acids and aldehyde analogues,71,72 which are further oxidized to yield dicarboxylic acids.73,74 Consequently, the sea-air emission of organic compounds associated with SSA are likely a mixture of more abundant fatty acids, dicarboxylic acids, \( \omega \)-oxocarboxylic acids and less abundant hydroxy FAs. Azelaic acid, a specific photochemical oxidation product of marine biogenic unsaturated fatty acids,73–75 also exhibited similar latitudinal variability with LMW-fatty acids in TSP (Figure 1j) due to a common source contribution from the ocean surface. However, these latitudinal trends are contrary to those of sea-salt (Figure 1k), which showed higher concentrations in the TSP from southern latitudes due to prevailing high wind speed. Consequently, the mixing of lipids in the SSML with the underlying ocean waters of the South Pacific results in overall lower abundances of these \( n \)-fatty acids associated with sea-salt particles.

3.4. Molecular Distributions of Hydroxy FAs. The molecular distributions of β-hydroxy FAs revealed a predominance of C\(_9\) over C\(_{10}\) and C\(_{11}\) over C\(_{12}\) homologues (Figure 2a). However, these distributions are contrary to those observed over Chichijima Island in the N. Pacific (i.e., C\(_{16}\) > C\(_{12}\) and/or C\(_{14}\)),1 where we found higher abundances for even-C numbered β-hydroxy FAs. This could be due to differences in the impact of ocean biological activity (e.g., phytoplankton bloom), which affects both the abundances and molecular distributions of the lipids in the SSA.31,52,68,76 The phytoplankton/bacterial cells lyse during the bubble bursting sample.
process and release LPS-bound β-hydroxy FAs\textsuperscript{31,77} and n-fatty acids into the water-column.\textsuperscript{47,78} Likewise, microbial oxidation of n-fatty acids within the sunlit surface ocean could also form corresponding β-hydroxy FAs.\textsuperscript{10,11,70,79} Consequently, hydroxy FAs (i.e., specific to bacterial/phytoplankton cells) occur in lower abundance than n-fatty acids (i.e., originate from bulk of the phytoplankton) in seawater, SSML, and SSA. Cochran et al.\textsuperscript{31} detected C\textsubscript{9}–C\textsubscript{18} β-hydroxy FAs and witnessed a sudden shift in the molecular distribution of n-fatty acids in the SSA (i.e., higher concentrations of some odd-C homologues) during a phytoplankton bloom. Trichodesmium blooms usually occur in the western Pacific during summer/autumn seasons.\textsuperscript{80,81} Therefore, higher abundances of odd-C numbered β-hydroxy FAs (C\textsubscript{9} > C\textsubscript{10} and C\textsubscript{11} > C\textsubscript{12}) in marine aerosols could be due to microbial/chemical degradation of n-fatty acids associated with SSA. Similar distributions for all the TSP during KH92-4 along with the presence of only LMW hydroxy FAs (< C\textsubscript{20}) emphasize their oceanic origin and minor contribution from terrestrial sources.

ω-Hydroxy C\textsubscript{9}–C\textsubscript{30} FAs have revealed the molecular characteristics of even-to-odd C predominance (C\textsubscript{16} > C\textsubscript{17} > C\textsubscript{14}) during KH92-4 (Figure 2b) along with the predominance of LMW-homologues (C\textsubscript{9}–C\textsubscript{20}). However, the concentration of ω-hydroxy C\textsubscript{11} FA exceeded that of C\textsubscript{16} in one TSP collected near Australia (QFF554). The epicuticular plant waxes of cutin contain ω-hydroxy C\textsubscript{16} and C\textsubscript{18} FAs, whereas suberin is composed of ω-hydroxy C\textsubscript{16}–C\textsubscript{26} FAs.\textsuperscript{37} In general, marine-derived organic matter contributes only to LMW ω-hydroxy FAs, while plant waxes also account for HMW ω-hydroxy FAs. Overall, similar trends in the molecular distributions between continental and marine type samples along with the occurrence and/or predominance of LMW hydroxy FAs suggest a major input from marine sources. This finding is further corroborated by the molecular distributions of other lipids (e.g., n-fatty acids and n-alkanes) emitted from surface seawater (Figure 2c,d).

The molecular distributions of n-fatty acids (Figure 2c) have revealed a predominance at palmitic acid (C\textsubscript{16}) followed by stearic acid (C\textsubscript{18}) and myristic acid (C\textsubscript{14}). We found rather low concentrations for HMW n-fatty acids (C\textsubscript{21}–C\textsubscript{32}) than that for LMW homologues. These results are consistent with other studies from the Pacific Ocean.\textsuperscript{31,35,60,82} The carbon preference index of n-fatty acids (CPI\textsubscript{n-FAs} ≈ (C\textsubscript{8} + C\textsubscript{10} + C\textsubscript{12} + C\textsubscript{14} + C\textsubscript{16} + C\textsubscript{18} + C\textsubscript{20} + C\textsubscript{22})/(C\textsubscript{9} + C\textsubscript{11} + C\textsubscript{13} + C\textsubscript{15} + C\textsubscript{17} + C\textsubscript{19} + C\textsubscript{21} + C\textsubscript{23}))\textsuperscript{31} is useful for underpinning their origin (i.e., whether anthropogenic or biogenic). Here, the CPI\textsubscript{n-FAs} > 1 indicates more biogenic origin through biological synthesis of even-C homologues of n-fatty acids. The CPI\textsubscript{n-FAs} values (6–17) in TSP suggest the biogenic sources and are comparable to those documented for the nascent sea salt particles (2–14).\textsuperscript{17,31}

Furthermore, the impact of ocean biological activity on n-fatty acid composition in marine aerosols is evident by the mass ratio of oleic acid (C\textsubscript{18:1}) to stearic acid (C\textsubscript{18}). The C\textsubscript{18:1}/C\textsubscript{18} ratio in marine aerosols serves as a proxy to evaluate the relative significance of terrestrial versus marine input of biogenic n-fatty acids (i.e., higher plants vs marine planktonic/microbial sources). Oleic acid is less stable and oxidized to result in dicarboxylic acids during long-range transport.\textsuperscript{72,74} Although the C\textsubscript{18:1}/C\textsubscript{18} ratios are lower for the aged aerosols transported from E. Asia to the N. Pacific (av. 0.42,\textsuperscript{13} 0.15\textsuperscript{17}) compared to those between 20°N and 20°S (0.35 ± 0.30) in pristine marine aerosols. Therefore, the C\textsubscript{18:1}/C\textsubscript{18} ratio is useful for assessing the photochemical aging of fatty acids (i.e., whether “fresh” or “old”).\textsuperscript{17} Here, we found lower C\textsubscript{18:1}/C\textsubscript{18} ratios between 35°N and 20°S (0.35 ± 0.30) compared to those between 20°S and 40°S (1.5 ± 0.6). This observation implies a strong influence of continental lipids from E. Asia.
and/or the mixing with those of oceanic origin over the tropical Pacific during KH92-4 cruise.

Nevertheless, the HYPLIT backward air mass trajectories originated mostly from the pelagic ocean (Figure S2). This result means that marine microbial lipids are probably the dominant source of airborne hydroxy FAs and n-fatty acids during KH92-4. These contrasting features (lower ratios of C_{18:1}/C_{18} over the WNP with marine origin of AMBTs) may suggest that marine derived unsaturated fatty acids are subjected to atmospheric oxidation during atmospheric transport.\(^2\) Interestingly, we found that C_{18:1}/C_{18} ratios inversely correlated with ambient temperature (Figure S7a).

Relatively high ambient temperatures over the WNP during KH92-4 might have resulted in lower C_{18:1}/C_{18} ratios. Overall, the C_{18:1}/C_{18} ratios from this study (0.09–2.62; av, 0.91; Table 1) highlight a significant contribution from marine biogenic lipids in the SSA followed by photochemical oxidation in the atmosphere.

Another useful proxy for assessing the terrestrial versus marine lipid contribution in TSP in the MABL is molecular distributions and CPI of n-alkanes (i.e., defined as (C_{21} + C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35})/(C_{20} + C_{22} + C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34})).\(^6\) However, the distributions of n-alkanes from biogenic plant waxes, in general, exhibit a strong odd carbon predominance with CPI_{n-alkanes} (4–15),\(^8,^9,^26\) while such a feature is absent for those originating from a fossil-fuel combustion source (CPI_{n-alkanes} ≈ 0.8 ± 0.1).\(^3,^7\) Additionally, the weak odd-C predominance in the molecular distributions with a CPI_{n-alkanes} close to unity (1–2) in remote marine aerosols also indicate contributions from oceanic microorganisms/recycled organic matter.\(^8\) The molecular distributions of n-alkanes in TSP during the KH92-4 cruise showed weak odd-C predominance between C_{23} and C_{31} (Figure 2d).

These CPI_{n-alkanes} (1.07–1.84; av, 1.37 ± 0.25) values, however, suggest a pronounced influence of oceanic biological sources and/or contribution from traces of petroleum derived hydrocarbons in the slicks of surface seawater.

### 3.5. Relative Abundances of Hydroxy FAs

We have examined the relative abundances of LMW (i.e., ΣC_{10}–C_{20}) and HMW (i.e., ΣC_{21}–C_{30}) ω-hydroxy FAs in total mass concentrations of Σ(C_{9}–C_{30}) to assess the significance of continental versus oceanic sources. LMW homologues (ΣC_{21}–C_{30}) accounted for ~58–100% of total ω-hydroxy FAs (Σ(C_{9}–C_{30}); Table 1), suggesting the marine biogenic origin. In the case of β-hydroxy FAs, we could observe only LMW homologues (C_{9}–C_{20}) due to a specific contribution from LPS of marine GNB/heterotrophic bacteria. We observed a predominance of β-hydroxy FAs in total hydroxy FAs (61–100%, av, 92%) over the remote Pacific Ocean (Figure 3a).

The absence of α-isomers and the predominance of β-hydroxy FAs followed by ω-hydroxy FAs over the western Pacific (i.e., contrary to those distributions in the East Asian outflow)\(^3,^4,^8,^9,^22\), characterize a contribution from oceanic sources. We also observed higher relative abundances of LMW n-fatty acids during the KH92-4 cruise, again suggesting a major input from oceanic sources (Figure 3b).

In the MABL, LMW n-fatty acids (C_{9}–C_{20}) can be derived from either plant waxes or marine-derived organic matter.\(^6\) In contrast, HMW n-fatty acids mostly originate from higher plant waxes but not from oceanic phyto detritus/microbial organic matter.\(^2\) Therefore, mass ratios of terrestrial to aquatic n-fatty acids\(^89\) (TAR_{n-FAs} ≈ (C_{22} + C_{24} + C_{26} + C_{28} + C_{30} + C_{32})/(C_{10} + C_{12} + C_{14} + C_{16} + C_{18} + C_{20})) and ω-hydroxy FAs (TAR_{ω-hydroxy-FAs} = (C_{22} + C_{24} + C_{26} + C_{28} + C_{30})/(C_{12} + C_{14} + C_{16} + C_{18} + C_{20})) are useful for deciphering the contribution from land-derived versus marine-derived lipids. If TAR_{n-FAs}/ω-hydroxy-FAs is greater than unity, it implies a major input of n-fatty acids/hydroxy FAs from allochthonous sources (i.e., from terrestrial plant waxes). If the ratio is less than unity, it indicates a major input from marine sources (i.e., the Pacific Ocean). The ratios of TAR_{n-FAs} range from 0.01 to 0.66 (Table 1), emphasizing important marine sources (the North Atlantic, 0.07–0.13;\(^37\) California coast, 0.004–1.11;\(^17\) North Pacific, 0.00; Yellow Sea, 0.4;\(^17\) the values were estimated from fatty acid data from the round-the-world cruise\(^17\)). However, the TAR_{ω-hydroxy-FAs} ratios are computed for the TSP samples in which both HMW and LMW ω-hydroxy FAs were detected (QF638=0.3, collected near Japan; QFF553:1.5, QFF555:0.7, both were collected near Australia). For all other samples, we could observe only LMW ω-hydroxy FAs. The advantage of these ratios for the qualitative source apportionment, for instance, is evident by the relatively high TAR_{ω-hydroxy-FAs} (1.4) in a TSP influenced by air masses from Australia, possibly indicating the input from terrestrial plant waxes.

### 3.6. Factors Affecting the Distributions of n-Fatty Acids and Hydroxy FAs

Hydroxy FAs and n-fatty acids, the ubiquitous surfactants crucial for the formation of the SSMI\(^89–92\) are autochthonous lipid components produced by marine phytoplankton and/or microbial degradation of organic matter.\(^6,^9,^34\) The trapped air bubbles in the surface waters, because of the wind stress, readily scavenge these lipids.\(^16,^66,^82,^95,^96\) Volkman et al.\(^70\) suggested that hydroxy FAs are the oxidative products of relatively more abundant and corresponding long chain fatty acids in the SSMI. On the basis of the origin of AMBTs, the predominance of LMW homologues in both hydroxy FAs and n-fatty acids as well as their TAR_{ω-hydroxy-FAs}/n-FAs we thus hypothesize that hydroxy FAs in marine aerosols originate from the microbial/photocatalytic oxidation of microbial/plankton-derived n-fatty acids.

Mochida et al.\(^22\) found that most abundant fatty acids (C_{10}, C_{16}, C_{14}, C_{18}) are in the coarse mode (i.e., 1–10 μm) with a positive linear relationship of LMW n-fatty acids with wind speed and sea-salt abundances from the North Pacific.\(^5,^16\) However, their study suggested that n-fatty acids are not the major surfactants associated with SSA over the western North Pacific based on their estimated surface area coverage.\(^16,^82\) In contrast, we observed here a weak but significant (R² = 0.32; P < 0.05; we excluded one TSP with rather high wind speed from the regression) negative correlation between wind speed and LMW n-fatty acids during KH92-4 cruise. Also, the total mass concentrations of LMW n-fatty acids during KH92-4 are much higher than those reported over the North Pacific (0.78–24 ng m⁻²).\(^3,^5,^82\) All these observations highlight that there exists not only a considerable spatial variability in the LMW n-fatty acids/sea-salt ratios between N. and Western Pacific but also a missing mechanism or major controlling process for the sea-to-air emission of n-fatty acids associated with SSA.

Because of the differences in the formation pathways (i.e., film versus jet droplets)\(^31,^68,^82,^97\), the composition of lipids in marine aerosols will be affected and, hence, reflected in the LMW n-fatty acids/sea-salt ratios. Mochida et al.\(^22\) observed a strong seasonality of LMW n-fatty acids/sea-salt ratio over the N. Pacific with higher values in summer (4.6 ± 1.8 × 10⁻⁴) and spring (3.7 ± 2.9 × 10⁻⁴) compared to winter (2.1 ± 1.3 × 10⁻⁴) and autumn (1.8 ± 1.3 × 10⁻⁴).\(^3,^22\) Therefore, we have investigated the dependence of LMW FAs/sea-salt mass...
The LMW \( n \)-fatty acids/sea-salt ratios (3.4 \( \times \) \( 10^{-4} \) to 1.2 \( \times \) \( 10^{-3} \); av, 4.1 \( \times \) \( 10^{-3} \)) during KH92-4 are 1 order of magnitude higher than those reported by Mochida et al.\(^8\). Additionally, we observed a rapid decrease in the mass ratios of LMW \( n \)-fatty acids to sea-salt with an increase in wind speed (i.e., averaged for the sampling periods; Figure 4a), followed by a power law. For this fit, we excluded three TSP collected over the pelagic waters near Japan (538, 540, 541) due to the likely influence from East Asia (Figure S2). Furthermore, higher ratios of LMW \( n \)-fatty acids/sea-salt in the TSP collected along the cruise track in the Northern Hemisphere are under the influence of lower wind speeds than those in the Southern Hemisphere (Figure S6). However, Gantt et al.\(^9\) reviewed the wind speed dependence of organic mass fraction associated with SSA and suggested that higher wind speeds (>8 m s\(^{-1}\)) often result in the destruction of SSML (i.e., rich in \( n \)-fatty acids) by mixing with the underlying surface ocean. Therefore, we observed that low mass ratios of LMW \( n \)-fatty acids to sea-salt decreased significantly over the South Pacific (i.e., due to high wind speed) compared to those over the North Pacific (Figure S6a).

The predominance of LMW homologues and molecular distributions of \( n \)-fatty acids (i.e., even-C predominance) clearly indicate a major input from oceanic microbial/
planktonic lipids to MABL. If both TC and LMW n-fatty acids were originated from the marine-derived organic matter, then we could make a good correlation between them. However, we found a moderate linear regression between TC and LMW n-fatty acids ($R^2 = 0.34$; see Figure S7b). Therefore, both the absorptia and ordinate are more or less normalized with the Na+ in SSML (here, sea-salt $\approx$ [salinity/Na+]$_{sea-water}$ $\times$ [Na+]$_{air}$). This normalization process somewhat minimizes the compositional changes of organic compounds associated with SSA due to any physical/chemical processes occurring in the marine atmosphere. We found a significant linear relationship ($R^2 = 0.81$) between LMW-fatty acids/sea-salt and TC/Na+ (Figure 4b). Because TSP samples (QFF538) collected near Japan showed high TC content due to a likely influence from East Asian outflow, we excluded the data from the regression analysis.

We found a significant correlation ($R^2 = 0.85$) between the total mass of LMW n-fatty acids and azelaic acid in TSP (Figure 4c). Remineralization of the dissolved/particulate organic matter by heterotrophic bacteria releases the surface-active lipids (e.g., n-fatty acids, unsaturated fatty acids) into the water column. However, the mono/polyunsaturated fatty acids (e.g., oleic acid) in seawater rapidly oxidizes to form initially oxocarboxylic acids, which are later converted to dicarboxylic acid (e.g., azelaic acid). Therefore, the linear relationship between LMW n-fatty acids and azelaic acid (Figure 4d) in TSP could be due to their common origin from marine-derived organic matter. We also found that oleic acid/stearic acid ratio ($C_{18:1}/C_{18}$) exhibited a nonlinear (power) anticorrelation with azelaic acid (Figure 4c). In particular, the $C_{18:1}/C_{18}$ ratios showed opposite latitudinal trends to that of LMW n-fatty acids/sea-salts (Figure S5b). High surface winds prevailed over South Pacific during KH92-4, coinciding with an increase in high $C_{18:1}/C_{18}$ ratio and sea-salt load but with lower mass ratios of LMW n-fatty acid/sea-salt.

A comparison of total mass concentrations of n-fatty acids and hydroxy FAs with other compound classes (e.g., dicarboxylic acids and oxocarboxylic acids and sugars) in TC demonstrates that n-fatty acids and dicarboxylic acids are the two major organic components in the remote open ocean (Figure 4e). However, Russell et al. documented relatively high abundances of organic material from the surface ocean to the marine atmosphere but cannot explain such shifts in the molecular distributions of hydroxy FAs/n-fatty acids. Cochran et al. observed a similar abrupt variability in the molecular distributions of fatty acids in SSA during a phytoplankton bloom. Therefore, the combination of oceanic biological activity and wind speed governs the atmospheric abundances and molecular distributions of hydroxy FAs and n-fatty acids over the western Pacific.

Climate models often use the parametrizations of wind speed driven sea-salt production and biogenic nonsea-salt SO$_4^{2-}$ concentrations (i.e., DMS oxidation product) over the open ocean to constrain the indirect effects of natural aerosols due to their hygroscopic nature and link with cloud nucleation processes. However, the transmission electron microscope (TEM) images of pristine oceanic aerosols from the high and low latitudes have revealed ubiquitous coatings of organic compounds in the SSML on deliquescent sea-salt particles. In this study, the wind speed dependence of both sea-salt concentrations and LMW n-fatty acids/sea-salt ratios as well as the biological activity in the surface ocean clearly affect the sea-to-air emission of fatty acids over the Pacific Ocean. If fatty acids in the SSML are, indeed, coated on nascent sea spray aerosols as monolayers, they might hinder the water-uptake of the particles (barrier effect) as evident by the recent laboratory experiments focusing on the CCN activity of palmitic ($C_{16}$) and stearic ($C_{18}$) acids. Understanding the relative proportions and molecular distributions of hydroxy FAs and n-fatty acids in marine aerosols from the remote ocean, as described in this study, under varying biological activity in the ocean surface is fundamental for better parametrization/representation of climate models.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.8b00161.

Figures of the surface wind directions, the origin of air mass back trajectories and pollution rose diagrams of investigated lipid compounds and the latitudinal variability of characteristic fatty acid ratios along with their wind speed data; significant linear correlations among the chemical constituents presented in this study (PDF)

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■ REFERENCES


(39) Draxler, R.; Rolph, G., HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory); Model access via NOAA ARL READY Website. NOAA Air Resources Laboratory, Silver Spring, MD, 2003.


(69) Ikawa, M. Algal polynsaturated fatty acids and effects on plankton ecology and other organisms. UNH Center For Freshwater Biology Research 2004, 6, 1−44.


