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Hydroxy fatty acids in marine aerosols as microbial tracers: 4-year study on β- and ω-hydroxy fatty acids from remote Chichijima Island in the western North Pacific

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HIGHLIGHTS

- A biomarker based approach for bacterial transport through aeolian pathway.
- Seasonal, temporal & molecular distributions of β– & ω–hydroxy fatty acids.
- Ubiquitous occurrence of hydroxy fatty acids in marine aerosols.
- Continental & marine sources equally contribute to these hydroxy fatty acids.

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ABSTRACT

To better understand the long-range atmospheric transport of microbial aerosols from Asia to the western North Pacific, marine aerosols were collected from Chichijima Island (27°04′N; 142°13′E) on a biweekly basis during 1990–1993. These samples were investigated for β– and ω–hydroxy fatty acids (FAs) as terrestrial biomarkers of Gram-negative bacteria (GNB) and higher plants, respectively. The average concentrations of β–hydroxy (C_8–C_{31}) and ω–hydroxy (C_{11}–C_{28}) FAs show pronounced seasonal variability with maxima in spring (300 ± 70 pg m^{-3}) and winter (650 ± 330 pg m^{-3}), respectively. Airmass back trajectories clearly indicate the continental outflow from Asia during winter to spring, whereas maritime airmasses dominate in summer to autumn over Chichijima. It is noteworthy that atmospheric abundances of β–hydroxy FAs and, thus, the estimated mass concentration of GNB have not been significantly varied between polluted (continental) and pristine (oceanic) airmasses during the study period. However, the relative source strength observed from cluster analysis of β–hydroxy FAs in the polluted continental airmassess vary significantly among seasons (winter: 98%, spring: 63%, summer; 11%, autumn: 26%). In addition, there were distinguishable differences between polluted continental and pristine maritime airmasses with regard to C-number predominance. The even C-number predominance of β– and ω–hydroxy FAs (~80 and 98% of total mass concentration, respectively) in marine aerosols could be due to their significant contribution from GNB, terrestrial plants and soil microorganisms. These results have implications towards assessing the atmospheric transport of bacterial and plant lipids in the continental outflow over the open ocean.

1. Introduction

A wide range of hydroxy fatty acids (FAs) are found in lipid fractions isolated from a variety of organisms (Downing, 1961) including bacteria (Wilkinson, 1988), algae (Blokker et al., 1998) and higher plants (Pollard et al., 2008; Molina et al., 2006). Several studies have been carried out to assess the abundances of hydroxy FAs in environmental samples such as lacustrine and marine sediments (Eglinton et al., 1968; Cardoso and Eglinton, 1983; Kawamura and Ishiwatari, 1984 a,b; Kawamura and Ishiwatari, 1982) and lake waters (Kawamura et al., 1987) as well as marine aerosols (Kawamura, 1995). Despite having their wide spread occurrence, unfortunately these compounds have received little attention from atmospheric chemists. In general, hydroxy FAs can be categorized

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into different classes on the basis of the number and position of the hydroxyl (OH) group. In the literature, the position of OH group in hydroxy FAs reported so far, are mainly limited to α–, β–, C–9, (ω–l)–, and ω–positions. Among these, aliphatic α–, β– and ω–monohydroxy FAs have been used as tracers of soil microorganisms (Kawamura, 1995), bacteria (Lee et al., 2004) and terrestrial plants (Kawamura et al., 2003) in ambient aerosols, respectively. Likewise, hydroxy FAs have been used as geochemical tracers to evaluate microalgal (Gelin et al., 1997), bacterial and terrestrial plant contributions to sediments (Cardoso and Eglinton, 1983).

Long chain β–hydroxy FAs (C_{10}–C_{18}) are important structural constituents of lipopolysaccharides (LPS) and lipid A, especially in the cell wall of Gram-negative bacteria (GNB). These β–hydroxy FAs are essentially associated with bacterial endotoxin activity (Wilkinson, 1988). Studies have been performed for the quantification and characterization of endotoxins and GNB in ambient aerosols by using β–hydroxy FAs as biomarkers (Lee et al., 2004; Hines et al., 2003; Laitinen et al., 2001). Similarly, long chain aliphatic β–hydroxy FAs have also been reported as intermediates in the β–oxidation of monocarboxylic acids by microorganisms in the old lacustrine sediments from the English Lake district (Eglinton et al., 1968).

It has been suggested that ω–hydroxy FAs (C_{11}–C_{28}) are the pivotal structural components of cell wall of plants (Pollard et al., 2008; Molina et al., 2006) and green algae (Blokker et al., 1998). A possible bacterial source was also identified by Skerratt et al. (1992) who found C_{26}, C_{28} and C_{30} (ω–1)–hydroxy FAs in methane utilizing bacteria. Recent scientific work has suggested that some microalgae can be a potential source of mid-chain hydorxy FAs (C_{30}–C_{34}) in marine environments (Gelin et al., 1997). Thus, these compounds can also be used as biomarkers for soil microorganisms and higher plant metabolites in ambient aerosols. Rather few studies exist in the literature that focuses on tracing the pathways of atmospheric hydroxy FAs in remote marine aerosols (e.g., Kawamura, 1995). Such studies are useful in understanding the changes in atmospheric circulation over the geological past and to assess the long-range atmospheric transport of microorganisms along with the continentally derived particulate matter.

Several studies have documented the impact of Asian outflow to the western North Pacific during winter and spring in delivering the airborne particulates and trace gases. However, to the best of our knowledge, no single study exists in the literature for assessing the long-range atmospheric transport of soil microbes in the continental outflow from Asia to the open ocean waters of the North Pacific. In this regard, we aim to trace the presence of soil microbes in aerosols collected from the Asian outflow in the western North Pacific using certain biomarkers. The present study was carried out over remote marine island, Chichijima, located in the western North Pacific to observe the changes in the long-range atmospheric transport of bacterial tracers to the ocean.

In this study, we made an attempt to use hydroxy FAs as a proxy to understand the linkage between the terrestrial components and those in the oceans and pelagic sediments. In a previous study, Kawamura et al. (2003) have documented the chemical compositions of marine aerosols collected from a remote island, Chichijima during 1990–1993. We have investigated these aerosol samples for the atmospheric abundances of hydroxy FAs in order to assess the long-range transport of terrestrial microbes.

2. Material and methods

2.1. Aerosol collection and prevailing meteorology

Aerosol samples were collected on a biweekly basis from April 1990 to November 1993 at the Ogasawara downrange station of the Japan Aerospace Exploration Agency (JAXA, elevation: 254 m a.s.l.) in Chichijima (27°04′N; 142°13′E) in the western North Pacific (Fig. 1). For this study, bulk aerosol (TSP) samples (N = 69) were collected using a high volume air sampler and quatz filter with a nominal flow rate of 1.0 m^3 min^{-1} (Kawamura et al., 2003). In general, the collection period for each aerosol sample varied in between 4 and 6 days. The air sampler was setup on the top (5 m above the ground) of the base of the parabola antenna for the satellite tracking. During the study period, the relative humidity changed from 60 to 90% (av. ~78%). In general, the sampling site is characterized by prevailing westerlies in winter and spring, whereas trade winds dominate in summer and autumn seasons.

All samples used in this study were collected on a precombusted (500 °C, 3 h) quartz fiber filter (PALLFLEX 2500QAT-UP, 20 × 25 cm^2). After collection, quartz filters were placed into a precleaned glass jar equipped with Teflon liner and screw cap, transported to the laboratory and stored at −20 °C until the analysis of chemical constituents. Prior to the chemical analyses, samples were kept in the desiccator for near about overnight to remove the moisture content. Owing to technical difficulties arose in the high volume air sampler, aerosol samples were not collected in winter and autumn seasons of year 1990–91 and 1993–94. Overall, we have categorized the each year samples into respective seasons, winter (December–February), spring (March–May), summer (June–August) and autumn (September–November).

2.2. Sample preparation for the quantification of hydroxy FAs

The analytical protocol used for assessing the atmospheric abundances of hydroxy FAs is adapted from Kawamura et al. (2003). Briefly, an aliquot of filter was extracted with methanolic KOH under reflux (~2 h) and the neutral fraction was seperated by extraction with n-hexane/methylene chloride (10:1) mixture. Then, the acid fraction was isolated with methylene chloride (i.e., CH_2Cl_2) after the acidification of the remaining solution with 6 M HCl. The isolated acids were converted to methyl esters using 14% BF_3 in methanol (SUPELCO Analytical). Soon after, methyl ester derivatives of FAs (FAMEs) were further separated into three subfractions using silica gel column chromatography. The third fraction (A-3) containing hydroxy FAs was then derivatized with N,O-*bis*-(trimethylsilyl) trifluoroacetamide (BSTFA) (SUPELCO Analytical) to derive the OH groups to trimethyl silyl (TMS) ethers. After reaction, 50 μL

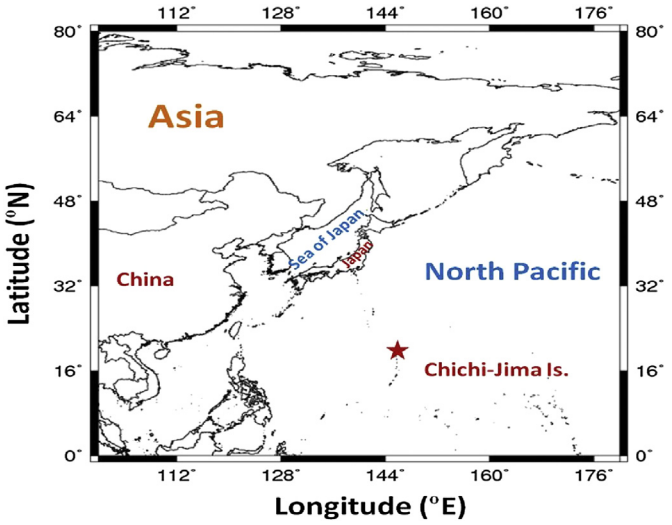

Fig. 1. Map with the sampling site (Chichijima Island) used for the collection of aerosols from the western North Pacific.