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Carbon Isotopic Composition of Fatty Acids in the Marine Aerosols from the Western North Pacific: Implication for the Source and Atmospheric Transport

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A combined molecular and isotopic approach was used in this study to reveal the source and transport of aerosols at a remote oceanic site. Fatty acid distributions and stable carbon isotopic compositions of individual fatty acids were determined in the aerosol samples collected at Chichi-Jima in the western North Pacific over a period of 41 months. Fatty acid concentration and isotopic composition $\delta^{13}\text{C}$ (vs PDB) exhibited temporal variations. Concentrations of fatty acids (C_{12} – C_{34}) ranged from 7.6 to 20.7 ng/m³. The concentrations of lower molecular weight (LMW) fatty acids (C_{12} – C_{19}) tend to decrease in winter and increase in summer, whereas the higher molecular weight (HMW) C_{20} – C_{34} fatty acids exhibited a reversed trend. Compound-specific isotopic analysis revealed that the LMW fatty acids exhibited consistently less negative $\delta^{13}\text{C}$ values than the HMW fatty acids. However, both the LMW and HMW fatty acids displayed a similar trend of temporal variations in $\delta^{13}\text{C}$, suggesting that the fatty acids experienced similar atmospheric pathways and transport processes to the remote marine atmosphere, whereas the difference in absolute $\delta^{13}\text{C}$ reflects the different sources of the fatty acids.

Introduction

Atmospheric organic aerosols play an important role in climate forcing, directly and indirectly (1, 2). In the past several decades, the source and long-range transport of carbonaceous aerosols have been a subject of intensive research (3–11). Different approaches have been used to quantitatively assess the importance of such long-range transport in the global aerosol carbon budget. For example, the C_1 – C_{10} mono- and C_2 – C_{10} dicarboxylic acids in the atmosphere have been used as signature compounds to trace the source, transport, and production/destruction processes of aerosols (12–15). Monocarboxylic acids are derived from direct vegetation emission (16), biomass burning (17), anthropogenic sources (i.e., motor vehicle exhaust), and

perhaps mostly from the photochemical reactions in the atmosphere (12). Dicarboxylic acids are known to be formed from gas-phase precursors under photochemical smog conditions (14). These compounds have been used to fingerprint the source of aerosols in rural, urban, and marine atmospheres (12, 16–18). However, less attention has been paid to use fatty acids (C_{12} and above in chain length) in the previous aerosol studies.

Fatty acids (monocarboxylic acids) are widely distributed in all living organisms and can also be produced from human activities such as vehicle emissions (19, 20), paved road dusts (20), combustion of fossil fuel and biomass (21–23), and cooking operations (24). These compounds have been identified in organic aerosols in urban and semiurban atmospheres (Tokyo (25); Beijing (8); New York (26); Los Angeles (20); Kuala Lumpur (27); Nigeria, (11); Hong Kong (22); Vienna (28)), in rural sites (11), remote sites (Antarctica (10)), and at sites affected by biomass burning (forest fire (29)). Fatty acids are more advantageous than C_1 – C_{10} mono- and dicarboxylic acids in determining the source and transport of organic aerosols in that (1) they are chemically more stable, less volatile, and are less likely to be oxidized in the atmosphere; and (2) their sources are limited to biological and anthropogenic activities but not from photochemical reactions in the troposphere. Therefore, they are more specific in source identification of organic aerosols. Hence, fatty acids have been used as biomarkers for long-range transport of aerosols from eroded plants (4).

Alternatively, stable carbon isotope analysis of bulk organic carbon has been used to determine the source and long-range transport of continental aerosols to remote oceanic sites (5, 7, 30). Because of the difference in plant physiology and carbon fixation pathways, C_3 plants (–20‰ to –32‰) have a distinctly different isotope signature from C_4 plants (–9‰ to –17‰) (31, 32). Additional variations in isotopic composition of aerosols can be attributed to anthropogenic inputs (7) or biomass burning (33, 34). More recently, compound-specific isotope analysis (CSIA) of *n*-alkanes and fatty acids has been used to pinpoint the source of rural and urban aerosols (11). The CSIA technique has the potential to allow for the determination of individual compounds. It has a clear advantage to the bulk isotope analysis in that isotope signature concurrent with structural and distributional information can be gathered (35). This technique has been widely used in organic geochemistry (36–41). However, the use of CSIA in aerosol research is relatively limited.

Recently, the CSIA has been used to determine the isotope fractionation of fatty acids associated with biomass burning (33, 34). The CSIA technique, while useful, has limitations, when applied to atmospheric chemistry (11), in that many biomarker compounds (e.g., alkanes, fatty acids) are derived from a number of different sources. In addition to the “inherited” difference in carbon source (physiology and biochemical metabolism of source organisms (31, 35)), biomarkers are frequently transported with particles in the atmosphere, which adds further uncertainties about the sources of these compounds. Fortunately, unlike isotopic measurements of sedimentary lipids which represent a geologic time-averaged signal (35), the isotopic ratios of individual biomarkers in aerosols are more indicative of the source of these compounds as the transport of aerosols from the continents to oceans takes only a few days (from the Asian continent to the western Pacific (42)). In this paper, we utilize a combined molecular and isotopic approach in characterizing organic aerosols from a remote open ocean

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site in the western North Pacific to reveal the seasonality of molecular and isotopic signatures in the marine aerosols. The results are discussed with reference to the interpretation of sources and transport of aerosols under different meteorological regimes in an open ocean site.

Experimental Section

Extraction, Derivatization, and Analysis of Fatty Acids. Marine aerosol samples were collected on a precombusted (500 °C, 3 h) Pallflex quartz fiber filter (20 × 25 cm) using a high volume air sampler (1000 m³/min) over a period of 41 months (from April 1990 to November 1993) at Chichi-Jima, the western North Pacific (27°04'N, 142°13'E). Detailed procedures were described in Kawamura et al. (43). The sampling time was approximately 100 h to collect enough material for chemical analysis. A total of 69 aerosol samples were collected at the site. After the sample collection, a quartz filter was placed in a precleaned glass jar with a Teflon-lined screw cap and stored in a freezer at -20 °C until analysis.

An aliquot of the filters was extracted under a reflux for 2 h with 100 mL of 0.1 M KOH in methanol, containing ca. 5% distilled water. The analytical method was described in Kawamura et al. (43). Briefly, the extracts were isolated by filtration with a precleaned Whatmann GF/A filter. The residue was further extracted with methanol and then methylene chloride under ultrasonication for 3 min. The extracts were combined and concentrated under vacuum and then separated into neutral and acidic fractions. Acidic components were extracted with methylene chloride from the total extract after acidifying it to pH = 1 with 6 M HCl (9). The acidic fraction was then derivitized to methyl esters using 14% BF₃/methanol. Monocarboxylic acid methyl esters were purified on silica gel column chromatography. The fatty acid methyl esters (FAME) were analyzed on a Carlo Erba Mega 5160 gas chromatograph (GC) equipped with a cool on-column injector, fused silica capillary column (HP-5, 30 m × 0.32 mm i.d. × 0.25 μm) and an FID detector. Compound identification was confirmed using a GC/MS (Thermoquest, Voyager) with similar GC column conditions. An *n*-C16 FAME was used as an external standard for quantification. Analytical errors of the procedures were within 15%. Laboratory procedural blanks showed that blank levels were less than 1% of the samples.

Stable Carbon Isotope Analysis. Isotopic ratios of FAMES were determined using an HP 6890 gas chromatograph coupled with a Finnigan MAT Delta Plus isotope ratio mass spectrometer by a Finnigan MAT combustion furnace containing Cu and Ni wires which were doped with oxygen and maintained at a temperature of 850 °C. The GC was equipped with an HP-5MS fused silica capillary column (30 m × 0.325 mm i.d., 0.25 μm film thickness). The GC oven was programmed from 50 to 120 °C at 30 °C/min, from 120 to 300 °C at 5 °C/min, and maintained at 300 °C for 22 min. The flow rate for He carrier gas was set at 1.5 mL/min. Two microliters of sample solution spiked with cholestane as an internal standard of known isotopic composition were injected through an on-column injector. Peaks were simultaneously detected in Faraday collectors at *m/z* 44 (¹²C¹⁶O₂), 45 (¹³C¹⁶O₂ and ¹²C¹⁷O¹⁶O), and 46 (¹²C¹⁶O¹⁸O, ¹²C¹⁷O¹⁷O, and ¹³C¹⁷O¹⁶O), amplified, corrected for the presence of ¹⁷O at mass 45 using the Craig correction (44). The isotopic composition of fatty acids is reported in the delta notation relative to the Pee Dee Belemnite (PDB) standard as follows:

$$\delta^{13}\text{C} (\text{‰}) = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{PDB}} - 1] \times 10^3$$

Isotope values reported were determined by averaging duplicate analyses. For compounds with a peak height of 0.5–5 V, precision was typically ≤ 0.5‰. Isotopic composition of individual fatty acids was obtained after the correction for

the additional methyl carbon from methanol using the mass balance equation (39, 45)

$$\delta^{13}\text{C}_{\text{FAME}} = f_{\text{FA}}\delta^{13}\text{C}_{\text{FA}} + f_{\text{methanol}}\delta^{13}\text{C}_{\text{methanol}}$$

where $\delta^{13}\text{C}_{\text{FAME}}$, $\delta^{13}\text{C}_{\text{FA}}$, and $\delta^{13}\text{C}_{\text{methanol}}$ are the carbon isotopic composition of the FAME, the underivertized fatty acid, and the methanol, respectively, and f_{FA} and f_{methanol} are the fractions of carbon in the FAME due to the underivertized fatty acid and methanol, respectively. The isotopic composition of methanol was determined using bulk stable isotope analysis (-46.3‰).

Back-Trajectory Analysis. Back-trajectory analyses were conducted using the Fifth-Generation NCAR/Penn State mesoscale model (MM5). The trajectory calculation was based on backward tracking of a selected air parcel released at a target location, assuming the parcel was moving along the ambient airflow. The flow pattern was updated every 6 h.

Results and Discussion

Because of the unique geographic location and meteorological condition of the sampling site in the western North Pacific, the data are discussed as two seasons: winter (from November to April, including early spring) and summer (from May to October, including fall).

Distribution and Concentrations of Fatty Acids. Chain length of fatty acid detected in aerosols ranges from C₁₂ to C₃₄ (Figure 1). The fatty acid homologous series shows bimodal distribution with C_{max} at C₁₆ and C₂₄/C₂₈. The concentrations of fatty acids in aerosols varied from season to season. For the sake of presentation and discussion, the fatty acids are grouped as C_{12–19} representing lower molecular weight (LMW) fatty acids from C₁₂ to C₁₉, and C_{20–34} for higher molecular weight (HMW) fatty acids from C₂₀ to C₃₄ (Table 1). The concentrations of C_{12–19} fatty acids were lower in the winter, ranging from 4.0 to 11.8 ng/m³ (average 8.8 ng/m³) and higher in the summer (6.5–11.8 ng/m³, average 11.1 ng/m³) (Table 1; Figure 2). In contrast, the C_{20–34} fatty acids exhibited maximum concentrations in the winter (4.0–9.4 ng/m³, average 6.0 ng/m³) and minimum concentrations in the summer (2.0–5.0 ng/m³, average 3.0 ng/m³). Overall, total concentrations of fatty acids were higher in the winter and lower in the summer, and the trend is more significant when normalized to total carbon (TC) (Table 1). The concentrations of fatty acids at the Chichi-Jima site are similar to those observed at an open ocean site (Marshall Islands, (3)), slightly lower than those found in aerosols collected over the eastern equatorial Pacific (46), but is 2–3 orders of magnitude lower than those found in the urban atmosphere (e.g., Hong Kong, (22); western United States, (6)), suggesting that continental material is a major source of marine aerosol at the Chichi-Jima site.

TC content of the aerosols was also determined (47). The TC content showed a seasonal trend similar to the C_{20–34} fatty acids (Figure 2). The summer season was characterized by low TC (0.40–0.50 μg C/m³) and winter season by high TC content (0.71–1.45 μg C/m³) (Table 1). It seems that the concentrations and distribution patterns of fatty acids reflect the source strength and transport processes of aerosols. The LMW fatty acids were derived, at least in part, from marine organisms, and the C_{20–34} fatty acids may be from terrestrial plant input (6). The detection of unsaturated fatty acids C_{16:1} and C_{18:1} in the aerosols (Table 1; Figure 1) is indicative of recent biological origin (6), because unsaturated fatty acids are unstable. They can be oxidized rapidly and are not frequently detected in the marine atmosphere (18). The marked high concentrations of C_{16:1} and C_{18:1} fatty acids in the aerosol samples in this study indicate that there might also be some contributions from anthropogenic source such as meat cooking, which can produce C_{18:1} fatty acids (24).

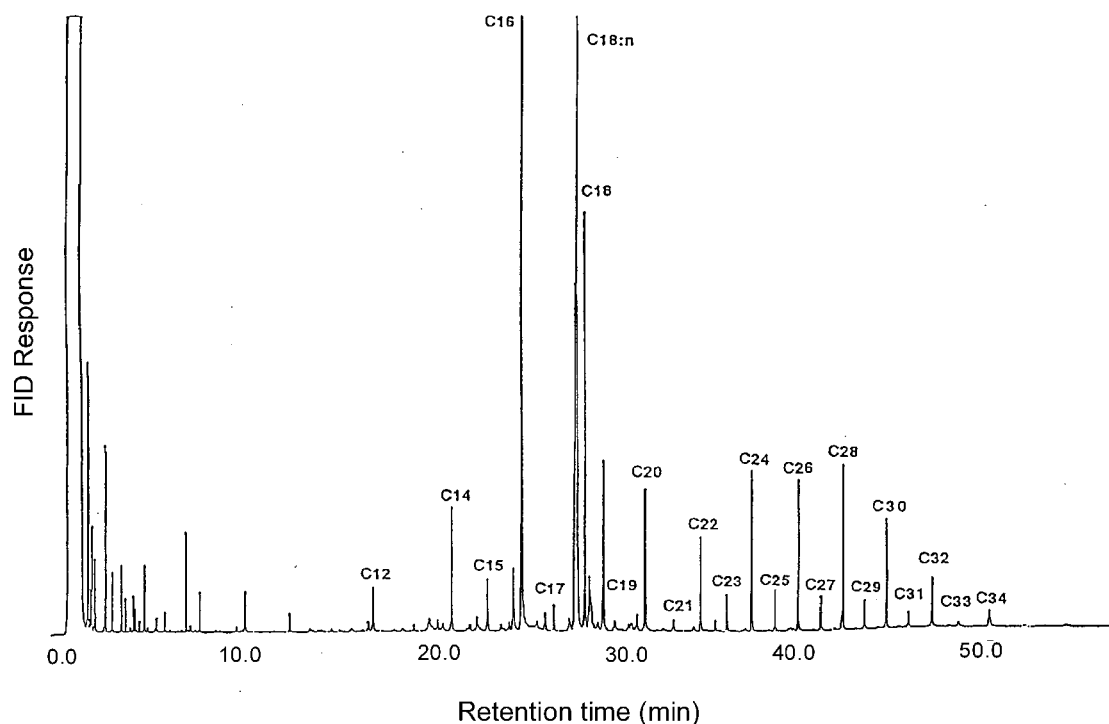


FIGURE 1. Typical GC-FID chromatogram of fatty acids isolated from marine aerosol sample QF207, collected at Chichi-Jima, March 4–7, 1991.

TABLE 1. Summarized Data of Air Temperature (T , °C), Total Carbon (TC, $\mu\text{g}/\text{m}^3$), and Concentration (ng/m^3) of Fatty Acids and Carbon Preference Index (CPI, dimensionless)

season ^a	number of samples	air T (°C)	TC ($\mu\text{g}/\text{m}^3$)	concn (ng/m^3)		normalized ^b concn	CPI ^c
				ΣC_{12-19}	ΣC_{20-34}		
winter 90	2	19.9	1.45 ± 0.3	10.3 ± 5.3	9.4 ± 7.1	13.1	9.8
summer 90	12	26.5	0.47 ± 0.9	11.0 ± 8.0	2.0 ± 1.2	27.7	23.6
winter 91	5	21.5	0.94 ± 1.2	11.8 ± 5.6	4.0 ± 0.8	16.8	17.5
summer 91	10	27.2	0.50 ± 1.6	15.7 ± 7.5	5.0 ± 4.7	41.4	24.7
winter 92	10	19.9	0.78 ± 1.1	8.9 ± 4.7	5.6 ± 7.2	18.6	15.2
summer 92	9	25.0	0.43 ± 1.7	11.1 ± 9.0	2.7 ± 2.4	32.1	23.7
winter 93	10	19.0	0.71 ± 0.5	4.0 ± 1.3	4.8 ± 3.6	12.3	10.9
summer 93	11	26.6	0.40 ± 1.0	6.5 ± 3.2	2.1 ± 1.4	21.5	18.5

^a Summer: May–October; winter: November–April. ^b Concentration of fatty acids normalized to total carbon (TC), ng of fatty acid/ μg of C. ^c $\text{CPI}_{\text{FA}} = 2\Sigma\text{even}(\text{C}_{14-32})/[\Sigma\text{odd}(\text{C}_{13-31}) + \Sigma\text{odd}(\text{C}_{15-33})]$.

However, on the basis of the very low concentration of unresolved complex mixture of hydrocarbons (43), the contributions from anthropogenic sources are negligible.

Additional evidence for recent origin of LMW fatty acids comes from the carbon preference index (CPI), which was calculated for each sample using the formula defined here (48):

$$\text{CPI}_{\text{FA}} = 2 \frac{\Sigma \text{even}(\text{C}_{14-32})}{[\Sigma \text{odd}(\text{C}_{13-31}) + \Sigma \text{odd}(\text{C}_{15-33})]}$$

The CPI values range from 9.8 to 24.7 (Table 1), significantly higher than those found in sediments (49, 50). The strong even carbon number predominance likewise suggests a recent biologic origin of the fatty acids (49) that had undergone little or no compositional changes. Interestingly, the CPI also exhibits systematic changes from season to season (Table 1), with lower values in winter and higher values in summer. Furthermore, LMW C_{12-19} fatty acids have much higher CPI values than HMW C_{20-34} fatty acids (data not shown).

Overall, the variations of the patterns of fatty acid concentration, CPI, and total carbon content reflect the

source intensity and transport processes of the marine aerosols. We chose the Chichi-Jima (27.4°N, 142.1°E) as our study site because the island is located in a unique meteorological regime such that the Japan Jet dominates the atmospheric flow in the western North Pacific in the winter and results in the westerly outflow from Asia (42). The westerlies are centered at 30°N (51) and peak in winter (42). The strong and persistent Asian outflow exerts a major influence on the atmospheric chemistry in the western North Pacific. Lipid aerosols were possibly produced by the wind stress to the plants involving wind-blown particles such as soil and dust (4, 52) in the Asian continent and transported by the westerlies to the western North Pacific (43, 52). Therefore, in the winter season, the total carbon content as well as the concentrations of HMW fatty acids are much higher than in the summer season. Reports from Gregory et al. (42) suggest that pollutants can be transported from Asia thousands of kilometers to the open ocean. It is therefore not surprising that the CPI values are correspondingly lower in the winter.

Although long-chain fatty acids seem to be characteristic to higher plants, there are no compounds that are uniquely of marine origin. Polyunsaturated fatty acids characteristic

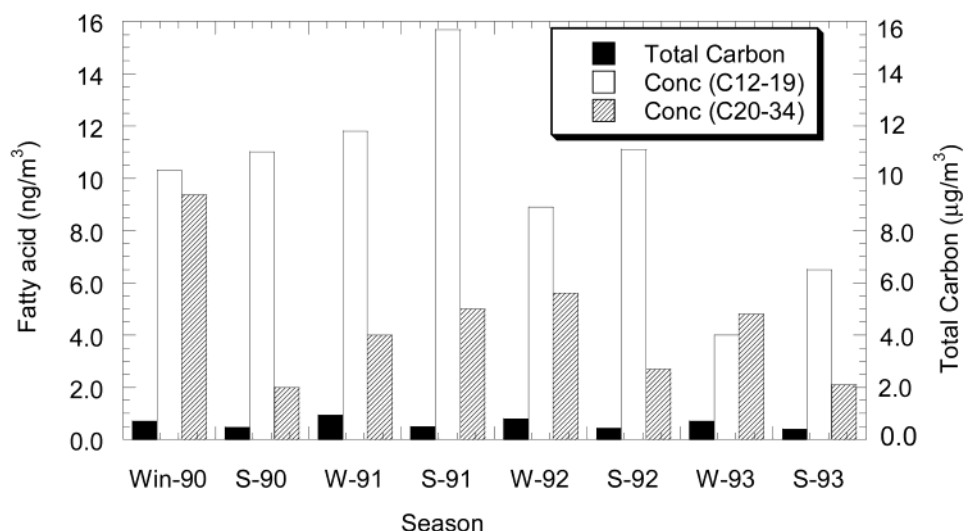


FIGURE 2. Concentration distribution of fatty acids (C_{12-34}) in marine aerosol collected at Chichi-Jima from April 1990 to November 1993. The annual data are divided into winter (Nov–April) and summer (May–Oct). See text for explanation.

TABLE 2. Isotopic Compositions of Fatty Acids Isolated from Aerosol Samples Collected from Chichi-Jima ($27^{\circ}04' N$, $142^{\circ}13' E$), Western North Pacific

fatty acid C number	$\delta^{13}C$ of fatty acid							
	winter 90	summer 90	winter 91	summer 91	winter 92	summer 92	winter 93	summer 93
12	<i>a</i>	-24.9 ± 0.5	-26.1 ± 0.1	-24.9 ± 1.4	-27.0 ± 1.2	-26.1 ± 2.4	-26.4 ± 2.2	-27.7
14	-25.1 ± 0.7	-25.1 ± 1.1	-25.7 ± 0.2	-24.9 ± 0.9	-26.5 ± 1.5	-26.1 ± 1.1	-26.1 ± 1.9	-25.3 ± 1.2
15	-24.4 ± 0.6	-24.9 ± 1.3	-25.4 ± 0.7	-24.4 ± 1.4	-26.7 ± 1.2	-25.7 ± 0.9	-26.0 ± 0.8	-24.8 ± 1.0
16:1		-25.9 ± 0.7	-25.3 ± 0.3	-23.8 ± 1.0	-25.0 ± 0.8	-25.6 ± 0.9	-24.7 ± 0.6	-25.1 ± 0.8
16	-25.1 ± 0.8	-26.4 ± 1.2	-27.5 ± 0.9	-25.5 ± 1.2	-27.7 ± 1.2	-27.3 ± 1.5	-27.0 ± 0.7	-26.3 ± 1.4
17		-24.4 ± 0.9	-26.3 ± 1.0	-24.9 ± 1.8	-27.1 ± 2.0	-25.7 ± 0.6	-27.0 ± 1.7	-25.4 ± 0.5
18:1	-24.0 ± 1.4	-26.0 ± 1.8	-26.3 ± 0.7	-25.7 ± 2.3	-26.8 ± 1.1	-26.6 ± 1.0	-26.1 ± 1.4	-25.5 ± 1.0
18	-24.5 ± 0.1	-26.1 ± 0.9	-26.8 ± 1.3	-24.8 ± 1.5	-27.4 ± 1.0	-26.6 ± 1.0	-26.2 ± 0.9	-25.8 ± 1.9
19	-26.5^b	-25.6 ± 2.1	-24.6 ± 1.9	-24.9 ± 1.2	-27.3 ± 1.7	-26.2 ± 1.3	-26.6 ± 1.3	-26.0 ± 1.3
20	-26.5 ± 2.7	-28.4 ± 1.2	-28.5 ± 0.9	-27.2 ± 1.7	-29.7 ± 0.8	-27.8 ± 1.2	-29.0 ± 1.4	-27.4 ± 1.7
21	-28.0	-29.9 ± 2.0	-30.0 ± 3.3	-28.2 ± 2.1	-29.0 ± 1.7	-29.5 ± 2.9	-29.6 ± 1.7	-32.1
22	-27.4 ± 1.3	-28.4 ± 2.4	-28.5 ± 0.5	-27.9 ± 1.3	-29.6 ± 0.7	-28.7 ± 1.1	-29.3 ± 0.8	-28.1 ± 2.6
23	-29.0	-28.2 ± 2.0	-28.7 ± 1.0	-28.1 ± 1.7	-29.8 ± 0.9	-28.9 ± 2.0	-29.2 ± 2.0	-29.1 ± 2.0
24	-27.6 ± 1.3	-28.0 ± 1.1	-28.5 ± 0.7	-27.7 ± 1.2	-29.7 ± 0.9	-28.5 ± 1.2	-30.1 ± 0.9	-27.6 ± 2.0
25	-28.6 ± 1.6	-26.6 ± 3.0	-28.6 ± 1.0	-27.4 ± 2.3	-29.7 ± 0.7	-28.2 ± 1.3	-29.1 ± 2.1	-28.3 ± 0.8
26	-27.9 ± 3.5	-29.4 ± 1.0	-29.4 ± 0.2	-28.8 ± 1.7	-30.8 ± 0.7	-29.5 ± 1.2	-30.6 ± 1.5	-28.2 ± 2.7
27	-28.6	-29.3 ± 2.9	-29.0 ± 0.8	-27.5 ± 3.4	-29.9 ± 1.6	-29.6 ± 1.7	-29.6 ± 1.6	-30.5 ± 0.8
28	-30.4	-29.0 ± 1.6	-28.8 ± 0.5	-28.2 ± 3.2	-30.1 ± 0.8	-29.6 ± 0.8	-30.2 ± 0.8	-29.2 ± 2.2
29	-28.9	-31.8 ± 1.0	-30.1 ± 0.7	-29.3 ± 3.3	-30.0 ± 1.0	-29.0 ± 2.0	-30.3 ± 1.2	-30.4 ± 0.4
30	-28.3 ± 0.2	-28.5 ± 1.8	-29.0 ± 0.8	-29.4 ± 2.2	-30.4 ± 0.7	-30.6 ± 0.8	-30.3 ± 0.9	-29.4 ± 2.5
31	-30.5		-29.6 ± 1.0	-28.2 ± 2.7	-29.8 ± 2.1	-29.2 ± 2.2	-30.2 ± 1.4	-28.9 ± 3.9
32	-28.9 ± 0.1	-28.8 ± 2.2	-28.7 ± 0.7	-28.3 ± 3.2	-29.9 ± 1.0	-29.4 ± 1.0	-30.1 ± 1.4	-29.4 ± 3.2
33	-27.5		-30.8 ± 0.9	-28.2 ± 2.6	-30.5 ± 1.6	-30.0	-31.7 ± 3.0	-30.7
34	-29.0	-26.9 ± 2.4	-30.1 ± 2.4	-28.5 ± 3.0	-30.7 ± 1.1	-29.4 ± 0.8	-30.5 ± 1.0	-28.2 ± 4.0

^a Not detected. ^b Detected in only one sample (see Table 1 for number of samples).

of marine origin (e.g., diatom (53)) were not detected in the aerosol samples. The in situ production of microbial fatty acids (from sea-slicks or within the atmosphere) may have contributed, to some extent, to the much higher CPI values observed in the summer (Table 1). However, the major cause of the temporal trends of fatty acid concentration, TC content, and CPI values may be ascribed to the meteorological conditions. In the summer/fall season, the Asian influence to the remote marine atmosphere is reduced substantially (42). Instead, the trade winds are more significant, transporting aerosols from tropical America (54, 55). The uniform trend of the increase of TC content in aerosol from summer to winter is an indication of the increase of the source strength of organic aerosols at Chichi-Jima when the source regions shifted from tropical America in the summer to Asia in the winter.

Carbon Isotopic Composition of Fatty Acids. Compound-specific isotope analysis provides further constraints on the

source and transport of fatty acids of marine aerosols. Both groups of fatty acids (LMW and HMW) showed different characteristics in isotopic composition. The $\delta^{13}C$ values of HMW fatty acids varied from -30.0‰ to -28.2‰ with a mean of $-29.1\text{‰} \pm 0.7\text{‰}$ (Table 2, Figure 3). These values are comparable to those $\delta^{13}C$ of Nigeria aerosol samples reported by Simoneit (11) but with less variation, suggesting a more consistent source of aerosols. Organic carbon of marine aerosols of continental origin is characterized by a $\delta^{13}C$ of $\sim -25.5\text{‰}$ (5, 7). Fatty acids of C_3 higher plants origin are generally depleted in ^{13}C relative to plant tissue by $\sim 5\text{‰}$ (50). Thus, the mean $\delta^{13}C$ value of -29.1‰ of the fatty acids of the Chichi-Jima aerosols indicates a dominant source of higher plants with C_3 metabolism (49).

The LMW fatty acids exhibited considerably less negative $\delta^{13}C$ values than HMW fatty acids (Figure 3). The average $\delta^{13}C$ values of C_{12-19} fatty acids ranged from -26.9‰ to -24.8‰ , with a mean of -25.8‰ . The lower $\delta^{13}C$ values

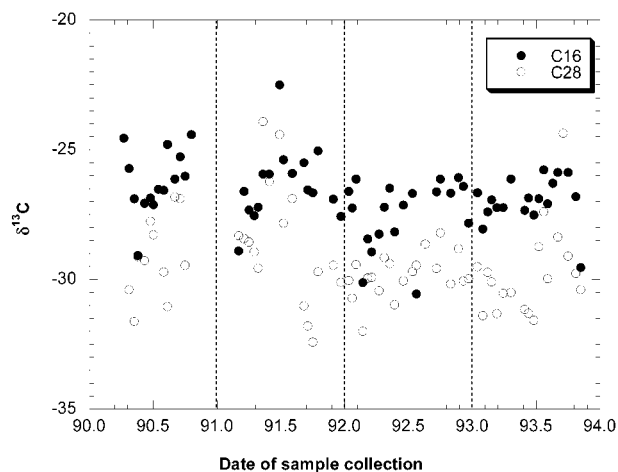


FIGURE 3. Distribution of carbon isotopic composition ($\delta^{13}\text{C}$) of C_{16} and C_{28} fatty acids in aerosol samples collected at Chichi-Jima Island between 1990 and 1993.

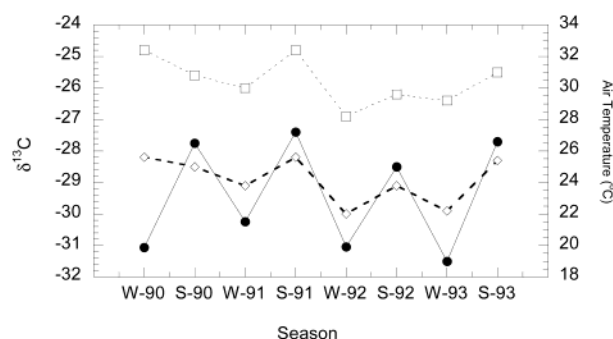


FIGURE 4. Seasonal variations of $\delta^{13}\text{C}$ of lower molecular fatty acids (C_{12-19} , square) and higher molecular weight (C_{20-34} , diamond) fatty acids, together with air temperature (filled circle).

suggest an input of the fatty acids derived from marine biota (50), given that fatty acids are generally depleted in ^{13}C by $\sim 4\text{--}5\text{‰}$ (31) and that organic carbon in the sea in the low latitude ranges ($40^{\circ}\text{S}\text{--}50^{\circ}\text{N}$) has a $\delta^{13}\text{C}$ of -21‰ (5, 56). The formation of marine aerosols may be resulted from sea-to-air emission (57), which can be enhanced by seasonal storms (typhoon) that are active in the summer in the western North Pacific near Chichi-Jima (43). Indeed, the positive correlation between aerosol mass and sodium concentrations supports the contention ($R = 0.58$; Kawamura et al. 1997, unpublished data).

Examination of the $\delta^{13}\text{C}$ of the fatty acids revealed that the HMW fatty acids exhibited systematic depletion in ^{13}C as compared to the LMW fatty acids (average 3.3‰ , Figure 4). The increased depletion of ^{13}C in fatty acids with increasing chain length observed in this study is similar to, but is lower than, that observed in ancient lacustrine sediments [4.6‰ ; (58)]. A similar trend of decreasing $\delta^{13}\text{C}$ with chain length was observed on alkanes in modern and fossil plant leaves (32, 59, 60). Assuming that the LMW fatty acids and HMW ones were from the same C_3 plant source, the increasing depletion of ^{13}C with chain length suggests that there was little or no significant carbon isotopic fractionation associated with aerosol transport (7). It again demonstrated the usefulness of the CSIA technique in studying the atmospheric transport of organic aerosols.

Both groups of fatty acids displayed strong temporal variations in $\delta^{13}\text{C}$ (Figure 4). Less negative $\delta^{13}\text{C}$ values of fatty acids were observed in the summer aerosols (higher air temperature), whereas more negative $\delta^{13}\text{C}$ values were characteristic of the winter aerosols (lower air temperatures),

irrespective of the type of the fatty acids (LMW or HMW). It is remarkable that the same variation trends of $\delta^{13}\text{C}$ were observed for both LMW and HMW fatty acids (Figure 4). The distribution patterns suggest that the fatty acids of the remote marine aerosols at the Chichi-Jima site may have experienced similar atmospheric transport pathways and processes and that the aerosols were possibly derived from consistent sources. Yet, the difference in absolute $\delta^{13}\text{C}$ values of the same fatty acids between winter and summer seasons reflects the difference in the $\delta^{13}\text{C}$ of the source terms. The fatty acids of the aerosols were an admixture of two major sources: terrestrial C_3 and C_4 plants. The relative contributions from the C_3 and C_4 plant sources are determined by the meteorological conditions of the site at different seasons. In the winter season, the contributions of higher plants from the Asian continent to the western North Pacific area were more significant based on trajectory analysis (Figure 5, path a). As a result, the concentrations of HMW fatty acids are much higher in the winter season than in the summer season (Table 2), because of the proximity of the Island site to the Asian continent. The $\delta^{13}\text{C}$ values of HMW fatty acids (from C_3 plants) are correspondingly lower (more negative) in the winter than in the summer. In fact, the LMW fatty acids, which can also be derived in part from higher plants, exhibit the same lower $\delta^{13}\text{C}$ values in the winter. For example, the difference between summer and winter seasons in $\delta^{13}\text{C}$ values (Table 2) $\Delta\delta$ ($\delta^{13}\text{C}_{\text{winter}} - \delta^{13}\text{C}_{\text{summer}}$) of the C_{28} fatty acid was -1.4‰ (1990), -0.6‰ (1991), -0.5‰ (1992), and -1.0‰ (1993). For the C_{16} fatty acids, the $\Delta\delta$ are $+1.3\text{‰}$ (1990), -2.0‰ (1991), -0.4‰ (1992), and -0.7‰ (1993). Similar trends were observed in $\delta^{13}\text{C}$ of other fatty acids. As the trade winds are dominated (Figure 5, path b) in the summer, the major source of organic aerosols was presumably from the North and Central Americas, where a diverse C_4 flora exists today (61). As a result, the $\delta^{13}\text{C}$ of fatty acids in the summer were less negative, as a whole (Figure 4). It is speculated that, because of the distant source from the Americas, the relative contributions from marine source also increased in the summer as compared to the winter. Thus, the concentration of the HMW fatty acids in the Chichi-Jima aerosols decreased in the summer (Table 1, Figure 2). In contrast, the concentrations of LMW fatty acids relatively increased.

Relative Source Strength of Marine Aerosols at Chichi-Jima through Isotope Constrain. From the previous discussion, it seems that fatty acids in marine aerosols at the Chichi-Jima site were mainly from terrestrial C_3 and C_4 plants, with minor contributions of marine origin. To determine the relative contributions of fatty acids from C_3 and C_4 plants, we collected C_3 plants (Japanese yew tree) as well as C_4 corn leaves in Sapporo, Japan, and analyzed the $\delta^{13}\text{C}$ of fatty acids isolated from the plants (Table 3). The $\delta^{13}\text{C}$ values of fatty acids of corn leaves varied widely, from -18.4‰ (C_{20} fatty acid) to -26.6‰ (C_{12} fatty acid). The fatty acids separated from plant waxes of the C_3 plants showed relatively less variations in $\delta^{13}\text{C}$ (Table 3). Here, we used C_{28} fatty acid as an example to calculate the relative contribution of fatty acids from C_3 and C_4 plants and assume that C_3 and C_4 plants have the $\delta^{13}\text{C}$ values of -30.9‰ and -20.8‰ , respectively (Table 3). Assuming that there is little or no significant isotopic fractionation occurs during aerosol transport over the ocean, we can calculate the relative proportions of contribution from each source to aerosol in different seasons based on the $\delta^{13}\text{C}$ of C_{28} fatty acid (Table 3) using the following equations (5, 30):

$$C_{\text{FA}} = C_3 + C_4 \quad (1)$$

$$C_{\text{FA}}\delta^{13}\text{C}_{\text{FA}} = \delta^{13}\text{C}_3 \times C_3 + \delta^{13}\text{C}_4 \times C_4 \quad (2)$$

where C_{FA} is the total concentration of a fatty acid, C_3 and

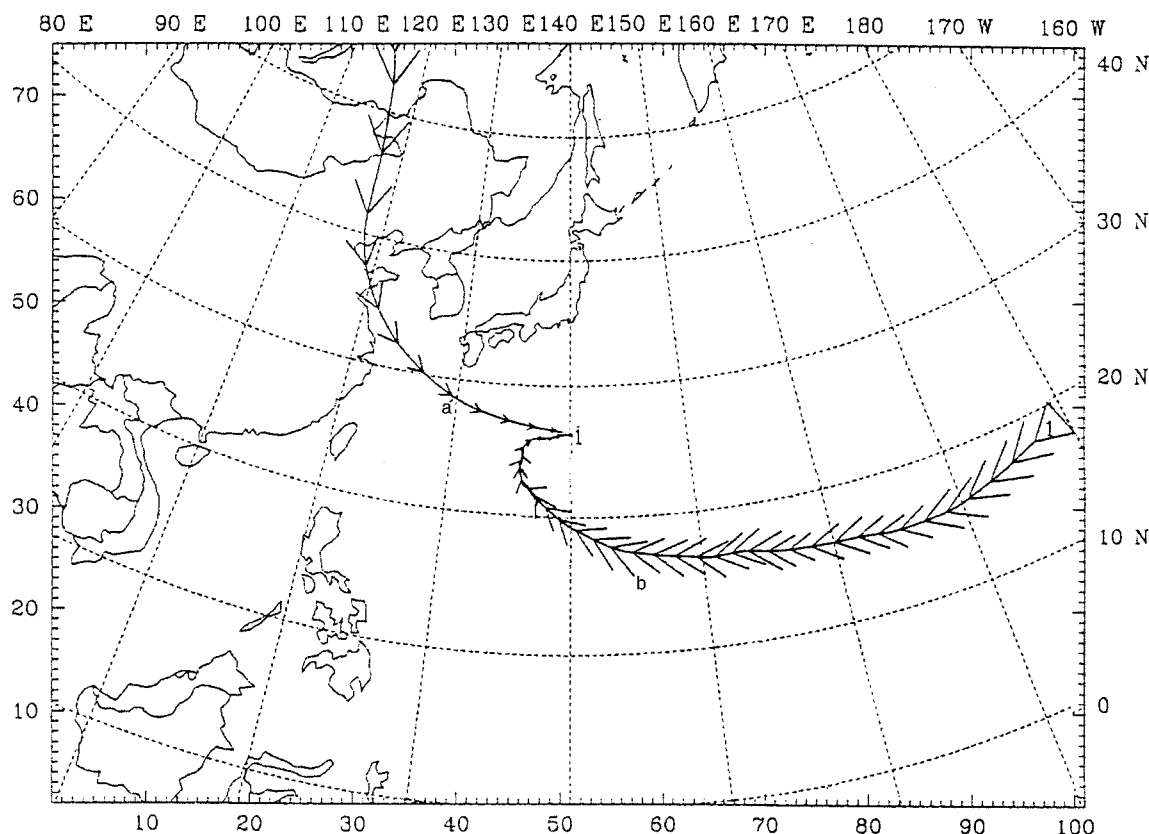


FIGURE 5. Backward air mass trajectory analyses of the winter season (path a, Jan 1992) and summer season (path b, Aug 1992) at the Chichi-Jima site. The trajectory calculation is based on backward tracking of a selected air parcel released at a target location, assuming that the parcel is moving with the ambient airflow. The flow pattern is updated every 6 h.

TABLE 3. Stable Carbon Isotopic Compositions (per mil) of Fatty Acids from C₃ (Japanese Yew Tree) and C₄ Plants Collected in Sapporo, Japan^a

fatty acid C number	C ₃ plant (yew)		C ₄ plant (corn)	
	average ^b	std dev ^c	average	std dev
14			-24.2	0.2
15			-20.2	0.2
16	-29.7	0.4	-24.2	0.2
17			-19.0	0.5
18			-22.8	0.4
19			-12.8	0.2
20	-29.3	0.7	-18.4	0.2
21			-18.5	0.2
22	-31.5	0.6	-19.7	0.2
23			-19.9	0.3
24	-32.3	0.1	-23.0	0.1
25	-29.1	0.2	-21.5	0.1
26	-29.5	0.3	-23.3	0.1
27	-31.0	0.2	-21.7	1.0
28	-30.9	0.2	-20.8	0.2
29	-30.7	0.2	-22.8	0.6
30	-30.8	0.3	-21.0	0.2
31			-23.3	0.9
32	-31.0	0.5	-23.4	0.4
33			-24.3	0.8
34	-31.0	0.6	-24.9	0.3
35			-23.2	0.3
36			-22.4	0.8

^a The plant leaves were extracted with methylene chloride/methanol (v/v, 5:1), and then the extracts were saponified using 0.5 M KOH/MeOH. The fatty acids were isolated and purified by the methods described in the text. ^b Average of three measurements. ^c Standard deviation.

C₄ are fatty acid concentrations from C₃ and C₄ plants, and $\delta^{13}\text{C}_3$ and $\delta^{13}\text{C}_4$ are isotopic composition of the fatty acid

TABLE 4. Calculated Source Input from End Members of C₃ (-30.9‰) and C₄ (-20.8‰) Plant Origins (see Table 2), Using C₂₈ Fatty Acids as an Example

	W-90	S-90	W-91	S-91	W-92	S-92	W-93	S-93
$\delta^{13}\text{C}_{28}$	-30.4	-29.0	-28.8	-28.28	-30.1	-29.6	-30.2	-29.2
C ₃	94	80	78	73	91	86	92	82
C ₄	6	20	22	27	9	14	8	18

from C₃ and C₄ plant sources, respectively. The calculated contributions of the two major sources are shown in Table 4. It can be seen that, for C₂₈ fatty acid, C₃ plants contribute the major part of the fatty acids (73–94%) and that contributions of C₄ plants range from 6% to 27% (Table 4). In the winter season, C₃ plants contribute over 90% of the C₂₈ fatty acid (except in 1991, 78%) with C₄ plants contribute 6–9%. The exceptionally higher contributions of C₄ plants in the winter of 1991 can be attributed to the forest fires in Indonesia due to El Niño (43). In contrast, the summer season was characterized by the increased contributions of C₄ plants (14–27%).

This study demonstrates that compound-specific isotopic analysis of fatty acids combined with fatty acid composition is useful in determining the source and strength of remote marine aerosols. However, specific characteristics of each source need to be defined in order to resolve the origin of these fatty acids and then the source of aerosols. It is apparent that there were no significant isotopic fractionations associated with atmospheric transport of aerosols. Hence, the isotopic composition of individual fatty acids can be used to determine the source and source region of aerosols.

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