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Seasonal changes in stable carbon isotopic composition of *n*-alkanes in the marine aerosols from the western North Pacific: Implications for the source and atmospheric transport

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Abstract

To constrain seasonal changes in the long-range atmospheric transport of land-derived lipid biomarker compounds, we investigated the compound-specific stable isotopic composition of marine aerosol *n*-alkanes collected from 1990 to 1993 at a remote island, Chichi-Jima (27°04′N, 142°13′E), in the western North Pacific. Compound-specific isotope analysis revealed, in particular, strong seasonal changes in the $\delta^{13}C$ values of the C_{29} and C_{31} *n*-alkanes (biomarkers for higher plants). Lighter $\delta^{13}C$ values were observed in winter (typically −32 to −34‰), with a transition to heavier values in summer (typically −28 to −31‰). Using a mixing equation and typical end members for C_3 and C_4 plants, we found that this is due to relative increases in the contributions from C_4 plants in the summer season. Using backward air-mass trajectory analyses, it was shown that the Asian continent was the major source region for C_3 plant material during winter/spring, whereas Indonesia/Australia and possibly the Americas were the major source regions for C_4 material during the summer/autumn. Also observed was an enhanced atmospheric transport of *n*-alkanes from C_4 plants in 1991 summer/autumn during a strong El Nino event, which was associated with forest and bushfires in Indonesia and Australia. In addition to providing information on contemporary processes, this study also provides a base for future paleoclimatological work in ocean sediments.

1. Introduction

Analytical advances during the last few decades have made possible studies describing in detail the molecular and isotopic composition of the organic component of aeolian materials. A result of this work has been the demonstration that homologous series of high molecular weight (HMW) *n*-alkanes, *n*-alcohols, and fatty acids are typical land-derived lipid biomarkers[1] (LDLBs) found in atmospheric dust (Conte and Weber, 2002; Fang et al., 2002; Gagosian et al., 1987; Kawamura, 1995; Kawamura et al., 2003; Matsumoto et al., 2001; Sicre and Peltzer, 2004), marine sediments (Gagosian and Peltzer, 1986; Huang et al., 2000; Ikehara et al., 2000; Ohkouchi et al., 1997a,b, 2000; Schefuss et al., 2003b; Westerhausen et al., 1993; Zhao et al., 2003), and lacustrine sediments (Huang et al., 1999, 2001; Street-Perrott et al., 1997; Zhang et al., 2004).

These lipids are synthesized by terrestrial higher plants as constituents of the epicuticular waxes (Eglinton et al., 1962; Eglinton and Hamilton, 1967). Particulate matter containing such compounds may be deflated to the troposphere either directly, by being sloughed off plant surfaces by winds (especially by sandblasting), or alternately they may be eroded from the soil reservoir during dust storms (Simoneit et al., 1977; Simoneit and Eglinton, 1977). Therefore, plant-wax lipids form a significant component of the "aerosol veil," even above remote ocean areas such as the North Pacific (Gagosian and Peltzer, 1986; Gagosian

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[1] The term "biomarker" refers to an organic compound with an unambiguous link to a known natural product. In this case, the biomarkers are compounds emanating from the epicuticular waxes of terrestrial higher plants.

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et al., 1981; Kawamura, 1995; Kawamura et al., 2003), South Pacific (Gagosian et al., 1987; Sicre and Peltzer, 2004), and Atlantic (e.g., Conte and Weber, 2002; Simoneit et al., 1991, 1977).

The refractory nature of some LDLB compounds (e.g., HMW *n*-alkanes, *n*-alcohols, and *n*-monocarboxylic acids) (e.g., Cranwell, 1981; Kawamura, 1995) means that information contained within them (e.g., isotopic composition of the source material) may be preserved in modern and geological samples without suffering major modification. Studies of contemporary LDLB samples may elucidate a number of modern earth processes, such as long-range atmospheric transport, circulation (Kawamura, 1995; Ohkouchi et al., 1997a) and deposition of organic carbon (OC) (Gagosian and Peltzer, 1986; Kawamura, 1995; Prahl and Muehlhausen, 1989) (including organic pollutants (Simoneit, 1997, 2002)) as well as the relative contributions to aerosol OC from C_3 and C_4 plant sources (Chesselet et al., 1981; Conte and Weber, 2002; Fang et al., 2002; Ohkouchi et al., 1997a; Prahl and Muehlhausen, 1989; Schefuss et al., 2003a). Moreover, in addition to providing information on processes of contemporary importance, such studies also provide a base for paleoclimatological work (Bird et al., 1995; Ohkouchi et al., 1997b; Prahl and Muehlhausen, 1989; Schefuss et al., 2003b; Westerhausen et al., 1993).

Higher plant *n*-alkanes typically have carbon chain-lengths ranging from C_{25} to C_{35} and a strong predominance of odd-carbon-number over even-carbon-number homologues (C_{27}, C_{29}, and C_{33} are most common) (Eglinton et al., 1962; Eglinton and Hamilton, 1967; Kolattukudy, 1976). High molecular weight *n*-alkanes are more resistant to degradation than shorter-chain homologues and other *n*-alkyl components (order of stability: *n*-alkanes > *n*-alkanoic acids > *n*-alkanols) (Cranwell, 1981). The carbon isotopic analysis of tissues from plants using the different pathways of photosynthetic carbon fixation, C_3, C_4, and CAM, shows different levels of ^{13}C depletion (Smith and Epstein, 1971). This carbon isotopic heterogeneity between plant types is also observed within specific compound classes, including *n*-alkanes (Chikaraishi and Naraoka, 2003; Collister et al., 1994). Thus, compound-specific carbon isotope (CSIA) analyses of leaf-wax lipids can determine the plant types from which the lipids were derived because the isotopic signature of C_3 plant *n*-alkanes (ca. −30 to −40‰ vs. Vienna Pee Dee Belemnite) is distinctly different from that of C_4 plant *n*-alkanes (ca. −17 to −24‰) (Chikaraishi and Naraoka, 2003; Collister et al., 1994; O'Leary, 1981; Rieley et al., 1993). There are around 250,000 species of C_3 plant which includes most trees, shrubs, and cool/temperate grasses and sedges (Sage, 2001). C_4 plant species consist mostly of warm temperate to tropical grasses and sedges, and are less abundant (around 7500 species), but nevertheless dominate primary productivity in many tropical and sub-tropical regions (Sage, 2001). Maize is an abundant agricultural C_4 species. CAM plants—which include succulents such as cacti—have intermediate $\delta^{13}C$ values, but form a much smaller proportion of the global biomass (Cerling and Quade, 1993; Spicer, 1989). The stable carbon isotope compositions of *n*-alkanes have been used to determine relative contributions by C_3/C_4 plant material in marine sediments (Bird et al., 1995; Huang et al., 2000; Kuypers et al., 1999; Schefuss et al., 2003b) and aerosol dust in the eastern Atlantic (Schefuss et al., 2003a). To date, no CSIA analysis of *n*-alkanes in dust in the western Pacific has been conducted.

Here, we present data on the seasonal variations of stable carbon isotope compositions of *n*-alkanes from aerosols collected from Chichi-Jima in the western North Pacific (see Fig. 1). We compare the variations in carbon isotope compositions of the *n*-alkanes collected at Chichi-Jima with air-mass-back trajectory analysis and a new modelled distribution map of global C_3/C_4 abundance (Still et al., 2003) (Fig. 1). The data provide an insight into the higher plant and anthropogenic sources and transport pathways of terrigenous lipid materials in the continental dust carried out to the ocean. Moreover, in addition to providing information on contemporary processes, this study also provides a base for future paleoclimatological work in ocean sediments. *n*-Alkanes are particularly refractory, therefore CSIA of *n*-alkanes in sediments can help to resolve paleo-wind patterns and deposition of OC over the Pacific. Alternately, if wind patterns can be constrained (e.g., by modelling) sedimentary *n*-alkanes could reveal changes in the evolution of past C_3/C_4 plant abundances and hence the carbon isotopic discrimination of terrestrial photosynthesis—an important parameter for accurate estimates of paleo-ρCO_2 (Conte and Weber, 2002).

2. Experimental and geographic setting

2.1. Geographic setting and sampling

Chichi-Jima is a small island (~8 × 5 km in size) located at 27°04′N; 142°13′E, approximately 2000 km east of the Asian continent and around 1000 km south of Tokyo (Fig. 1). The region is strongly influenced by the Asian monsoon, Kawamura et al. (2003) reported that during the sampling period—from April 1990 to November 1993—the wind systems were characterized by westerlies during the winter to spring seasons (November to April), whereas trade winds dominated in summer to autumn (May to October). During this period 69 aeolian dust samples were collected on a biweekly basis at the Satellite Tracking Center of National Aeronautic and Science Development Agency (NASDA). NASDA is located near a hilltop (elevation, 254 m). The sampling station was fixed upon the raised base of a satellite tracking parabola at the top of the hill, well elevated above local topography and vegetation. The climate of Chichi-Jima is sub-tropical with an annual rainfall of 850 mm. The biomass is dominated by C_3 plants (>99% Toyoda, 1981). There are a few species of C_4 plant, mostly sedges which are found in streams near the

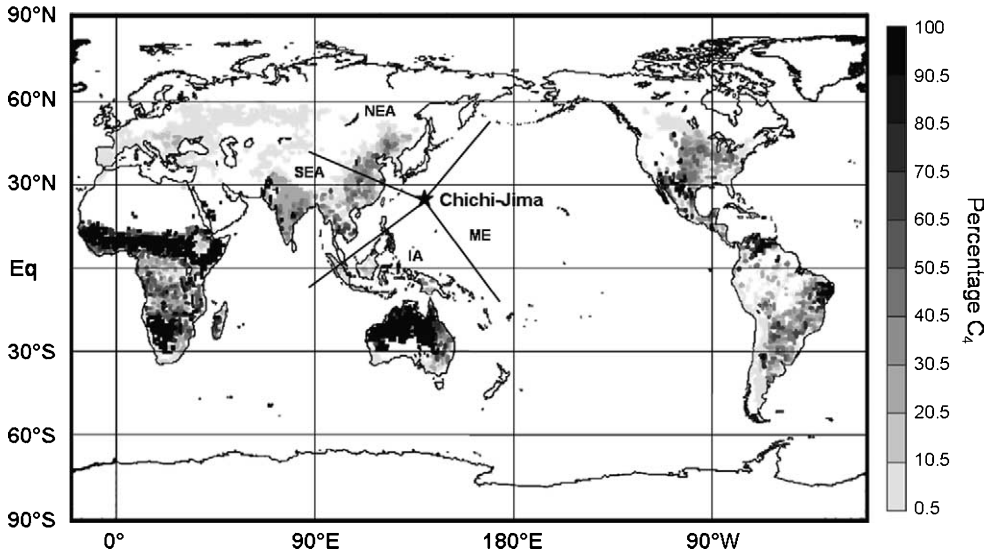

Fig. 1. Global map showing the sampling location (Chichi-Jima) in the western Pacific, the global C_4 percentage of terrestrial biomass, and the source areas of the four major air-mass trajectories. *Abbreviations:* NEA, North east Asia; SEA, South east Asia; IA, Indonesia and Australia; ME, Marine easterlies. The C_4 biomass is adapted from (Still et al., 2003), the C_4 biomass fraction was modelled by combining remote-sensing products, physiological modelling, a spatial distribution of global crop fractions, and national harvest area data for major crop types.

coast (Toyoda, 1981). It is highly unlikely that there would be a significant C_4 plant seasonal influence on the aerosols collected at the elevated sampling station.

2.2. Distribution of n-alkanes in aerosols

Kawamura et al. (2003) previously reported the concentrations and molecular distributions of the *n*-alkanes (0.17–14 ng m^{-3}, average 1.7 ngm^{-3}) collected at Chichi-Jima, along with other lipid classes. The seasonal data are summarized in Table 1. The *n*-alkanes were characterized by a strong odd-carbon number predominance as defined by the Carbon Preference Index (CPI), which is the ratio of the abundance of odd-carbon number *n*-alkanes to even-carbon number *n*-alkanes (CPI ratios, average 4.5) with a maximum at C_{29} or C_{31}, indicating that terrestrial higher plant waxes were the primary source. Fig. 2 illustrates a typical *n*-alkane GC-ir-MS trace, as seen in most of the samples. Absolute concentrations generally increased in winter/spring and decreased toward summer/autumn season, except for the El Niño year of 1991 when the concentrations were relatively high in the summer/autumn (Kawamura et al., 2003). Such a seasonal trend suggested that atmospheric transport of terrestrial organic materials over the western North Pacific is enhanced during winter/spring season probably due to the strong westerly winds. CPI values were generally high suggesting a minimal contribution from petroleum residues/pollution (Kawamura et al., 2003). Unresolved complex mixtures of hydrocarbons (UCM) were detected in some samples, the UCM consisting of cyclic/branched-chain hydrocarbons which cannot be resolved into peaks during gas chromatography.

Table 1
Summarized data for total carbon (TC, μg/m^3), concentration of *n*-alkanes, carbon preference index (CPI, dimensionless), unresolved carbon mixture (UCM), and ACL

Season[a]	Number of samples	TC (μg/m^3)	Concentration (ng m^{-3}) (SD)			CPI[b] (SD)	UCM[c] (SD)	ACL[d] (SD)
			$\sum C_{19-26}$	$\sum C_{27-40}$	$\sum$*n*-alkanes			
Winter 90	2	1.45 ± 0.3	2.6 (1.2)	8.8 (3.5)	11.4 (4.8)	3.8 (0.8)	8.4 (1.9)	29.6 (0.1)
Summer 90	12	0.47 ± 0.9	2.6 (0.3)	9.3 (1.0)	11.9 (1.3)	5.8 (3.4)	3.3 (1.8)	29.8 (0.5)
Winter 91	5	0.94 ± 1.2	1.2 (0.1)	7.4 (0.5)	8.6 (0.5)	4.9 (2.6)	4.8 (2.5)	29.5 (0.2)
Summer 91	10	0.50 ± 1.6	2.9 (0.2)	15.2 (1.6)	18.1 (1.8)	3.7 (3.4)	12.4 (16.8)	30.1 (0.3)
Winter 92	10	0.78 ± 1.1	3.5 (0.4)	23.2 (3.7)	26.7 (4.1)	3.8 (1.7)	3.8 (4.1)	29.8 (0.1)
Summer 92	9	0.43 ± 1.7	1.2 (0.2)	9.7 (1.4)	10.9 (1.5)	5.0 (2.6)	2.4 (1.2)	29.7 (0.3)
Winter 93	10	0.71 ± 0.5	3.9 (0.3)	21.0 (1.6)	24.9 (1.8)	4.2 (2.0)	3.8 (2.0)	29.8 (0.2)
Summer 93	11	0.40 ± 1.0	1.2 (0.1)	9.2 (0.8)	10.4 (0.9)	4.0 (0.9)	6.6 (6.7)	30.0 (0.6)

The brackets show one standard deviation. Data from Kawamura et al. (2003).
[a] Summer, May–October; winter, November–April.
[b] $CPI_{n\text{-alkanes}} = 2\sum\text{odd}\ (C_{25-35})/[\sum\text{even}\ (C_{24-34}) + \sum\text{even}(C_{26-36})]$.
[c] Unconsolidated carbon mixture in ng m^{-3}.
[d] Average chain length: the concentrated-weighted mean carbon chain length C_{27}–C_{33}.

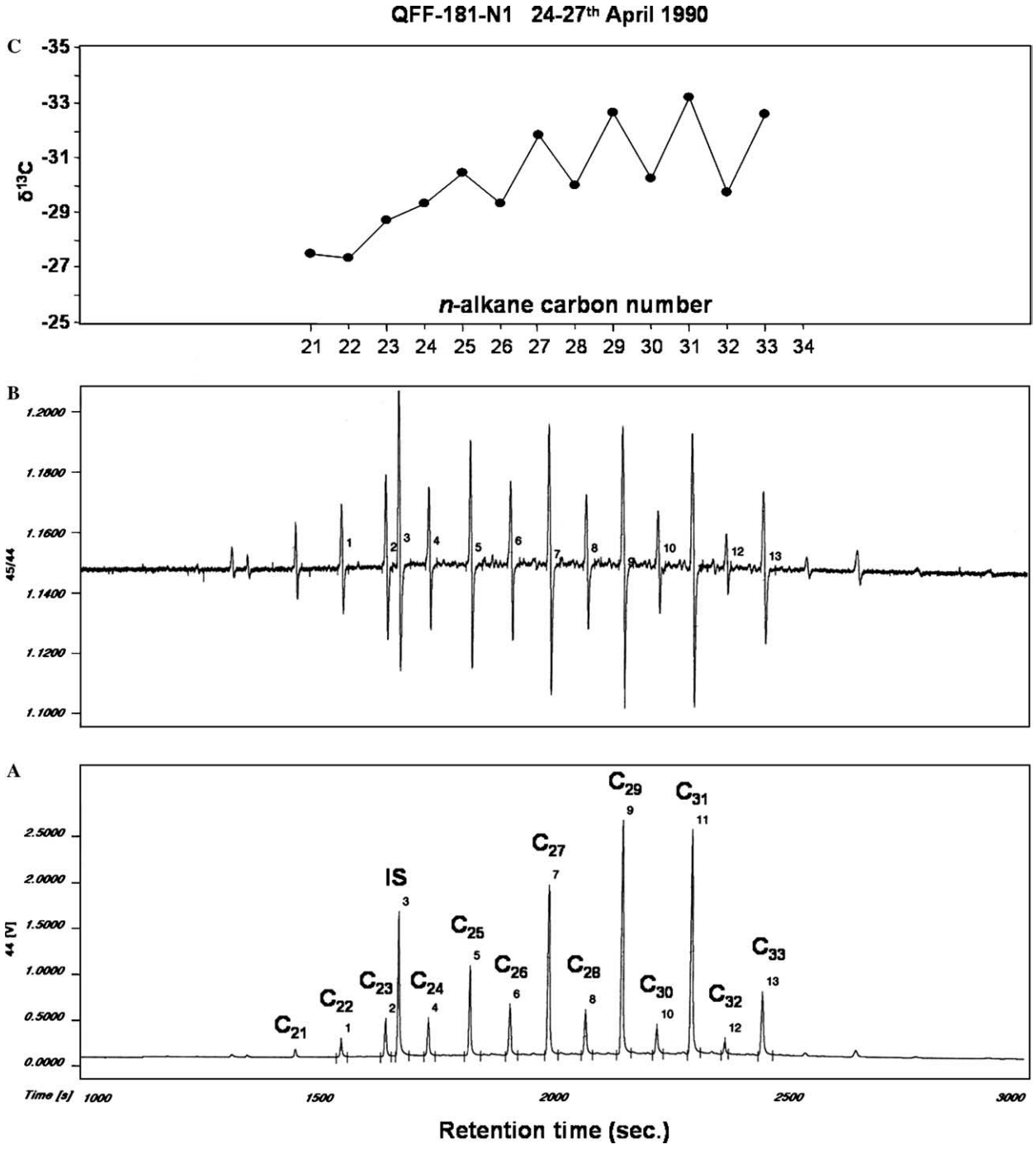

Fig. 2. A typical GC-ir-MS trace of m/z 44 (A), ratio of m/z 45–44 (B), and $\delta^{13}C$ (C) values for a homologous series of n-alkanes from a marine aerosol sample (QFF-181-N1) collected at Chichi-Jima, 24–27th April, 1990. IS, internal standard (C_{20} fatty acid methyl ester). The signal of m/z 45 is multiplied by 100 times.

UCM hydrocarbons are emitted to the atmosphere by the incomplete combustion of fossil fuels (e.g., Boyer and Laitinen, 1975; Simoneit and Mazurek, 1981) and are typically abundant in aerosol and rainwater samples from the urban atmosphere (e.g., Kawamura and Kaplan, 1991; Kawamura et al., 1995; Simoneit, 1984; Simoneit et al., 1988). The presence of UCMs may demonstrate the influence of polluted air from Asian countries at Chichi-Jima. However, the concentrations were 2 or 3 orders of magnitude lower than for urban samples, thus confirming (as with the high CPI values) the relatively low levels of pollution at the remote Chichi-Jima site. There were no clear seasonal trends of the CPI ratios or UCM concentrations (Kawamura et al., 2003).

The average chain length (ACL: the concentrated-weighted mean carbon chain length) of the n-alkanes quantifies the relative dominance of the C_{max} homologue (in this case either C_{29} or C_{31}). The index showed a seasonal trend,

with values increasing from spring to autumn (relatively more C_{31} than C_{29}) (Kawamura et al., 2003). Kawamura et al. (2003) suggested that this reflected the seasonal changes in source regions and transport pathways.

2.3. Extraction and analysis of n-alkanes

Aerosol samples were collected on a precombusted (500 °C, 3 h) Pallflex quartz fiber filter (20 × 25 cm) using a high volume air sampler (1 m^3 min^{-1}). Detailed sampling and analytical procedures were described in Kawamura et al. (2003). The sampling time was approximately 100 h to collect enough material for chemical analysis. After the sample collection, the quartz filter was placed in a pre-cleaned glass jar with a Teflon-lined screw cap and stored in a freezer at −20 °C until analysis. An aliquot of the filters (10–20%) was extracted under reflux for 2 h with 100 mL of 0.1 M KOH in methanol, containing ca. 5% distilled water. The residue was further extracted with methanol and then methylene chloride under ultrasonification for 3 min. The extracts were combined and concentrated under vacuum and then separated into neutral and acidic fractions using the methods of Kawamura (1995). The neutral fraction was further separated into four sub-fractions using a silica gel column chromatography, that is, aliphatic hydrocarbons/*n*-alkanes (N1), aromatic hydrocarbons (N2), aldehydes and ketones (N3), and alcohols (N4) by elution with *n*-hexane, *n*-hexane/methylene chloride (2:1) mixture, methylene chloride and methylene chloride/methanol (95:5) mixture, respectively. Sub-fractionation of the acid classes is detailed in Kawamura et al. (2003) and Fang et al. (2002).

The *n*-alkanes were analyzed on a Carlo Erba Mega 5160 gas chromatograph (GC) equipped with a cool on-column injector, fused silica capillary column (Chrompack, CP-Sil 5CB 60 m × 0.32 mm i.d. × 0.25 μm) with an FID detector. The oven program was 70–120 °C at 30 °C/min and to 300 °C (22 min) at 5 °C/min. Structural identification was confirmed using a GC/MS (Thermoquest, Voyager) with similar GC column conditions. Authentic *n*-C_{29} alkane was used for quantification, recoveries being better than 80%. Analytical errors of the procedures were within 15%. Laboratory procedural blanks showed that blank levels were less than 1% of the samples.

2.4. Stable carbon isotope analysis

Isotopic ratios of *n*-alkanes were determined using a 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 a cool on-column injector and a HP-5MS fused silica capillary column (30 m × 0.32 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 1.6 mL/min. Two microliters of sample solution spiked with C_{20} methyleicosanoate (C_{20} FAME) as an internal standard of known isotopic composition was injected through an on-column injector. Peaks were simultaneously detected in Faraday collectors at *m*/*z* 44 ($^{12}C^{16}O_2$), 45 ($^{13}C^{16}O_2$ and $^{12}C^{17}O^{16}O$), and 46 ($^{12}C^{16}O^{18}O$, $^{12}C^{17}O^{17}O$, and $^{13}C^{17}O^{16}O$), amplified, and corrected for the presence of ^{17}O at mass 45 using the Craig correction (Craig, 1957). The isotopic composition of *n*-alkanes is reported in the delta notation, relative to the Vienna Pee Dee Belemnite (Vienna PDB) standard, as follows:

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

Isotope values reported were determined by averaging duplicate analyses whenever concentrations were sufficient. A minority of the samples (30%) contained only enough material for a single isotopic analysis of the dominant C_{29} and C_{31} homologues. For the duration of the analysis the condition of the machine was checked by injection of an external standard of *n*-alkanes (mixture of various carbon numbers from C_{15} to C_{33}) of known isotopic composition. This gave a reproducibility of ∼0.5‰ for all compounds (e.g., $\delta^{13}C$ 0.45, 0.5, and 0.57‰ for C_{27}, C_{29}, and C_{31}, respectively). The isotopic composition of sample *n*-alkanes was calculated by co-injection with a non-coeluting internal standard (C_{20} FAME) of known isotopic composition ($\delta^{13}C$ −26.21‰).

2.5. Back-trajectory analysis

Back-trajectory analyses were conducted using a 6-hourly 40-year reanalysis data of the European Centre of Medium-range Weather Forecasts (ERA40) (Simmons and Gibson, 2000) and a trajectory model developed by Hatsushika and Yamazaki (2003). The ERA40 data used in this study have a horizontal resolution of 2.5 × 2.5° in latitude and longitude, and 23 layers from 1000 to 1 hPa. Near the surface, its standard levels are 1000, 925, 850, 775 hPa, and so on. The wind data at 10 m above the surface are also used. Trajectories are calculated in order to determine how and from where tropospheric air arrived at Chichi-Jima during sampling periods. Considering the low resolution of the data and uncertainty in analyzed winds, initial positions of air parcels are allocated within a 2° area centered at Chichi-Jima with an interval of 0.5° and parcels are set at three levels, i.e., 1000, 925, and 850 hPa. In total, 75 (=5 × 5 × 3) parcels were allocated around Chichi-Jima. Back-trajectories are calculated once a day starting at 12UTC during a sampling period. The parcel is transported by the three-dimensional wind field of the 6-hourly ERA40 reanalysis data. Linear interpolation is employed in the temporal and horizontal directions, and spline interpolation is adopted for the vertical direction. The time step of the back-trajectory calculations is

20 min. Ten-day back-trajectories were calculated and some samples were also investigated for 20 days.

3. Results and discussion

3.1. Stable isotopic compositions of n-alkanes

Fig. 2 shows a typical GC-ir-MS trace for *n*-alkanes isolated from the Chichi-Jima aerosols. Results of the stable isotopic measurements for the major *n*-alkanes are given in Table 2. The stable isotopic compositions of the dominant HMW *n*-alkanes (C_{29}, C_{31}) fell in the range −26.6 to −34.4‰ indicating that all the samples consisted primarily of varying relative amounts of C_3 and C_4 plant-derived leaf-wax lipids (Table 2). In general, for the dominant C_{29} and C_{31} *n*-alkanes, lighter $\delta^{13}C$ values were observed in winter (typically −31 to −34‰), with a transition to heavier values in summer (typically −28 to −33‰) (Fig. 3). The seasonal isotopic trend for the C_{29} and C_{31} *n*-alkanes had no strong linear relationship to the seasonal concentration (ng m^{-3}) trend previously observed by Kawamura et al. (2003). Linear regressions (R^2) for the C_{29} and C_{31} *n*-alkanes were 0.19 and 0.14, respectively. If only the summer samples are used, then the relationship is slightly stronger, with more of the higher concentration samples being associated with lighter $\delta^{13}C$ values, but the relationship was still not very significant (C_{29}, $R^2 = 0.23$; C_{31}, $R^2 = 0.29$). The stable isotopic composition of the *n*-alkanes was also independent of the *n*-alkane molecular distributions, there being no significant correlation between $\delta^{13}C$ values of the C_{29} or C_{31} *n*-alkanes against UCM, ACL or CPI (all $R^2 < 0.12$).

Within individual samples the odd-numbered *n*-alkanes are relatively more depleted in ^{13}C with increasing chain length, a typical isotopic distribution being illustrated in Fig. 2C. In general, the C_{29} and C_{31} alkanes were the most ^{13}C depleted compounds in each sample. The longer-chain odd-numbered compounds, C_{33} and C_{35}, if measurable, were isotopically enriched relative to C_{29} and C_{31}.

Fang et al. (2002) previously reported the compound-specific $\delta^{13}C$ values measured in the fatty acid compound class extracted from the same Chichi-Jima sample set. The isotopic values measured by Fang et al. (2002) for the HMW fatty acids were also consistent with those of a higher plant source of varying relative amounts of C_3 and C_4 lipids (−30 to −28.2‰ with a mean of -29.1 ± 0.7). They suggested that heavier ^{13}C values (−26.9 to −24.8‰, with a mean of −25.8) measured in the LMW fatty acids (C_{12}–C_{19}) may have indicated a contribution from marine biota (Fang et al., 2002), as marine organic carbon in the 40–50°N latitude range has a $\delta^{13}C$ of around −21‰ (Chesselet et al., 1981; Fontugne and Duplessy, 1978). *n*-Alkanes synthesized by aquatic algae typically have C_{15} or C_{17} as the dominant homologue (Blumer et al., 1971; Gelpi et al., 1970), but these LMW compounds were not present as aerosol particles in concentrations measurable by GC-FID or GC-ir-MS. This suggests that input of marine algal *n*-alkanes to the Chichi-Jima aerosols was minimal and that the *n*-alkane compound class was dominated by non-marine (terrestrial) sources.

As well as marine derived *n*-alkanes a significant contribution of anthropogenic *n*-alkanes to the aerosols collected at Chichi-Jima is also a possibility. There is no consensus on the most appropriate method to assess and/or correct for non-higher plant contributions. Some previous authors have used CPI ratios to calculate the contribution of non-higher plant *n*-alkanes (Ishiwatari et al., 1994; Schefuss et al., 2003a). However, we are not satisfied that a natural higher plant-wax end member can be assigned to the mixing equation used by this method—given that natural CPI values vary so greatly (e.g., 1.4–40.3 in Chikaraishi and Naraoka, 2003; Collister et al., 1994). In order to avoid the uncertainties involved in using the molecular distributions to assess the contribution from non-higher plant sources, we simply excluded the samples which had a significant UCM, defined arbitrarily as >10 ng m^{-3}. This led to the exclusion of five samples from the analysis (QFF-218, -436, -434, -212, and -395).

3.2. Backward trajectories and sources of C_4 plant-derived wax lipids in aerosols

In general, lighter $\delta^{13}C$ values were observed in winter (typically −31 to −34‰), with a transition to heavier values in summer (typically −28 to −33‰) (Fig. 3). The difference in the $\delta^{13}C$ of the same *n*-alkanes between the winter and summer seasons may reflect a seasonal variability in the source areas and/or atmospheric transport pathways and hence differential source areas. The isotopic composition of plants can change in response to seasonal environmental stimuli. Lighter values of $\delta^{13}C$ for the C_{29} and C_{31} *n*-alkanes in several deciduous tree species have been observed in autumn leaves compared with leaves sampled at the start of the growing season ($\Delta\delta^{13}C$ −0.6 to −5) (Chikaraishi et al., 2004; Lockheart et al., 1997). Spring lipids may be isotopically heavier due to the remobilization of stored carbohydrate at the beginning of the growing season (Lockheart et al., 1997). However, such phenomena cannot explain the observed seasonal signal at Chichi-Jima, which is the opposite in sign (*n*-alkanes become isotopically heavier from the spring to autumn).

Conte and Weber (2002) reported a seasonal isotopic variation in plant-wax *n*-alkanols and *n*-alkenoic acids (ablated from a wide region of North America and collected in aerosols at Bermuda) which was characterized by a progression, from spring to autumn, of lighter to heavier $\delta^{13}C$ values (+5–6‰) and is therefore similar to the seasonal signal at Chichi Jima. The seasonality of the North American plant-wax $\delta^{13}C$ is suggested to be a function of: (1) decreasing isotopic discrimination in C_3 plants as moisture becomes limiting; (2) C_3 plant species and genotypes with greater water use efficiency (which have lower ^{13}C discrimination and therefore heavier $\delta^{13}C$) become

Table 2
Collection details, source area, molecular distribution and isotopic data for aerosol samples collected from Chichi-Jima between 1990 and 1993

Sample	Season	Date	Source allocation[a]	C_{25}–C_{35} conc. (ng m^{-3})	UCM	ACL	CPI	$\delta^{13}C$ values			%C_4 (C_{29})	%C_4 (C_{31})
								C_{27}	C_{29}	C_{31}		
QFF-181	Winter 90	4/9-12/90	NEA	8.1	7.0	29.6	4.3	−31.81	−32.62	−33.21	16	15
QFF-183	Summer 90	5/7-10/90	ME	1.2	4.0	29.3	9.8	−29.45	−30.47	−31.33	31	27
QFF-184		5/21-24/90	ME	4.5	3.6	29.1	5.9	−31.21	−32.41	−33.39	18	13
QFF-185		6/5-8/90	ME	0.7	2.4	29.4	3.8	−30.14	−30.88	−32.02	28	23
QFF-187		6/25-28/90	ME	0.8	4.4	29.8	3.0		−31.34	−32.65	25	18
QFF-189		7/16-19/90	ME	0.3	4.8	29.3	3.3		−31.02	−30.48	27	33
QFF-193		9/17/-20/90	ME	0.4	5.8	31	7.1		−28.63	−28.40	43	47
QFF-194		10/1-4/90	ME	0.5	5.3	29.7	3.2	−29.16	−30.48	−32.75	31	18
QFF-207	Winter 91	3/4-7/91	ME	1.0	3.9	29.5	2.4	−29.19	−31.75	-30.97	22	30
QFF-208		3/18-21/91	NEA	1.6	8.2	29.6	2.0	−30.34	−32.04	−32.37	20	20
QFF-209		4/1-4/91	NEA	2.0	6.8	29.2	5.5	−32.21	−32.66	−31.80	16	24
QFF-210		4/16-20/91	SEA	2.1	2.6	29.5	7.9	−30.24	−30.88	−31.40	28	27
QFF-211		4/29-5/2/91	SEA	1.1	2.6	29.7	6.6	−30.46	−30.73	−31.94	29	23
QFF-214	Summer 91	5/31-6/3/91	SEA	1.0	9.4	30.1	2.1	−28.28	-29.31	-29.15	38	42
QFF-216		6/28-7/1/91	IA	2.2	9.2	30.1	2.1	−28.31	−28.69	−30.00	42	36
QFF-217		7/8-11/91	IA	0.8	9.4	29.7	2.3	−30.20	−31.01	−30.94	27	30
QFF-219		8/21-24/91	IA	0.2	3.8	30.1	3.9	−28.08	−27.23	−27.56	52	52
QFF-220		9/6-9/91	IA	0.7	2.8	30.5	13.1	−29.07	−30.00	−29.95	34	36
QFF-221		9/6-9/91	IA	4.0	4.8	30.5	1.8	−33.12	−33.38	−34.44	11	6
QFF-222		9/30-10/2/91	ME	0.4	6.3	29.6	3.2	−29.09	−29.48	−29.23	37	41
QFF-223		10/15-18/91	NEA	0.7	4.9	29.8	3.7	−31.22	−32.82		15	
QFF-393	Winter 92	12/6-10/91	NEA	1.1	2.1	29.7	0.3	−30.92	−32.55	−31.92	17	23
QFF-396		1/24-28/92	NEA	1.8	4.1	29.8	4.1	−30.81	−32.88	−32.64	15	18
QFF-397		2/3-9/92	NEA	0.8	1.1	29.8	3.1	−32.38	−33.35	−32.71	12	18
QFF-399		2/21-25/92	NEA	13.4	5.2	30.1	7.4	−32.02	−33.14	−31.66	13	25
QFF-400		3/9-13/92	SEA	1.2	1.6	29.8	3.8	−30.44	−32.83	−31.83	15	24
QFF-401		3/19/-23/92	SEA	1.4	1.9	29.6	3.7	−31.10	−33.05	−32.36	14	20
QFF-402		4/10-15/92	NEA	2.3	3.1	29.7	4.2	−31.58	−32.17	−32.84	19	17
QFF-403		4/24-28/92	SEA	1.1	1.4	29.8	4.0	−31.43	−33.29	−34.32	12	7
QFF-404	Summer 92	5/8-12/92	NEA	0.8	1.5	29.8	11.4	−30.22	−30.68	−32.56	29	19
QFF-405		5/25-29/92	SEA	4.3	2.3	29.2	6.5	−30.04	−33.49	−32.89	11	17
QFF-406		6/17-20/92	ME	0.7	2.9	29.7	3.3	−29.52	−29.96	−29.32	34	41
QFF-407		7/13-17/92	IA	0.6	4.2	29.5	3.3	−31.49	−32.44	−30.94	18	30
QFF-408		7/26-30/92	ME	0.3	2.7	29.7	3.2		−29.11	−28.66	40	45
QFF-410		8/18-23/92	IA	0.1	0.2	30.3	3.8	−29.95	−30.83	−30.51	28	33
QFF-412		9/19-23/92	IA	0.3	2.3	29.4	4.6	−28.47	−29.80	−30.02	35	36
QFF-413		10/2-7/92	ME	0.2	1.7	29.9	3.5		−29.11	−32.10	40	22
QFF-414		10/30-11/4/92	NEA	2.8	3.4	29.8	5.0	−30.55	−30.83	−32.68	28	18
QFF-415	Winter 93	11/20-24/92	NEA	1.1	2.3	30.1	7.2	−30.35	−31.03	−29.86	27	37
QFF-417		12/21-25/92	NEA	4.2	4.2	29.7	4.4	−32.32	−33.71	−33.21	9	15
QFF-418		1/16-20/93	SEA	1.1	2.0	29.6	2.2	−29.54	−31.71	−31.52	22	26
QFF-419		1/29-2/2/93	NEA	6.3	5.5	29.9	7.7	−33.53	−34.26	−33.79	6	11
QFF-420		2/12-16/93	NEA	2.1	7.2	29.6	2.7	−29.87	−31.42	−31.65	24	25
QFF-421		2/26-3/2/93	NEA	1.1	2.6	29.7	3.0	−31.47	−33.42	−33.15	11	15
QFF-422		3/13-17/93	NEA	2.0	6.8	29.9	4.9	−30.87	−32.45	−31.76	18	24
QFF-423		3/29-4/1/93	NEA	1.1	2.7	29.6	1.2	−30.73	−32.12	−32.07	20	22
QFF-424		4/20-24/93	NEA	2.6	2.9	29.5	3.9	−31.69	−32.87	−33.65	15	12
QFF-426	Summer 93	5/29-6/2/93	SEA	0.5	3.2	29.6	3.5	−29.91	−33.49	−32.23	11	21
QFF-427		6/11-16/93	IA	1.6	2.4	29.5	6.1	−29.75	−31.55	−32.92	24	17
QFF-430		7/26-30/93	ME	0.9	5.7	30.8	4.8	−28.64	−28.32	−26.56	45	59
QFF-431		8/6-10/93	IA	0.4	2.6	29.9	3.0		-30.05	-30.07	33	36
QFF-433		9/3-7/93	IA	0.2	6.7	29.8	2.9	−29.40	−28.83	−28.77	42	44
QFF-437		12/6-10/93	NEA	0.7	1.6	29.9	3.3	−30.94	−32.57	−32.67	17	18

Data except for $\delta^{13}C$ and source allocation are from Kawamura et al. (2003). n.d., not determined, only isotopic data for the C_{27}, C_{29}, and C_{31} *n*-alkanes are shown measurements for other carbon numbers were sparse and have been omitted.

[a] Predominant source area in the 10-day back-trajectory. Acronyms are: NEA, Northeast Asia; SEA, Southeast Asia; Marine Easterlies; IA, Indonesia and Australia.

photosynthetically more active in late summer; (3) C_4 plants also become photosynthetically more active in late summer. It is highly likely that there could be some seasonal change in the ecosystem composition of the source areas for the aerosols collected at Chichi-Jima. However, we expect that, given the strong seasonality recorded in the pre-

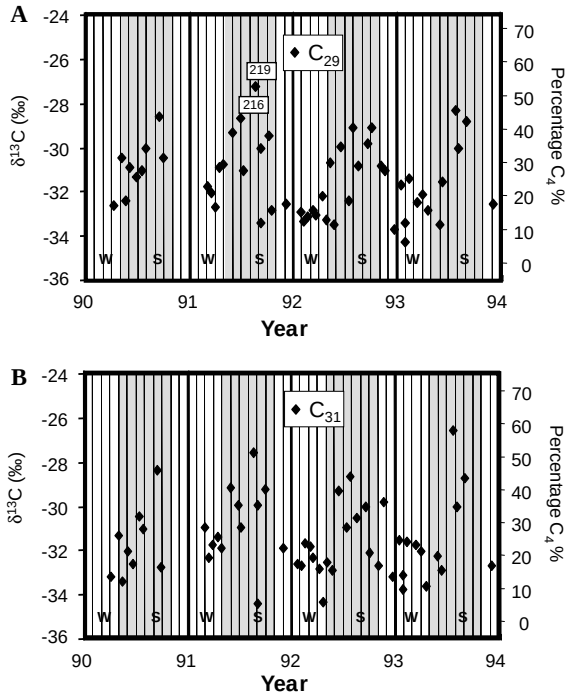

Fig. 3. Distribution of carbon isotopic composition ($\delta^{13}C$, left axis) of (A) C_{29} and (B) C_{31} *n*-alkanes and estimates of the percentage contribution of C_4 plant material (%C_4, right axis) in aerosol samples collected at Chichi-Jima Island between 1990 and 1993. Gray shading delimits the summer (May–October) and white the winter seasons (November–April).

vailing winds at Chichi-Jima (Kawamura et al., 2003), changes in transport pathways may be more important for the seasonal $\delta^{13}C$ signal at Chichi-Jima than at Bermuda (which is dominated by North American air masses advected by westerlies). We suggest that, every year, for a particular season the *n*-alkanes may be derived from relatively consistent sources and the aerosols are transported by similar atmospheric transport pathways and processes. In order to explore these different processes in more detail, we estimated the source contributions of C_3 and C_4 plant material (derived from the *n*-alkane $\delta^{13}C$) and the transport pathways (by back-trajectory analysis).

Assuming that there is no significant isotopic fractionation during aerosol transport over the ocean, the relative contributions to the *n*-alkanes from terrestrial C_3 and C_4 plants can be estimated by using a two-component mixing equation (Chesselet et al., 1981):

$$C_{alk} = C_3 + C_4$$

$$C_{alk}\delta^{13}C_{alk} = \delta^{13}C_3 \times C_3 + \delta^{13}C_4 \times C_4$$

where C_{alk} is the total concentration of an *n*-alkane, C_3 and C_4 are *n*-alkane concentrations from C_3 and C_4 plants, and $\delta^{13}C_3$ and $\delta^{13}C_4$ are the isotopic composition of the *n*-alkanes from C_3 and C_4 plant sources, respectively. The end member values for the mixing equation were averages taken from the literature and from measurements made at the Institute of Low Temperature Science (ILTS) (see Table 3): for C_{29}, C_4 plant *n*-alkanes = −20.0‰ and C_3 plant *n*-alkanes = −35.1‰; for C_{31}, C_4 plant *n*-alkanes = −20.4‰ and C_3 plant *n*-alkanes = −35.4‰ (Chikaraishi and Naraoka, 2003; Collister et al., 1994; Huang et al., 1997; Lichtfouse et al., 1994; Lockheart et al., 1997). This results in estimates of C_4 plant contribution varying from 6 to 52% for the individual winter samples and 6–59% for the individual summer samples (Table 2 and Fig. 3, right axis). There is a significant degree of natural variability in the $\delta^{13}C$ of C_3 and C_4 plant samples, standard

Table 3
Stable carbon isotopic compositions (per mil) of *n*-alkanes from C_3 and C_4 plants

Plant type	Source	C_{29} $\delta^{13}C$ (SD)	C_{31} $\delta^{13}C$ (SD)
C_3 plants	Collister et al. (1994)	−35.4‰ (1.7)	−36.1‰ (1.3)
	9 species		
	Chikaraishi and Naraoka (2003)	−35‰ (2.7)	−35.2‰(2.9)
	22 species		
	Lockheart et al. (1997)	−36.1‰ (1.1)	
	1 species		
	Huang et al. (1997)	−33.3 (0.1)	−33.1 (0.2)
	1 species		
	ILTS this paper	−33.7‰	
	1 species		
	Mean	−35.1‰ (2.3)	−35.4‰ (2.6)
C_4 plants	Collister et al. (1994)	−21.5‰ (4.3)	−20.2‰ (2.3)
	3 species		
	Chikaraishi and Naraoka (2003)	−19.2‰ (2.4)	−20.2‰ (2.3)
	7 species		
	Lichtfouse et al. (1994)	−18.4	
	1 species		
	ILTS this paper	−19.6‰	−20.3‰
	1 species		
	Mean	−20.0‰ (2.4)	−20.4‰ (2.1)

For measurements made at ILTS, plant leaves were extracted with DCM/MeOH (5:1) and then the extracts were saponified using 0.5 M KOH/MeOH. The *n*-alkanes were isolated and analyzed by the methods described in the text.

Table 4
Calculated % C_4 source input of plants from end members[a] of C_3 and C_4 plants

Compound	W-90	S-90	W-91	S-91	W-92	S-92	W-93	S-93
C_{29} *n*-alkane (this paper)	16	29	23	32	14	29	17	31
C_{31} *n*-alkane (this paper)	15	26	25	35	19	29	21	35
C_{28} fatty acid Fang et al. (2002)	6	20	22	27	9	14	8	18

[a] For the C_{28} fatty acid Fang et al. (2002) used end members of −30.9 for C_3 plants and −20.8‰ for C_4 plants.

deviations for the end members were between 2.1 and 2.6‰ (Table 3) which is equivalent to a variability of 14–17% in the estimation of the C_4 plant fraction.

Fang et al. (2002) estimated C_4 plant contributions to the Chichi-Jima aerosols from the isotopic composition of the C_{28} fatty acid. They detected a similar seasonal trend of relatively higher inputs of C_4 material in the summer than the winter seasons (Table 4). The absolute estimates of mean seasonal C_4 contributions are consistently lower when calculated from the C_{28} fatty acid $\delta^{13}C$ (%C_4 of 6–27) (Fang et al., 2002) than from the *n*-alkanes (%C_4 of 15–35%) (this paper); however, the offset is not significant as it is less than the uncertainty of the end members (14–17%). The natural variability of $\delta^{13}C$ within C_3 and C_4 plants highlights the fact that caution is needed in interpreting absolute source input contributions calculated from end member models. However, despite some uncertainties, it is still useful to convert the $\delta^{13}C$ values to percentage C_4 estimates for clarity when discussing relative C_3/C_4 changes.

3.3. C_3 and C_4 plant contribution and air mass source categories

The relative contributions from the C_3 and C_4 plant sources are determined by the regional meteorological conditions, and C_3/C_4 production and deflation to the atmosphere in the source areas. Comparison of composite back-trajectory analysis maps and source area pie-charts (Fig. 4) with a global modelled distribution map of the fraction of C_4 biomass (Still et al., 2003) (Fig. 1) reveals the potential source areas of eroded plant material that may be responsible for the seasonal changes in the C_{29} and C_{31} *n*-alkane $\delta^{13}C$ values observed at Chichi-Jima. Each sample was allocated an air-mass source category, based on the dominant source area observed in the 10-day back trajectory. The categories were: Northeast Asia (NEA), Southeast Asia (SEA), Indonesia and Australia (IA), and Marine easterlies (ME) (Fig. 1, Table 2). Ninety-six percent of winter samples fall into the SEA or NEA source area categories, in contrast, only 21% of the summer samples were of NEA or SEA origin, being of IA (30%) and ME (49%) origin, respectively (Table 2). The yearly seasonal source area distributions are shown in Fig. 4C. In general, in winter/spring, air masses tended to originate in north Asia where for large regions C_4 plants comprise 0% of the mean annual biomass (Fig. 1) (Still et al., 2003). In contrast in summer/autumn, backward trajectories show a greater diversity of source areas: less air masses originated in north Asia, instead they were more often marine (easterly trades) Southeast Asian, Indonesian, and sometimes (1991 and 1992) Australian in origin. In the latter regions, C_4 plants form a more significant proportion of the annual mean biomass than in northern and western Asia, for example: up to 50% in eastern Chinese provinces such as Hebei and Shanxi, up to 70% in parts of Thailand and Cambodia, and up to 100% in much of northern Australia (Fig. 1) (Still et al., 2003).

Box plots of the C_{29} and C_{31} $\delta^{13}C$ data for each of these major source areas are illustrated in Fig. 5. They show that samples in the NEA and SEA categories were significantly isotopically lighter (median values of around −32 to −33‰) than those of the ME and IA categories (median values of around −30 to −31‰). This confirms that a major portion of the isotopically heavier values recorded at Chichi-Jima during the summer–autumn is a function of material carried by the IA and ME air mass sources. The interquartile ranges (25–75% of the data) also demonstrate that—on the basis of CSIA measurements of the *n*-alkanes—it is largely possible to discriminate between samples with an Asian continental source (NEA or SEA) and the easterly (ME) or southerly (IA) sources. However, using this method further categorization was not possible—there was a major overlap of the interquartile ranges of the NEA and SEA categories, and of the IA and ME categories (Fig. 5).

Overall, it seems that the extreme changes in the $\delta^{13}C$ of the aerosol *n*-alkanes at Chichi-Jima are a function of the major seasonal changes in the prevailing wind systems. However, it can also be seen from Fig. 5 that there is significant variation (between 1 and 3‰ for the interquartile range) in isotopic values within the individual source area categories. We suggest that this portion of the variability at Chichi-Jima is a function of seasonal changes within the source areas, i.e., carbon isotopic discrimination in C_3 plants decreasing as moisture becomes limiting, and plant species and genotypes with higher water use efficiency (lower discrimination) comprising a greater proportion of photosynthesis in summer and autumn (Conte et al., 1992).

The lack of significant difference between SEA and NEA categories and between IA and ME categories may be due to the entrainment and mixing by air masses of *n*-alkanes from wide geographic areas. This suggests that paleoclimatic reconstructions using sedimentary material recovered from the Chichi-Jima sector of the western Pacific may record C_3/C_4 plant abundance changes over wide geographical areas.

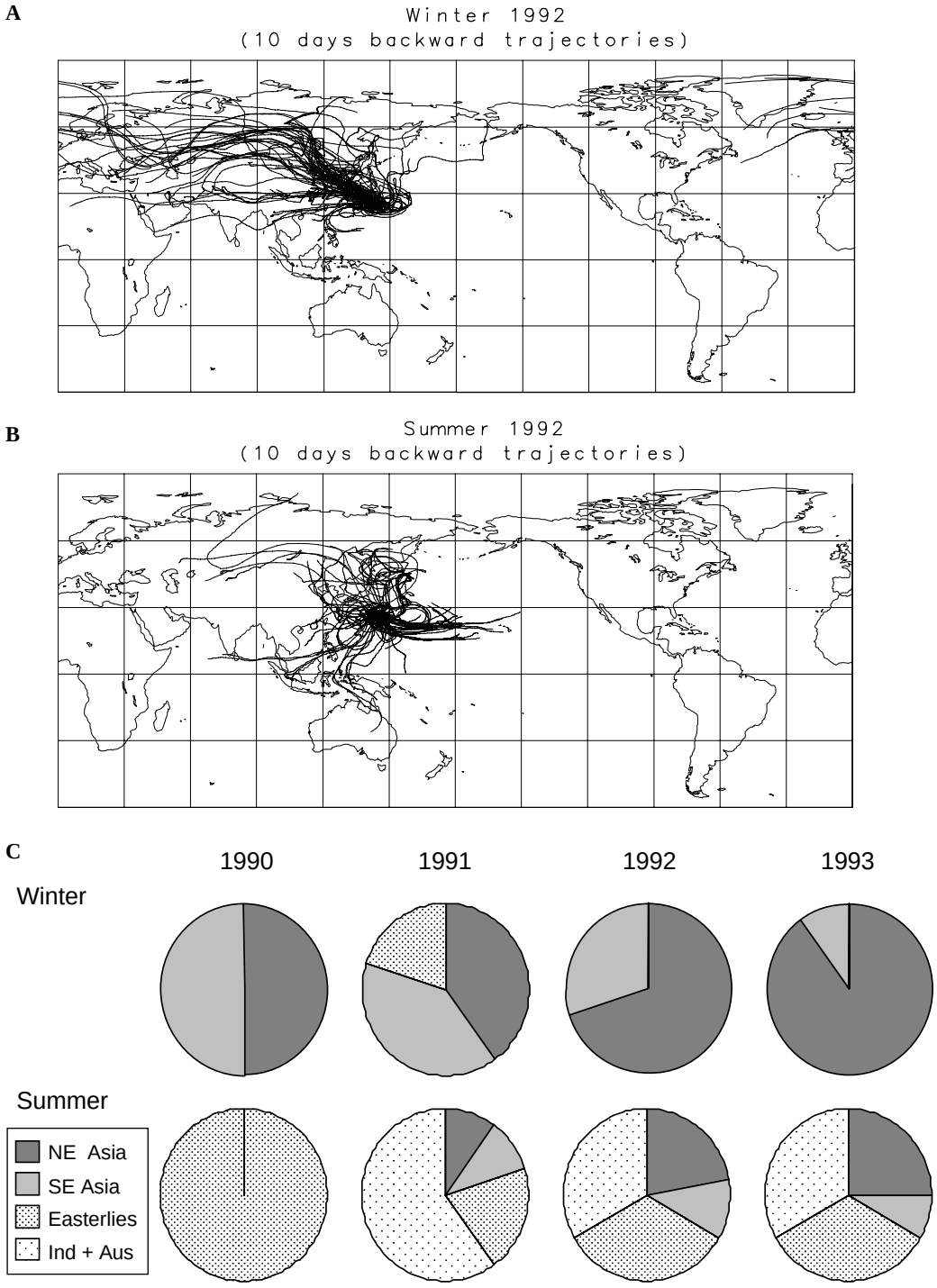

Fig. 4. Examples of the composite seasonal 10-day back-trajectory analyses for (A) Winter 1992 and (B) Summer 1992 sampling periods. (C) Pie-charts representing the distribution of the source areas for each season as defined by the percentage of dominant back-trajectories found within each sampling period. Back-trajectory analysis was conducted using a 40-year reanalysis data of the European Centre of Medium-range Weather Forecasts (ERA40) (Simmons and Gibson, 2000) and a trajectory model developed by Hatsushika and Yamazaki (2003). The trajectory calculations were based on backward tracking of air parcels released at the target location (for the sampling periods) assuming the parcel was moving along the ambient airflow. The flow pattern was updated every 6 h.

To explore the possibility for various combinations of higher plant biomarker parameters to further discriminate between the different source areas, we looked at a matrix of scatterplots (not shown). A number of combinations of parameters showed a significant separation of the NEA and SEA categories from the IA and ME categories (e.g., $\delta^{13}C$ of C_{24} fatty acids vs $\delta^{13}C$ of C_{29} *n*-alkanes; $\delta^{13}C$ of C_{31} *n*-alkanes vs UCM) but no combinations could further separate out the NEA from SEA categories or the IA from ME categories.

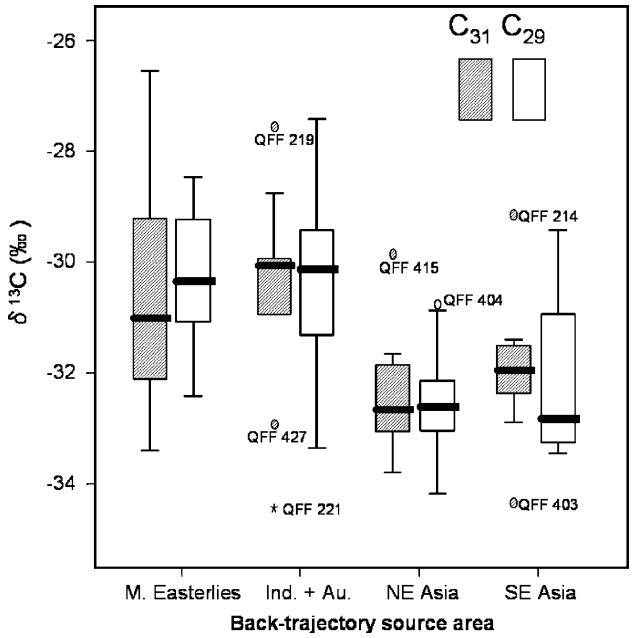

Fig. 5. Box plots of the carbon isotopic composition ($\delta^{13}C$) of C_{29} and C_{31} *n*-alkanes in aerosol samples collected at Chichi-Jima Island between 1990 and 1993, categorized by back-trajectory source area. Each box shows the median (black line), the interquartile range (box), and the min and max values that are not outliers (whiskers), mild outliers (circles), and extreme outliers (stars).

Prior to this comparison of the global C_4 biomass with back-trajectory analysis Fang et al. (2002) had suggested that the increase in C_4 inputs in the summer at Chichi-Jima was a result of material carried by the easterly trade winds from the North and Central Americas, where a diverse C_4 flora exists (Still et al., 2003; Teeri and Stowe, 1976) (Fig. 1). Indeed, 6 of the 8 isotopically heaviest *n*-alkane samples (>29.5‰ or around >40% C_4) were of marine easterly (ME) origin (Table 2). However, even 20-day back-trajectory analysis did not place the source air-mass parcels in the Americas (data not shown). Therefore, while there may be a high proportion of C_4 material of American provenance in these samples, we cannot confirm the thesis of Fang et al. (2002) that it is transported directly to Chichi-Jima by specific meteorological events. Rather we suggest that the easterly winds are transporting C_4 material from aged continental air, which has been previously advected to form part of the "aerosol veil" above the eastern Pacific. Our analysis further suggests that the increase in C_4 contribution observed in the summer seasons at Chichi-Jima was also the result of a relatively less C_4-poor material being transported from north Asia and a relatively more C_4-rich material being transported from Southeast Asia and Australia (Fig. 4) as well as from the Americas.

Previously Kawamura et al. (2003) noted that absolute concentrations (ng m^{-3}) of terrestrial biomarkers were generally lower in the summer to autumn seasons due to the predominance of maritime trade winds. However, higher concentrations were recorded during the summer and autumn of 1991. During this period the highest proportion of C_4 material at Chichi-Jima was discovered for the C_{29} *n*-alkane (Fig. 3). The year of 1991 was characterized by a strong El Niño event, expressed meteorologically by weaker subtropical high-pressure systems in the western Pacific and more frequent development of tropical low systems (typhoons). The back-trajectories demonstrated that more air masses associated with this year originated in Southeast Asia, including Indonesia, Kalimantan, and Australia (see Fig. 4C and Kawamura et al., 2003). The C_4 contributions to aerosols at Chichi-Jima were therefore enhanced by emissions from these areas. Samples QFF-216 and QFF-219 (Fig. 6) had high concentrations of C_4 plant material (45 and 55%, respectively, for the C_{29} *n*-alkane), these samples also had back-trajectories which reached Indonesia (QFF-216) northern Australia (QFF-219) (see Fig. 6), a region with a biomass of up to 100% C_4 plants over large areas (Still et al., 2003). Also during the 1991 El Niño event, the air over the western equatorial Pacific became dry and hot, and many forest fires occurred in southeast Asia (Kita et al., 2000) and Australia (Verdon et al., 2004), as well as the following year. During the forest fires and biomass burning, lipid class compounds, originally present as leaf waxes, could have been significantly emitted as smoke particles (without severe oxidative degradation) via volatilization (Abas et al., 1995; Oros and Simoneit, 2001). Thereafter lipids associated with smoke produced by smoldering and flaming processes may have been uplifted by convection and transported long distances over the Pacific Ocean, hence, enhancing the input of C_4 plant material detected at Chichi-Jima.

4. Conclusions

- The *n*-alkane class—in the remote marine aerosols collected from the western North Pacific—contains predominantly long-chain compounds with a strong dominance of odd-carbon numbered compounds. These lipids are derived from epicuticular waxes of terrestrial plants and indicate the importance of vegetation sources for organic matter in aerosols.
- Using Compound-Specific Isotope Analysis (CSIA) of the dominant C_{29} and C_{31} *n*-alkanes, lighter $\delta^{13}C$ values were observed in winter (−31 to −34‰) with a transition to heavier values in summer (−28 to −33‰).
- Comparison of backward trajectory analysis and a global modelled distribution map of C_3/C_4 biomass showed that higher plant *n*-alkanes transported from the east Asian continent were isotopically distinct from those of a marine easterly or Indonesian/Australian origin.
- Variability observed within individual source area categories suggested that seasonal changes within source areas contributed to some of the $\delta^{13}C$ variability in the Chichi-Jima *n*-alkanes. However, the dominant factor

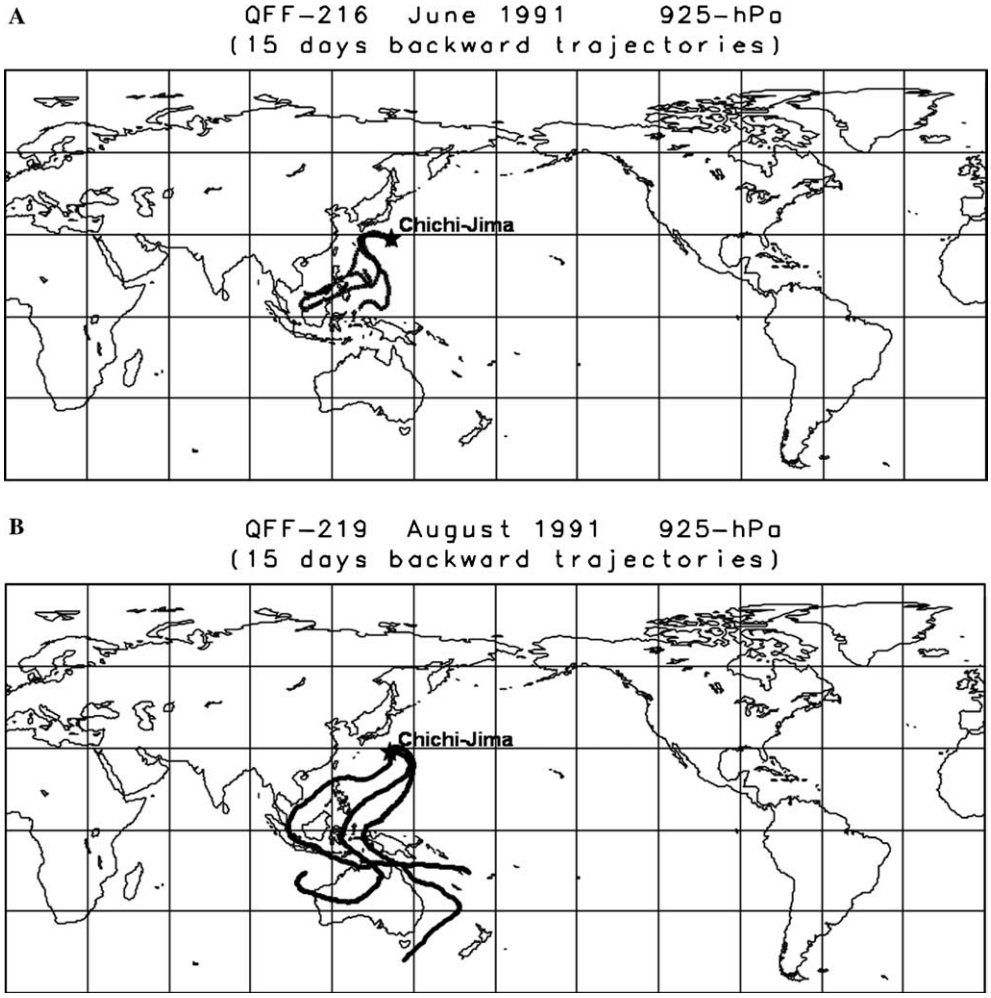

Fig. 6. Composite seasonal 15-day Back-trajectory analyses for (A) QFF-216 and (B) QFF-219. Back-trajectory analysis was conducted using a 40-year reanalysis data of the European Centre of Medium-range Weather Forecasts (ERA40) (Simmons and Gibson, 2000) and a trajectory model developed by Hatsushika and Yamazaki (2003). The trajectory calculations were based on backward tracking of air parcels released at the target location (for the sampling periods) assuming the parcel was moving along the ambient airflow. The flow pattern was updated every 6 h.

controlling the extremes of the seasonal signal at Chichi-Jima was changes in air-mass source area, which delivered different proportions of C_3/C_4 plant material.

- In general in winter/spring, more air masses transported C_3 material from north Asia, whereas in summer/autumn relatively more air masses transported material from south east Asia, Indonesia, and Australia where C_4 plants are more abundant. Marine easterlies were also an important source of isotopically heavier *n*-alkanes in the summer, which may have been transported from the Americas. The highest mean C_4 contributions in the summer of 1991 may have been enhanced by strong El Niño conditions which influenced meteorology and biomass burning emissions.

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