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Contributions of modern and dead organic carbon to individual fatty acid homologues in spring aerosols collected from northern Japan

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[1] Radiocarbon (^{14}C) and stable carbon isotope ratios ($\delta^{13}C$) have been used as proxies to evaluate the contributions of modern/fossil carbon and marine/terrestrial organic matter, respectively, in geochemical samples. However, there are few such studies in atmospheric aerosols. Here, we measured ^{14}C contents and $\delta^{13}C$ of individual *n*-fatty acids in an aerosol sample collected from northern Japan in spring 2001 during Asian dust season. Our results show that the distribution of fatty acids in the spring aerosols was characterized by a strong even/odd carbon number predominance with two maxima at C_{16} and C_{26}. Their $\delta^{13}C$ (range: −30.6 to −20.5‰) showed higher values (average: −24.5‰) for lower molecular weight (LMW) fatty acids ($C_{16} - C_{19}$) and lower values (average: −29.7‰) for higher MW (HMW) fatty acids ($C_{20} - C_{32}$). This difference suggests that LMW acids are mainly derived from lacustrine and/or marine algal sources whereas HMW acids are predominantly from terrestrial C_3 higher plants. $\Delta^{14}C$ values of fatty acids were found to range from −96.9 to +122.9‰ with lower values for HMW acids and higher values for LMW acids. LMW acids in the aerosols contain only modern carbon. In contrast, HMW acids $\geq C_{24}$ were found to contain up to 9.7 wt% dead carbon, although their major portion (up to 92.3%) is composed of modern carbon. Backward trajectory analyses indicated that the source regions of the spring aerosols were dominated by central and north China (62%). This study suggests that the old fatty acids in the spring aerosols are most likely originated from the loess deposits in China via long-range atmospheric transport over the western North Pacific, although their contribution to the aerosols was relatively small.

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1. Introduction

[2] Past Asian dust events are considered to have been concordant with the climate changes in East Asia based on the analysis of the Japan Sea sediments for inorganic components, in which millennial-scale variability of Asian dust events is apparently associated with the variation in summer monsoon precipitation in central to East Asia [*Irino and Tada*, 2000]. *Kyotani et al.* [2005] reconstructed the fluctuation of the eolian dust fluxes (Kosa aerosols) during the last 100 years by using a data set from lacustrine sediments in Japan. A significant amount of Chinese loess (Kosa) is occasionally transported over the Japanese Islands and the North Pacific [e.g., *Huebert et al.*, 2003; *Kawamura et al.*, 2004] to North America [*Cahill*, 2003] in spring. The present-day Asian dusts have been investigated, for example, for inorganic components in various grain sizes [*Mori et al.*, 2002] and $PM_{2.5}$ [*Tsai and Chen*, 2006]. Asian dusts also contain various organic compounds of higher plant origin. *Guo et al.* [2003] studied the distributions of fatty acids in total suspended particles collected in China during a dust season and reported a significant contribution (38.7–45.5%) of higher plant waxes to total fatty acids in aerosols.

[3] A compound-specific radiocarbon analysis (CSRA) technique was developed over a decade ago [*Eglinton et al.*, 1996] and applied to various geochemical samples such as marine sediments [e.g., *Drenzek et al.*, 2007] and soil samples [e.g., *Lichtfouse et al.*, 1997; *Lichtfouse*, 2000; *Smittenberg et al.*, 2006; *Matsumoto et al.*, 2007]. *Matsumoto et al.* [2001, 2004] also applied the technique to atmospheric aerosol samples collected in Sapporo during the summer season and reported the compound specific radiocarbon contents of fatty acids. The radiocarbon contents in terrestrial fatty acids showed that the carbon ages are not always recent. Long-chain fatty acids of terrestrial higher plant origin were found to contain a significant amount of dead carbon (averaged age: up to 5000 years old) probably due to a long-range atmospheric transport of wind blown dusts from Asian

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arid regions. The old fatty acids may be stored in geochemical reservoirs such as loess deposits in China and are mobilized by winds to be emitted to the air and long-range transported over the Japanese Islands and the North Pacific. However, there is no study on the radiocarbon contents of *n*-fatty acids for the aerosols collected in spring when Asian dust outflow is maximized in the western North Pacific.

[4] In this study, we collected an aerosol sample in Sapporo in spring when strong Asian dust events were observed [*Huebert et al.*, 2003]. The aerosols were analyzed for the radiocarbon contents of individual fatty acids and their molecular composition and stable carbon isotopic ($\delta^{13}C$) compositions. We also analyzed simulated Asian dust sample (CJ-2) to compare with the spring aerosols for molecular and isotopic compositions of fatty acids. Based on the $\Delta^{14}C$ and $\delta^{13}C$ data and comparison to the loess deposit sample, we discuss the contribution of dead and modern carbon to the aerosol fatty acids, which may be both influenced by loess deposits in spring and vegetation in Asia via long-range atmospheric transport to northern Japan.

2. Sampling and Method

2.1. Sample Collection and Lipid Extraction From Aerosols and CJ-2

[5] The aerosol sample was collected using a precombusted quartz fiber filter (450°C, 4 hrs) and a high-volume air sampler (flow rate: ~600–800 L/min) on the roof of the Institute of Low Temperature Science, Hokkaido University, Sapporo for a month from 30 March to 29 April 2001. During the spring season, Asian soil dusts are often transported to the western North Pacific by strong westerly winds [*Huebert et al.*, 2003]. Sapporo (43°N, 141°E) is located in the western part of Hokkaido Island, Japan, and is a good site for collecting air masses delivered from Siberia, China, and surrounding oceans [*Aggarwal and Kawamura*, 2008]. The sampler was set up so as to avoid entraining building emissions. During the sampling period a large-scale Asian dust event was observed over the Japanese Islands and the western North Pacific [*Huebert et al.*, 2003]. Total volume of the air sample was 48,550 m^3 and total aerosol mass collected was 2.62 g; the averaged total aerosol mass concentration was 53.9 $\mu g\ m^{-3}$.

[6] This filter sample (QFF 2048) was extracted with dichloromethane/methanol (2:1, v/v) under ultrasonication to separate lipid class compounds. The extracts were saponified with 0.5 M KOH in methanol and neutral lipids were extracted with *n*-hexane/dichloromethane (10:1, v/v). Acidic lipids were then extracted with dichloromethane at pH 1 and were methylated with 14% BF_3/methanol. Monocarboxylic acid methyl esters were eluted with *n*-hexane/dichloromethane (1:2) on a silica gel column (300–400 mesh, deactivated with 1% H_2O). An aliquot of the ester fraction was analyzed by gas chromatography with flame ionization detection (GC-FID) to determine the molecular composition and concentrations, and their stable carbon isotope compositions were measured using isotope ratios mass spectrometry (GC/IRMS). A blank filter (combusted quartz filter) was analyzed by the method used for the sample. The result showed only small peaks of C_{16} and C_{18} acids. More details on the method are given elsewhere [*Matsumoto et al.*, 2001].

[7] A simulated Asian dust sample was analyzed for molecular and stable isotopic compositions of fatty acids to compare with the spring aerosol sample (QFF2048). The surface (0–6 cm depth) loess deposits were collected at the southeast of the Tengger Desert (40°N; 116°E) in the Ningxia Hui autonomous region of China and a dust fraction by filtering <100 μm was named as CJ-2 [*Nishikawa et al.*, 2000]. The CJ-2 sample (0.50 g) was extracted following the method described above. The monocarboxylic acid methyl ester fraction was analyzed by GC-FID for the molecular distributions whereas their stable carbon isotopic compositions were determined by GC/IRMS.

2.2. The ^{14}C Analysis of Individual Fatty Acids

[8] In order to isolate individual fatty acids for ^{14}C age determination by accelerator mass spectrometer (AMS), we employed a preparative capillary GC (PCGC) system equipped with a cooled injector (CIS4, Gerstel, Germany), megabore column, zero-dead-volume effluent splitter, and cryogenic preparative fraction collector (PFC, Gerstel). The injection volume was 25 μl and the CIS is programmed from 25°C (0.5 min) to 350°C at 12°C s^{-1} and held at 350°C for 6 min. The GC oven temperature was programmed from 50°C (1 min) to 120°C at 30°C min^{-1}, from 120°C to 310°C at 6°C min^{-1} and then held at 310°C for 30 min. Individual compounds were isolated on a HP-5 fused silica megabore column (30 m × 0.53 mm i.d. film thickness 1.0 μm). Helium was used as carrier gas. Using an automatic sampler, 70 consecutive PCGC runs were performed in order to isolate microgram quantities of the individual fatty acids. After the PCGC separation, fatty acid methyl esters (FAMEs) were purified on a silica gel column by eluting any methyl silicones potentially contaminated from the GC column liquid phase with *n*-hexane/dichloromethane (2:1) mixture. The GC chromatogram showed a very flat base line without hump of methyl silicone contaminants. We isolated C_{16}, C_{18}, C_{20}, C_{24}, C_{26}, C_{28} and C_{30} + C_{32} acid fractions. Their purities were determined to be 98–100% by GC-FID.

[9] The isolated FAME fractions from the aerosols were combusted in the presence of CuO (800°C, 2 h) and the purified CO_2 was then converted to a graphite target using a technique of microscale ^{14}C analysis [*Uchida et al.*, 2000]. The amounts of isolated FAME fractions ranged from 49 μgC (C_{20}) to 239 μgC (C_{16}). The IAEA ^{14}C standards (C_1 and C_6) and NBS oxalic acid (Hox II, RM-49) were used as the reference standard samples. The details of CSRA, accuracy and precision (±2~31‰, ±200~230 years) are discussed by *Uchida et al.* [2000, 2004]. The ^{14}C analyses of graphite targets were conducted at the AMS facility (NIES-TERRA) of the National Institute for Environmental Studies. To calculate $\Delta^{14}C$ values of fatty acids, we corrected the value of individual esters using a simple mass balance equation among $\Delta^{14}C$ values of certain fatty acid, methyl group of derivative reagent (14% BF_3/methanol, $\Delta^{14}C$ = −998‰) and corresponding methyl ester. Unfortunately, we were not able to conduct ^{14}C measurements for fatty acids in the loess sample (CJ-2) due to the limited amounts of sample.

2.3. Backward Trajectory Analysis

[10] Backward trajectory analyses were conducted for the period of aerosol collection using the Meteorological Data Explorer (METEX), developed by Jiye Zeng at the Centre for

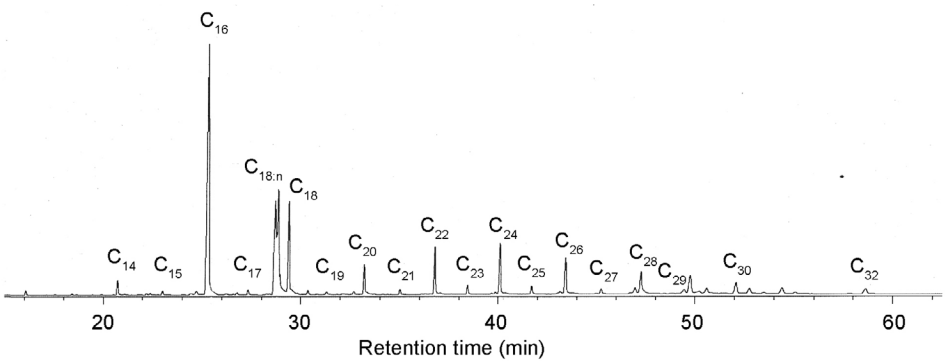


Figure 1. A gas chromatogram of fatty acid methyl ester fraction isolated from the spring aerosols (QFF2048) collected in Sapporo, northern Japan, during Asian dust season (30 March to 29 April 2001).

Global Environmental Research (CGER), National Institute of Environmental Studies (NIES). METEX includes programs for calculating air mass trajectory, extracting meteorological data in various binary formats, and plotting trajectory results and meteorological data (http://db.cger.nies.go.jp/metex/index.html). Data sets are used from European Centre for Medium-Range Weather Forecast (ECMWF), National Centers for Environmental Prediction (NCEP), and Japan Meteorological Agency (JMA). Backward trajectories are calculated for 10 days once a day starting at 1200 UTC during a sampling period. The time step of the backward trajectory calculations is 60 min.

3. Results and Discussion

3.1. Distribution of Fatty Acids in Spring Aerosols

[11] To illustrate the molecular range of the fatty acids, a gas chromatogram of fatty acid methyl ester fraction is shown for the spring aerosol sample (Figure 1). Their distribution showed an even-carbon-numbered predominance and a bimodal pattern with peaks at n-C_{16} and n-C_{24}. Concentrations of total fatty acids are 1160 ng m^{-3} with a maximum at n-C_{16}. Similar molecular distributions have been typically observed in aerosol samples from continents [*Simoneit et al.*, 1991; *Matsumoto et al.*, 2001, 2004; *Wang et al.*, 2006; *Fu et al.*, 2008], aircraft [*Simoneit et al.*, 2004] and remote oceans [*Conte and Weber*, 2002; *Kawamura et al.*, 2003; *Bendle et al.*, 2007; *Mochida et al.*, 2007], riverine and estuarine sediments [e.g., *Naraoka and Ishiwatari*, 2000] and marine sediments [e.g., *Ohkouchi et al.*, 1997; *Dahl et al.*, 2005] as well as a soil sample [*Matsumoto et al.*, 2007]. Fatty acids in higher plant leaves are characterized by a strong even carbon number predominance of fatty acids [*Eglinton and Hamilton*, 1967], but they rarely contain odd-carbon-number species (e.g., *Zea mays*; *Taxus cuspidata* [*Fang et al.*, 2002]). The existence of odd-numbered components suggests that fatty acids in the aerosols are derived not only from terrestrial plants, but also from various geochemical reservoirs such as soils and sediments, in which odd carbon fatty acids are produced by microbial α-oxidation of even carbon numbered fatty acids [*Yano et al.*, 1971; *Kawamura and Ishiwatari*, 1984; *Matsumoto et al.*, 2007].

[12] Carbon preference index (CPI), which is defined by the abundance ratio of even over odd carbon numbered C_{20} to C_{32} fatty acids, is 5.36. This CPI value is much lower than that of terrestrial higher plant (e.g., CPI = 19.1 [*Matsumoto et al.*, 2007]), but higher than or close to the soil sample collected near the sampling site (CPI = 4.57 [*Matsumoto et al.*, 2007]). In soils and sediments, microbial α-oxidation of fatty acids decreases their CPI values [*Kawamura and Ishiwatari*, 1984; *Matsumoto et al.*, 2007]. The relatively low CPI values suggests that fatty acids in the aerosols are derived from both fresh higher plants and soil organic matter. Alternatively, α-oxidation of HMW fatty acids in the atmosphere during long-range transport could lower the CPI values. The distributions of fatty acids in spring sample are compared with those of summer aerosol samples (Summer I [*Matsumoto et al.*, 2001] and Summer II [*Matsumoto et al.*, 2004]) (Figure 2), which were all collected in the same site. The CPI value (5.36) of the spring aerosols is similar to those of the Summer I (5.45) and II (4.12) samples. Although the

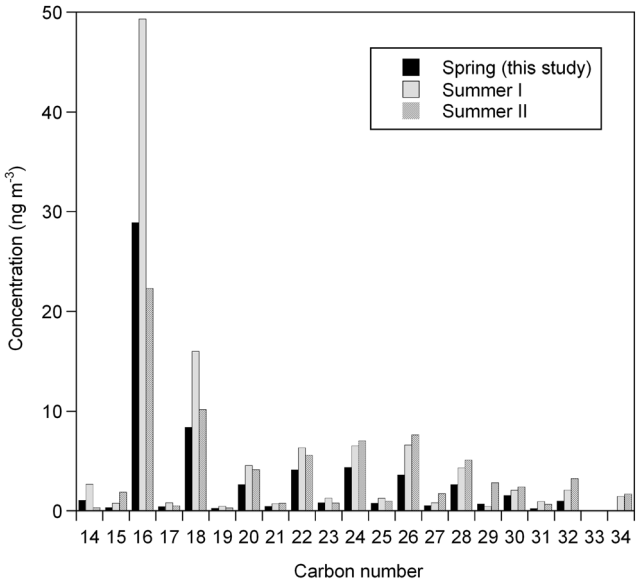


Figure 2. Chain length distributions of fatty acids in the spring aerosols (30 March to 29 April 2001) in comparison with summer aerosol I (18 June to 2 July 1999 [*Matsumoto et al.*, 2001]) and II (1–21 June 2001 [*Matsumoto et al.*, 2004]) samples, which were collected on the same site in northern Japan.

Table 1. Concentrations and Carbon Isotopic Compositions for Individual Fatty Acids (FA) in the Spring Aerosol Sample (QFF2048) Collected in Northern Japan During Asian Dust Season

Fatty Acids	ng m^{-3}	μg/g-aerosols	$\delta^{13}C$ (‰)	Standard Deviation (1σ)
14	1.04	19.3	−22.3	0.3
15	0.32	5.9	−21.6	0.6
16	28.92	536.1	−26.5	0.6
17	0.42	7.7	−20.5	1.0
18	8.37	155.2	−24.3	0.4
19	0.24	4.5	−27.0	0.3
20	2.61	48.4	−28.3	0.6
21	0.42	7.9	−29.0	0.3
22	4.11	76.1	−29.7	0.2
23	0.79	14.6	−29.3	1.2
24	4.34	80.5	−29.9	0.3
25	0.75	13.9	−29.7	1.6
26	3.58	66.3	−30.4	0.4
27	0.50	9.2	−29.5	2.9
28	2.62	48.6	−30.4	0.2
29	0.67	12.4	n.d.[a]	
30	1.54	28.5	−30.6	0.7
31	0.22	4.2	n.d.	
32	0.97	18.0	−29.4	0.8
Total	62.42	1157.2		
CPI(C_{20} − C_{32})[b]	5.36			

[a]Not determined because of very small GC peak.
[b]CPI (C_{20} − C_{32}) = [Σeven(C_{20} − C_{30})FA + Σeven(C_{22} − C_{32})FA]/2Σodd (C_{21} − C_{31})FA.

molecular compositions are similar, concentrations of HMW fatty acids in the spring sample are lower than in Summer I by 55% and Summer II by 66%. Since the bloom season of terrestrial higher plants in East Asia is in summer, this result seems reasonable.

3.2. Stable Carbon Isotopic Composition of Fatty Acids and Their Sources

[13] Stable carbon isotopic compositions of fatty acids are given in Table 1. Their $\delta^{13}C$ values range from −30.6‰ (*n*-C_{30}) to −20.5‰ (*n*-C_{17}). The higher $\delta^{13}C$ values (−27.0 to −20.5‰) were found in LMW fatty acids <*n*-C_{20} whereas the lower values were obtained for HMW fatty acids (−30.6 to −28.3‰). Higher values of C_{14} to C_{19} acids were reported in remote marine aerosols [*Fang et al.*, 2002] and marine sediments [e.g., *Naraoka and Ishiwatari*, 2000; *Uchida et al.*, 2005] from the western North Pacific, and in lacustrine sediments from Lake Haruna [*Chikaraishi and Naraoka*, 2005]. However, such higher $\delta^{13}C$ ratios have not been reported in terrestrial C_3 higher plant waxes [e.g., *Matsumoto et al.*, 2007], but were reported in aquatic C_3 plants and phytoplankton samples from Lake Haruna [*Chikaraishi and Naraoka*, 2005]. Thus, LMW fatty acids (C_{14} − C_{19}) in the spring aerosols may originate from the combination of lacustrine sediments and algal plants. It is more likely that these acids would originate from marine aerosols during air mass passage over the Japan Sea. HMW fatty acids (≥C_{20}) show lower $\delta^{13}C$ values (−30.6 to −28.3‰), which are equivalent to or slightly higher than those of the leaf waxes of terrestrial C_3 plant origin [*Fang et al.*, 2002; *Matsumoto et al.*, 2007]. This similarity suggests that HMW fatty acids in the spring aerosols originated from terrestrial higher plants and their debris in soils.

[14] The $\delta^{13}C$ values of fatty acids (C_{16} − C_{32}) in the spring aerosol sample were compared with those of the previously studied summer samples (Summer I and II) (Figure 3). The $\delta^{13}C$ values of HMW fatty acids in the spring sample are equivalent to or lower than those of summer samples, except for the higher value of the C_{17} acid. In particular, the $\delta^{13}C$ values of HMW fatty acids in the spring sample are slightly lower than those of Summer I and II samples by on average 0.60‰ and 0.94‰, respectively, although the difference is similar to the standard deviations (Table 1).

3.3. Simulated Asian Dust Sample CJ-2

[15] In order to compare the molecular distributions and concentrations of fatty acids in the spring aerosols as well as their stable carbon isotopic compositions with those of Asian dusts, we analyzed the simulated Asian dust sample (CJ-2) prepared from loess deposits. As shown in Figure 4, its molecular distribution is characterized by even/odd predominance with two peaks at C_{16} and C_{24}. Although its distribution is generally similar to that of the spring and summer aerosol samples (Figure 2), the simulated dust sample showed lower relative abundances of C_{16} and higher abundances of C_{20} − C_{30}, in particular C_{28}. This can be explained by a selective microbial degradation of LMW fatty acids over HMW acids in soils. Table 2 gives the concentrations of fatty acids in the dust sample (CJ-2) and their $\delta^{13}C$ compositions. The concentration of total fatty acids (28.4 μg/g-dust) is much lower than that (1157 μg/g-aerosols) of the spring aerosol sample, suggesting that the aerosol material is more likely to contain lipid-rich pollen than the simulated dust sample would be. However, the differences between the simulated dust and ambient aerosol samples can be explained by a preferential deposition of coarse particles mainly com-

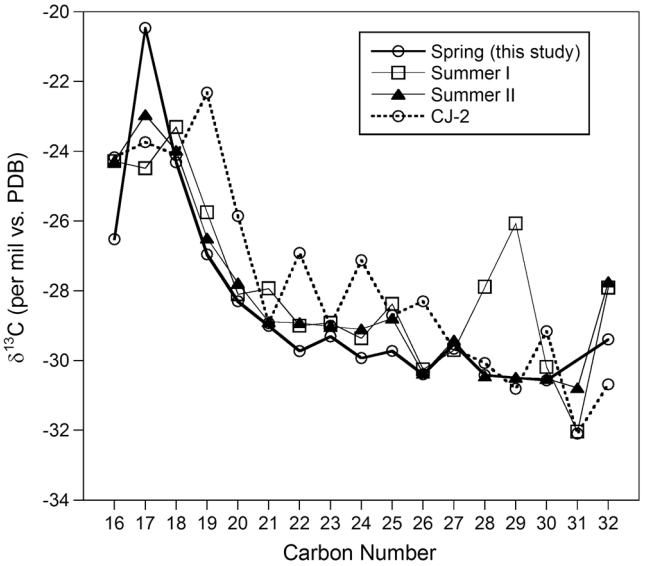


Figure 3. Chain length variations of stable carbon isotopic ratios ($\delta^{13}C$) of fatty acids in spring aerosols (30 March to 29 April 2001) in comparison with summer aerosol samples (I and II) collected in northern Japan and Chinese loess sample (CJ-2). For data of summer samples, see the caption of Figure 2.

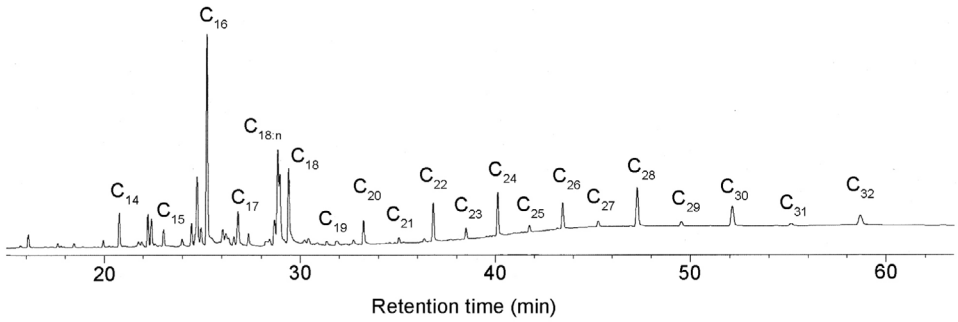


Figure 4. A gas chromatogram of fatty acid methyl ester fraction isolated from simulated Asian dusts (CJ-2) (loess deposits) that were collected from the Tengger Desert (40°N; 116°E) in China.

posed of mineral dusts during the long-range atmospheric transport. The CJ-2 sample contains more coarse particles (diameter <100 μm) than the atmospheric aerosols, which generally show two modes maximizing at 0.5–1 μm and 10 μm in diameter [*Nishikawa et al.*, 2000]. Fatty acids in the remote marine atmosphere are characterized by bimodal size distributions with peaks at submicrometer (~0.5 μm) and super micrometer (~5 μm) modes [*Mochida et al.*, 2007].

[16] The $\delta^{13}C$ values of fatty acids in the simulated dusts (CJ-2) ranged from −30.8‰ (n-C_{29}) to −22.3‰ (n-C_{19}). Higher molecular weight fatty acids (C_{20} − C_{32}) showed more negative values (−25.9‰ to −32.1‰, average: −29.0‰) than those of lower molecular weight (C_{14} − C_{19}) fatty acids (−22.3‰ to −24.2‰, average: −23.2‰). This difference indicates that HMW fatty acids in the loess deposits are predominantly of terrestrial C_3 plant origin. In contrast, lower molecular weight (C_{14} − C_{19}) fatty acids may be in part derived from fossil aquatic plants, in which the isotopic ratios are higher than those of terrestrial fatty acids [*Chikaraishi et al.*, 2004]. In fact, $\delta^{13}C$ values of LMW fatty acids in the CJ-2 sample are equivalent to those of aquatic higher plants [*Chikaraishi et al.*, 2004] and some lacustrine phytoplankton [*Chikaraishi and Naraoka*, 2005]. The debris of aquatic plants could have been deposited in lake sediments and mobilized as dusts when the lake dried in the past. Interestingly, these $\delta^{13}C$ values of loess deposits are similar to those of the spring aerosol sample (Table 1); the averaged $\delta^{13}C$ values for LMW fatty acids in the aerosols versus in the loess deposits are −23.7‰ versus −23.2‰ while those of HMW acids are −29.7‰ versus −29.0‰.

[17] Although the $\delta^{13}C$ values are generally similar between the spring aerosol and loess (CJ-2) samples within the difference of 2.0‰ for most of the fatty acids (Figure 3), large differences were recognized for few major fatty acids such as C_{16}, C_{20}, C_{22}, and C_{24}. The lower isotopic values of C_{16} (by −2.3‰), C_{20} (−2.4‰), C_{22} (−2.8‰) and C_{24} (−2.8‰) fatty acids in the aerosols than in the loess deposits (Figure 3) may suggest that the real aerosols have more contributions from terrestrial higher plants in the source regions in Asia. Further, local emissions of plant wax in northern Japan and their contributions to the atmospheric aerosols may also be important in addition to the inputs of modern and dead carbon from the Asian continent, in which the dead carbon components likely originated from the loess deposits in the arid regions in China and Mongolia.

3.4. Radiocarbon Content in Individual Fatty Acids

[18] $\Delta^{14}C$ values of fatty acids in the spring aerosols range from −96.9 (C_{30} + C_{32}) to +122.9 (C_{16}) ‰ (Table 3). The value of n-C_{16} fatty acid indicates modern carbon corresponding to 1992–1995 [*Levin and Kromer*, 1997] (global and hemispheric average $\Delta^{14}C$ [*Hua and Barbetti*, 2004]) or to 1957–1958, when nuclear bomb tests were carried out. C_{18} and C_{20} acids that have positive $\Delta^{14}C$ values are likely derived from living organisms. In contrast, fatty acids ≥C_{24} show negative values (−90 to −5‰). Old carbon characterized by negative $\Delta^{14}C$ values of the fatty acids ≥C_{24} has been reported in marine surface sediments [*Uchida et al.*, 2005] and surface soil [*Matsumoto et al.*, 2007]. Continent-derived organic carbon is believed to be a significant source of the organic matter in deep-sea sediments [*Gagosian and Peltzer*, 1986; *Kawamura*, 1995].

[19] It has been recognized that Asian soil dusts are transported long distances over the central North Pacific to North America [*Kawamura and Gagosian*, 1990; *Perry et al.*, 1999;

Table 2. Concentrations and Stable Carbon Isotopic Ratios ($\delta^{13}C$) of Fatty Acids in a Simulated Asian Dust Sample (CJ-2)

Fatty Acids	μg/g-dusts	$\delta^{13}C$ (‰)	Standard Deviation (1σ)
14	1.30	−22.5	1.2
15	0.63	−22.4	0.6
16	8.50	−24.2	0.1
17	0.51	−23.7	0.7
18	3.42	−24.1	0.5
19	0.17	−22.3	n.d.[a]
20	1.18	−25.9	0.9
21	0.26	−28.9	3.9
22	1.92	−26.9	0.2
23	0.55	−29.0	1.1
24	2.13	−27.1	0.6
25	0.34	−28.7	1.4
26	1.43	−28.3	0.7
27	0.32	−29.7	1.0
28	2.54	−30.1	0.6
29	0.31	−30.8	0.9
30	1.65	−29.2	0.6
31	0.21	−32.1	0.0
32	1.04	−30.7	1.0
Total	28.41		
CPI (C_{20} − C_{32})[b]	5.42		

[a]No data because of only one analysis.
[b]CPI (C_{20} − C_{32}) = [Σeven(C_{20} − C_{30})FA + Σeven(C_{22} − C_{32})FA]/2Σodd (C_{21} − C_{31})FA.

Table 3. The ^{14}C Data for Individual Fatty Acids in the Spring Aerosol Sample Collected in Sapporo, Northern Japan

Fatty Acids	Purity[a] (%)	$\Delta^{14}C$ (‰)	^{14}C Age (Years Before 1950)
16	100	123	modern
18	99	79	modern
20	98	46	modern
22	99	n.d.[b]	
24	99	−18	140
26	100	−71	590
28	100	−5	40
30+32	100	−100	820

[a]Purity was determined by GC-FID.
[b]Not determined. Approximately 50–240 μg of fatty acid methyl esters were used for ^{14}C measurements.

Cahill, 2003]. Thus, the old fatty acid $\geq C_{24}$ in the spring aerosols may be derived by long-range atmospheric transport of loess deposits that originated from the arid regions in Asia. It is of interest to note that the longest-chain fatty acids ($C_{30} + C_{32}$) show the oldest ^{14}C age of 819 years (Table 3). The longer-chain fatty acids could likely escape microbial degradation in the soils/sediments, and thus older carbon can survive more within the longer-chain acids. In contrast, shorter-chain acids are more easily decomposed in sediment/soil systems by microbial oxidation during early diagenesis [e.g., *Kawamura and Ishiwatari*, 1984]. The ^{14}C age of C_{28} acid was found to be younger than that of C_{26} (Table 3). This finding may suggest a contribution from contemporary sources to C_{28} species.

[20] The weight-averaged $\Delta^{14}C$ values of HMW fatty acids in the spring sample are compared with those of summer aerosol samples I and II (Table 4). The weight-averaged value of the spring aerosols was calculated to be −56‰, which is equivalent to Summer II sample (−63‰), but higher than that of Summer I sample (−243‰). These comparisons indicate that the HMW fatty acids in the spring and summer aerosols contain a different amount of old carbon. Summer I sample showed a larger depletion of ^{14}C possibly due to more contribution from geochemical reservoirs (soil organic matter) such as loess containing abundant dead carbon and a smaller contribution from northern Asian regions where fresh vegetations dominate. We presume that transport of dead carbon from loess deposits over northern Japan should be sporadic and event-dependent, as suggested by air mass trajectories (section 3.5).

[21] Because spring aerosols are associated with Asian soil dusts that often originate from arid regions in China and Mongolia, we initially expected to have more dead carbon components in the spring aerosols than the summer aerosols. Being different from the initial expectation, the spring aerosols did not clearly show a depletion of ^{14}C. Instead, they have modern carbon compositions that are dominated by HMW fatty acids. This study suggests that modern carbon that originated from vegetation in northeast China and Siberia largely contribute to the terrestrial fatty acids in the spring aerosols. In addition to ablation of leaf wax esters, biomass burning may be an important source for HMW fatty acids since levoglucosan (tracer of biomass burning) was detected abundantly in the Sapporo aerosol samples collected in August 2005 [*Agarwal et al.*, 2010]. Further, pollen may be emitted in spring and long-range transported over northern Japan. Pollen contains HMW fatty acids abundantly as coating wax; however, due to their large particle sizes they are efficiently scavenged from the atmosphere by dry deposition and are unlikely transported long distances. Alternatively, local vegetation may be the principal source of the C_3 vascular plant fatty acids because their pollen starts to emit in early April in Sapporo.

3.5. Backward Trajectory Analysis and Contribution of Dead Carbon

[22] In order to better understand the source region of aerosols, backward trajectory analysis was carried out as shown in Figure 5. The trajectories for the spring sample indicate that 62% of the source regions are in the Asian continent including Russia, Mongolia, Gobi desert, and northeast China (Figure 5a). In contrast, the Summer I trajectories show that the contribution from the Asian continent was only 27%, and most of the air masses originated from the western North Pacific (Figure 5b). This pattern is consistent with the higher concentrations of C_{16} and C_{18} fatty acids in the Summer I sample (Figure 2), which are abundant in marine phytoplankton. This study may indicate that HMW fatty acids derived from Asian arid regions are not significant in Summer I sample although their concentrations are higher in both Summer I and II aerosols than spring aerosols (Figure 2). On the other hand, the backward trajectories for Summer II sample (Figure 5c) suggest that contribution of terrestrial higher plants from the Asian continent is small (21%) and the rest (79%) originates mainly from Hokkaido Island and the adjacent oceans.

[23] Although the spring aerosols mostly originated from the Asian continent, the dead carbon in the HMW fatty acids seems to be less significant in the spring than the summer samples (Table 4). Based on $\Delta^{14}C$ values (Table 3), we calculated the contribution of dead carbon to individual HMW fatty acids assuming that $\Delta^{14}C$ value = 0‰ for modern carbon in 1950 [*Kanke et al.*, 2004]. The contributions of dead carbon in the spring aerosols are 1.8% (C_{24}), 7.1% (C_{26}), 0.5% (C_{28}) and 9.7% ($C_{30} + C_{32}$). The values are fairly variable and are sometimes lower than those calculated for summer samples; 52% ($C_{24} + C_{26}$) and 3.3% ($C_{28} + C_{30} + C_{32}$) in Summer I aerosols and 1.2% ($C_{24} + C_{26}$) and 8.9% ($C_{28} + C_{30} + C_{32} + C_{34}$) in Summer II aerosols. These results may suggest that, although contribution of components containing dead carbon is highly variable depending upon meteorological conditions in the source regions, their contribution to the spring aerosols is rather insignificant. Instead,

Table 4. Weight Averages of $\Delta^{14}C$ Values Calculated for Higher Molecular Weight Fatty Acids[a]

Aerosol Sample	Identification Number	Fatty Acids	$\Delta^{14}C$ Weight Average (‰)
Spring (30 March to 29 April 2001)	QFF2048	$C_{24} - C_{32}$	−56
Summer I (18 June to 2 July 1999)	QFF1969	$C_{24} - C_{32}$	−243
Summer II (1–21 June 2001)	QFF2138	$C_{24} - C_{34}$	−63

[a]Data for Summer I and II samples are from *Matsumoto et al.* [2001] and *Matsumoto et al.* [2004], respectively.

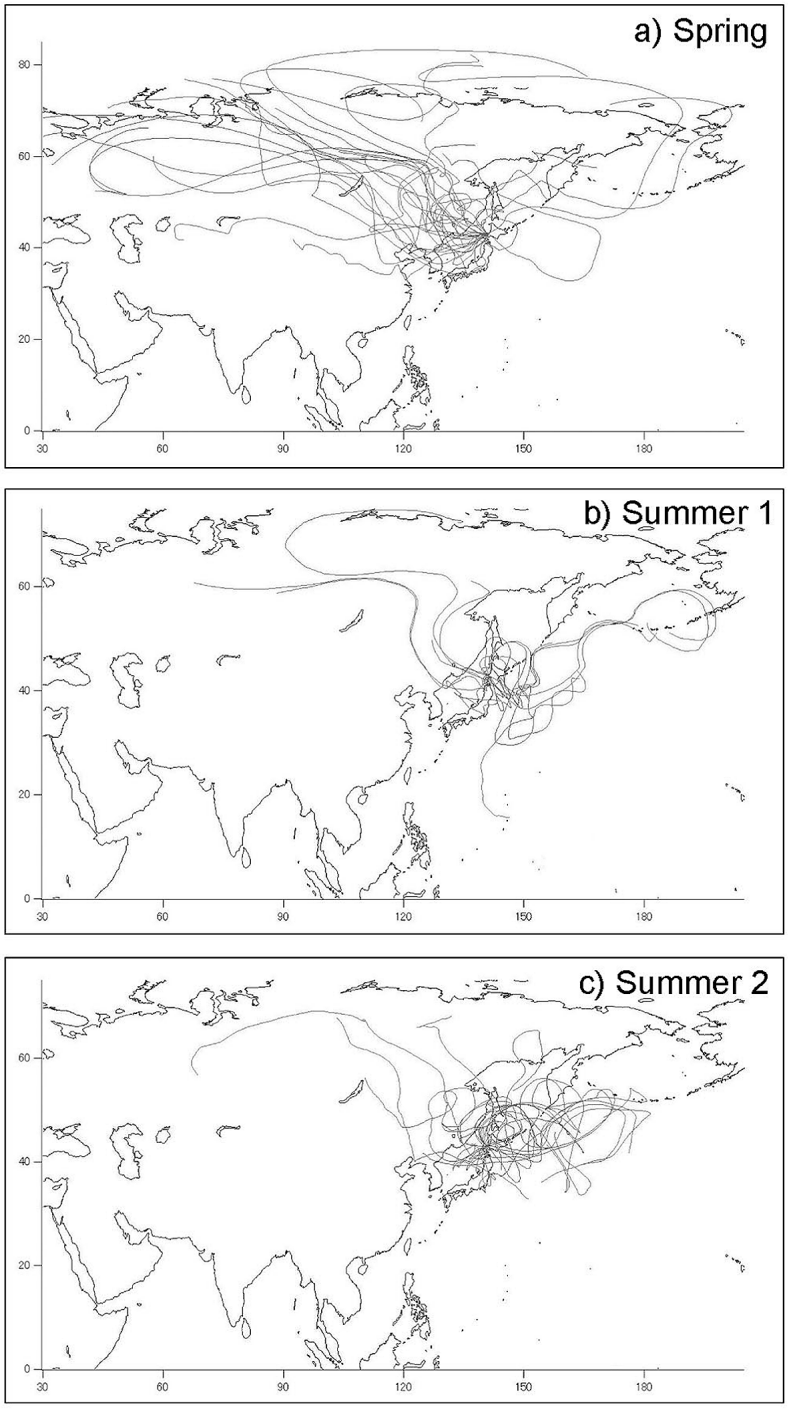


Figure 5. Results of 10 day air mass backward trajectory analyses for (a) spring (30 March to 29 April 2001), (b) Summer I (1–21 June 2001), and (c) Summer II (18 June to 2 July 1999) samples collected in northern Japan.

modern carbon significantly dominates the terrestrial fatty acids in the spring aerosols.

4. Summary and Conclusions

[24] We measured radiocarbon contents of individual fatty acids in the aerosol sample collected for a month (April) in Sapporo, northern Japan, when a strong Asian dust episode was observed. Their molecular distribution and stable carbon isotopic compositions were also measured. The results of the spring aerosols were compared with those of summer aerosol samples collected in the same location, together with a simulated dust sample prepared from Chinese loess deposits (CJ-2). We found similarities in the molecular distributions and stable carbon isotopic compositions between the spring aerosol and loess deposit samples, suggesting that the fatty

acids in the spring aerosols from Sapporo are influenced by the Asian dusts that originated from arid regions in China and vegetation in Siberia and North China. This conclusion is consistent with the results of air mass backward trajectory analyses for the sample.

[25] The measurements of $\Delta^{14}C$ in individual fatty acids in the spring aerosols showed that C_{16}, C_{18} and C_{20} fatty acids are composed predominantly of modern carbon and contribution of dead carbon is rather negligible. In contrast, HMW fatty acids such as C_{24}, C_{26}, C_{28}, C_{30} and C_{32} were found to contain dead carbon to varying degrees. In particular, averaged ^{14}C ages of C_{26}, C_{30} and C_{32} fatty acids were calculated to be 589–819 years old. The contribution of dead carbon to the HMW fatty acid carbon was calculated to be up to 9.7% of the carbon mass and the rest (>90.3%) is modern carbon. This study clearly demonstrates that the spring aerosols collected during the Asian dust season in northern Japan contain old organic carbon that probably originated from the loess deposits in the arid regions of China, an important geochemical reservoir of dead carbon in the form of higher plant waxes. However, the old components are diluted by modern material from contemporary higher plants and their debris in soils.

[26] Although contributions of dead carbon are not significant, old organic carbon may be sporadically transported from the loess deposit region in Asia over the western North Pacific. However, we consider that major portion of HMW fatty acids in spring aerosols is largely derived from modern terrestrial plant sources such as leaf waxes, biomass burning, pollen and their recent soil remains in central and north China and Siberia as well as local sources.

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References

Agarwal, S., S. G. Aggarwal, K. Okuzawa, and K. Kawamura (2010), Size distributions of dicarboxylic acids, ketoacids, α-dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in atmospheric particles over northern Japan: Implication for long-range transport of Siberian biomass burning and East Asian polluted aerosols, *Atmos. Chem. Phys.*, *10*, 5839–5858, doi:10.5194/acp-10-5839-2010.

Aggarwal, S. G., and K. Kawamura (2008), Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for photochemical aging during long-range atmospheric transport, *J. Geophys. Res.*, *113*, D14301, doi:10.1029/2007JD009365.

Bendle, J., K. Kawamura, K. Yamazaki, and T. Niwai (2007), Latitudinal distribution of terrestrial lipid biomarkers and n-alkane compound-specific stable carbon isotope ratios in the atmosphere over the western Pacific and Southern Ocean, *Geochim. Cosmochim. Acta*, *71*, 5934–5955, doi:10.1016/j.gca.2007.09.029.

Cahill, C. F. (2003), Asian aerosol transport to Alaska during ACE-Asia, *J. Geophys. Res.*, *108*(D23), 8664, doi:10.1029/2002JD003271.

Chikaraishi, Y., and H. Naraoka (2005), $\delta^{13}C$ and δD identification of sources of lipid biomarkers in sediments of Lake Haruna (Japan), *Geochim. Cosmochim. Acta*, *69*, 3285–3297, doi:10.1016/j.gca.2005.02.023.

Chikaraishi, Y., H. Naraoka, and S. R. Poulson (2004), Hydrogen and carbon isotopic fractionations of lipid biosynthesis among terrestrial (C_3, C_4 and CAM) and aquatic plants, *Phytochemistry*, *65*, 1369–1381, doi:10.1016/j.phytochem.2004.03.036.

Conte, M. H., and J. C. Weber (2002), Long-range atmospheric transport of terrestrial organic biomarkers to the western North Atlantic, *Global Biogeochem. Cycles*, *16*(4), 1142, doi:10.1029/2002GB001922.

Dahl, K. A., D. W. Oppo, T. I. Eglinton, K. A. Hughen, W. B. Curry, and F. Sirocko (2005), Terrigenous plant wax inputs to the Arabian Sea: Implications for the reconstruction of winds associated with the Indian Monsoon, *Geochim. Cosmochim. Acta*, *69*, 2547–2558, doi:10.1016/j.gca.2005.01.001.

Drenzek, N. J., D. B. Montluçon, M. B. Yunker, R. W. Macdonald, and T. I. Eglinton (2007), Constraints on the origin of sedimentary organic carbon in the Beaufort Sea from coupled molecular ^{13}C and ^{14}C measurements, *Mar. Chem.*, *103*, 146–162, doi:10.1016/j.marchem.2006.06.017.

Eglinton, G., and R. J. Hamilton (1967), Leaf epicuticular waxes, *Science*, *156*, 1322–1335, doi:10.1126/science.156.3780.1322.

Eglinton, T. I., L. I. Aluwihare, J. E. Bauer, E. R. M. Druffel, and A. P. McNichol (1996), Gas chromatographic isolation of individual compounds from complex matrices for radiocarbon dating, *Anal. Chem.*, *68*, 904–912, doi:10.1021/ac9508513.

Fang, J., K. Kawamura, Y. Ishimura, and K. Matsumoto (2002), Carbon isotopic composition of fatty acids in the marine aerosols from the western North Pacific: Implication for the source and atmospheric transport, *Environ. Sci. Technol.*, *36*, 2598–2604, doi:10.1021/es015863m.

Fu, P., K. Kawamura, K. Okuzawa, S. G. Aggarwal, G. Wang, Y. Kanaya, and Z. Wang (2008), Molecular characteristics, sources and temporal variations of summertime organic aerosols in the troposphere over Mt. Tai, North China Plain, *J. Geophys. Res.*, *113*, D19107, doi:10.1029/2008JD009900.

Gagosian, R. B., and E. T. Peltzer (1986), The importance of atmospheric input of terrestrial organic material to deep sea sediments, *Org. Geochem.*, *10*, 661–669, doi:10.1016/S0146-6380(86)80002-X.

Guo, Z. G., L. F. Sheng, J. L. Feng, and M. Fang (2003), Seasonal variation of solvent extractable organic compounds in the aerosols in Qingdao, China, *Atmos. Environ.*, *37*, 1825–1834, doi:10.1016/S1352-2310(03)00064-5.

Hua, Q., and M. Barbetti (2004), Review of tropospheric bomb ^{14}C data for carbon cycle modeling and age calibration purposes, *Radiocarbon*, *46*, 1273–1298.

Huebert, B. J., T. Bates, P. B. Russell, G. Shi, Y. J. Kim, K. Kawamura, G. Carmichael, and T. Nakajima (2003), An overview of ACE-Asia: Strategies for quantifying the relationships between Asian aerosols and their climatic impacts, *J. Geophys. Res.*, *108*(D23), 8633, doi:10.1029/2003JD003550.

Irino, T., and R. Tada (2000), Quantification of aeolian dust (Kosa) contribution to the Japan Sea sediments and its variation during the last 200 ky, *Geochem. J.*, *34*, 59–93.

Kanke, H., M. Uchida, T. Okuda, M. Yoneda, H. Takada, Y. Shibata, and M. Morita (2004), Compound-specific radiocarbon analysis of polycyclic aromatic hydrocarbons (PAHs) in sediments from an urban reservoir, *Nucl. Instrum. Methods, Sect. B*, *223–224*, 545–554.

Kawamura, K. (1995), Land-derived lipid class compounds in the deep-sea sediments and marine aerosols from North Pacific, in *Biogeochemical Processes and Ocean Flux in the Western Pacific*, edited by H. Sakai and Y. Nozaki, pp. 31–51, Terra Sci., Tokyo.

Kawamura, K., and R. B. Gagosian (1990), Atmospheric transport of soil-derived dicarboxylic acids over North Pacific Ocean, *Naturwissenschaften*, *77*, 25–27, doi:10.1007/BF01131790.

Kawamura, K., and R. Ishiwatari (1984), Fatty acid geochemistry of a 200-meter sediment core from Lake Biwa, Japan, *Geochim. Cosmochim. Acta*, *48*, 251–266, doi:10.1016/0016-7037(84)90249-7.

Kawamura, K., Y. Ishimura, and K. Yamazaki (2003), Four years' observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific, *Global Biogeochem. Cycles*, *17*(1), 1003, doi:10.1029/2001GB001810.

Kawamura, K., M. Kobayashi, N. Tsubonuma, M. Mochida, T. Watanabe, and M. Lee (2004), Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in *Geochemical Investigation in Earth and Space Science: A Tribute to Issac R. Kaplan*, *Geochem. Soc. Publ. Ser.*, vol. 9, edited by R. J. Hill et al., pp. 243–265, Elsevier Sci., New York.

Kyotani, T., S. Koshimizu, and H. Kobayashi (2005), Short-term cycle of eolian dust (Kosa) recorded in Lake Kawaguchi sediments, central Japan, *Atmos. Environ.*, *39*, 3335–3342, doi:10.1016/j.atmosenv.2005.01.026.

Levin, I., and B. Kromer (1997), Twenty years of atmospheric $^{14}CO_2$ observations at Schauinsland Station, Germany, *Radiocarbon*, *39*, 205–218.

Lichtfouse, É. (2000), Compound-specific isotope analysis (CSIA). Application to archaeology, biomedical sciences, biosynthesis, environment, extraterrestrial chemistry, food science, forensic science, humic substances, microbiology, organic geochemistry, soil science and sport, *Rapid Comm. Mass Spectrom.*, *14*(15), 1337–1344, doi:10.1002/1097-0231(20000815)14:15<1337::AID-RCM9>3.0.CO;2-B.

Lichtfouse, É., G. Bardoux, A. Mariotti, J. Balesdent, D. C. Ballentine, and S. A. Macko (1997), Molecular, ^{13}C, and ^{14}C evidence for the allochthonous and ancient origin of C_{16}-C_{18} n-alkanes in modern soils, *Geochim. Cosmochim. Acta*, *61*, 1891–1898, doi:10.1016/S0016-7037(97)00021-5.

Matsumoto, K., K. Kawamura, M. Uchida, Y. Shibata, and M. Yoneda (2001), Compound specific radiocarbon and $\delta^{13}C$ measurements of fatty acids in a continental aerosol sample, *Geophys. Res. Lett.*, *28*, 4587–4590, doi:10.1029/2001GL013599.

Matsumoto, K., M. Uchida, K. Kawamura, Y. Shibata, and M. Morita (2004), Radiocarbon variability of fatty acids in semi-urban aerosol samples, *Nucl. Instrum. Methods, Sect. B*, *223–224*, 842–847.

Matsumoto, K., K. Kawamura, M. Uchida, and Y. Shibata (2007), Radiocarbon content and stable carbon isotopic ratios of individual fatty acids in subsurface soil: Implication for selective microbial degradation and modification of soil organic matter, *Geochem. J.*, *41*, 483–492.

Mochida, M., N. Umemoto, K. Kawamura, H. Lim, and B. J. Turpin (2007), Bimodal size distributions of various organic acids and fatty acids in the marine atmosphere: Influence of anthropogenic aerosols, Asian dusts, and sea spray off the coast of East Asia, *J. Geophys. Res.*, *112*, D15209, doi:10.1029/2006JD007773.

Mori, I. M., M. Nishikawa, H. Quan, and M. Morita (2002), Estimation of the concentration and chemical composition of Kosa aerosols at their origin, *Atmos. Environ.*, *36*, 4569–4575, doi:10.1016/S1352-2310(02)00489-2.

Naraoka, H., and R. Ishiwatari (2000), Molecular and isotopic abundances of long chain *n*-fatty acids in open marine sediments of the western North Pacific, *Chem. Geol.*, *165*, 23–36, doi:10.1016/S0009-2541(99)00159-X.

Nishikawa, M., Q. Hao, and M. Morita (2000), Preparation and evaluation of certified reference materials from Asian mineral dust, *Global Environ. Res.*, *4*, 103–113.

Ohkouchi, N., K. Kawamura, H. Kawahata, and A. Taira (1997), Latitudinal distributions of terrestrial biomarkers in the sediments from the central Pacific, *Geochim. Cosmochim. Acta*, *61*, 1911–1918, doi:10.1016/S0016-7037(97)00040-9.

Perry, K., D. Cahill, A. Thomas, R. C. Schnell, and J. M. Harris (1999), Long-range transport of anthropogenic aerosols to the National Oceanic and Atmospheric Administration baseline station at Mauna Loa Observatory, Hawaii, *J. Geophys. Res.*, *104*(D15), 18,521–18,533, doi:10.1029/1998JD100083.

Simoneit, B. R. T., G. Sheng, X. Chen, J. Fu, J. Sheng, and Y. Xu (1991), Molecular marker of extractable organic matter in aerosols from urban areas of China, *Atmos. Environ., Part A*, *25*, 2111–2129.

Simoneit, B. R. T., M. Kobayashi, M. Mochida, K. Kawamura, and B. J. Huebert (2004), Aerosol particles collected on aircraft flights over the northwestern Pacific region during the ACE-Asia campaign: Composition and major sources of the organic compounds, *J. Geophys. Res.*, *109*, D19S09, doi:10.1029/2004JD004565.

Smittenberg, R. H., T. I. Eglinton, S. Schouten, and J. S. Sinninghe Damsté (2006), Ongoing buildup of refractory organic carbon in boreal soils during the Holocene, *Science*, *314*, 1283–1286, doi:10.1126/science.1129376.

Tsai, Y. I., and C.-L. Chen (2006), Characterization of Asian dust storm and non-Asian dust storm $PM_{2.5}$ aerosol in southern Taiwan, *Atmos. Environ.*, *40*, 4734–4750, doi:10.1016/j.atmosenv.2006.04.038.

Uchida, M., Y. Shibata, K. Kawamura, M. Yoneda, A. Tanaka, T. Uehiro, and M. Morita (2000), Isolation of individual fatty acids from sediments for radiocarbon analysis using preparative capillary gas chromatography (PCGC) at NIES-TERRA, *Nucl. Instrum. Methods, Sect. B*, *172*, 583–588.

Uchida, M., Y. Shibata, M. Yoneda, T. Kobayashi, and M. Morita (2004), Technical progress in AMS microscale radiocarbon analysis, *Nucl. Instrum. Meth., Sect. B*, *223*, 313–317.

Uchida, M., Y. Shibata, K. Ohkushi, M. Yoneda, K. Kawamura, and M. Morita (2005), Age discrepancy between molecular biomarkers and calcareous foraminifera isolated from the same horizons of Northwest Pacific sediments, *Chem. Geol.*, *218*, 73–89, doi:10.1016/j.chemgeo.2005.01.026.

Wang, G., K. Kawamura, S. C. Lee, K. Ho, and J. Cao (2006), Molecular, seasonal and spatial distribution of organic aerosols from fourteen Chinese cities, *Environ. Sci. Technol.*, *40*, 4619–4625, doi:10.1021/es060291x.

Yano, I., Y. Furukawa, and M. Kusunose (1971), α-Oxidation of long chain fatty acids in cell free extracts of Arthrobacter simplex, *Biochim. Biophys. Acta*, *239*, 513–516.

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