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Compound specific radiocarbon and $\delta^{13}\text{C}$ measurements of fatty acids in a continental aerosol sample

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Abstract. Compound-specific radiocarbon analysis of individual fatty acids was conducted for a semi-urban aerosol sample using a preparative capillary gas chromatography (PCGC) system and an accelerator mass spectrometry (AMS). The aerosol fatty acids (C_{16} to C_{34}) showed a typical bimodal distribution with two maxima at C_{16} and C_{26} . Their carbon isotopic compositions ranged from -30.3‰ (C_{26}) to -23.3‰ (C_{18}), suggesting that they are derived from terrestrial higher plants and marine sources. Radiocarbon measurements of C_{16} - C_{22} fatty acids showed modern ^{14}C ages, suggesting that the acids are emitted from living higher plants and possibly from marine organisms. On the other hand, C_{24} - C_{26} fatty acids that are characteristic to terrestrial plant waxes showed ^{14}C ages of 5860 (± 200) years. This suggests that some portion of higher molecular weight fatty acids have been stored in geochemical reservoirs such as soils at least for hundreds to thousands of years and then emitted to the atmosphere. These aged fatty acids could be in part transported long distances from the Asian continent through the atmosphere.

1. Introduction

Fatty acids are ubiquitous in environmental samples including aerosols [Simoneit et al., 1977], rain/snow [Kawamura et al., 1996a], soils [e.g. Schnitzer and Neyroud, 1975], and lake [e.g. Kawamura et al., 1981] and marine sediments [e.g. Volkman et al., 1980]. They are biosynthesized by different types of organisms such as marine phytoplankton, terrestrial higher plants and bacteria [e.g. Bradshaw and Eglinton, 1993] and have been frequently used as biomarkers in the fields of atmospheric chemistry and organic geochemistry. Previous studies of aerosols have shown that distribution of fatty acids are characterized by even carbon numbered predominance with two peaks at C_{16} and C_{24} or C_{26} [Simoneit et al., 1977; Kawamura, 1995]. Lower molecular weight fatty acids (C_{16} , C_{18}) are mainly derived from marine organisms as well as terrestrial higher plants, whereas higher molecular weight fatty acids ($>\text{C}_{20}$) are more specific to terrestrial higher plant waxes [e.g. Gagosian et al., 1982]. Thus, fatty acids are useful indicators to evaluate the relative contribution from marine and terrestrial sources to the atmosphere [Simoneit et al., 1977; Gagosian et al., 1982; Kawamura, 1995] and to the pelagic sediments [Ohkouchi et al.,

1997].

In addition to the source information based on the organic molecular composition, we can extract additional information from their radiocarbon concentration, that is, the age of organic compounds after their photosynthetic production, by measuring ^{14}C concentration. Recently, compound specific radiocarbon analysis (CSRA) has become available in the field of environmental geochemistry [Eglinton et al., 1996]. Eglinton et al. [1997] showed that sedimentary alkanes gave a diversity of ^{14}C ages even in a same layer of sediments. Uchida et al. [2000] measured ^{14}C ages for individual fatty acids separated from the surface sediments of Tokyo Bay and reported that some higher molecular weight fatty acids such as C_{22} are old (up to 17 thousands years), although most abundant palmitic acid (C_{16}) showed modern age. These studies demonstrated that the diversity of ^{14}C ages for fatty acids is significant even in the same geochemical sample. This knowledge, however, suggests that the diversity of ^{14}C ages in the same compound class may provide further information on the transport mechanism of organic matter from the source region to the sampling areas.

In this study, we conducted the CSRA study for fatty acids separated from the continental aerosols collected from semi-urban area. We present here the ^{14}C ages of individual and/or group of fatty acids and discuss the ^{14}C results in terms of transport process and source regions. Atmospheric aerosols are now recognized to carry the continental materials over the remote oceans [Gagosian et al., 1982].

2. Sample and Method

An aerosol sample was collected using a pre-combusted quartz fiber filter (QFF 1969) on the roof of Institute of Low Temperature Science (15 m above the ground), Hokkaido University, from 18 June 1999 to 2 July 1999. Total air volume and the collected aerosol mass were 21470 m^3 and 0.894 g, respectively. The aerosols were extracted with CH_2Cl_2 / methanol (2:1, 100 ml, 3 times). The extracts were concentrated and saponified with 0.5M KOH / methanol (100 ml, 90°C, 1 h). After neutrals were removed, fatty acids were extracted with CH_2Cl_2 under pH \sim 1 condition. The acidic fraction was methylated with 14% BF_3 / methanol and then monocarboxylic (fatty) acid methyl esters were separated using silica-gel column chromatography. An aliquot of the methyl ester fraction was analyzed using a Carlo Erba 5160 mega series GC equipped with on-column injector and a HP-5 fused silica capillary column (30 m x 0.32 mm i.d. film thickness 0.25 μm). Hydrogen was used as carrier gas and the oven temperature was programmed from 70 to 120°C at 30°C min^{-1} , to 320°C at 6°C min^{-1} and held at 320°C for 20 min.

In order to isolate large quantities of individual fatty acids that are needed to determine ^{14}C ages using AMS, we employed a preparative GC system equipped with automated 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 injection was repeated 60 times through the PCGC operation. The CIS is programmed from 25°C (0.5 min) to 300°C at 12°C sec^{-1} and held at 300°C for 2 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 $3^{\circ}\text{C min}^{-1}$ and then held at 310°C for 20 min. Individual compounds were separated on a HP-5 fused silica megabore column (30 m x 0.53 mm i.d. film thickness 1.0 μm). Helium was used as carrier gas.

GC chromatograms of fatty acid methyl esters before and after PCGC injection are shown in Fig. 1a and Fig. 1b-f, respectively. Because $\text{C}_{20}\text{-C}_{32}$ fatty acids were not abundant enough to perform the AMS measurement for individuals, some target fatty acids are combined into the U tubes of the PFC as one fraction such as C_{20} plus C_{22} , C_{24} plus C_{26} , and C_{28} , C_{30} plus C_{32} (see Fig. 1). After the PCGC separation, fatty acid methyl esters were purified on a silica-gel column by eliminating the methyl silicone contaminants that eluted from the GC column liquid phase. We confirmed that amounts of C_{16} , $\text{C}_{18}\text{-C}_{22}$, $\text{C}_{24}\text{-C}_{26}$ and $\text{C}_{28}\text{-C}_{32}$ fatty acid fractions were more than 100 μg by GC analysis.

Fatty acid fractions were combusted to CO_2 in a quartz tube encasing CuO, Cu, Ag and purified fatty acid methyl esters. Refined CO_2 were then converted to graphite carbon target. ^{14}C in the graphite target was measured using AMS facility (NIES-TERRA) at National Institute for Environmental Studies, Tsukuba, Japan [Uchida et al., 2000]. To calculate ^{14}C values of fatty acids, we corrected the value of esters using a simple mass balance equation amongst ^{14}C values of fatty acid, methyl group of the derivative reagent ($\text{BF}_3/\text{methanol}$, $^{14}\text{C} = -998\text{‰}$) and their methyl ester.

Stable carbon isotope ratios were determined using a Finnigan MAT delta-plus mass spectrometer interfaced to a HP 6890 GC and a combustion reactor. Individual fatty acid methyl esters were separated using a HP-5 fused silica capillary column (60 m x 0.32 mm i.d. film thickness 0.25 μm) with an on-column injector. The GC oven was programmed from 50°C to 120°C at $30^{\circ}\text{C min}^{-1}$, then to 310°C at $3^{\circ}\text{C min}^{-1}$ and held at 310°C for 20 min. The combustion reactor, which was encased with fine CuO and Pt wires as catalysts, was held at 850°C . $^5\text{-cholestane}$, whose ^{13}C value had been independently determined, was co-injected as internal isotopic standard. The ^{13}C corrections from fatty acid methyl esters to fatty acids are calculated by a mass balance equation using ^{13}C value ($-46.32 \pm 0.14\text{‰}$) of methanol.

3. Results and Discussion

Table 1 gives abundances and ^{13}C values of fatty acids in the aerosol sample. The fatty acids showed bimodal distribution with two peaks at C_{16} and C_{26} . This distribution pattern is typical for the aerosol samples collected from continents and oceans [e.g. Simoneit et al., 1977, Kawamura, 1995, Zheng et al., 2000]. Orders of the fatty acid concentrations in the aerosols from Sapporo are equal to those from Hong Kong [Zheng et al., 2000].

The ^{13}C values ranged from -30.3‰ (C_{26}) to -23.3‰ (C_{18}). These results suggest that $\text{C}_{16}\text{-C}_{18}$ fatty acids (-24.3 to -23.3‰) may be derived mainly from marine organisms with lesser contribution from terrestrial plants, whereas $\text{C}_{24}\text{-C}_{34}$ fatty acids (-27.9 to -30.3‰) are derived from terrestrial C_3 higher plants. These interpretations are consistent with the direct and indirect evidences of ^{13}C values for various geochemical samples. For example, ^{13}C values for C_{16} and C_{18} fatty acids in marine algae range from -25.0 to -20.5‰ ($[\text{CO}_2]_{\text{aq}}$ up to $14.5\text{ }\mu\text{M}$, which is typical concentration in the open ocean; Riebesell et al., 2000).

^{13}C values for C_{16} and C_{18} fatty acids in terrestrial higher plants

range from -36.0 to -35.1 ‰ [C₃ plants; Ballentine et al., 1998]. On the other hand, ¹³C value for C₂₄ fatty acid of terrestrial higher plants is -33.8 ‰ [Ballentine et al., 1998]. Contributions of C₄ plants to the present aerosol fatty acids should be low because ¹³C values for C₂₄ fatty acids in C₄ plants are much heavier than those of the aerosol sample used in this study [C₂₄-C₃₄ fatty acids of *Zea Mays*: -24.9 to -20.8 ‰; Matsumoto et al., unpublished data].

Table 2 gives the purities of each fatty acid after the separation with PCGC, and their ¹⁴C values and ¹⁴C ages for the aerosol sample. The purity of individual fatty acids ranged from 98 % to 100 %, except for C₂₈-C₃₂ fatty acid fraction (94 %). We report here, for the first time, ¹⁴C ages of individual fatty acids in atmospheric aerosols. The results showed that ¹⁴C ages of the fatty acids have a wide diversity. The ¹⁴C ages of C₁₆ fatty acid and the mixture of C₁₈, C₂₀ and C₂₂ fatty acids gave modern carbon values, suggesting that these acids are emitted from microlayers of seawater surfaces that contain abundant fatty acids of phytoplankton and bacterial origin [Kawamura et al., 1996a]. On the other hand, ¹⁴C ages for the mixtures of C₂₄ and C₂₆ fatty acids and C₂₈, C₃₀ and C₃₂ fatty acids are 5900 and 270 years, respectively. Those ¹⁴C ages indicate that higher molecular weight fatty acids in the aerosols were not emitted directly from living terrestrial higher plants, but have been stored in certain reservoirs for hundreds to thousands years.

Soils are most likely candidate of reservoir for long chain fatty acids of leaf wax origin because they receive many litters from trees and other higher plants and store them as soil organic matter for geological time. The soil organic matter that is exposed to the air can be emitted to the atmosphere as wind blown dusts. However, CSRA measurements of fatty acids isolated from the soils collected near the sampling site showed that the fatty acid carbons are all modern [Matsumoto et al., unpublished data]. This indicates that the aged fatty acids detected in the present aerosol sample are not supplied from the local soil sources.

Alternatively, it is likely that aged fatty acids can be transported from the Asian continent over the sampling site because Asian dusts are well known to be transported frequently over the Pacific during spring to early summer [Duce et al., 1981, Gagosial et al., 1982]. Kawamura et al. [1996b] analyzed the arctic aerosols and reported that the concentrations of long chain dicarboxylic acids largely increased between April and May. Their molecular distributions are characterized by relatively low even/odd ratios, which are different from those of fresh soils, but are similar to aged soils such as Chinese loess. Although the arctic aerosol study suggested a long-range atmospheric transport of Asian dust, the atmospheric transport of Chinese loess from Asia over Japan should be more significant than over the Arctic. Thus, we consider that the atmospheric input of biogenic but old fatty acid carbon by wind blown dusts in Asian arid regions would be the likely source for the aged fatty acids in the aerosols collected over the Japanese Islands.

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Figure 1. Capillary gas chromatograms of fatty acid methyl esters separated from semi-urban aerosols, (a) before PCGC

analysis and (b-f) after purification using PCGC. The numbers superimposed on the chromatograms are carbon numbers of the fatty acids.

Table 1. Concentrations and carbon isotopic compositions for individual fatty acids in a semi-urban aerosol sample.

Carbon number	concentration (ng/m ³)	¹³ C (‰)	1 (‰)
16	22.3	-24.3	0.1
17	0.5	-24.5	0.6
18	10.2	-23.3	0.1
19	0.3	-25.8	0.2
20	4.1	-28.1	0.4
21	0.7	-27.9	0.8
22	5.6	-29.0	0.2
23	0.8	-28.9	0.5
24	7.0	-29.4	0.2
25	0.9	-28.4	0.0
26	7.6	-30.3	0.2
27	1.7	-29.7	0.7
28	5.1	-27.9	0.1
29	2.8	-26.1	1.2
30	2.4	-30.2	0.3
31	0.6	-32.0	2.6
32	3.2	-27.9	0.2
33	tr.*	tr.*	
34	1.7	-30.2	1.5

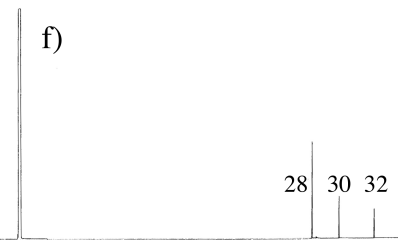
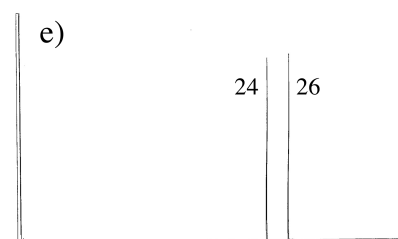
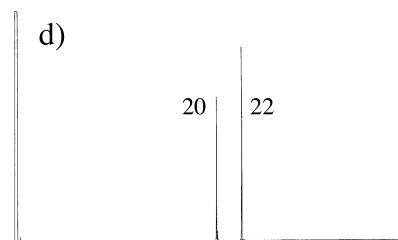
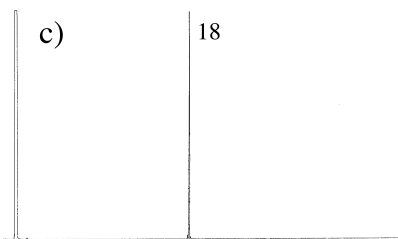
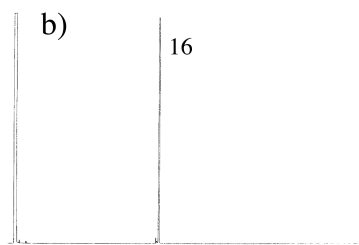
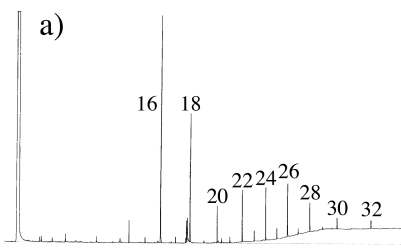
*trace.

Table 2. The ¹⁴C data for individual fatty acids in semi-urban aerosol sample.

Fraction (Carbon number of fatty acid)	Purity (%)*	yield (µg C)**	¹⁴ C (‰)	¹⁴ C Age (yrs. BP)	1 (yrs.)
C ₁₆	98	124	407	modern	98
C ₁₈ +C ₂₀ +C ₂₂	99	175	44.1	modern	132
C ₂₄ +C ₂₆	100	164	-518	5860	200
C ₂₈ +C ₃₀ +C ₃₂	94	134	-33	271	120

*Purity was determined when the individual fatty acids are obtained by PCGC system.

**yields calculated based on GC analyses of individual fatty acid fractions by PCGC analyses.



0 10 20 30 40
Retention time (min.)