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Compound-specific stable carbon and hydrogen isotopic compositions of *n*-alkanes in urban atmospheric aerosols from Tokyo

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Stable carbon ($\delta^{13}C$) and hydrogen (δD) isotopic compositions of *n*-alkanes in total suspended particles from Tokyo were measured to decipher their source and transport in the polluted urban atmosphere. The $\delta^{13}C$ and δD values of the C_{21} to C_{33} *n*-alkanes ranged from –25.5 to –32.8‰ and –55 to –157‰, respectively. The $\delta^{13}C$ values are within the range of those in terrestrial higher plants and fossil fuel. In contrast, the δD values of the C_{21} to C_{24} *n*-alkanes and the C_{26} to C_{32} even-carbon numbered *n*-alkanes are in the range of those typical to marine crude oil, indicating that these *n*-alkanes are primarily derived from the anthropogenic emission of petroleum hydrocarbons. Lower δD values were found in the C_{25} to C_{33} odd-carbon numbered *n*-alkanes than other homologues, suggesting that the long chain *n*-alkanes are significantly contributed from terrestrial higher plant waxes in addition to fossil fuel hydrocarbons. The δD values of the C_{29} and C_{31} *n*-alkanes show a strong negative correlation with CPI (carbon preference index), which enable us to eliminate fossil fuel contribution using a mass balance approach. Large seasonal variations in the δD values corrected for fossil fuel contribution and their relation to seasonal differences in air mass transport suggest that terrestrial higher plant-derived *n*-alkanes in the Tokyo aerosols likely originate from the raw leaves of local vegetation. The corrected δD values based on CPI of 10 are in good agreement with those in contemporary vegetation in Tokyo, indicating that local vegetation is more important as a source of terrestrial higher plant-derived *n*-alkanes in the polluted urban atmosphere.

Keywords: δD, $\delta^{13}C$, *n*-alkane, urban aerosols, Tokyo

INTRODUCTION

Homologous series of *n*-alkanes are ubiquitous in geochemical samples including atmospheric aerosols (Simoneit *et al.*, 1977). These *n*-alkanes are directly emitted from biological and anthropogenic sources to result in primary organic aerosols because of their chemical stability and low vapor pressure. In general, *n*-alkanes ranging from C_{10} to C_{35} with no carbon number preference are commonly found in fossil fuels and their combustion residues (Brassell *et al.*, 1978; Simoneit, 1984), whereas C_{25} to C_{35} *n*-alkanes with a strong odd carbon number predominance are the major components of terrestrial higher plant waxes (Eglinton and Hamilton, 1967).

Carbon number predominance of *n*-alkanes are usually expressed using the carbon preference index (CPI), which is defined as $\mathrm{CPI} = 0.5 \times [\Sigma(C_{25} - C_{35})_{odd}/\Sigma(C_{24} - C_{34})_{even} + \Sigma(C_{25} - C_{35})_{odd}/\Sigma(C_{26} - C_{36})_{even}]$, where C is abundance of each *n*-alkane (Bray and Evans, 1961). The CPI values of higher plant wax *n*-alkanes are generally >5, and the *n*-alkanes in soil and immature sediment also show similar CPI values if there is no serious input from pollutant. However, the values tend to decrease down to 1.0 in matured sediment and petroleum that generate *n*-alkanes with no carbon number preference during diagenesis and catagenesis. Hence, the CPI values are often used to identify specific sources of *n*-alkanes and to estimate relative contributions from higher plant waxes (CPI > 5) and fossil fuel hydrocarbons (CPI = 1; Simoneit and Mazurek, 1982; Kawamura and Kaplan, 1991) to atmospheric particles (Simoneit and Mazurek, 1982; Simoneit *et al.*, 1988; Kawamura *et al.*, 2003; Schefuß *et al.*, 2003; Simoneit *et al.*, 2004).

Stable carbon isotopic composition ($\delta^{13}C$) of long chain *n*-alkanes in atmospheric aerosols provides additional information on their sources (Simoneit, 1997). This is because the $\delta^{13}C$ values of terrestrial higher plant-derived *n*-alkanes are sensitive to the plant types from which they originate due to the isotopic differences (up to 20‰) between C_3 and C_4 photosynthetic carbon fixation pathways (Collister *et al.*, 1994). Indeed, studies on the $\delta^{13}C$ of *n*-alkanes in aerosols have revealed long-range atmospheric transport of varying amount of C_3 and C_4 plant materials over the Atlantic and the western Pacific (Conte and Weber, 2002; Schefuß *et al.*, 2003; Bendle *et al.*, 2006, 2007). The $\delta^{13}C$ values are especially useful in

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low to mid-latitudes where C_4 plant vegetation is dominant in tropical and subtropical arid regions (Sage, 2001), however, their ability to distinguish the source vegetation is limited in mid to high latitudes where relative contribution from C_4 plants are rather constant (6–35%; Fang *et al.*, 2002; Bendle *et al.*, 2006). In addition, the $\delta^{13}C$ values of terrestrial higher plant *n*-alkanes overlap with the range of those in crude oil (Simoneit, 1997), which makes it difficult to decipher inherent higher plant signals especially in polluted urban aerosols.

Recent observation in hydrogen isotopic composition (δD) of rainwater reveals a large (>100‰) spatial variation between low and high latitudes of the northern hemisphere (IAEA, 2001). Because terrestrial higher plant *n*-alkanes reflect the δD of precipitation waters on their D/H ratios with minor modification by local and regional meteorology (evapotranspiration, relative humidity and soil moisture; Sachse *et al.*, 2006), D/H ratios of the *n*-alkanes in atmospheric aerosols are expected to provide information on the latitude where their source vegetation grows. In addition, the δD values of terrestrial higher plants are generally much lower (Chikaraishi and Naraoka, 2003; Bi *et al.*, 2005; Sachse *et al.*, 2006; Pedentchouk *et al.*, 2008) than those of marine crude oil (Li *et al.*, 2001), indicating that vegetation signals may be distinguished from anthropogenic fossil fuel components in polluted urban aerosols.

Urban aerosols from Tokyo, Japan contain C_{17} to C_{40} *n*-alkanes with large amounts of unresolved complex mixture (UCM) of hydrocarbons in their aliphatic hydrocarbon fractions. The *n*-alkanes from C_{17} to C_{24} exhibited no odd/even carbon number predominance, whereas the *n*-alkanes from C_{25} to C_{35} showed a weak odd/even carbon number predominance, demonstrating that the *n*-alkanes originate from both terrestrial higher plant waxes and fossil fuel combustion residues (Kawamura *et al.*, 1995). The seasonal variation of carbon preference index (CPI), although small, implies that relative contributions of atmospheric *n*-alkanes from higher plants and fossil fuel combustion may vary seasonally (Kawamura *et al.*, 1995). This suggests that the samples may provide a good opportunity to assess the usefulness of isotopic measurements of *n*-alkanes in aerosols. Although the presence of co-eluting UCM in the Tokyo aerosols prevented accurate isotopic analysis for years, several methods are now available to remove UCM for the measurement of stable isotopes of individual *n*-alkanes (e.g., Ellis and Fincannon, 1998; Xu and Sun, 2005; Grice *et al.*, 2008).

In this study, we present $\delta^{13}C$ and δD values of individual *n*-alkanes in aerosols from Tokyo, Japan and compare the results with the molecular distribution of *n*-alkanes, air mass transport pathways and the isotopic compositions of local vegetation to better understand their source and transport in polluted urban atmosphere.

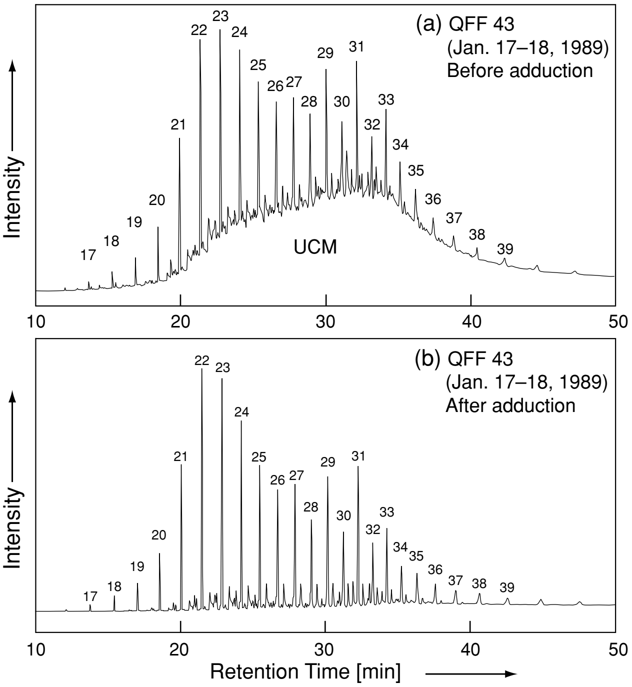

Fig. 1. Typical gas chromatograms of aliphatic hydrocarbon fractions in Tokyo aerosol (a) before and (b) after the urea adduction. (Numbers on the GC peaks indicate carbon numbers of n-alkanes, UCM = unresolved complex mixture of branched and cyclic hydrocarbons.)

SAMPLES AND ANALYTICAL METHODS

Samples

Urban aerosol samples (total suspended particles, n = 17) were collected on pre-combusted quartz filters (Pallflex 2500QAT, 20 cm × 25 cm) using a high-volume air sampler (Shibata HV1000) on the roof of the former Science building of Tokyo Metropolitan University in Setagaya, Tokyo, Japan (35.62°N, 139.66°E) from 19 April 1988 to 8 February 1989. Each filter sample was placed in a separate clean glass jar with a Teflon-lined cap and stored in a freezer (–20°C) until analysis.

Extraction and separation of n-alkanes

We used aliphatic hydrocarbon fractions that were ultrasonically extracted with CH_2Cl_2 (DCM) and isolated using a silica gel column chromatography by elution with *n*-hexane in 1989 (Kawamura *et al.*, 1995). To assess the potential deterioration of samples, three filter samples were extracted again in 2009 using DIONEX ASE-200 with 0.1 M KOH-methanol solution (10 ml × 3) and subsequent ultrasonication with DCM (10 min). The *n*-alkane fractions were analyzed by GC for the composition and concentration of *n*-alkanes. We confirmed that the results are not significantly different from those re-

Table 1. *Analytical errors of stable isotope ratios determined in this study*

Notation	$\delta^{13}C$	δD
Designation	$^{13}C/^{12}C$ ratios	D/H ratios
Unit	(‰ vs. PDB*)	(‰ vs. SMOW**)
Analytical error	±0.5‰	±5‰
Internal standard	C_{20} *n*-alkanoic acid methyl ester; $\delta^{13}C = -26.21$‰	C_{13} *n*-alkane; $\delta D = -79$‰

**Pee Dee Belemnite; **Standard Mean Ocean Water.*

ported in Kawamura *et al.* (1995). Unresolved complex mixture (UCM) was removed from the fraction using the urea adduction technique of Yamamoto and Kawamura (in press) (see Fig. 1). Although mono-methyl alkanes remain in the *n*-alkane fractions after the urea adduction, they can be isolated from *n*-alkanes on the capillary GC chromatogram. Any serious co-elution of these compounds on the *n*-alkanes was not observed in the GC/FID traces (Fig. 1).

The aliphatic hydrocarbon fractions were analyzed using a gas chromatography (GC) and GC/mass spectrometry (MS). GC analysis was performed using a Hewlett-Packard 6890 gas chromatograph equipped with an on-column injector, CP-Sil 5 CB fused silica capillary column (60 m × 0.32 mm i.d., 0.25 μm film thickness) and a flame ionization detector (FID). Helium was used as a carrier gas. The GC oven temperature was programmed from 50 to 120°C at 30°C/min, then to 310°C at 5°C/min and held isothermally for 45 min. GC/MS analysis was performed using a Hewlett-Packard 5973 Mass Selective Detector (quadrupole mass spectrometer) coupled to a Hewlett-Packard 6890 GC equipped with a HP-5MS fused silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The temperature program was the same as for GC analysis. The components were identified on the basis of comparison of their GC retention times and mass spectra with those of reference compounds.

Compound-specific stable isotope analyses

$^{13}C/^{12}C$ ratios of individual *n*-alkanes were determined using a HP 6890 GC coupled to a Finnigan MAT Delta Plus isotope ratio mass spectrometer via a Finnigan MAT combustion furnace maintained at a temperature of 850°C. The GC was equipped with HP-5MS fused silica column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The GC oven was programmed from 50 to 120°C at 10°C/min, and to 310°C at 4°C/min, and then held isothermally for 45 min. One to two μl of sample solution were injected into the GC via an on-column injector with an internal standard of known isotopic composition (C_{20} *n*-alkanoic acid methyl ester; $\delta^{13}C = -26.21$‰). The $\delta^{13}C$ values are expressed as per mil (‰) relative to the Pee Dee Belemnite (PDB). An external standard consisting of C_{16} to C_{30} *n*-alkanes of known isotopic compositions was daily injected into the GC/IRMS system to check the data quality and to ensure the analytical error of the *n*-alkanes remained below ±0.5‰ during the analyses (Bendle *et al.*, 2006).

D/H ratios for individual *n*-alkanes were determined using a Hewlett-Packard GC (HP 6890) connected to a Finnigan MAT Delta Plus XL mass spectrometer via a Finnigan MAT thermal conversion ceramic tube maintained at a temperature of 1450 °C. The GC was equipped with an on-column injector and DB-5MS fused silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The GC oven temperature was programmed from 50 to 120°C at 10°C/min, and to 310°C at 4°C/min, and then held isothermally for 45 min. Helium was used as a carrier gas at a flow rate of 1.8 ml/min. One to two μl of samples were injected with an internal standard (C_{13} *n*-alkane; $\delta D = -79$‰). The δD values are expressed as per mil (‰) relative to the Standard Mean Ocean Water (SMOW). Prior to the sample measurement, a standard mixture containing C_{16} to C_{30} *n*-alkanes was injected to the GC/TC/IRMS system to check the data quality and to ensure the analytical error to be ±5‰. Most measurements were duplicated and the reported isotopic data represent an averaged value of the duplicate analyses. Analytical errors in the measurements of $\delta^{13}C$ and δD are given in Table 1.

Air mass trajectory analysis

Ten-day back air mass trajectories were calculated twice a day for each of the samples using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Rolph, 2003; Rolph, 2003). The trajectories were calculated for air masses starting from the sampling site at 500 m height using the vertical velocity method and the reanalysis data (Aggarwal and Kawamura, 2008).

RESULTS

Stable carbon isotopic compositions ($\delta^{13}C$) of n-alkanes in the Tokyo aerosols

Stable carbon isotopic compositions ($\delta^{13}C$) of C_{21} to C_{35} *n*-alkanes in aerosols from Tokyo range from –25.5 to –32.8‰ (Table 2). The samples could be categorized into two distinctive groups, one with higher concentra-

Table 2. Stable carbon ($\delta^{13}C$) and hydrogen (δD) isotope compositions of individual n-alkanes, CPI, estimated δD values of leaf waxes, and the annual distribution of air mass trajectory sectors

Sample	B001	B004	QFF08	QFF09	QFF13	QFF22	QFF29	QFF32	QFF33	QFF34	QFF36	QFF38	QFF37	QFF39	QFF42	QFF43	QFF45
Start date	Apr. 19, 1988	Apr. 21, 1988	June 13, 1988	June 22, 1988	July 5, 1988	July 19, 1988	Aug. 22, 1988	Sep. 13, 1988	Oct. 3, 1988	Oct. 13, 1988	Nov. 7, 1988	Nov. 21, 1988	Dec. 2, 1988	Dec. 15, 1988	Jan. 3, 1989	Jan. 17, 1989	Feb. 7, 1989
CPI[a]	1.4	1.7	2.1	2.0	1.7	1.5	1.6	1.8	1.6	1.8	2.1	1.4	1.5	1.6	1.5	1.3	1.2
$\delta^{13}C$ (‰ vs. VPDB)																	
C_{21}	−27.6	−28.1	−28.1	−27.8	nd	−27.5	nd	−28.1	−27.2	−27.9	−27.3	−26.9	−28.6	−26.5	−26.3	−25.6	−26.9
C_{22}	−27.5	−27.7	−27.8	−27.5	−28.5	−27.5	−28.5	−27.7	−27.2	−27.7	−27.3	−26.7	−27.9	−26.4	−26.1	−25.5	−26.7
C_{23}	−28.0	−28.6	−28.3	−27.9	−28.5	−27.4	−28.2	−28.2	−27.1	−27.5	−27.7	−26.8	−27.8	−26.5	−26.3	−25.8	−26.9
C_{24}	−27.2	−27.2	−27.6	−27.4	−27.4	−26.9	−28.0	−27.6	−26.9	−27.4	−27.7	−26.9	−28.0	−26.5	−25.9	−25.6	−27.0
C_{25}	−28.1	−28.3	−28.7	−27.9	−27.8	−26.9	−28.3	−28.0	−27.0	−27.8	−28.5	−27.3	−28.2	−28.2	−26.8	−26.0	−27.1
C_{26}	−26.9	−26.8	−27.0	−27.0	−27.0	−26.6	−26.8	−27.4	−26.5	−27.5	−28.2	−27.2	−28.1	−26.8	−26.5	−26.0	−27.3
C_{27}	−28.7	−28.8	−28.5	−28.5	−28.3	−27.5	−27.8	−28.9	−27.7	−28.9	−30.0	−28.4	−29.0	−28.7	−27.3	−26.6	−27.7
C_{28}	−27.1	−27.5	−27.2	−27.9	−27.4	−26.9	−27.0	−28.0	−26.8	−27.7	−28.8	−28.0	−28.5	−27.4	−25.5	−26.1	−27.4
C_{29}	−30.2	−31.0	−30.5	−30.8	−30.5	−29.3	−28.8	−30.4	−29.3	−30.6	−31.5	−30.3	−31.1	−30.8	−29.1	−28.4	−29.8
C_{30}	−27.9	−28.8	−28.5	−28.6	−28.9	−27.8	−27.4	−28.1	−29.3	−28.8	−29.8	−29.0	−29.5	−28.4	−27.2	−28.8	−28.2
C_{31}	−31.7	−31.3	−32.5	−32.6	−32.3	−31.3	−30.8	−31.5	−31.3	−32.8	−32.4	−31.6	−32.5	−31.9	−31.4	−30.0	−31.2
C_{32}	−28.9	−27.6	−28.8	−28.8	−28.9	−28.2	−27.6	−28.2	−28.3	−28.4	−30.0	−29.0	−29.0	−28.7	−27.0	−27.3	−28.2
C_{33}	−30.1	−29.3	−30.7	−30.7	−30.3	−29.8	−29.4	−29.2	−30.0	−30.7	−31.2	−30.1	−31.1	−30.4	−29.9	−28.7	−30.0
C_{34}	−27.3	−27.9	−27.3	−27.8	−27.4	−27.2	−27.1	−28.0	−27.4	nd	−27.9	−27.1	−28.3	−27.4	−26.1	−26.9	−27.6
C_{35}	−27.3	−27.9	−27.9	−28.1	−27.3	−27.5	−27.2	−27.1	−27.0	nd	−28.2	−27.0	−29.0	−27.8	−26.1	−28.3	−27.5
δD (‰ vs. VSMOW)																	
C_{21}	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	−76	−85	−80	−74	nd	−71	−77
C_{22}	nd	nd	nd	−71	nd	nd	nd	nd	nd	−65	−76	−80	−79	−70	nd	−71	−78
C_{23}	−85	−94	−78	−80	nd	−80	−85	nd	−78	−80	−81	−82	−77	−72	nd	−73	−75
C_{24}	−81	−78	−88	−81	−85	−71	−82	−68	−77	−73	−81	−85	−77	−69	nd	−72	−76
C_{25}	−91	−95	−119	−96	−92	−84	−103	−88	−98	−84	−107	−91	−83	−84	nd	−79	−86
C_{26}	−83	−87	−92	−91	−86	−80	−93	−75	−88	−80	−99	−95	−83	−85	nd	−76	−81
C_{27}	−97	−116	−129	−117	−112	−94	−115	−112	−115	−115	−140	−113	−102	−115	nd	−97	−95
C_{28}	−92	−88	−92	−87	−95	−83	−94	−88	−95	−92	−104	−96	−85	−94	nd	−82	−84
C_{29}	−126	−140	−146	−139	−130	−118	−129	−136	−132	−141	−151	−138	−126	−144	−116	−110	−114
C_{30}	−81	−84	−82	−86	−88	−74	−93	−81	−85	−75	−100	−85	−79	−81	nd	−60	−74
C_{31}	−117	−129	−141	−143	−139	−128	−133	−135	−137	−138	−157	−133	−123	−138	−125	−115	−116
C_{32}	−58	−79	−69	−77	−81	−65	−91	−77	−80	−76	−88	−70	−74	−75	nd	−55	−62
C_{33}	−87	−104	−114	−108	−118	−94	−114	−122	−113	−114	−128	−97	−100	−98	−104	−85	−91
δD_{wax}[b]																	
C_{29}	−189	−179	−170	−170	−174	−168	−182	−173	−190	−172	−169	−170	−175	−181	−144	−155	−175
C_{31}	−150	−176	−166	−168	−169	−167	−181	−167	−180	−168	−186	−164	−178	−174	−147	−163	−169
Air mass trajectory (% of total trajectories)[c]																	
A	50	100	0	0	0	0	0	0	0	25	50	0	0	50	50	0	0
B	25	0	100	0	0	0	25	25	0	0	0	25	0	0	0	0	0
C	0	0	0	0	0	0	75	0	0	0	0	0	0	0	0	0	0
D	0	0	0	83	100	100	0	75	25	0	0	0	0	0	0	0	0
E	25	0	0	17	0	0	0	0	75	75	50	75	100	50	50	100	100

nd, not determined. [a] *$CPI = 0.5 \times [\Sigma(C_{25}-C_{35})_{odd}/\Sigma(C_{24}-C_{34})_{even}) + \Sigma(C_{25}-C_{35})_{odd})/\Sigma(C_{26}-C_{36})_{even}]$, where C is abundance of each n-alkane.* [b] *δD of n-alkanes that are corrected for fossil fule contribution based on CPI value of 10.* [c] *A, western trajectory from China and Far East Russia; B, trajectory over the vicinity of the Eastern China and Sea of Japan; C, trajectory from South Asia; D, oceanic; E, trajectory over land at >500 m altitude.*

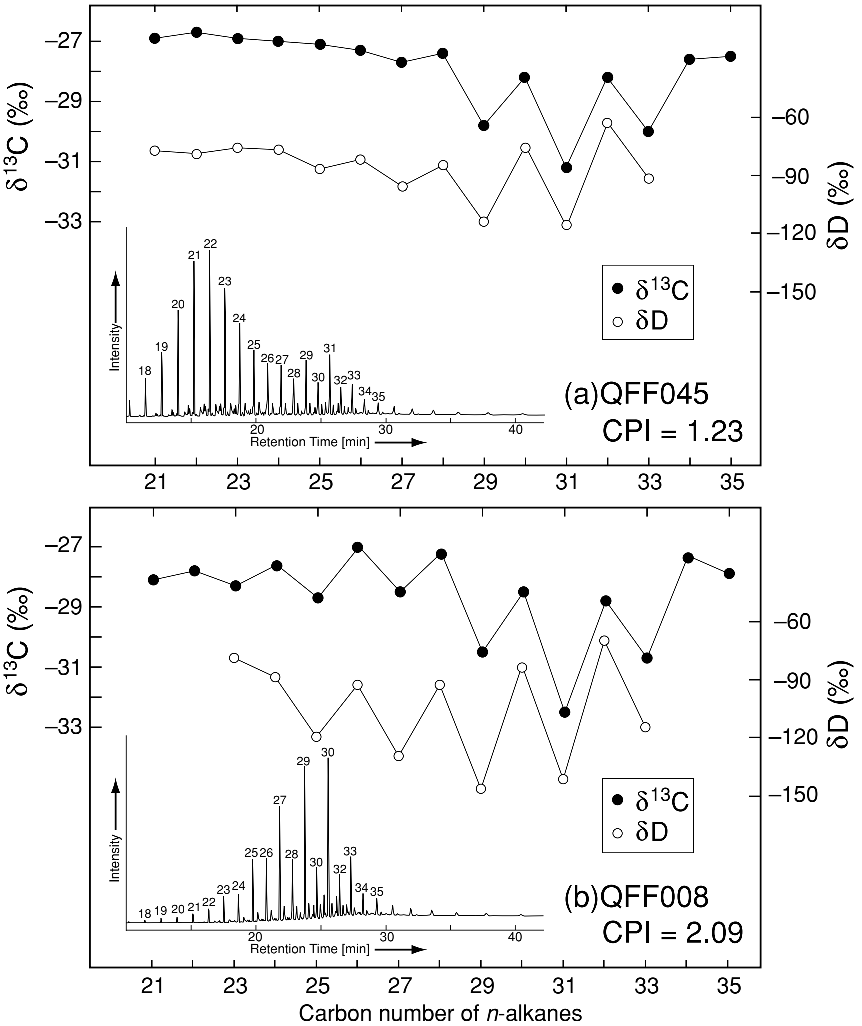

Fig. 2. Gas chromatographic traces of the adducted n-alkane fraction and the $\delta^{13}C$ and δD distributions of individual n-alkanes in (a) low CPI and (b) high CPI samples. Numbers on the GC peaks indicate carbon numbers of n-alkanes.

tion of C_{18} to C_{25} *n*-alkanes than those of C_{26} to C_{33} and low CPI values, and the other with higher concentration of C_{25} to C_{33} *n*-alkanes than those of C_{18} to C_{24} and high CPI values. A representative plot for each group is shown in Fig. 2.

When the CPI values are low, the $\delta^{13}C$ values are relatively constant (–27.0 ± 0.2‰) in a range of C_{21} to C_{26}. In contrast, the $\delta^{13}C$ values of C_{27} to C_{33} odd-carbon numbered *n*-alkanes are more depleted in ^{13}C by up to 3.0‰ compared to even-carbon number homologues, showing a sawtooth pattern for longer chain *n*-alkanes (Fig. 2a). On the other hand, the C_{21} to C_{35} odd-carbon numbered *n*-alkanes in the aerosol samples with high CPI values exhibit lower $\delta^{13}C$ values than those of low CPI samples by up to 1.6‰ (Fig. 2b). The C_{31} *n*-alkane is found as the most ^{13}C-depleted species in all the samples.

The $\delta^{13}C$ values of C_{27} to C_{33} odd-carbon numbered *n*-alkanes exhibit large seasonal variations with relatively high values (~–27.3‰) in summer (QFF22, 29), fall (QFF32, 33) and winter samples (QFF37, QFF39–45) (Table 2; Fig. 3a). We found that the $\delta^{13}C$ values of C_{29} and C_{31} *n*-alkanes and CPI are negatively related with each other (Fig. 4a). Correlation coefficient is 0.55 for C_{29} *n*-alkane ($p = 0.02$) and 0.60 for C_{31} *n*-alkane ($p = 0.01$).

Stable hydrogen isotopic compositions (δD) of n-alkanes in the Tokyo aerosols

Stable hydrogen isotopic composition (δD) of C_{21} to C_{33} *n*-alkanes in the Tokyo aerosols range from –55 to –157‰ (Table 2). The δD values of C_{21} to C_{24} *n*-alkanes are fairly constant (–78 ± 6‰), whereas the δD values of C_{25} to C_{33} odd-carbon numbered *n*-alkanes are more depleted in D by up to 100‰ compared to even-carbon number homologues, showing a sawtooth pattern for

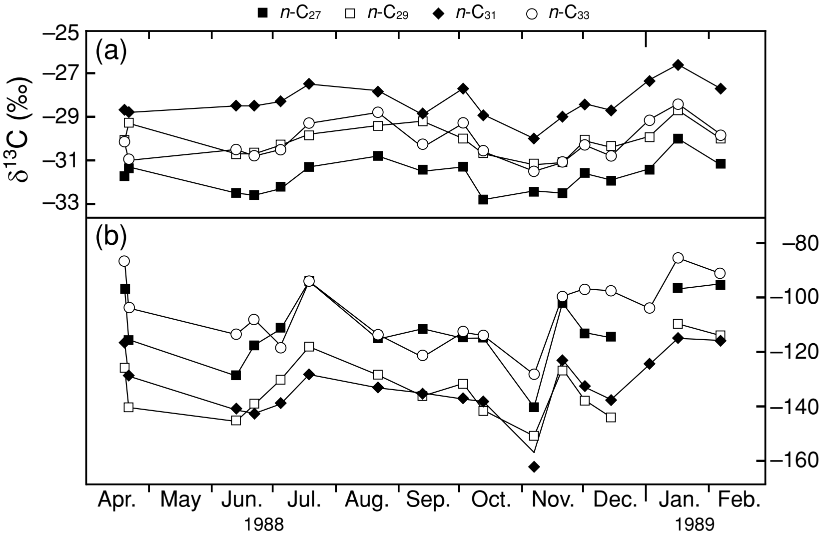

Fig. 3. Seasonal variations in (a) $\delta^{13}C$ and (b) δD of C_{27} to C_{33} odd-carbon number n-alkanes in the urban aerosols from Tokyo.

longer chain *n*-alkanes. The magnitude of the D-depletion is more significant in the high CPI samples than in the low CPI samples (Figs. 2a and b). The C_{29} or C_{31} *n*-alkanes are the most D-depleted compounds in all the samples.

The δD values of C_{27} to C_{33} odd-carbon numbered *n*-alkanes show large seasonal variations with relatively high values (~–85‰) in spring (B001), summer (QFF22) and winter samples (QFF37–45) (Table 2; Fig. 3b). The δD values of C_{29} and C_{31} *n*-alkanes and CPI are negatively related each other (Fig. 4b). Correlation coefficient is 0.82 for C_{29} *n*-alkane and 0.87 for C_{31} *n*-alkane ($p < 0.01$), which are higher than those for the *n*-alkane δ^{13}C values (Fig. 4). Although a systematic difference is observed in the δ^{13}C values between C_{29} and C_{31} *n*-alkanes (Fig. 4a), there is no such difference in the δD values (Fig. 4b).

Air mass back trajectories

Air mass trajectories were sorted into five categories in terms of the direction and passage of winds (Fig. 5). Trajectories classified as “category A” are characterized by long-range transport with westerly winds extended back to China and Far East Russia. Trajectories classified as “category B” is not a type of long-range transport, rather they represent air masses coming from the vicinity of the Eastern China Sea and Sea of Japan. Trajectories classified as “category C” are characterized by southwesterly winds that come from Southeast Asia through eastern China, whereas those classified as “category D” are characterized by easterly maritime winds from the low to middle latitudes in the Pacific Ocean. Trajectories classified as “category E” are mostly characterized by westerlies that extended back to the Asian continent, but they represent upper tropospheric transport without touching the continent at an altitude of <500 m.

Table 2 summarized the seasonal distribution of air mass trajectory sectors during the one-year sampling period. In general, summer (June to September) samples predominantly received air masses from the Pacific except for August when air mass reached from Southeast Asia via southeastern part of China. In contrast, spring (April) and winter (October to February) samples are predominantly associated with air masses from the Asian continent. Such seasonal changes in prevailing winds are consistent with those observed in the Northwest Pacific during a period of 1990–1993 (Kawamura *et al*., 2003; Bendle *et al*., 2006).

DISCUSSION

Sources of n-alkanes in urban aerosols from Tokyo

Homologous series of *n*-alkanes with low CPI in urban atmospheric aerosols are mainly derived from lubricants in vehicular exhaust and combustion residues of fossil fuels (mainly petroleum and coal) (Simoneit, 1984; Wang and Kawamura, 2005; Simoneit, 2006), although they can also be emitted from biomass burning (Standley and Simoneit, 1987; Schimidl *et al*., 2008a, b). The δ^{13}C values of C_{21} to C_{24} *n*-alkanes in the Tokyo aerosols (–28.1 to –25.6‰) are within the typical range of those in fossil fuels (Fig. 6). However, we cannot fully exclude the possibility that the *n*-alkanes are derived from sources other than fossil fuel hydrocarbons (e.g., those from biomass burning; Schimidl *et al*., 2008a, b) because the values are also in the range of those in terrestrial higher plants (Fig. 6). In contrast, the δD of the C_{21} to C_{24} *n*-

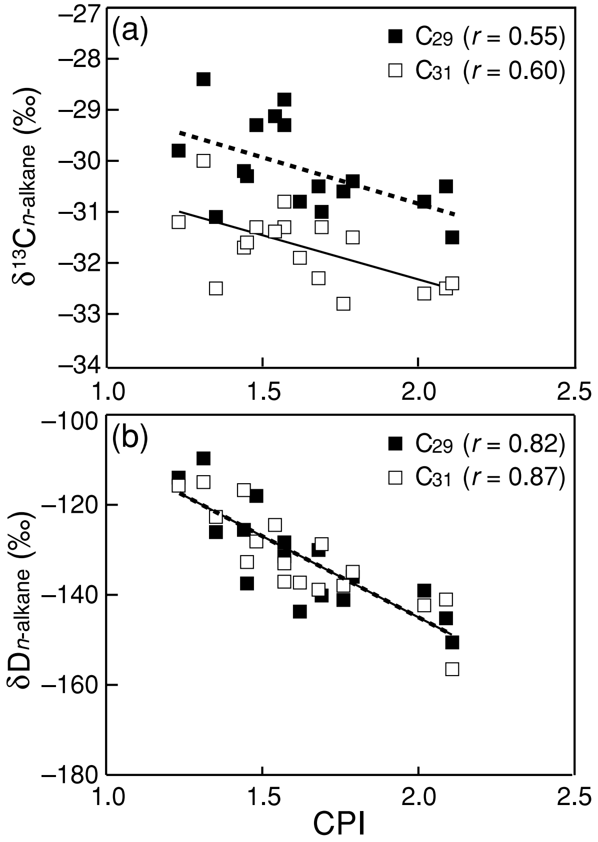

Fig. 4. Cross-plots of (a) the $\delta^{13}C$ of C_{29} and C_{31} n-alkanes and (b) the δD of C_{29} and C_{31} n-alkanes as a function of CPI values.

alkanes and the C_{26} to C_{32} even-carbon numbered *n*-alkanes are within the range of those typical to marine crude oil, and exhibit much higher values than those in terrestrial crude oil and higher plants (Fig. 6). Such δD distributions thus suggest that they likely originate from the anthropogenic emission of petroleum hydrocarbons.

On the other hand, the $\delta^{13}C$ and δD values of C_{25} to C_{33} odd-carbon numbered *n*-alkanes are lower than those of the C_{21} to C_{24} *n*-alkanes and the C_{26} to C_{32} even-carbon numbered *n*-alkanes (Fig. 6). Again, the $\delta^{13}C$ values are in both the ranges of terrestrial higher plant and fossil fuel *n*-alkanes, showing insufficient resolution for the recognition of their specific sources. The δD values of the *n*-alkanes are also within both ranges of those for marine crude oil and for C_3 and CAM plants (Fig. 6). However, the δD values of terrestrial higher plant-derived *n*-alkanes are generally lower than those of *n*-alkanes in marine crude oil (Fig. 6; Chikaraishi and Naraoka, 2003; Bi *et al.*, 2005; Sachse *et al.*, 2006; Pedentchouk *et al.*, 2008), and thus the lower δD values observed for the C_{25} to C_{33} odd-carbon numbered *n*-alkanes likely suggest a significant contribution from higher plant waxes in addi-

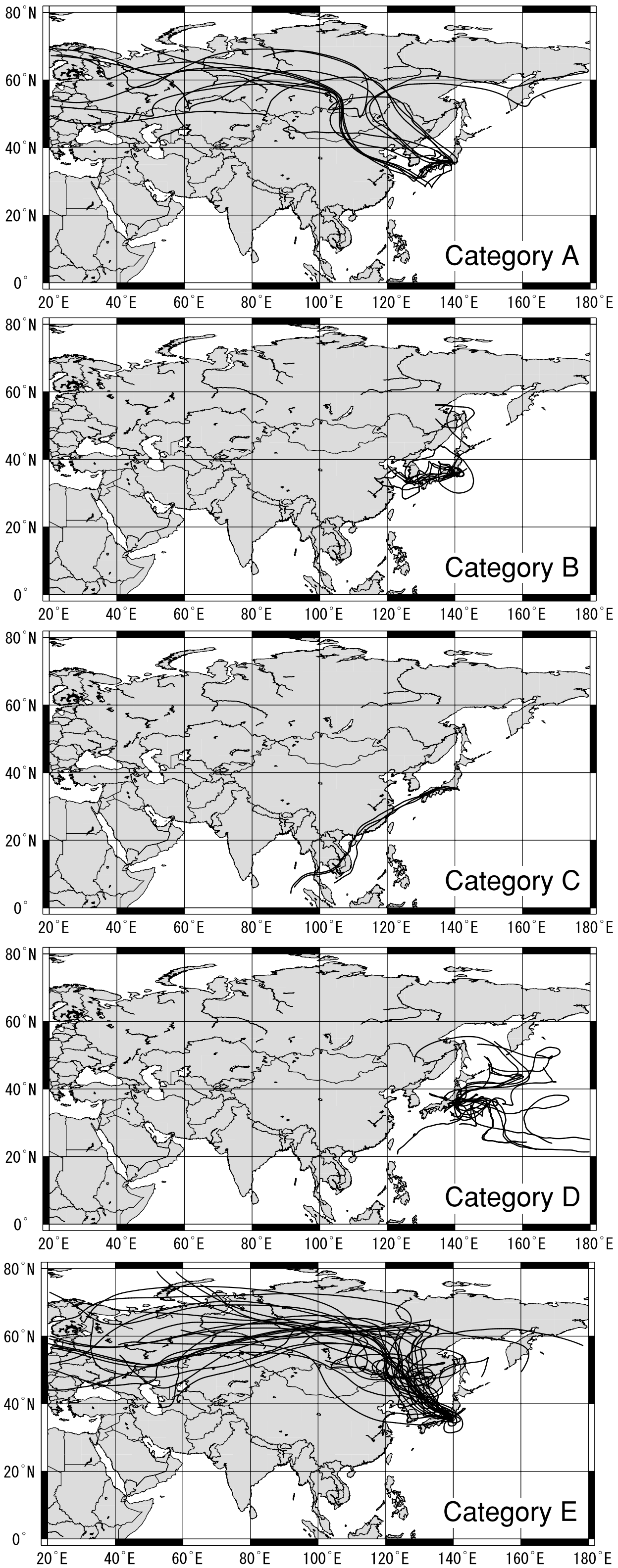

Fig. 5. Results of 10-day backward trajectory analysis for all the samples, which are grouped into five air mass categories.

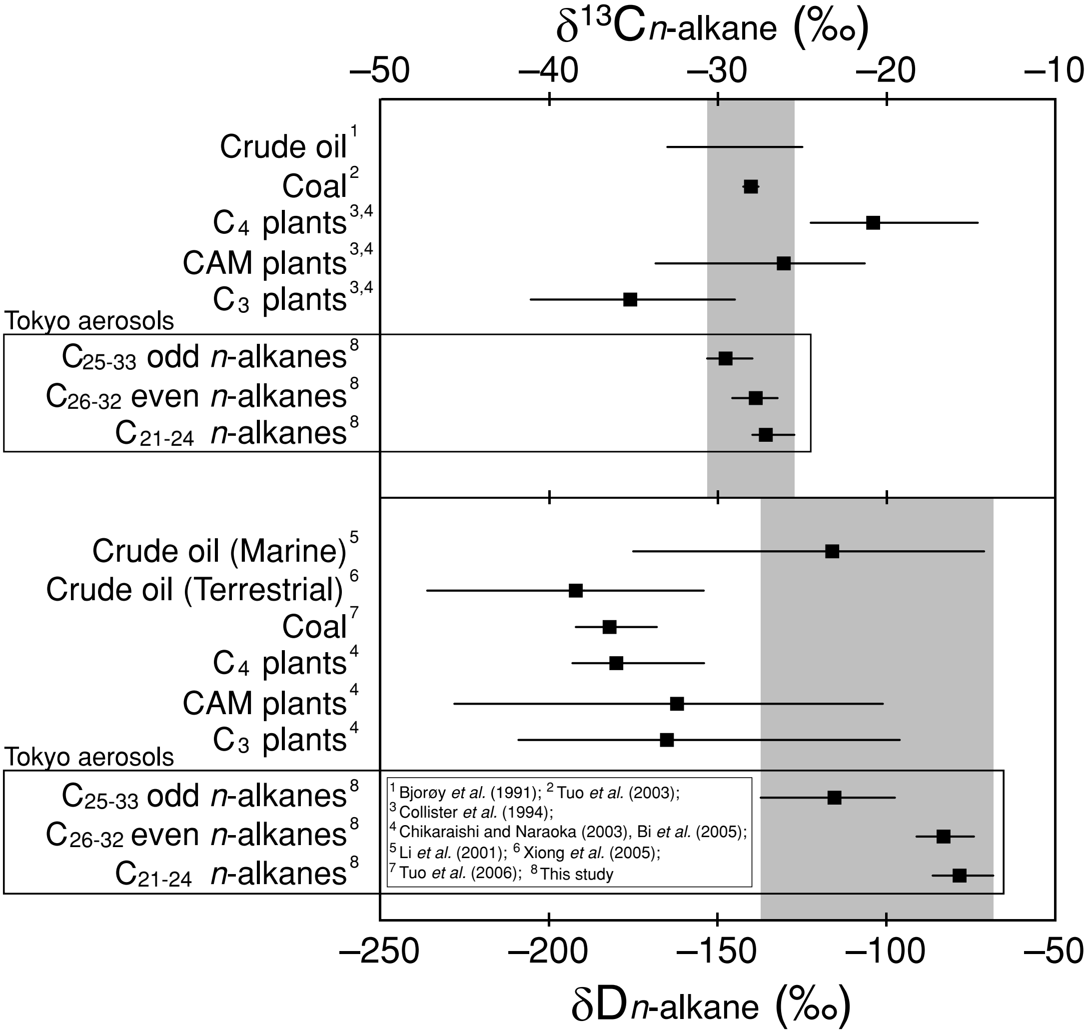

Fig. 6. Comparison of the averaged $\delta^{13}C$ and δD ranges of n-alkanes between the terrestrial higher plant and fossil fuel n-alkanes and the atmospheric n-alkanes from Tokyo.

tion to fossil fuel hydrocarbons. A good negative correlation between the *n*-alkane δD and CPI values indicates that the δD values are mainly controlled by a variable input from biogenic and anthropogenic hydrocarbon sources.

δD values of terrestrial higher plant-derived n-alkanes in urban aerosols from Tokyo

Previous studies on the stable carbon isotopic ratios ($\delta^{13}C$) of *n*-alkanes in environmental samples have evaluated the *n*-alkane contribution from non-higher plant sources (i.e., anthropogenic) based on CPI values (Ishiwatari *et al.*, 1994; Huang *et al.*, 2000; Schefuß *et al.*, 2003; Rommerskirchen *et al.*, 2006). However, it should be noted that this approach contains a certain uncertainty because the CPI values of vegetation can vary significantly in nature (1.4–40.3; Collister *et al.*, 1994; Chikaraishi and Naraoka, 2003).

In the urban aerosols from Tokyo, the *n*-alkane $\delta^{13}C$ values are negatively correlated with CPI values (Fig. 4a). However, the correlation is not so tight because of a large variability in the $\delta^{13}C$ values. Such a variability in the $\delta^{13}C$ values might be partly attributed to a substantial input from C_4 plant materials besides fossil fuel hydrocarbons, particularly in summer (Bendle *et al.*, 2006). In contrast, the *n*-alkane δD values show a strong negative correlation with CPI values (Fig. 4b), which enables us to estimate the inherent isotopic compositions of terrestrial higher plant waxes by eliminating the contribution of the long chain *n*-alkanes of fossil fuel origin.

Although no consensus has yet been achieved for the most appropriate method for the correction (Bendle *et al.*, 2006), we decided to use a mass-balance approach following the method described in Huang *et al.* (2000) as

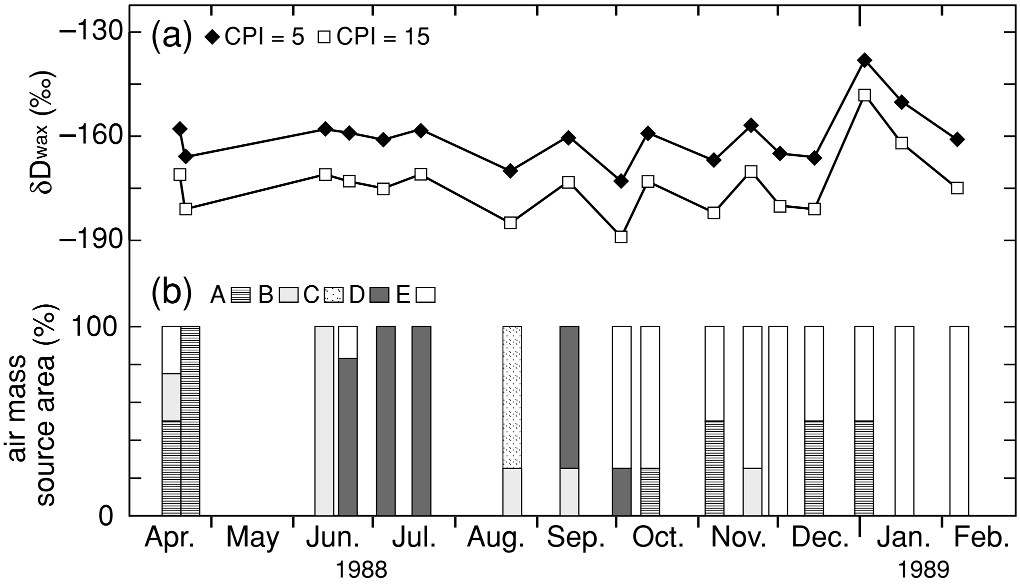

Fig. 7. Seasonal variations of the δD values estimated for terrestrial higher plant-derived n-alkanes (weighted mean of C_{29} and C_{31} n-alkanes) with the CPI of 5 and 15 (a) and the annual distribution of air mass trajectory sectors (b).

follows:

$$\delta D_{alk} C_{alk} = \delta D_w (C_{alk} - C_f) + \delta D_f C_f$$

where δD_w is the isotopic composition of terrestrial higher plant-derived *n*-alkanes, δD_{alk} and C_{alk} are the measured isotopic value and concentration of C_{29} or C_{31} *n*-alkanes, δD_f and C_f are the isotopic composition and the concentrations of fossil fuel *n*-alkanes, respectively. The weighted mean δD value of C_{22}, C_{23} and C_{24} *n*-alkanes (–77‰) is used as the δD_f because these *n*-alkanes are most abundant in fossil fuels but generally absent in terrestrial higher plant waxes. Although Li *et al.* (2001) reported a gradual increase in the δD values of *n*-alkanes (~20‰ in a range of C_{22} to C_{27}) with an increase in their carbon numbers of crude oil samples, the δD values of fossil fuel *n*-alkane that are obtained by a mass balance calculation in our samples are relatively constant (–79‰ ± 5‰) in a range of C_{22} to C_{28}. The C_f are calculated by assuming that the long chain *n*-alkanes are equally influenced by fossil fuel hydrocarbons as follows:

$$\mathrm{CPI} = C_{odd}/C_{even} = (C_{alk} - C_f)/(C_{30} - C_f)$$

where C_{30} are the measured abundance of C_{30} *n*-alkane, and C_{odd} and C_{even} are the concentrations of odd- and even-carbon numbered *n*-alkanes, respectively. We assume that CPI (odd/even ratios) for fossil fuel *n*-alkanes is 1, whereas that for terrestrial higher plant-derived *n*-alkanes ranges from 5 to 15, which are typical of modern higher plant waxes (Simoneit *et al.*, 1991).

The *n*-alkane δD values that are corrected by subtracting contribution of fossil fuel *n*-alkanes (weighted mean of the corrected δD of *n*-C_{29} and *n*-C_{31}) ranged from –138 to –189‰. These values are found to decrease with an increase in the CPI values from 5 to 15, which are assumed for terrestrial higher plant-derived *n*-alkanes (Fig. 7). Seasonal variations in the corrected δD values are much larger (~42‰) than the δD difference (~17‰) between the *n*-alkanes with CPI of 5 and 15 (Fig. 7), indicating that the δD variations cannot be explained solely by the uncertainty in the CPI estimates (5 to 15) for each sample (Bendle *et al.*, 2006).

In eastern China, Rao *et al.* (2009) reported that the δD of higher plant-derived *n*-alkanes in surface soil gradually decrease from low to high latitude reflecting spatial distribution of the δD of rainwater in East Asia (IAEA, 2001). Because the air mass trajectories show a large seasonal variability in the air mass source regions (Table 2), the variations in the corrected δD values could have been attributed to the *n*-alkane transport from the source vegetation in various latitudes of the Asian continent. However, the results do not show variations corresponding to differences in air mass transport (Fig. 7). Although the δD differences between their source regions could have been weakened by large seasonal variations in the δD values of leaf wax *n*-alkanes (up to 40‰; Sessions, 2006; Sachse *et al.*, 2009) that are equivalent to their latitudinal variations in East Asia (53‰ in 18°N–50°N; Rao *et al.*, 2009), the decoupling between the δD values and air mass source regions probably suggests that the contribution of *n*-alkanes transported from the Asian continent is not significant in the urban aerosols of Tokyo.

Recently, a δD study of plant leaf lipids in a forest around Lake Haruna, which locates *ca*. 100 km northwest of Tokyo, revealed large (~42‰) seasonal variations in the *n*-alkanes from raw leaf samples although those in soil samples did not show any significant (<2‰) variation (Chikaraishi and Naraoka, 2006). Hence, a large (~42‰) variation in the corrected δD values in our aerosol samples likely indicates that the terrestrial higher plant-derived *n*-alkanes in the Tokyo atmospheric aerosols originate from the waxes from raw leaves of local vegetation rather than those in soil. In support for this, calculated δD values for terrestrial higher plant-derived *n*-alkanes with CPI of 10 (Table 2), which is an averaged CPI value for vegetation in Tokyo (Chikaraishi and Naraoka, 2003), match well with the *n*-alkane δD values in growing leaves from Tokyo: –145 to –196‰ for C_{29} *n*-alkane and –134 to –186‰ for C_{31} *n*-alkane (Chikaraishi and Naraoka, 2003).

Although our δD results indicate that local vegetation are more important as a source of higher plant *n*-alkanes in the Tokyo aerosols, a good agreement between the corrected δD values and the values of the contemporary local vegetation suggest that the δD values of *n*-alkanes in aerosols can be used as a tracer for their source vegetation in polluted urban atmosphere in which their δ^{13}C values are not available for the recognition of higher plant signals. Because aliphatic hydrocarbons in the atmosphere over the East Asia-northwest Pacific regions are composed of varying amounts of terrestrial higher plant waxes and urban emissions (Kawamura, 1995; Kawamura *et al*., 2003; Simoneit *et al*., 2004), the δD measurements of atmospheric *n*-alkanes can provide a powerful tool for deciphering their source and transport pathways in the regions.

CONCLUSIONS

Stable carbon (δ^{13}C) and hydrogen (δD) isotopic compositions of individual *n*-alkanes were measured in aerosols collected from Tokyo to better understand the source and transport of *n*-alkanes in the polluted urban atmosphere. The δ^{13}C and δD values of the *n*-alkanes indicate that the C_{20} to C_{24} *n*-alkanes and the C_{26} to C_{32} even-carbon numbered *n*-alkanes are primarily originated from anthropogenic emission of petroleum hydrocarbons. In contrast, the C_{25} to C_{33} odd-carbon numbered *n*-alkanes are composed of a mixture of higher plant and petroleum components. A strong negative correlation between the δD values of the C_{29} and C_{31} *n*-alkanes and CPI enables us to estimate the inherent isotopic compositions of terrestrial higher plant waxes by eliminating the contribution from fossil fuel hydrocarbons. Although the δD values corrected for fossil fuel contribution suggest that the input of terrestrial higher plant-derived *n*-alkanes from local vegetation is more important in the Tokyo aerosols, the results of this study demonstrate that the δD approach has a great advantage over the δ^{13}C measurements to elucidate information on the source and transport of *n*-alkanes in the polluted urban atmosphere.

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