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 ($\delta D$) 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 $\delta D$ values of the C21 to C35 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 $\delta D$ values of the C35 n-alkanes and the C26 to C32 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 $\delta D$ values were found in the C25 to C35 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 $\delta D$ values of the C29 and C31 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 $\delta D$ 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 $\delta D$ 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: $\delta D$, $\delta^{13}C$, 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 C10 to C35 with no carbon number preference are commonly found in fossil fuels and their combustion residues (Brassell et al., 1978; Simoneit, 1984), whereas C25 to C35 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 CPI = 0.5 × [∑(C25 – C35)_{odd}/∑(C24 – C34)_{even} + ∑(C25 – C35)_{odd}/∑(C26 – C36)_{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 C3 and C4 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 C3 and C4 plant materials over the Atlantic and the western Pacific (Conte and Weber, 2002; Schefüß et al., 2003; Bendle et al., 2006, 2007). The $\delta^{13}C$ values are especially useful in...
low to mid-latitudes where C₄ 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 C₃ plants are rather constant (6–35%; Fang et al., 2002; Bendle et al., 2006). In addition, the δ¹³C 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 C₁₇ to C₄₀ n-alkanes with large amounts of unresolved complex mixture (UCM) of hydrocarbons in their aliphatic hydrocarbon fractions. The n-alkanes from C₁₇ to C₃₅ exhibited no odd/even carbon number predominance, whereas the n-alkanes from C₃₅ to C₄₀ 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 δ¹³C 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.

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 CH₂Cl₂ (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-
ported in Kawamura et al. (1995). Unresolved complex mixtures, one to two µl of sample solution were 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 (C13 n-alkane; δD = −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 C16 to C30 n-alkanes was injected into 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 δ13C 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 (δ13C) of n-alkanes in the Tokyo aerosols

Stable carbon isotopic compositions (δ13C) of C21 to C35 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 1. Analytical errors of stable isotope ratios determined in this study

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<td>Analytical error</td>
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<td>C13 n-alkane; δD = −79‰</td>
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*Pee Dee Belemnite; **Standard Mean Ocean Water.
Table 2. Stable carbon (δ¹³C) 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

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<td>nd, not determined. *CPI = 0.5 × (ΣC_{29} – C_{13})<em>{abundance} ΣC</em>{23} + (C_{23} – C_{19})<em>{abundance} ΣC</em>{25} + (C_{25} – C_{21})<em>{abundance} ΣC</em>{27}, where C_{abundance} is abundance of each n-alkane. δD of n-alkanes that are corrected for fossil fuel contribution based on CPI value of 10. 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 &gt;500 m altitude.</td>
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13C and δ

D of n-alkanes in Tokyo aerosols

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tion of C16 to C25 n-alkanes than those of C26 to C33 and low CPI values, and the other with higher concentration of C26 to C33 n-alkanes than those of C16 to C24 and high CPI values. A representative plot for each group is shown in Fig. 2.

When the CPI values are low, the δ

13C values are relatively constant (−27.0 ± 0.2‰) in a range of C21 to C26. In contrast, the δ

13C values of C27 to C33 odd-carbon numbered n-alkanes are more depleted in 13C 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 C21 to C35 odd-carbon numbered n-alkanes in the aerosol samples with high CPI values exhibit lower δ

13C values by up to 1.6‰ (Fig. 2b). The C21 n-alkane is found as the most 13C-depleted species in all the samples.

The δ

13C values of C27 to C33 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 δ

13C values of C29 and C31 n-alkanes and CPI are negatively related with each other (Fig. 4a). Correlation coefficient is 0.55 for C29 n-alkane (p = 0.02) and 0.60 for C31 n-alkane (p = 0.01).

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

Stable hydrogen isotopic composition (δD) of C21 to C33 n-alkanes in the Tokyo aerosols range from −55 to −157‰ (Table 2). The δD values of C21 to C33 n-alkanes are fairly constant (−78 ± 6‰), whereas the δD values of C25 to C33 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

δ

13C and δD of n-alkanes in Tokyo aerosols 423

Fig. 2. Gas chromatographic traces of the adducted n-alkane fraction and the δ

13C 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.
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 \( \delta^D \) 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 \( \delta^D \) 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 \( \delta^{13}C \) values (Fig. 4). Although a systematic difference is observed in the \( \delta^{13}C \) values between \( C_{29} \) and \( C_{31} \) \( n \)-alkanes (Fig. 4a), there is no such difference in the \( \delta^D \) 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 southwesternly 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 \( \delta^{13}C \) 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 \( \delta^D \) of the \( C_{21} \) to \( C_{24} \) \( n \)-
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 δ$^{13}$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 δ$^{13}$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$_{31}$ odd-carbon numbered n-alkanes likely suggest a significant contribution from higher plant waxes in addi-
tion to fossil fuel hydrocarbons. A good negative correlation between the \( \delta D \) and CPI values indicates that the \( \delta D \) values are mainly controlled by a variable input from biogenic and anthropogenic hydrocarbon sources.

\[ \delta D \text{ values of terrestrial higher plant-derived } n\text{-alkanes in urban aerosols from Tokyo} \]

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 \( \delta D \) 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. 6. Comparison of the averaged \( \delta ^{13}C \) and \( \delta D \) ranges of \( n \)-alkanes between the terrestrial higher plant and fossil fuel \( n \)-alkanes and the atmospheric \( n \)-alkanes from Tokyo.](image-url)
follows:

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

where $\delta D_w$ is the isotopic composition of terrestrial higher plant-derived $n$-alkanes, $\delta D_{\text{alk}}$ and $C_{\text{alk}}$ are the measured isotopic value and concentration of $C_{29}$ or $C_{31} n$-alkanes, $\delta D_f$ and $C_f$ are the isotopic composition and the concentrations of fossil fuel $n$-alkanes, respectively. The weighted mean $\delta D$ value of $C_{22}$, $C_{23}$ and $C_{24} n$-alkanes ($-77\,\permil$) is used as the $\delta D_f$ 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 $\delta D$ values of $n$-alkanes ($\sim 20\,\permil$ in a range of $C_{22}$ to $C_{27}$) with an increase in their carbon numbers of crude oil samples, the $\delta D$ values of fossil fuel $n$-alkane that are obtained by a mass balance calculation in our samples are relatively constant ($-79\,\permil \pm 5\,\permil$) 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:

$$\text{CPI} = \frac{C_{\text{odd}}}{C_{\text{even}}} = \frac{C_{\text{alk}} - C_f}{C_{30} - C_f}$$

where $C_{30}$ are the measured abundance of $C_{30} n$-alkane, and $C_{\text{odd}}$ and $C_{\text{even}}$ 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 $\delta D$ values that are corrected by subtracting contribution of fossil fuel $n$-alkanes (weighted mean of the corrected $\delta D$ of $n-C_{29}$ and $n-C_{31}$) ranged from $-138$ to $-189\,\permil$. 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 $\delta D$ values are much larger ($\sim 42\,\permil$) than the $\delta D$ difference ($\sim 17\,\permil$) between the $n$-alkanes with CPI of 5 and 15 (Fig. 7), indicating that the $\delta D$ 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 $\delta D$ of higher plant-derived $n$-alkanes in surface soil gradually decrease from low to high latitude reflecting spatial distribution of the $\delta D$ 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 $\delta D$ 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 $\delta D$ differences between their source regions could have been weakened by large seasonal variations in the $\delta D$ values of leaf wax $n$-alkanes (up to $40\,\permil$; Sessions, 2006; Sachse et al., 2009) that are equivalent to their latitudinal variations in East Asia ($53\,\permil$ in $18^\circ$N–$50^\circ$N; Rao et al., 2009), the decoupling between the $\delta D$ 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 C29 n-alkane and ~134 to ~186‰ for C13 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 δ13C 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; Simoncit 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 (δ13C) 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 δ13C and δD values of the n-alkanes indicate that the C29 to C34 n-alkanes and the C29 to C34 odd-carbon numbered n-alkanes are primarily originated from anthropogenic emission of petroleum hydrocarbons. In contrast, the C35 to C37 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 C29 and C31 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 δ13C measurements to elucidate information on the source and transport of n-alkanes in the polluted urban atmosphere.

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REFERENCES


