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Carbon isotope evidence for oil-pollution in long chain normal alkanes in Tokyo Bay sediments

MINORU UZAKI, KEITA YAMADA and RYOSHI ISHIWATARI
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan

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Carbon isotope compositions of long-chain n-alkanes (C_{27} - C_{33}) in selected samples from a Tokyo Bay sediment core (0 - 3 m in depth) were determined by gas chromatography/isotope ratio mass spectrometry (GC-IRMS). $\delta^{13}C$ values of the n-alkanes in the shallow sections (0 - 40 cm in depth, present ~ 1965 AD) range from $-31.5$ to $-28.2\%$o relative to the PDB standard, showing that even carbon-numbered n-alkanes are isotopically heavier than the odd numbered ones. The n-alkanes in the deeper sections (190 - 220 cm in depth) show the values ranging from $-29.6$ to $-31.4\%$ (average value: $-30.7\pm0.6\%$) without any significant difference among the n-alkanes. The results of n-alkanes in the shallow sections are explained by an addition of oil-derived n-alkanes to higher plant wax n-alkanes observed in the deeper sections.

INTRODUCTION
Since Matthews and Hayes (1978) developed a technique using gas chromatography coupled with isotope ratio mass spectrometry (GC-IRMS) for analyses of carbon isotopes ($^{12}C$ and $^{13}C$) of individual organic compounds, many studies have demonstrated the usefulness of this technique in the examination on organic geochemical cycles in ancient environments (Freeman et al. 1990; Hayes et al. 1990; Kohnen et al. 1992; Micke and Leplat 1991). Little is known, however, on the $\delta^{13}C$ values of n-alkanes in recent environments and their significance in environmental studies. Rieley et al. (1991) reported $\delta^{13}C$ values of odd carbon-numbered C_{25} - C_{33} n-alkanes from a lake sediment ranging from $-30.1$ to $-35.9\%$o (relative to PDB) and concluded that these were derived from deciduous leaf waxes. Kennicutt and Brooks (1990) determined $\delta^{13}C$ values of unusually even carbon dominated n-alkanes in continental shelf sediments offshore North Island, New Zealand and suggested the different origins of odd and even carbon-numbered n-alkanes. These studies indicate that carbon isotopic examinations are quite useful for pursuing sources of n-alkanes in geochemical samples. No study has been reported, however, on carbon isotopic composition of n-alkanes in environmentally polluted sediments. Since n-alkanes in young sediments are more or less contain those by oil pollution, this study is aimed to determine $\delta^{13}C$ values of individual n-alkanes in polluted sediments (Tokyo Bay sediments) by the use of a GC-IRMS method and to show usefulness of the method in the pollution studies.

MATERIALS AND METHODS

Samples
Tokyo Bay sediments were selected for this study because these are well-documented by studies of organic pollution in this area by us and other research groups (Ishiwatari et al. 1983; Ohta et al. 1983; Takada et al. 1984, 1992; Yun 1989; Yun et al. 1983).

Tokyo Bay has been receiving discharges of
many kinds of pollutants from Tokyo Metropolitan and adjacent areas through four major rivers (Rivers Edogawa, Arakawa, Sumidagawa and Tamagawa). A daily input of organic carbon into the bay through the rivers was estimated to be 410 tons in 1976 (Ishiwatari et al. 1983).

A 3 m-long sediment core sample G81-7 (depth from 0 to 3 m under water depth of 16 m) was taken at 35°33.3’N; 139°49.6’E (10 km off the mouth of River Arakawa, located in the inner part of the bay) in 1981. The core sample was cut at every 10 cm in depth on board, and stored in a freezer at −20°C until analysis. The age of the sediment in the surface sections (0 ~ 40 cm in depth) was estimated to be about 15 years old using the sedimentation rate (0.58 g cm⁻² yr⁻¹) determined by a lead-210 method (Matsumoto 1983). The year of 1707 AD was noted at the depth of 170 cm by the presence of volcanic ash from the eruption of Mt. Fuji.

Method
The procedures for recovery of saturated hydrocarbons from sediment samples were described elsewhere (Yun 1989). Briefly, a freeze-dried sediment sample (3 ~ 10 g) was soxhlet-extracted by a mixture of benzene and methanol (6:4) for 18 hrs. After evaporation of the solvents from the extract, saturated hydrocarbons were obtained in the n-hexane fraction by column chromatography using silica gel. For the separation of n-alkanes from the saturated hydrocarbons, the n-hexane eluate was transferred into a glass ampoule, evaporated and dissolved in 1 ml of iso-octane. Pellets of molecular sieve 5 A were added into the iso-octane solution. The glass ampoule was sealed and heated at 100°C for 18 hrs. After wash with n-hexane, the pellets were dissolved by HF solution, and n-alkanes were recovered by extraction with n-hexane.

The carbon isotope compositions of n-alkanes were measured by using a Finnigan Mat GC-IRMS combined with a delta-S mass spectrometer. In a typical GC analysis, one µl of n-alkane solution was injected into a DB-5 chemically-bonded fused silica capillary column (30 m x 0.32 mm i.d.) of the GC with a splitless mode. Helium was used as carrier gas. The GC oven temperature was programmed from 60 to 120°C at the rate of 30°C min⁻¹ and then to 310°C at 5°C min⁻¹. The injector temperature was 300°C. Normal alkanes emerged from the GC column were continuously introduced into the a CuO furnace where individual n-alkanes were successively combusted to CO₂. The intensities of masses 44, 45 and 46 corresponding to ¹²C₁₆O₂, ¹³C₁₆O₂ and ¹²C¹⁸O₁₆O, respectively, thus prepared, were measured simultaneously, from which the ¹²C/¹³C ratios were determined. The ¹³C values of n-alkanes were checked by measuring a mixture of standard n-alkanes (C₁₀ ~ C₄₁) provided by Chevron Oil Field Research Co (Hayes et al. 1990). For calibration of ¹³C values of the standards, a CO₂ reference gas was automatically introduced into the IRMS in pulses before and after n-alkane peaks. The n-alkane sample injections and the IRMS measurements were repeated three or four times in most cases. The carbon isotope ratios were expressed in unit of ¹³C relative to the PDB standard. The precision in measurements for the standards was within 0.4‰ and 0.6‰ for most sediment samples.

RESULTS AND DISCUSSION
Analytical results of carbon isotope compositions of individual C27 ~ C33 n-alkanes from different depth sections are given in Table 1 and Fig. 1(a). The reason why we selected n-alkanes of the carbon range (C27 ~ C33) is that these n-alkanes are abundant in most sediments, oils contaminating aquatic environment and higher-plant n-alkanes. Therefore, these n-alkanes are suitable to evaluate the mixing of n-alkanes from different sources.

The ¹³C values vary from −28.2 to −31.5‰. A marked difference in the ¹³C values was found between the shallow (0 ~ 40 cm) and deeper sections (190 ~ 220 cm in depth). Normal alkanes in the deeper sections show the ¹³C values ranging from −29.6 to −31.4‰, where
Table 1. Analytical results of carbon isotope composition of individual n-alkanes in Tokyo Bay sediments. Core sample; G81-7, Location: 35°33.3’N 139°49.6’E, water depth 16 m.

<table>
<thead>
<tr>
<th>Sample depth (cm)</th>
<th>Organic Carbon (% of dry sediment)</th>
<th>δ¹³C (%) of bulk organic matter</th>
<th>δ¹³C (%) of each n-alkane</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>1.38</td>
<td>-19.8</td>
<td>C₂₇ -30.0</td>
</tr>
<tr>
<td>10-20</td>
<td>1.05</td>
<td>-20.4</td>
<td>C₂₈ -28.6</td>
</tr>
<tr>
<td>20-30</td>
<td>1.24</td>
<td>-30.0</td>
<td>C₂₉ -28.6</td>
</tr>
<tr>
<td>30-40</td>
<td>1.00</td>
<td>-20.4</td>
<td>C₃₀ -30.0</td>
</tr>
<tr>
<td>190-200</td>
<td>0.67</td>
<td>-30.6</td>
<td>C₃₁ -31.4</td>
</tr>
<tr>
<td>210-220</td>
<td>0.79</td>
<td>-30.4</td>
<td>C₃₂ -31.0</td>
</tr>
</tbody>
</table>

Fig. 1. a) δ¹³C values of C₂₇−C₃₃ n-alkanes as function of carbon number and b) n-alkane distribution in different depths of Tokyo Bay sediment. Core sample; G81-7, Location: 35°33.3’N 139°49.6’E, water depth 16 m.

The number of n-alkanes analyzed is 14 and the average value: -30.7 ± 0.6‰. Normal alkanes in the deeper sections may be natural in origin, because the δ¹³C values fall in a range for deciduous leaf-wax n-alkanes of higher plants reported previously. According to Rieley et al. (1991), δ¹³C of C₂₅ to C₃₃ odd carbon-numbered n-alkanes range from -30.1 to -38.4‰.

The carbon isotopes of n-alkanes in the shallow sections are slightly heavier (-31.5 to -28.2‰) than those in the deep sections. Moreover, the δ¹³C values of n-alkanes expressed as a function of carbon-number show a zigzag pattern, where even carbon number n-alkanes are isotopically heavier than odd carbon-numbered n-alkanes.

This zigzag pattern indicates that n-alkanes in the shallow sections had not been derived from a single source, because no mechanism has been presented to produce differences in δ¹³C between even carbon-numbered alkanes and odd carbon-numbered ones from a single source. A plausible explanation for this zigzag pattern is a mixing mechanism of unpolluted and polluted (oil-pollution) n-alkanes, whose relative abundances of odd carbon-numbered n-alkanes to
even carbon-numbered ones are different. Normal alkanes of oil-pollution origin are isotopically heavier than those of higher-plant wax origin.

The $\delta^{13}C$ difference between the shallow and deeper sections in the Tokyo Bay sediment is consistent with the results obtained from a GC n-alkane analysis. As shown in Fig. 1(b), carbon preference indices (CPI, which are defined here the ratio of odd carbon-numbered n-alkanes to even ones C$_{27}$ to C$_{33}$) show 2.2~2.3 for the shallow sections and 4.5~4.6 for the deeper sections, respectively. The n-alkane concentrations in the shallow sections are 2~3 times higher than those in the deeper sections. The approximate depositional years of the 40~50 cm sections are estimated from the sedimentation rate from 1960 to 1965 AD when oil-pollution of Tokyo Bay has probably become intense. The CPI values and n-alkane concentrations clearly indicate a considerable portion of n-alkanes in the shallow sections was derived from oil pollution.

Normal alkanes in petroleum are generally composed of almost equal amount of even and odd carbon-numbered molecules (CPI=1) (Hunt 1979). Therefore, we estimated 38 ± 10% of the total n-alkanes in shallow sediments with CPI of 2.3 are pollution-derived ones using a simple mixing model of pollution-derived n-alkanes (CPI=1.0) and higher-plant n-alkanes in the 190~220 cm sections (CPI=4.5 ± 0.4).

According to the simple mixing model of the two endmembers, the $\delta^{13}C$ value of n-alkane with carbon number $n$ in a sediment section ($\delta^{13}C_n$, %) is expressed by the following equation:

$$\delta^{13}C_n = \delta^{13}C_{n_o} \times f_{n_o} + \delta^{13}C_{n_k} \times (1-f_{n_o})$$

where, $\delta^{13}C_{n_o}$ is $\delta^{13}C$ of oil-derived n-alkane with carbon number $n$ (C$_n$), $\delta^{13}C_{n_k}$ $\delta^{13}C$ of higher-plant derived n-alkane with C$_n$ and $f_{n_o}$ the fraction of oil-derived n-alkane with C$_n$ in the total n-alkane with C$_n$, respectively.

It can be assumed here that $\delta^{13}C$ of higher plant endmember is represented by those of n-alkanes in the deeper sections (190~220 cm in depth), where the $\delta^{13}C$ values are in the range of $-29.6$ and $-31.4\%$ (average: $-30.7 \pm 0.6\%$) for n-alkanes with C$_{27}$~C$_{33}$. However, since $\delta^{13}C$ values of the other endmembers (oil-derived n-alkanes) are unknown, $f_{n_o}$ of oil-derived n-alkane in the total n-alkane for each n-alkane can not be calculated. Judging from the zigzag distribution of $\delta^{13}C$ value in n-alkanes as a function of their carbon number, carbon isotopes of oil-derived n-alkanes with C$_{27}$~C$_{33}$ may be isotopically heavier than those of higher plant endmember. If the fraction (38%) of oil-derived n-alkanes in the total n-alkanes in shallow sections estimated from CPI values is correct, $\delta^{13}C$ value of oil-derived n-alkanes would be approximately $-28\%$. This value for oil-derived n-alkanes seems appropriate, because even carbon-numbered n-alkanes in the range of C$_{29}$ and C$_{24}$ are generally the least abundant in higher plant n-alkanes and the average $\delta^{13}C$ value of these n-alkanes measured in the same core sample is $-27.9 \pm 0.6\%$.

$\delta^{13}C$ values of individual long-chain n-alkanes in petroleum have become measured just recently (Sofer et al. 1991). Limited data seem to show that their $\delta^{13}C$ values are variable depending on their source types (marine vs. lacustrine) and locations of occurrence. Reasons for variable $\delta^{13}C$ values of petroleum n-alkanes are not known yet. Extensive collection of $\delta^{13}C$ data of n-alkanes from different petroleums and higher-plant waxes etc. is needed before reliable discussions are made on the origin and behavior of individual n-alkanes in the aquatic environment and their historical variations.

**CONCLUSION**

The present study revealed that $\delta^{13}C$ values of long-chain n-alkanes in Tokyo Bay sediments gave a distinct difference between oil-polluted and unpolluted sections. The results can be explained by a mixing model of higher plant wax n-alkanes with oil-derived ones. This study shows that GC-IRMS measurements of individual n-alkanes give a useful criterion on oil pollution which is better than the CPI of n-alkanes obtained by a GC method.
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REFERENCE


