Land-derived lipid class compounds in the deep-sea sediments and marine aerosols from North Pacific

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Abstract—Deep-sea sediments from western to central North Pacific as well as marine aerosols from western North Pacific were analyzed for lipid class compounds including n-alkanes, fatty alcohols, monocarboxylic acids, dicarboxylic acids, and hydroxy fatty acids using capillary gas chromatography (GC) and GC-mass spectrometry. The distributions of n-alkanes (C\text{20}–C\text{35}) in the sediments were characterized by the predominance of C\text{31}, C\text{29} and C\text{27} with a carbon preference index (CPI: odd/even ratio) of 4.79–5.85. A similar distribution (with lower CPI value) was observed in the marine aerosols, suggesting that organic matter of terrestrial higher plant origin are long-range transported to the remote atmosphere and to deep-sea sediments. Fatty alcohols in both aerosols and sediments showed molecular distributions with a strong even-to-odd carbon number predominance with two maxima at C\text{16} and C\text{22} or C\text{26}. Fatty acids showed similar bimodal distributions with maxima at C\text{16} and C\text{26} or C\text{28}. These results demonstrated that North Pacific deep-sea sediments are influenced by both marine and terrestrially derived organic matter. The longitudinal distributions of terrigenous lipids such as n-C\text{29} alkane, n-C\text{26} alcohol, C\text{29} sterols, n-C\text{32} fatty acid, C\text{24} \alpha,\omega-dicarboxylic acid and C\text{24} \omega-hydroxyacid, C\text{30} (\omega-1)-hydroxy acid detected in the deep-sea sediments indicated that their concentrations generally decreased from western to central North Pacific, supporting atmospheric transport of terrestrial organic matter from the Asian continents to central North Pacific and subsequent supply to the underlying deep-sea sediments via air-to-sea interface.

INTRODUCTION

Eolian dust fallout in open ocean has been first described in the Atlantic Ocean by DARWIN (1846). The mineralogical studies of pelagic sediments raised the importance of atmospheric transport of terrestrial materials to deep-sea sediments, which has long been a major issue of oceanography (e.g., REX and GOLDBERG, 1958; BLANK et al., 1985; SCHRAMM and LEINEN, 1987). Long-range transport of terrigenous materials through the atmosphere has recently been substantiated by both organic and inorganic chemical studies of remote marine aerosols. SIMONEIT et al. (1977) studied organic matter in eolian dusts over the Atlantic Ocean and reported n-alkanes, fatty acids and n-alcohols, whose molecular distributions indicated a significant contribution from terrestrial higher plant vegetation over the remote marine atmosphere. Long-range atmospheric transport of soil dust from Asia to the tropical and central North Pacific has also been demonstrated by inorganic study of

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the marine aerosol samples collected at remote islands including Enewetak Atoll (DUCE et al., 1980; UEMATSU et al., 1983, 1985). Atmospheric transport of continentally derived materials to the tropical North Pacific has also been proposed with detailed analyses of n-alkanes, n-alcohols and fatty acids (GAGOSIAN et al., 1981; PELTZER and GAGOSIAN, 1989).

The studies of lipid class compounds in remote marine aerosols clearly showed that continentally derived materials are transported over the open ocean and suggest that the organic matter associated with aeolian dusts significantly contribute to the total organic carbon in deep-sea sediments (GAGOSIAN and PELTZER, 1985). Long-chain, even-carbon predominant series of n-fatty acids can be used as terrestrial higher plant tracers because they are characteristic constituents of surface leaf waxes of higher plants (KOLLATUKUDY, 1976; GAGOSIAN, 1986). Higher plants also biosynthesize homologous series of long-chain (C20 to >C30) even-carbon predominant n-alcohols and odd-carbon predominant n-alkanes as their wax components (KOLLATUKUDY, 1976). There are many studies on lipids in estuarine and coastal sediments (e.g., VOLKMAN et al., 1983; SALIOT et al., 1991 and references therein). However, only few studies of lipid class compounds have been reported in oceanic sediments at great distances from continents (FARRINGTON and TRIPP, 1977; PRAHL et al., 1989) and there is no reported study in western to central North Pacific, where significant amounts of organic matter associated with Asian dusts are expected to be transported through the atmosphere (BLANK et al., 1985; GAGOSIAN and PELTZER, 1985).

In this study, we conducted a detailed analysis of lipid class compounds (n-alkanes, fatty alcohols, fatty acids, dicarboxylic acids, and hydroxyacids) in the deep-sea sediments collected from western to central North Pacific as well as marine aerosols collected from western North Pacific. Comparing their molecular distributions between the aerosol and sediment samples and longitudinal distributions in the deep-sea sediments, we evaluate the importance of west-to-east atmospheric transport of terrestrial organic matter over the central North Pacific and underlying deep-sea sediments. Microbial decomposition and alteration of lipid compounds in the deep-sea sediments during early diagenesis will also be discussed.

EXPERIMENTAL

Sediments

Sediment samples were used from four box core samples collected from the North Pacific sites during the R/V Hakuho-Maru cruise (KH-80-2) in 1980 (YANG et al., 1986). Figure 1 shows sampling sites of the sediments. Table 1 gives latitude, longitude and water depth of the sampling location as well as the depth of sediment samples used. Water depths of the sampling sites were between 5381 and 5654 m. The sediment samples are red clay type and calcium carbonate was already dissolved. Sedimentation rates have been determined to be 0.4 to 1 cm/kyr by means of natural radionuclide (YANG et al., 1986).

The dried samples (6 g) were extracted under a reflux with 50 ml 0.1 M KOH in methanol, containing ca. 20% distilled water. The extracts were isolated by
Land-derived lipid class compounds

Fig. 1. Sampling locations of deep-sea sediments (Sts. 5, 6, 8, 9) and marine aerosols (QFF 94).

Table 1. Description of the deep-sea sediment samples from North Pacific and their organic carbon and nitrogen contents (mg/g-dry sedi.)

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>St.5</th>
<th>St.6</th>
<th>St.8</th>
<th>St.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latitude</td>
<td>40°00.2'N</td>
<td>39°02.5'N</td>
<td>38°03.3'N</td>
<td>39°00.0'N</td>
</tr>
<tr>
<td>Longitude</td>
<td>150°00.0'E</td>
<td>166°00.3'E</td>
<td>179°45.7'W</td>
<td>170°00.8'W</td>
</tr>
<tr>
<td>Water depth, m</td>
<td>5509</td>
<td>5654</td>
<td>5548</td>
<td>5381</td>
</tr>
<tr>
<td>Sediment section, cm</td>
<td>10-12</td>
<td>0-1</td>
<td>7-9</td>
<td>15.5-19.5</td>
</tr>
<tr>
<td>Total carbon, mg/g</td>
<td>3.45</td>
<td>4.44</td>
<td>3.13</td>
<td>2.46</td>
</tr>
<tr>
<td>Total organic carbon, mg/g</td>
<td>2.50</td>
<td>3.05</td>
<td>1.79</td>
<td>1.34</td>
</tr>
<tr>
<td>Total nitrogen, mg/g</td>
<td>0.53</td>
<td>0.68</td>
<td>0.54</td>
<td>0.44</td>
</tr>
<tr>
<td>Org.C/N weight ratio</td>
<td>4.8</td>
<td>4.5</td>
<td>3.3</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Total organic carbon was determined after treatment with 2M HCl solution overnight.

filtration with a pre-cleaned Whatmann GF/A filter. The residue was further extracted with methanol and then methylene chloride under ultrasonication. The extracts were combined and concentrated by a rotary evaporator under a vacuum. Neutral components were isolated from the total extracts by an extraction with n-hexane/methylene chloride mixture. They were further divided into four fractions by
means of a silica gel column chromatography (KAWAMURA and GAGOSIAN, 1987a), by eluting with (1) n-hexane (N-1: aliphatic hydrocarbons), (2) n-hexane/methylene chloride (2:1) mixture (N-2: polycyclic aromatic hydrocarbons), (3) methylene chloride (N-3: aldehydes and ketones) and (4) methylene chloride/methanol (95:5) mixture (N-4: alcohols).

Acidic components were extracted with methylene chloride from the remaining solution after acidifying it (pH = 1) with 6 M HCl. The acidic fraction was concentrated and the carboxylic acids were derivatized to methyl esters with 14% BF$_3$/methanol at 100°C for 30 min. The methyl esters were divided into three sub-fractions on the silica gel column by eluting with n-hexane/methylene chloride (1:2) mixture (A-1: monocarboxylic acid methyl esters), methylene chloride/ethyl acetate (98:2) mixture (A-2: dicarboxylic acid dimethyl esters) and methylene chloride/methanol (95:5) mixture (A-3: hydroxyacid methyl esters).

Aerosols

Marine aerosol sample was collected in the western North Pacific during R/V Hakuho-Maru cruise in August 9–13, 1989 using a high volume air sampler. The air sampler was operated on the upper deck of the vessel (ca. 14 m above the sea surface) under a control of the wind sector (±45°) and wind speed (≥5 m/sec) system to avoid contamination from the ship exhausts (KAWAMURA and USUKURA, 1993). Sampling location is shown in Fig. 1. During the sample collection, weather conditions continued to be very clear and fine with a dominant wind direction from the west (Asian continents). Aerosol particles were collected on a pre-combusted (500°C, 3 hrs) quartz fiber filter and the filter sample was stored in a pre-cleaned glass jar with a Teflon-lined cap at –20°C prior to analysis. One quarter of the filter was extracted with 50 ml 0.1 M KOH in methanol, containing ca. 20% distilled water. The extracts were concentrated and separated into neutral and acidic fractions. Each fraction was further divided into sub-fractions as described above.

GC and GC-MS analyses

Each sub-fraction was concentrated and dried by using a rotary evaporator and a nitrogen blow-down system and finally dissolved in 50 or 100 µl n-hexane. Alcohol (N-4) and hydroxyacid methyl ester (A-3) fractions were silylated with BSTFA to derivatize hydroxy group to trimethyl silyl (TMS) ether. Two µl of each fraction were injected to the capillary gas chromatograph (Carlo Erba Vega 6000 or Hewlett Packard 5890) installed with on-column injector, fused silica capillary column (DB-5, 0.32 mm x 30 m x 0.25 µm) and an FID detector. Column oven temperature was programmed from 50°C (1 min.) to 120°C at 30°C/min. and then to 310°C at 6°C/min. Hydrogen and helium were used as a carrier gas for Carlo Erba GC and Hewlett Packard GC, respectively. GC data were processed by Shimadzu C-R7A or Hewlett Packard 3396A integrator.

Identification of the compounds were performed by comparing gas chromatographic retention times with those of authentic standards. Samples were further analyzed by a Finnigan-MAT INCOS-50 or ITS-40 GC-mass spectrometer installed
with the similar column described above. Mass spectral identification was confirmed by comparing the obtained mass spectra with those of authentic standards or mass spectra stored in the INCOS data library system.

**Carbon and nitrogen analyses**

Total carbon, total organic carbon and total nitrogen (organic nitrogen plus fixed-ammmonium nitrogen) were measured using a Yanagimoto MT-3 CHN corder. Total organic carbon and total nitrogen contents were obtained after inorganic carbon (carbonates) was removed by treatment with 2 M HCl solution overnight. As seen in Table 1, the deep-sea sediments contained negligible amounts of carbonate carbon.

**RESULTS AND DISCUSSION**

In both marine aerosol and deep-sea sediment samples, n-alkanes, n-alcohols, sterols, mono- and di-carboxylic acids and hydroxy fatty acids were detected. Tables 2 and 3 summarize a range of carbon numbers, maximum carbon number ($C_{\text{max}}$), carbon preference index (CPI) and concentrations of the lipid class compounds in the marine aerosol and deep-sea sediment samples, respectively.

**Molecular distributions of lipids and long-range atmospheric transport**

1. **Long-chain n-alkanes**

Normal alkanes ($C_{19}-C_{42}$) were detected in the marine aerosols with a maximum at $C_{31}$ (Fig. 2). The lower molecular weight n-alkanes (e.g., $C_{20}-C_{26}$) showed no odd-to-even carbon number predominance, suggesting that they originate from combustion of fossil fuels (SIMONEIT and MAZUREK, 1982). In contrast, higher molecular weight n-alkanes ($C_{27}-C_{33}$) showed a strong odd-to-even carbon number predominance. The distribution of lower n-alkanes is similar to those observed in urban aerosols from Tokyo (KAWAMURA et al., 1995). The marine aerosol sample (QFF94) did not show a hump of unresolved complex mixture of hydrocarbons.

Table 2. Concentrations (ng m$^{-3}$) of lipid class compounds in the marine aerosol sample (QFF 94) from North Pacific

<table>
<thead>
<tr>
<th>Compound class</th>
<th>Range</th>
<th>$C_{\text{max}}$</th>
<th>CPI</th>
<th>Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Alkanes</td>
<td>C19-C42</td>
<td>C31</td>
<td>2.44 (C22-C35)</td>
<td>3.96</td>
</tr>
<tr>
<td>H-Alk</td>
<td>C22-C35</td>
<td>C31</td>
<td>4.37</td>
<td>3.50</td>
</tr>
<tr>
<td>n-Alcohols</td>
<td>C14-C32</td>
<td>C26</td>
<td>10.6 (C20-C30)</td>
<td>3.65</td>
</tr>
<tr>
<td>H-Alc</td>
<td>C20-C32</td>
<td>C26</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Sterols</td>
<td>C27-C29</td>
<td>C27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fatty acids</td>
<td>C12-C38</td>
<td>C16, C28</td>
<td>8.80</td>
<td></td>
</tr>
<tr>
<td>LFA</td>
<td>C12-C19</td>
<td>C16</td>
<td>14.0 (C12-C19)</td>
<td>2.36</td>
</tr>
<tr>
<td>HFA</td>
<td>C20-C32</td>
<td>C28</td>
<td>4.06 (C20-C32)</td>
<td>6.00</td>
</tr>
<tr>
<td>Dicarboxylic acids</td>
<td>C8-C32</td>
<td>C26, C28</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>H-Dicarboxylic acids</td>
<td>C20-C32</td>
<td>C26, C28</td>
<td>2.01 (C20-C32)</td>
<td>0.93</td>
</tr>
<tr>
<td>$\omega$-Hydroxy acids</td>
<td>C12-C30</td>
<td>C16, C22</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>H-$\omega$-Hydroxy acids</td>
<td>C20-C30</td>
<td>C16, C22</td>
<td>3.22 (C20-C30)</td>
<td>0.42</td>
</tr>
<tr>
<td>($\omega$-1)-Hydroxy acids</td>
<td>C20-C26</td>
<td>C22</td>
<td>7.1 (C20-C26)</td>
<td>0.05</td>
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</table>
Table 3. Concentrations (ng/g-dry sedi.) of lipid class compounds in the deep-sea sediments from western to central North Pacific

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compound class</th>
<th>Range</th>
<th>Cmax</th>
<th>CPI</th>
<th>ng/g</th>
<th>Cmax</th>
<th>CPI</th>
<th>ng/g</th>
<th>Cmax</th>
<th>CPI</th>
<th>ng/g</th>
<th>Cmax</th>
<th>CPI</th>
<th>ng/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-Alkanes</td>
<td>C22-C35</td>
<td>C31</td>
<td>4.69</td>
<td>310</td>
<td>C31</td>
<td>4.79</td>
<td>430</td>
<td>C31</td>
<td>5.56</td>
<td>350</td>
<td>C31</td>
<td>5.85</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>n-Alcohols</td>
<td>C14-C30</td>
<td>C26, C16</td>
<td>510</td>
<td>C16, C22</td>
<td>440</td>
<td>C16, C26</td>
<td>270</td>
<td>C16, C26</td>
<td>230</td>
<td>C16, C26</td>
<td>230</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H-n-Alc</td>
<td>C20-C30</td>
<td>C26</td>
<td>4.38</td>
<td>380</td>
<td>C22</td>
<td>4.97</td>
<td>300</td>
<td>C26</td>
<td>8.67</td>
<td>200</td>
<td>C26</td>
<td>4.34</td>
<td>180</td>
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<tr>
<td>Sterols</td>
<td>C27-C29</td>
<td>C29</td>
<td>97</td>
<td></td>
<td>C29</td>
<td>110</td>
<td>C29</td>
<td>66</td>
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<td>22</td>
<td>C29</td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>C12-C32</td>
<td>C16, C28</td>
<td>3750</td>
<td></td>
<td>C16, C26</td>
<td>7310</td>
<td>C16, C28</td>
<td>2110</td>
<td>C16, C28</td>
<td>1530</td>
<td>C16, C28</td>
<td>1530</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-LFA</td>
<td>C12-C19</td>
<td>C16</td>
<td>5.2</td>
<td>1900</td>
<td>C16</td>
<td>7.68</td>
<td>5070</td>
<td>C16</td>
<td>4.93</td>
<td>1020</td>
<td>C16</td>
<td>4.24</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>n-HFA</td>
<td>C20-C32</td>
<td>C28</td>
<td>3.03</td>
<td>1850</td>
<td>C26</td>
<td>3.6</td>
<td>2250</td>
<td>C26</td>
<td>3.39</td>
<td>1090</td>
<td>C26</td>
<td>3.22</td>
<td>830</td>
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<tr>
<td></td>
<td>br-FA</td>
<td>C13, C15, C17</td>
<td>C15</td>
<td>220</td>
<td>C15</td>
<td>410</td>
<td>C15</td>
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<td>C15</td>
<td>45</td>
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<tr>
<td>Dicarboxylic acids</td>
<td>C7-C34</td>
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<td>4150</td>
<td></td>
<td>C9</td>
<td>4400</td>
<td>C11</td>
<td>2490</td>
<td>C11</td>
<td>1760</td>
<td></td>
<td>C11</td>
<td>1760</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H-Di</td>
<td>C20-C32</td>
<td>C24</td>
<td>1.24</td>
<td>1920</td>
<td>C20</td>
<td>1.18</td>
<td>1580</td>
<td>C22</td>
<td>1.18</td>
<td>980</td>
<td>C27</td>
<td>1.21</td>
<td>760</td>
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<td>β-Hydroxyacids</td>
<td>C12-C20</td>
<td>C16</td>
<td>110</td>
<td></td>
<td>C18</td>
<td>110</td>
<td>C12</td>
<td>52</td>
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<td>C16</td>
<td>42</td>
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<tr>
<td>α-Hydroxyacids</td>
<td>C10-C32</td>
<td>C16, C24</td>
<td>480</td>
<td>450</td>
<td>C16, C24</td>
<td>230</td>
<td>C16, C28</td>
<td>170</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>H-ω-Hydroxyacids</td>
<td>C20-C32</td>
<td>C24</td>
<td>2.2</td>
<td>270</td>
<td>C24</td>
<td>2.49</td>
<td>250</td>
<td>C24</td>
<td>2.14</td>
<td>140</td>
<td>C28</td>
<td>2.47</td>
<td>98</td>
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<tr>
<td>(ω-1)-Hydroxyacids</td>
<td>C22-C30</td>
<td>C26</td>
<td>&gt;20</td>
<td>140</td>
<td>C26</td>
<td>&gt;20</td>
<td>140</td>
<td>75</td>
<td>C28</td>
<td>&gt;20</td>
<td>19</td>
<td></td>
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</tr>
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</table>
(UCM), although other marine aerosol samples from western North Pacific sometimes showed UCM hydrocarbons (Kawamura and Tanaka, unpublished results). However, the carbon preference index for the C_{22}–C_{35} alkanes (CPI: ratio of the amounts of odd-carbon n-alkanes to those of even-carbon n-alkanes) was 2.4, suggesting a combination of terrestrial higher plant waxes and petroleum hydrocar-
bons. The CPI values are known to be 5–10 for terrestrial higher plant waxes and an
unity for petroleum hydrocarbons and combustion residues of fossil fuels (SIMONEIT
and MAZUREK, 1982; KAWAMURA and KAPLAN, 1991). Aerosol studies from urban
Tokyo showed that CPI values of n-alkanes ranged from 1.1 to 2.8 with an average
of 1.5 (KAWAMURA et al., 1995).

Concentration of n-alkanes in the marine aerosol sample QFF 94 (ca. 4
ng m\(^{-3}\)) is within the concentrations (0.9–4.7 ng m\(^{-3}\)) obtained in the western North
Pacific (12°N–34°N) (Kawamura and Tanaka, unpublished results). Higher concen-
trations (4–29 ng m\(^{-3}\)) have been reported in the western North Pacific (OHTA and
HANNA, 1985). However, the present value is much higher than those reported from
tropical North Pacific aerosols (0.02–0.16 ng m\(^{-3}\), GAGOSIAN et al., 1981) and from
aerosols off the Coast of Peru (0.3–0.6 ng m\(^{-3}\), SCHNEIDER and GAGOSIAN, 1985).

Similar distributions of n-alkanes were obtained in deep-sea sediments from the
North Pacific (Fig. 2(b)). However, even-carbon numbered n-alkanes were less
abundant and thus CPI values were much higher (4.8–5.8, see Table 3) than the
marine aerosol sample (QFF 94, CPI = 2.4). These results suggest that the sediment
samples were not contaminated either from anthropogenic sources during sampling
or analytical procedures, and the surface sediments (St. 6) are not seriously influ-
enced by the recent global pollution. The results also indicate that the North Pacific
deep-sea sediments are significantly influenced by the terrestrial higher plant waxes,
which are probably transported to remote marine atmosphere, dry- and/or wet-
deposited over the open ocean and settled down on the ocean floor.

(2) n-Alcohols and Sterols

Normal fatty alcohols (C\(_{14}\)–C\(_{32}\)) were detected in the western North Pacific
aerosol sample (Fig. 3(a)). Distribution of the n-alcohols is characterized by a strong
even-to-odd carbon number predominance with a maximum at C\(_{26}\). The n-alcohols
are most likely derived from waxes of terrestrial higher plants (SIMONEIT et al., 1977;
GAGOSIAN et al., 1981). Concentration of total n-alcohols (4.4 ng m\(^{-3}\)) is similar to
those (2.8–6.7 ng m\(^{-3}\)) obtained in the western North Pacific aerosols collected
during another cruise (12°N–34°N) (Kawamura and Tanaka, unpublished results).
The concentrations of n-alcohols in the western North Pacific are higher than those
(0.07–0.25 ng m\(^{-3}\)) reported in the remote marine aerosol samples from tropical
North Pacific (Eniwetak Atoll) (GAGOSIAN et al., 1981) and those (0.25–0.28
ng m\(^{-3}\)) from marine aerosols off the Coast of Peru (SCHNEIDER and GAGOSIAN, 1985).
The results suggest that fatty alcohols of terrestrial higher plant origin are transported
to the western North Pacific atmosphere probably from Asian continents.

Normal alcohols were also detected in the deep-sea sediments from western to
central North Pacific (Fig. 3(b)). Their distribution pattern is similar to that of the
marine aerosols (Fig. 3(a)), suggesting that n-alcohols in deep-sea sediments were
supplied from terrestrial higher plant sources probably through atmospheric trans-
port. However, lower molecular weight alcohols such as C\(_{16}\) are relatively more
abundant in the marine sediments, suggesting a contribution from marine phyto-
plankton to the sediments. Total concentrations of n-alcohols (C\(_{14}\)–C\(_{30}\)) were 230–
510 ng/g-dry wt. sediment, whose values are similar to n-alkanes (Table 3).
Fig. 3. Capillary gas chromatograms of TMS ethers of alcohols separated from (a) marine aerosol (QFF 94) and (b) deep-sea sediments (St. 8, depth 7–9 cm).
Although there is no reported concentrations of n-alcohols in the open ocean deep-sea sediments, the obtained values seem to be fairly high.

Sterols (C_{27} cholesterol, C_{27} cholestanol and C_{29} \( \beta \)-sitosterol) were detected in the marine aerosols, although their concentrations (0.12 ng m\(^{-3}\)) are much lower than n-alcohols (Table 2). \( \beta \)-Sitosterol has been proposed as a source marker of terrestrial higher plants (GAGOSIAN, 1986). These sterols have been reported in continental aerosols from California, Oregon and central Africa and C_{29} sterol was found to be more abundant than C_{27} sterol in the warmer climatological regions (SIMONEIT et al., 1983). Cholesterol may be in part derived from animals such as marine zooplankton (TISSOT and WELTE, 1984).

In the marine sediments, stigmasterol (C_{29}) was detected in addition to cholesterol and \( \beta \)-sitosterol (Fig. 3(b)). Stigmasterol is abundantly present in higher plants (TISSOT and WELTE, 1984). High abundance of C_{29} sterols in the sediments indicate an important contribution of terrestrial higher plant lipids to deep-sea sediments. However, abundance of C_{29} sterols relative to fatty alcohols such as C_{28} seems to be higher in the deep-sea sediments than the aerosols (Figs. 3(a) and (b)). This might suggest that a part of the sterols in the sediments is supplied to the open ocean by horizontal transport process in the ocean and/or produced by the marine organisms (VOLKMAN, 1986).

(3) Monocarboxylic acids

As shown in Fig. 4, molecular distribution of normal fatty acids in marine aerosols indicates a strong even-to-odd carbon number predominance with two maxima at C_{16} and C_{28}. Lower molecular weight fatty acids (C_{12}–C_{19}) are generally present in organisms including marine phytoplankton whereas higher molecular weight fatty acids (C_{20}–C_{32}) are characteristic of terrestrial higher plants (KOLLATUKUDY, 1976) and not found in marine organisms as major species (GAGOSIAN, 1986). Thus, abundant presence of C_{20}–C_{32} fatty acids in the western North Pacific aerosols indicate atmospheric transport of terrestrial organic matter over the open ocean. Similar distribution patterns have been reported in the continental aerosols from western United States (SIMONEIT and MAZUREK, 1982), West Africa (SIMONEIT et al., 1988), and China (SIMONEIT et al., 1991) as well as Japanese Islands (Kawamura and Kobayashi, unpublished results). Fatty acids in a range of C_{12}–C_{32} have also been reported in marine aerosols from equatorial Pacific (GAGOSIAN et al., 1981), eastern North Pacific (KAWAMURA and GAGOSIAN, 1990b) and off the Coast of Peru (SCHNEIDER and GAGOSIAN, 1985).

Fatty acids in the deep-sea sediment samples showed an even-to-odd carbon number predominance with maxima at C_{26} and C_{28} or C_{26} (Fig. 4(b)). Their distribution patterns are very close to that of the marine aerosol sample (Fig. 4(a)), indicating that solvent extractable fraction in the deep-sea sediments is contributed from terrestrial higher plants. Similarity of the chain-length distributions of fatty acids between marine aerosols and deep-sea sediments suggest that air-to-sea fallout (dry and wet) of aerosol particles in the remote atmosphere is an important transport process of terrigenous organic matter to deep-sea sediments. Higher fatty acids (C_{20}–C_{32}) have abundantly been reported in lacustrine Lake Biwa sediments and were
Fig. 4. Capillary gas chromatograms of monocarboxylic acid methyl esters isolated from (a) marine aerosol (QFF 94) and (b) deep-sea sediments (St. 5, depth 10–12 cm).
used as tracers for reconstruction of vegetational changes in the past (KAWAMURA and ISHIWATARI, 1984). Long-chain fatty acids were also used to reconstruct past changes in the terrestrial inputs to the eastern equatorial Pacific sediments (PRAHL et al., 1989).

Although both marine aerosol and deep-sea sediment samples showed a similar molecular distribution, branched chain fatty acids such as iso and anteiso C\textsubscript{15} are relatively more abundant in the marine sediments than the aerosol sample (Figs. 4(a) and (b)). Because branched chain fatty acids are characteristic to bacterial lipids (KANEDA, 1967; KAWAMURA and ISHIWATARI, 1984), fatty acids in the deep-sea sediments seem to have been largely influenced by microbial activity in the water column during a vertical transport and in sediments after deposition.

(4) Dicarboxylic acids

Homologous series of $\alpha,\omega$-dicarboxylic acids (C\textsubscript{8}–C\textsubscript{34}) were detected in the marine aerosol sample. Their molecular distribution is characterized by a strong peak of azelaic acid (C\textsubscript{9}) and relatively abundant presence of C\textsubscript{22}–C\textsubscript{28} diacids, which showed a weak even-to-odd carbon number predominance (Fig. 5(a)). Similar distributions have been reported in marine aerosols from the eastern North Pacific (KAWAMURA and GAGOSIAN, 1990a). The predominance of C\textsubscript{9} diacid in the marine aerosols has been explained as a result of photochemical oxidation of unsaturated fatty acids such as oleic acid which contains double bond predominantly at C-9 position (KAWAMURA and GAGOSIAN, 1987b). In contrast, long-chain dicarboxylic acids (C\textsubscript{20}–C\textsubscript{32}) have been proposed to be produced in soils by microbial terminal oxidation of plant-derived fatty acids and soil particles containing long-chain diacids have been considered to be injected to the atmosphere by winds and long-range transported to the remote marine atmosphere (KAWAMURA and GAGOSIAN, 1990a).

$\alpha,\omega$-Dicarboxylic acids (C\textsubscript{8}–C\textsubscript{34}) were also detected in the deep-sea sediments (Fig. 5(b)), however, their distribution is not similar to that of the marine aerosols (Fig. 5(a)), being different from the cases of n-alkanes, n-alcohols and fatty acids. The dicarboxylic acids in deep-sea sediments showed a smooth distribution with no predominant peak. The difference suggests that origin of sedimentary diacids is different from that of marine aerosols. However, a weak even-to-odd carbon number predominance was observed in a range of C\textsubscript{20}–C\textsubscript{32} (CPI for C\textsubscript{20}–C\textsubscript{32} diacids: 1.18–1.24, see Fig. 5(b) and Table 3), whose concentrations are fairly high: comparative to long-chain fatty acids (see Table 3). These results suggest that major portion of dicarboxylic acids is produced in sediments by microbial terminal ($\omega$- and $\omega$-1) oxidation of long-chain compounds such as fatty acid, which can produce both even and odd carbon number diacids from even carbon number fatty acids (KAWAMURA and ISHIWATARI 1984). This is similar to the mechanisms proposed in soils (KAWAMURA and GAGOSIAN, 1990a). Thus, long-chain dicarboxylic acids may hold an information of inputs of terrigenous organic matter to the deep-sea environment.

(5) Hydroxyacids

Three types of hydroxy fatty acids ($\beta$, $\omega$- and ($\omega$-1)-) have been detected in the marine aerosol sample, as $\omega$-hydroxyacids being a dominant group (Fig. 6(a)). This is the first report of the hydroxy fatty acids in a remote marine aerosol sample. The
(a) Diacids (Aerosols)

(b) Diacids (Sediments)

Fig. 5. Capillary gas chromatograms of $\alpha,\omega$-dicarboxylic acid dimethyl esters isolated from (a) marine aerosol (QFF 94) and (b) deep-sea sediments (St. 5, depth 10–12 cm).
ω-hydroxyacids showed a distribution pattern of a strong even-to-odd carbon number predominance (CPI for C₂₀–C₃₀: 3.22, see Table 2). ω-Hydroxyacids have been reported in terrestrial higher plants as cutin and suberin components (EGLINTON and HUNNEMAN, 1968) and in lacustrine and marine sediments (CARDOSO and EGLINTON, 1983; KAWAMURA and ISHIWATARI, 1984). The results indicate that ω-hydroxyacids probably associated with soil dust particles are transported to the open

(a) Hydroxy acids (Aerosols)

(b) Hydroxy acids (Sediments)

Fig. 6. Capillary gas chromatograms of TMS ether derivatives of hydroxy acid methyl esters isolated from (a) marine aerosol (QFF 94) and (b) deep-sea sediments (St. 5, depth 10–12 cm). Peaks of ω-hydroxy acids are shaded.
ocean. The soil particles were found to contain homologous series of \( \omega \)-hydroxyacids (Kawamura and Gagosian, 1987, unpublished results), which are probably produced by microbial terminal oxidation of fatty acids and other lipids. This is similar to the case of long-chain dicarboxylic acids, which are partly produced by microbial activity in soils, as stated above.

\( \omega \)-Hydroxyacids were also detected in the deep-sea sediments together with \( \beta \)- and (\( \omega \)-1)-hydroxyacids, as shown in Fig. 6(b). Even-to-odd carbon number predominance (CPI values: 2.2–2.5, see Table 3) was observed in the \( \omega \)-hydroxyacid distributions, however, CPI values are lower than that of the marine aerosols (3.2, Table 2). \( \beta \)- and (\( \omega \)-1)-hydroxy acids, which are relatively less abundant in the aerosol sample, are as abundant as \( \omega \)-hydroxyacids in the sediments. This suggests that \( \beta \)- and (\( \omega \)-1)-hydroxyacids are in part produced in the sediments by microbial oxidation of lipid class compounds. In fact, \( \beta \)-hydroxyacids are known as important constituents of bacterial cell wall and abundantly present in recent sediments (e.g., Kawamura and Ishiwatari, 1982). The long-chain \( \omega \)- and (\( \omega \)-1)-hydroxyacids may provide information of inputs of terrestial higher plants and soil dust particles over the pelagic sediments.

**Early diagenesis in deep-sea sediments**

The abundant presence of branched chain fatty acids and \( \beta \)-hydroxy acids in the sediment samples suggests that organic materials are significantly subjected to microbial degradation and modification in the deep-sea sediments. Studies of recent sediments have shown that plankton-derived lipids such as lower molecular weight fatty acids (C\(_{16}\), C\(_{18}\)) are rapidly decomposed and resynthesized in water column and surficial sediments by a microbial activity (e.g., Matsuda and Koyama, 1977; Kawamura et al., 1987). However, terrestrial lipids such as higher molecular weight (C\(_{20}\)–C\(_{32}\)) fatty acids, n-alcohols and n-alkanes are refractory to microbial degradation during an early diagenesis, thus, they are preserved in sediments over a geological time (e.g., Kawamura and Ishiwatari, 1984).

Figure 7(a) plots concentration ratios of low to high molecular weight fatty acids (C\(_{16}\)/C\(_{28}\) and \( \Sigma (C_{12}–C_{19})/\Sigma (C_{20}–C_{32}) \)) as a function of sediment depth. In spite that sediment samples used were collected at different sites in the North Pacific, the results show a decreasing trend with depth, supporting a selective degradation of lower carbon-number lipids in the surface sediments. This indicates that plankton-derived lipids which escaped microbial degradation during settling in the water column, are subjected to decomposition in the deep-sea surface sediments. In contrast, higher carbon-number lipids stayed rather constant with depth (see Table 3). Higher molecular weight lipids of terrigenous origin appear to be stable in the marine sediments (Volkman et al., 1986).

Figure 7(b) shows a vertical trend of CPI values (ratio of the amount of even carbon number fatty acids to that of odd carbon number fatty acids) for lower (LFA: C\(_{12}–C_{19}\)) and higher (HFA: C\(_{20}–C_{32}\)) fatty acids. The CPI values for LFA decrease with depth, probably as a result of microbial \( \alpha \)-oxidation of fatty acids, which produces odd carbon number fatty acids from even carbon number fatty acids.
Interestingly, CPI values of HFA seem to decrease slightly from the surface to deeper sediments, suggesting that HFA are in part subjected to \( \alpha \)-oxidation in the surface layers of deep-sea sediments. The present author, however, believes that HFAs are refractory to the bacterial attack in the sediments and major portion of longer chain lipid compounds is preserved in the sediments with no severe modification. Consequently, lipids in the deep-sea sediments from North Pacific should provide informations of long-range atmospheric transport of terrestrial higher plants and soil organic matter.

**Longitudinal distributions of terrestrial lipids in the North Pacific deep-sea sediments**

Figure 8 presents concentrations of selected lipid compounds of terrestrial
Fig. 8. Longitudinal distributions of terrestrial lipid compounds in the western to central North Pacific sediments.

origin in the western to central North Pacific sediments. Their longitudinal distributions indicate that concentrations of the terrestrial lipid compounds generally decrease from the west to east. Because sampling sites of the sediments studied are located under the pathway of westerlies (see Fig. 1), terrestrial lipids in the North Pacific sediments are most likely supplied through atmospheric transport from source regions of Asian continents. The longitudinal decrease of terrestrial lipids in the pelagic sediments from west to east suggests that the terrigenous materials transported over the Pacific Ocean are scavenged from the atmosphere by dry and wet deposition processes. Based on the averaged concentrations of terrestrial lipid class compounds in the deep-sea sediment samples, sea-to-sediment fluxes of the lipids in the North Pacific were calculated assuming a sedimentation rate of 0.5 cm/1000 yr and the bulk sediment density of 0.5 (g dry sediment)/(cm³ wet sediment) (Yang et al., 1986; Kawamura et al., 1990). Table 4 gives estimated annual fluxes (0.09–1.5 µg m⁻² yr⁻¹) for terrestrial n-alkanes, n-alcohols, n-fatty acids, α,ω-di-carboxylic acids, ω-hydroxyacids, and (ω-1)-hydroxyacids.

Air-to-sea fluxes of terrestrial lipids were also estimated using the results of QFF94 aerosol sample (Table 2) and assuming a deposition velocity of 0.15 cm/sec for marine aerosol particles (Slinn and Slinn, 1980; Gagosian and Peltzer, 1986). Estimated air-to-sea fluxes of terrestrial n-alkanes, n-alcohols and n-fatty acids at western north Pacific were 160 µg m⁻² yr⁻¹, 170 µg m⁻² yr⁻¹, and 280 µg m⁻² yr⁻¹, respectively. Air-to-sea fluxes of dicarboxylic acids, ω-hydroxyacids, and
Table 4. Estimated water-to-sediment fluxes of terrestrial lipid compounds in North Pacific based on the analyses of deep-sea sediment samples

<table>
<thead>
<tr>
<th>Lipid class compounds</th>
<th>C-numbers</th>
<th>Water-to-Sediment Flux (μg m⁻²yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Alkanes</td>
<td>C20-C33</td>
<td>0.33</td>
</tr>
<tr>
<td>n-Alcohols</td>
<td>C20-C32</td>
<td>0.27</td>
</tr>
<tr>
<td>n-Fatty Acids</td>
<td>C20-C32</td>
<td>1.5</td>
</tr>
<tr>
<td>Dicarboxylic Acids</td>
<td>C20-C32</td>
<td>1.3</td>
</tr>
<tr>
<td>ω-Hydroxyacids</td>
<td>C20-C30</td>
<td>0.19</td>
</tr>
<tr>
<td>(ω-1)-Hydroxyacids</td>
<td>C20-C30</td>
<td>0.09</td>
</tr>
</tbody>
</table>

(ω-1)-hydroxyacids were calculated to be 43, 20 and 2 μg m⁻²yr⁻¹, respectively. The estimated air-to-sea fluxes are 2–3 orders of magnitudes greater than the water-to-sediment fluxes obtained for central North Pacific (Table 4). Although these results indicate that atmospheric transport is a potentially important pathway to carry the terrestrial lipids to the deep-sea sediments, their air-to-sea flux in the western North Pacific are unexpectedly high in comparison with the sea-to-sediment flux in the central North Pacific. This is probably due to a usage of the western North Pacific aerosol sample, whose terrestrial lipid concentrations may be exceptionally high because of the sampling site close to Asian continents and a strong wind from the west during sample collection.

Much lower values have been reported in the tropical Pacific for air-to-sea flux of terrestrial lipids. Gagosian and Peltzer (1986) measured terrestrial lipids in the marine atmosphere at Eniwetok Atoll (11°20’N, 162°20’E) and estimated air-to-sea flux of C₂₁–C₃₆ n-alkanes (25 μg m⁻²yr⁻¹), C₂₁–C₃₂ alcohols (4.2 μg m⁻²yr⁻¹) and C₁₉–C₃₂ fatty acids (8.4 μg m⁻²yr⁻¹). These values at Eniwetok Atoll seem to be more realistic to explain sea-to-sediment flux of terrestrial lipids in the open ocean.

Although there is no aerosol data set at present available to flux calculation in the central North Pacific, these considerations suggest that a long-range atmospheric transport of terrestrial organic matter contributes significantly to the abundant presence of terrigenous lipids in the bottom sediments of central North Pacific and plays an important role in controlling the accumulation of the terrestrial organic matter in the pelagic sediments. Although riverine input of terrigenous lipids cannot be ruled out, the present author considers that atmospheric inputs overwhelm riverine inputs in the central Pacific Ocean.

CONCLUSIONS

Molecular distributions of n-alkanes, fatty alcohols, fatty acids, dicarboxylic acids and hydroxy fatty acids in deep-sea sediment samples from the central North Pacific showed a predominance of longer carbon-chain numbered compounds: a strong signature of terrestrial higher plants and soil organic matter. Similar distributions of the lipid class compounds were also observed in the Pacific aerosol sample. Longitudinal distributions of terrestrial lipids in the deep-sea sediments showed a decreasing trend from western to central North Pacific. The results of the
present study indicated that terrestrial organic materials originated from Asian continents are long-range transported over the western to central North Pacific through the atmosphere and settled down to the deep-sea sediments. Flux estimation of terrestrial lipids over the North Pacific Ocean suggested that long-range atmospheric transport of terrigenous materials mostly derived from Asian continents is an important process, which significantly contributes to the accumulation of terrestrial materials in the pelagic bottom sediments.

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REFERENCES


