Combined use of Δ^{14}C and δ^{13}C values to trace transportation and deposition processes of terrestrial particulate organic matter in coastal marine environments

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Abstract

Accelerator mass spectrometry was used to measure radiocarbons of riverine suspended particles and sediments from the estuary, continental shelf and slope off the coast of Tokachi River in Japan. The spatial distribution of Δ^{14}C and δ^{13}C values of sedimentary organic matter was divided into those of (1) estuary, (2) continental shelf, and (3) continental slope. For shelf sediments, respective maxima can be seen for Δ^{14}C value, C/N ratio and organic carbon content at a station near the river mouth. The mean grain size of surface sediments also exhibits a similar trend. The δ^{13}C values show a minimum near the river mouth. The shelf composition does not appear to be a simple mixture of terrestrial and marine origin. From the above data, it is considered that the spatial distribution of Δ^{14}C and δ^{13}C values may reflect variations in dispersion and deposition processes together with the size fractionation of riverine suspended particles, the resuspension of sediments, and differences in the contribution of marine organic matter.

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1. Introduction

Global riverine discharge of dissolved and particulate terrestrial matter represents a substantial source of organic carbon to the ocean (Meybeck, 1993; Hedeges et al., 1997). Continental margins are recognized as the dominant reservoir for organic carbon burial in the marine environment. Total organic carbon comprises materials that are derived from both marine and terrestrial sources. An accurate inventory for terrestrial and marine organic carbon in continental margin sediments is important for quanti-
tative understanding of biogeochemical cycles. A variety of geochemical approaches have been employed to define the mixing ratio of marine and terrestrial organic matter, including $\delta^{13}C$ and lignin biomarker analyses (e.g., Hedges and Parker, 1976; Hedges and Mann, 1979; Prahl et al., 1994).

The $\delta^{13}C$ tracer has proven to be simple and very useful for dissolved organic carbon (DOC) and particulate organic carbon (POC) in riverine, estuarine and marine environments (Hedges and Parker, 1976; Prahl et al., 1994). It has been utilized to estimate relative amounts of biological materials derived from terrestrial and marine sources. This method is based on a general enrichment of $^{12}C$ in terrestrial organic matter compared with marine materials. Nevertheless, a considerable overlap exists in the $\delta^{13}C$ values of several major sources of DOC and POC within these aquatic environments. For this reason, we require an additional tracer to determine the fate of organic matter and to estimate the contribution of terrestrial organic matter to continental margins. Radiocarbon abundances have become an additional indicator of terrestrial versus marine sources because nuclear weapons testing in the 1950s and 1960s injected large quantities of $^{14}C$ into the atmosphere. There are different $\Delta^{14}C$ signatures of contemporary marine dissolved inorganic carbon (DIC) and atmospheric CO$_2$ (Nydal and Lovseth, 1983). The $\Delta^{14}C$ values of organic matter in river suspended particles range from $-980$ to $+75\%$ (Kao and Liu, 1996; Raymond and Bauer, 2001), but plankton and particulate organic carbon in marine environments have enriched $^{14}C$ values ranging from $-45$ to $+110\%$ (Williams et al., 1992; Wang et al., 1998; Bauer et al., 2001). Therefore, the simultaneous use of $\Delta^{14}C$ and $\delta^{13}C$ values adds a second dimension to isotopic studies of carbon cycling in surface aquatic environments, especially to the study of the fate and geochemical behavior of particulate organic carbon at continental margins.

The $\Delta^{14}C$ values of dissolved and particulate organic matter have been measured by several authors using accelerator mass spectrometry to elucidate dynamics of organic carbon in river systems (e.g., Hedges et al., 1986; Raymond and Bauer, 2001; Nagao et al., 2004) and marine environments (e.g., Druffel and Williams, 1990; Wang et al., 1996; Megens et al., 2001). Radiocarbon of organic matter in sediment trap samples has also been used to study the lateral transport of materials derived from sea margins (e.g., Anderson et al., 1994; Nakatsu et al., 1997; Honda et al., 2000). However, the application of this method to marine sediments is limited (e.g., Goni et al., 1997; Megens et al., 2002).

This study applies a combined use of $\Delta^{14}C$ and $\delta^{13}C$ to surface sediments from the river mouth, continental shelf, and slope off the coast of Hokkaido. This study is intended to test the utility of a combined $\Delta^{14}C$ and $\delta^{13}C$ approach to better understand the fate of terrestrial particulate organic matter that is released from the river to the coastal marine environment.

2. Materials and methods

2.1. Study area

The Tokachi River runs through southeastern Hokkaido, a large northern island in Japan. The 156-km-long river has a watershed of 9010 km$^2$. It originates at Mt. Tokachi-dake (2077 m) of the Taisetsu Mountain Range located in the middle of Hokkaido. It flows through the broad Tokachi Plain, which includes old and new alluvial fans and stream terraces. Geological features of the plain are mainly volcanic rocks with unconsolidated sediments along. The soil in this area consists mainly of ando soil and lowland soil (Otowa, 1985). Mean annual precipitation during the 22 years from 1979 to 2000 is recorded as 947 mm at the Urahoro observatory, which is located near the Moiwa sampling site (Japan Meteorological Agency, 2004).

The Tokachi River’s mean annual water discharge is recorded as 220 m$^3$/s (129–330 m$^3$/s) at a water flow monitoring station at the Moiwa Bridge in 1970–1998 (Ministry of Land, Infrastructure, and Transport, 2004). Water discharge in the spring snow-melt season is up to four times greater than that of the winter season (Ministry of Land, Infrastructure, and Transport, 2004).

Fig. 1 depicts the offshore Tokachi area studied in this paper. The Oyashio current flows off the Hokkaido Island coast from northeast to southwest. The Oyashio region has high primary production (380–2500 mgC/m$^2$/day; Shiomoto et al., 1994; Kasai et al., 1998). Off the coast near the Tokachi River, a
shore current flows from northeast to southwest—the same direction as the Oyashio current (Ohtani, 1971, 1991). A survey of sediment compositions from the shelf and slope off the coast of the Tokachi River indicated high contents of organic carbon and silt–clay fraction of the siliceous sediments at the oxygen minimum zone (Okamura, 2003). Two submarine canyons (the Kushiro canyon and the Hiroo canyon) appear to have no effect on the spatial distribution of organic matter.

2.2. Sampling

Sediment samples were collected from two transects (Lines A and B) off the coast of the Tokachi River using a K-Grab sampler during the cruise of GH-02 R/V Hakurei-Maru II in August 2002 (Fig. 1). Line A runs along the southeast coast of Hokkaido Island. Line B is perpendicular to the shoreline extending across the shelf and slope. Surface sediments at 0–3 cm depth were used to analyze organic carbon content, carbon isotopes ($^{13}$C and $^{14}$C) and total nitrogen content. The sediment samples were stored at room temperature for grain size analyses and stored at $-30 \, ^{\circ}C$ on board for organic analyses. Estuarine sediments were collected at three points of the Tokachi River mouth on 4 August 2003. The water depths at three points were about 3–6.5 m. Salinity was nearly 0 practical salinity units (psu) for the surface water and 2–26 psu for the bottom water. Sediment samples were freeze-dried; then they were ground using a glass mortar or an agate mortar.

Samples for surface river water were collected at a station near the Moiwa bridge in April, May, June, and August 2003. This point is located ca. 20 km inland from the sea. There was no tidal influence at this sampling station. About 100 l of water were taken into polyethylene containers and then transferred to the laboratory. Suspended particles in river water samples were concentrated with a single-flow continuous-flow centrifuge with a flow rate of 15 l/h (Nagano et al., 2003). The inside temperature was maintained at 10–20 $^{\circ}C$ to avoid transformation of solids. The solid sample was dried at room temperature. The continuous flow method is less efficient for separating low-density particulate matter than filtration (Hermans et al., 1992). Nevertheless, in this study, the recovery of suspended particles was 100% or more in comparison with that of filtration because of high turbidity ranging from 13 to 95 mg/l during the sampling period.

2.3. Analyses

Organic carbon contents for the suspended particles, estuarine and marine sediments were deter-
mined using a Leco WR-112 total organic carbon (TOC) analyzer and a Fisons NA1500 elemental analyzer. Prior to analysis, inorganic carbonates were removed by adding 0.1 M HCl, rinsing with Milli-Q water, and drying again. Total nitrogen content was measured using the elemental analyzer.

$^{14}$C measurements were performed by accelerator mass spectrometry (AMS) at the Tono Geoscience Center of Japan Nuclear Cycle Development Institute (Xu et al., 2000). Sediment samples were first converted to CO$_2$ and purified cryogenically. The purified CO$_2$ was then reduced to graphite with H$_2$ over Fe and its $^{14}$C/12C ratio was measured with an NEC 15SDH-2 AMS system. The $^{14}$C activities are determined with respect to the international standard of oxalic acid. Final $^{14}$C activities are reported in $^{14}$C age using the conventional $^{14}$C half-life.

$^{13}$C values were determined for sub-samples of the CO$_2$ gas generated during graphite production, using an isotope ratio mass spectrometer (Micromass, dual-inlet Optima). The precisions of measurements were $\pm 0.5\%$ for $^{14}$C and $\pm 0.2\%$ for $^{13}$C (Xu et al., 2000).

Grab samples were washed through a 63-$\mu$m sieve to separate sand and gravel fractions from silt and clay fraction, then dried and weighed. Sand and gravel fractions were sieved and weighed at 0.25 grain size intervals. Grain size distributions were determined using the hydrometer method. The mean grain size was calculated using a graphical method (Folk and Ward, 1957).

3. Results and discussion

3.1. General characteristics of particulate and sedimentary organic matter

The organic carbon contents of riverine suspended particles and estuarine sediments (1.3–4 wt.%) are higher than those of the shelf (0.29–1.37%) and slope sediments (0.67–1.93%) (Table 1). The C/N molar ratios also vary among these four groups. These values were 9.6 $\pm$ 1.2 for the riverine suspended particles, 16.4 $\pm$ 2.6 for the estuary sediments,

$^{14}$C value and $\pm 0.2\%$ for the $^{13}$C value (Xu et al., 2000).

<table>
<thead>
<tr>
<th>Location</th>
<th>Station No.</th>
<th>Water depth (m)</th>
<th>Org. C (%)</th>
<th>C/N (mol/mol)</th>
<th>$^{13}$C (%)</th>
<th>$^{14}$C (%)</th>
<th>$^{14}$C age (year B.P.)</th>
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<td>$-215$</td>
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<td>$-26.3$</td>
<td>$-242$</td>
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<td>$-160$</td>
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<td></td>
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<td>$-26.5$</td>
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<td>8.36</td>
<td>$-21.0$</td>
<td>$-167$</td>
<td>1468</td>
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</table>

$^a$ The river water samples were collected from the surface of the Tokachi River.
10.7 ± 1.3 for the shelf, and 8.3 ± 0.4 for the slope sediments (Table 1). Although the sediment sample collected at Site 166 was located on the shelf, its C/N ratio (8.0) was close to that of the slope sediments.

3.2. $\Delta^{14}C$ and $\delta^{13}C$ values of particulate and sedimentary organic matter

3.2.1. Riverine and estuary data

The estuary sediments and riverine suspended particles from the Tokachi River have $\delta^{13}C$ values ranging from $-27.3$ to $-25.0\%_o$ (Table 1). These $\delta^{13}C$ values in the present study were consistent with the literature data ($-33.7\%_o$ to $-25.0\%_o$) (Raymond and Bauer, 2001; Megens et al., 2001; Kao et al., 2003). Data of sedimentary organic matter from the estuarine and riverine particulate organic matter are scattered and depleted in $^{13}C$ compared to the shelf and slope sediments (Fig. 2).

The $\Delta^{14}C$ values of organic matter in riverine suspended particles and estuarine sediments ranged from $-242$ to $-101\%_o$ and from $-205$ to $-157\%_o$, respectively (Table 1). The averaged value was $-180 \pm 62\%_o$ for the riverine suspended particles and $-173 \pm 27\%_o$ for the estuarine samples. There is no difference in $\Delta^{14}C$ values of the riverine POM and the estuarine samples. These values were within the reported values for the organic matter of terrestrial origin ($-980\%_o$ to $+75\%_o$) (Raymond and Bauer, 2001). As shown in Fig. 3, it appears to be a positive correlation between $\Delta^{14}C$ and $\delta^{13}C$ values of POM in the Tokachi River waters from April to August in 2003.

The measured $\Delta^{14}C$ and $\delta^{13}C$ values of riverine suspended particles and estuarine surface sediments in this study can be used to estimate those of land-derived organic matter in the coastal sea off the Tokachi River. During the snowmelt season, the Tokachi River showed its highest water discharge (Ministry of Land, Infrastructure, and Transport, 2004), and the amounts of suspended particles in April and May in 2003 were 5–10 times higher than those in the June and August samples. Thus, even with the limited data of $\Delta^{14}C$ and $\delta^{13}C$ values of riverine and estuarine samples in this study, average $\Delta^{14}C$ and $\delta^{13}C$ values of the land-derived suspended organic carbon discharged from the Tokachi River system are estimated to be $-177 \pm 47\%_o$ and $-26.0 \pm 0.6\%_o$, respectively. These values are close to those from similar environments in Scotland: surface soil organic matter from peat and riparian have $\delta^{13}C$ values of $-27.7$ to $-26.8\%_o$ and $\Delta^{14}C$ of $-298$ to $-160\%_o$ (Palmer et al., 2001). The organic matter in riverine suspended particles and estuarine sediments from the Tokachi area may be derived mainly from old soil organic matter of $C_3$ land plants.

3.2.2. Continental slope data

The $\delta^{13}C$ values of sedimentary organic carbon in the outer shelf at Site 191 and the slope region were almost constant ($-20.9 \pm 0.1\%_o$) (Table 1). These enriched values agree well with previously reported data for marine sediments (Hedges and Parker, 1976;
Ruttenberg and Goni, 1997), δ13C values of the slope sediments were constant, while a negative correlation exists between δ13C values and organic carbon contents for the continental shelf sediments (Fig. 2).

The surface sediments from the continental slope have Δ14C values ranging from −167 to −124‰ with an averaged value of −146 ± 16‰ (Table 1). These Δ14C values are greater than those from the Gulf of Mexico Basin: −393 to −277‰ at water depth of 74 to 1470 m (Goni et al., 1997). Sediments from water depth greater than 100 m and the coastal site at Site 166 display higher and relatively constant Δ14C and δ13C values in comparison with those of the estuarine and shelf sediments (Figs. 3 and 4). The narrow range of δ13C values (−21.0 to −20.8‰) and the younger values for Δ14C (−146 ± 16‰) suggest that organic matter in the sediment from the continental slope originates almost entirely from marine sources.

### 3.3. Factors controlling differences in Δ14C and δ13C values of coastal sea sediments

Plankton in surface seawater showed enriched Δ14C values ranging from +55 to +200‰, indicating the presence of bomb 14C (Bauer et al., 2001; Megens et al., 2001). The Δ14C values of suspended and settling particulate organic matter (POM) in surface seawater from the northwestern Pacific Ocean were from −44 to +27‰ and from −59 to +37‰, respectively (Nakatsuka et al., 1997; Honda et al., 2000). Organic matter collected in the first four samples from the 130-m trap at the mid-Atlantic Bight had a flux-weighted mean Δ14C value of +35‰, but the fifth sample contained much older carbon (ca. −140‰) because of a massive resuspension event (Anderson et al., 1994). Therefore, it is likely that the contribution of fresh materials, such as debris of plankton from surface waters, is higher in the slope sediments than shelf sediments in the Tokachi River coast.

The observed variations in Δ14C and δ13C values of surface sediments can be affected by the transportation and deposition processes in the water column, and bioturbation of surface sediments. Also, different time intervals could be represented by the samples, depending on the sedimentation rate. The sedimentation rate at the site near Site 149 was 0.11 g/cm²/year (K. Suzuki, personal communication), corresponding to 0.22–0.44 cm/year for the surface sediment with the porosity of 0.8–0.9 and density of 2.5 g/cm³. This value is similar to that of coastal sea

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Fig. 4. Distribution of Δ14C and δ13C values of organic matter in surface sediments from various water depths of the northwestern Pacific off the coast near the Tokachi River.
sediments (0.43 ± 0.19 cm/year) from the Funka Bay in Hokkaido, Japan (Matsumoto and Togashi, 1980), and is much higher than those at similar water depths from other coastal areas (0.005–0.013 cm/year) (e.g., Tanaka et al., 1991; Ruttenberg and Goni, 1997). From the above data, the thickness of 3-cm depth interval of surface sediments from the shelf and slope off the Tokachi River corresponds to a maximum period of 30 years. Bioturbation effects may be negligible for variations in Δ¹⁴C and δ¹³C values because of the high sedimentation rate.

The distinct marine Δ¹⁴C and δ¹³C values of the slope sediments suggest that a long, year-around shore current from northeast to southwest along the southeast coast of Hokkaido (Ohtani, 1971, 1991) prevented the transport of riverine organic particles toward the offshore under normal water discharge conditions of the Tokachi River. Large scatters in Δ¹⁴C and δ¹³C values of the shelf sediments suggest that older organic matter was resuspended, transported laterally, and deposited on the shelf.

3.4. Transport and deposition of terrestrial organic matter to continental shelf sediments

Organic carbon in the shelf sediments is a mixture of materials contributed from shoreline erosion, riverine suspended particles, resuspended sediments, and organic matter produced in the water column (Hedges and Parker, 1976; Anderson et al., 1994; Colman et al., 2002). The size and density of the suspended particles can markedly influence the dispersal pattern of terrestrial organic matter in coastal marine environments (Pralh, 1985; Keil et al., 1994; Mayer, 1994). The size distribution and the surface area are useful as conservative properties to evaluate the rate of riverine POM in the coastal ocean (Hedges and Keil, 1995).

We examined the relationship between bulk organic matter and the mean grain size of surface sediments to elucidate the transport and deposition processes of land-derived organic matter in the coastal marine environments off the Tokachi River. Fig. 5 shows variations in isotopic data (Δ¹⁴C and δ¹³C values), C/N molar ratios, organic carbon contents and mean grain size of the shelf sediments along Line A in this study (Fig. 1). Respective maxima can be seen for Δ¹⁴C value, C/N ratio and organic carbon content at Site 201 near the river mouth. On the other hand, the mean grain size of surface sediments and the δ¹³C values show an inverse relationship with a minimum at the station near the river mouth. A pattern of the Δ¹⁴C values is similar to those of C/N ratio and organic carbon content, except for Site 166, which shows all these values similar to those of the slope sediments.

It has been shown that the Δ¹⁴C and δ¹³C values of riverine particles and estuarine surface sediments vary considerably with their particle size (Hedges et al., 1986; Krusche et al., 2002; Megens et al., 2002). The coarse fraction of suspended particulate matter in the Amazon River has an average C/N molar ratio varying from 21 to 35 (Hedges et al., 1994) and radiocarbon content close to that of atmospheric CO₂ (Hedges et al., 1986). Similar results were reported for riverine suspended particles from the Piracicaba River in Brazil (Krusche et al., 2002). Devol and Hedges (2001) considered that the coarse fraction was the least degraded, resembling relatively fresh tree leaves.

![Fig. 5. Δ¹⁴C and δ¹³C values, organic carbon contents, C/N ratio and mean grain size of surface sediments along line A off the coast near the Tokachi River. Sampling sites were located at approximately 25 km from the coast of the Tokachi area in Japan.](image-url)
In a sediment from the Ems-Dollard estuary, the sedimentary organic matter in the fine fractions with $<20 \, \mu m$ has $\Delta^{14}C$ and $\delta^{13}C$ values, which are considerably higher than those in the coarse fractions (Megens et al., 2002). They observed a clear, positive correlation between the $\Delta^{14}C$ and $\delta^{13}C$ values of the fractions. In this study, the $\Delta^{14}C$ values of surface sediments along Line A have a negative correlation with the $\delta^{13}C$ value (Fig. 5). This relationship differs from that of previous results (Hedges et al., 1986; Krusche et al., 2002; Megens et al., 2002). However, a similar relationship to that observed in this study was reported for POC in the Santa Clara River during high flow events (Masiello and Druffel, 2001). The mean grain size of riverine suspended particles varies with the flow rate. Surface sediments at Sites 189 and 201, which are located near the mouth of the river, are classified as sandy silt sediments (Okamura, 2003), exhibiting relatively young $^{14}C$ age (Table 1 and Fig. 5). Sediments at other sampling sites (Sites 166, 178, 210, 219, and 227) at Line A are classified as very fine sand (Okamura, 2003). These results suggested that the size fractionation of suspended particles during transportation caused the observed patterns for $\Delta^{14}C$ and $\delta^{13}C$ values. The isotopic values of the shelf sediment from the northernmost site (Site 166) suggest that the organic matter is largely of marine origin (Figs. 2–5), due probably to the dominant coastal current from northwest.

Our results lead us to conclude that variations in $\Delta^{14}C$ and $\delta^{13}C$ values of the coastal marine sediments near the Tokachi River are caused by several factors: (a) sources and different contributions of organic matter (marine versus terrestrial), (b) size fractionation of riverine particles (Prahl, 1985; Keil et al., 1994), (c) current-induced dispersion and deposition processes, and (d) resuspension of surface sediments (Anderson et al., 1994; Colman et al., 2002). The predominance of one over the other between marine and terrestrial organic matter differs at each location, but we cannot estimate the percentage of each fraction. The discrepancy also exists between this study and the previous results from riverine suspended particles and estuarine sediments (Hedges et al., 1986; Krusche et al., 2002; Megens et al., 2002). Detailed elucidation of the transportation and deposition behavior of particulate organic matter from the river to coastal sea requires measurements of $\Delta^{14}C$ and $\delta^{13}C$ values of size-fractionated samples from suspended and settling particles, and marine sediments.

4. Summary

We selected a sampling line along the southeast coast of the Tokachi region in Japan and a seaward transect across the shelf and slope to study land-derived particulate organic carbon in a coastal marine environment. The $\Delta^{14}C$ and $\delta^{13}C$ values of sediment samples can be divided into three groups: (1) estuary, (2) continental shelf, and (3) continental slope. The $\delta^{13}C$ values of sedimentary organic carbon from the slope vary little from $-21.0$ to $-20.8\%e$ and display only a weak trend with water depth. The $\Delta^{14}C$ values ranged from $-167$ to $-124\%e$, which are slightly higher than those of estuary samples. These enriched $\delta^{13}C$ values indicate the dominance of autochthonous marine over terrestrially organic matter. On the other hand, shelf sediments had a wide range of $\Delta^{14}C$ ($-275$ to $-164\%e$) and $\delta^{13}C$ values ($-27.7$ to $-24.5\%e$) in comparison with those of estuary and slope sediments. A maximum and minimum were observed at a station near the Tokachi River mouth for the $\Delta^{14}C$ and $\delta^{13}C$ values, respectively. The riverine and estuarine sediments are distinct from that of the slope, but the shelf sediments appear to be more complex. Organic matter originates from both marine and riverine–estuarine environments. Scattering in $\Delta^{14}C$–$\delta^{13}C$ values of the shelf sediments may show differences in the predominance of sources together with size fractionation by the hydrodynamic sorting during transportation.

Our results indicate that the combined $\Delta^{14}C$ and $\delta^{13}C$ measurements of the surface sediments from coastal regions can provide unique information on the sources and age of sediments. This technique can serve as a convenient tool for tracing and identifying the fate of bulk POM that is discharged from rivers to the ocean.

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