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Fluxes, source and transport of organic matter in the western Sea of Okhotsk: Stable carbon isotopic ratios of *n*-alkanes and total organic carbon

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Abstract

Settling particles and surface sediments collected from the western region of the Sea of Okhotsk were analyzed for total organic carbon (TOC), long-chain *n*-alkanes and their stable carbon isotope ratio ($\delta^{13}\text{C}$) to investigate sources and transport of total and terrestrial organic matter in the western region of the sea. The $\delta^{13}\text{C}$ measurements of TOC in time-series sediment traps indicate lateral transport of resuspended organic matter from the northwestern continental shelf to the area off Sakhalin via the dense shelf water (DSW) flow at intermediate depth. The *n*-alkanes in the surface sediments showed strong odd carbon number predominance with relatively lighter $\delta^{13}\text{C}$ values (from -33 to -30 ‰). They fall within the typical values of C3-angiosperms, which is the main vegetation in east Russia, including the Amur River basin. On the other hand, the molecular distributions and $\delta^{13}\text{C}$ values of *n*-alkanes in the settling particles clearly showed two different sources: terrestrial plant and petroleum in the Sea of Okhotsk. We reconstructed seasonal change in the fluxes of terrestrial *n*-alkanes in settling particles using the mixing model proposed by Lichtfouse and Eglinton (1995). Results of the terrestrial *n*-alkane fluxes indicate that there are two transport pathways of terrestrial plant *n*-alkanes to sediments off Sakhalin, the Sea of Okhotsk. One is lateral transport of resuspended particles with lithogenic material from the northwestern continental shelf by the DSW flow. Another is the vertical transport of terrestrial plant *n*-alkanes, which is independent of transport of lithogenic material. The latter may include dry/wet deposition of aerosol particles derived from terrestrial higher plants possibly associated with forest fires in Siberia.

Key words: terrestrial organic matter, terrestrial biomarker, hydrocarbons, stable carbon isotope, settling particles, sediment, Sea of Okhotsk

1. Introduction

Input of terrestrial organic matter to the ocean is estimated to be 400 Tg yr⁻¹ by riverine transport (Schlesinger and Melack, 1981) and 20 Tg yr⁻¹ by atmospheric transport (Buat-Ménard et al., 1989). Therefore, rivers are the primary pathway for the transport of fresh organic matter from land to the coastal oceans, together with fresh waters and mineral matter, representing 70 % of the world's solid inputs to the marine realm (Milliman 1991), and 0.7 % of the terrestrial net primary production (Schlesinger and Melack, 1981; Ittekkot, 1988). Delta and coastal regions play a key role in the global carbon cycle since they are the main repository of inputs of terrestrial organic matter delivered by rivers to marine sediments (Bernier, 1989; Hedges and Keil, 1995). On the other hand, the atmosphere is another important transport pathway of terrestrial organic matter for the open ocean environments. It is important to investigate the sources and long-range transport of terrestrial organic matter in the ocean to better understand the global carbon cycle. Moreover, terrestrial plant-derived biomarkers deposited in marine sediments can also provide spatially integrated information about terrestrial plant ecosystems and terrestrial biosphere functions in the past. Hence, it is of geochemical interest that how fluvial and atmospheric transports of terrestrial organic matter are recorded in marine sediments for reconstructing terrestrial environments from sedimentary records. However, transport pathways and the fate of terrestrial organic matter in the ocean are not fully understood (Hedges et al., 1997).

Several methods have been proposed for inferring the source of organic matter in marine environments. Stable carbon isotopes of bulk organic matter ($\delta^{13}\text{C}_{\text{org}}$) is a useful tool for identifying sources of organic matter. For example, $\delta^{13}\text{C}_{\text{org}}$ are often used to distinguish between marine and terrestrial-plant sources of sedimentary organic matter, because the $\delta^{13}\text{C}_{\text{org}}$ of land plants using the C3 photosynthetic pathway is approximately -27‰, whereas marine phytoplankton typically have $\delta^{13}\text{C}_{\text{org}}$ values between -20 and -22 ‰ in tropical and temperate regions (Schefuß et al., 2003; Rommerskirchen et al., 2003). However, $\delta^{13}\text{C}_{\text{org}}$ is often insensitive for estimating the contribution of terrestrial organic matter input in high latitude oceans. At low temperature, the solubility of CO₂ increases, and thus its availability to the

phytoplankton increases, resulting in much larger fractionation. As a consequence, phytoplankton living in cold oceans tend to have lighter $\delta^{13}\text{C}$ whose value often overlaps with that of terrestrial C3 plants (Popp et al., 1999; Trull and Armand 2001). On the other hand, the molecular level analyses for lignin phenols and long-chain lipids (unique biomarkers of terrestrial plants) are much more specific and sensitive. Odd carbon numbered *n*-alkanes (C_{25} - C_{35}) are widely used as tracers for inputs of terrestrial organic matter to the ocean environment. Positive correlations ($r^2 > 0.88$) between concentrations of ΣC_{25-31} *n*-alkanes and TOC have been reported in the sediments of river basins (Prahel et al., 1994; Fernandes and Sicre, 2000), suggesting that terrestrial-plant *n*-alkanes can be a widely representative biomarker of terrestrial organic matter input.

The Sea of Okhotsk, which is located in the northwestern Pacific rim, is one of the largest marginal seas in the world and is also characterized as a region where seasonal sea ice reaches the lowest latitudes (Kimura and Wakatsuchi, 2000). This sea has a general cyclonic current system with peculiar conditions of water exchange with the North Pacific via the straits of the Kuril Islands. The Sea of Okhotsk is the source region of the North Pacific Intermediate Water (NPIW) (Tally and 1991; Wong et al., 1998). When sea ice is formed on the northwestern continental shelf, cold brine waters are rejected and sink to the bottom of the shelf to make dense shelf water (DSW) (Martin et al., 1998; Gladyshev et al., 2000). Annual mean production rate of the DSW has been estimated to be 0.5 Sv and 0.67 Sv by Gladyshev et al. (2000) and Itoh et al. (2003), respectively. The DSW spreads into intermediate depths (200-500 m), mixing horizontally with Okhotsk Sea Intermediate Water (OSIW) and further penetrates into the North Pacific intermediate layer via the Bussol Strait. The Amur River, which is one of the largest rivers of eastern Eurasia, is thought to play an important role as the major source of terrestrial organic matter to the Sea of Okhotsk (see Fig. 1). Annual fluxes of fresh waters from the Amur River are estimated to be $300 \text{ km}^3 \text{ yr}^{-1}$ (Ogi et al., 2001), carrying a terrestrial input of dissolved organic carbon (DOC) to the continental margin estimated to be 2.5 TgC yr^{-1} (Nakatsuka et al., 2004a), which is comparable to that of largest rivers in the world (Spitzzy and Leenheer, 1991; Telang et al., 1991). Because the Sea of Okhotsk is adjacent to the eastern rim

of Eurasia, long-range atmospheric transport of organic matter from the land might also be important, especially in offshore regions.

Previous field observations have revealed that the Sea of Okhotsk has an effective transport system of entraining particles from the bottom of the northwestern shelf into the adjacent deeper basin. This is associated with the formation of sea ice and the DSW in the northwestern shelf (Nakatsuka et al., 2002; Nakatsuka et al., 2004b). The DSW contains a large amount of resuspended particles, due to strong tidal mixing on the shelf (Kowalik and Polyakov, 1998). This upper shelf resuspended matter is effectively transported to the southern deeper basin through the intermediate layers. Results from time-series sediment traps deployed in the western region of the Sea of Okhotsk clearly showed that a large amount of biogenic and lithogenic particles deposited on the northwestern continental shelf are exported to the open ocean interior by the intermediate water flow (Nakatsuka et al., 2004b). Estimated transports of dissolved organic carbon (DOC) and particulate organic carbon (POC) by the DSW flow are 13.6 and 0.9 TgC yr⁻¹, respectively (Nakatsuka et al., 2004a). These fluxes are much higher than the sinking POC fluxes from proximal surface waters, suggesting that the organic carbon flux by the DSW plays an important role in biogeochemical cycles in the sea. However, the sources and export process of terrestrial organic matter are still unclear in the Sea of Okhotsk.

In this study, we provide spatiotemporal distributions of $\delta^{13}\text{C}_{\text{org}}$ and terrestrial biomarker distributions (high molecular weight *n*-alkanes), together with their compound-specific $\delta^{13}\text{C}$ values in sediments and settling particles collected from the western Sea of Okhotsk, in order to investigate the sources and transport processes affecting particulate terrestrial organic matter in the sea.

2. Materials and methods

2.1. Samples

Four sediment trap systems (Mclane Mark78G) were moored at two sites (M4 and M6)

off Sakhalin Island in the Sea of Okhotsk during the XP-98 and 99 cruises of R/V Professor *Khromov* of the Far Eastern Regional Hydrometeorological Research Institute in Uladivostok, Russia, as a part of the Joint Japanese-Russian-U.S. research project of the Sea of Okhotsk (see Fig. 1). Table 1 presents station data of the sediment traps used in this study. The upper traps were deployed at 260-280 m depth. The lower traps were deployed at about 200 m (M4) and 100 m (M6) above the ocean floor. Trap sample cups were pre-poisoned with a 5 % formaldehyde solution buffered by sodium tetraborate to prevent *in situ* bacterial degradation of trapped materials. A total of 168 samples of settling particles was collected, refrigerated and brought to the shore-based laboratory. Each sample was sieved through a 1 mm mesh to remove zooplankton swimmers, split into 10 fractions and stored again at -20 °C until chemical analysis. We analyzed a total of 168 samples for total organic carbon (TOC) and $\delta^{13}\text{C}_{\text{org}}$, and 120 samples for aliphatic hydrocarbons. Sediment samples were also collected along the western coastline of the Sea of Okhotsk by a multiple-core sampler during the cruises (see Table 2). Surface 0-1 cm sections of sediment cores were analyzed for TOC, aliphatic hydrocarbons and their stable carbon isotopic compositions.

2.2. Bulk elemental and $\delta^{13}\text{C}_{\text{org}}$ analyses

For analyses of TOC and $\delta^{13}\text{C}_{\text{org}}$, sediment trap samples were dried and homogenized with a pestle and mortar. TOC contents were determined with a Fisons NA 1500 CNS analyzer after HCl treatment to remove calcium carbonate. Analysis of $\delta^{13}\text{C}_{\text{org}}$ was conducted with a Finnigan-MAT Delta Plus isotope-ratio mass spectrometer interfaced to a Fisons NA 1500 CNS analyzer. Values of isotopic ratios were corrected for procedural blanks and expressed in per mille relative to the standard Pee Dee Belemnite (PDB): $\delta^{13}\text{C} = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{PDB}} - 1] \times 10^3$. Analytical errors (reproducibility) of TOC and $\delta^{13}\text{C}_{\text{org}}$ measurements were within 0.04 % and 0.2 ‰, respectively.

2.3. Aliphatic hydrocarbon extraction

Total lipids of settling particles were extracted from wet samples sequentially with MeOH, CH₂Cl₂/MeOH (2:1) and CH₂Cl₂/MeOH (95:5) under ultra sonication for 5 min. The extracts were saponified with 1.0 M KOH/MeOH. Neutral components were isolated by extraction with *n*-C₆H₁₄/CH₂Cl₂ (10:1). The aliphatic hydrocarbon fraction was further separated from other fractions on a Pasteur pipette column packed with silica gel (BIO-SIL A, 200-400 mesh, 0.25 g, 2 cm × 5 mm i.d.) deactivated with 1 % distilled water (Kawamura et al., 1995). Aliphatic hydrocarbons were eluted with *n*-C₆H₁₆ (2 ml). Total lipids of sediments were extracted from the homogenized dry samples with CH₂Cl₂/ MeOH (95:5) and with accelerated solvent extractor (Dionex: ASE 200) at 100 °C and 1000 psi for 15 min. Treatment for the separation of the aliphatic hydrocarbon fraction was the same as that for settling particles. Subsequently, the aliphatic hydrocarbon fraction was separated into saturated and unsaturated aliphatic hydrocarbon fractions by AgNO₃-impregnated silica gel (10 wt%) chromatography (BIO-SIL A, 200-400 mesh, 0.25 g, 2 cm × 5 mm i.d.) for compound-specific δ¹³C measurement of long-chain *n*-alkanes. Saturated hydrocarbons were eluted with *n*-C₆H₁₆ (2 ml). For the quantification and δ¹³C measurement of aliphatic hydrocarbons, an internal standard (C₂₄D₅₀ *n*-alkane) was added to the subfractions before the injection to the GC. Recoveries of *n*-alkanes (C₂₉ and C₃₂) were > 90 %.

2.4. Gas chromatography (GC) and GC/mass spectrometry (MS) analyses

Quantification of aliphatic hydrocarbons was performed with a HP6890 GC equipped with an on-column injector, a CPSIL-5 CB fused silica capillary column (60 m × 0.32 mm i.d.) and a flame ionization detector. The GC oven temperature programme was 50 °C to 120 °C at 30 °C min⁻¹ and then 120 °C to 310 °C at 5 °C min⁻¹. The identification of each compound was achieved by GC/MS. The GC/MS measurements were carried out with a Finnigan Trace GC/MS equipped with an on-column injector and a DB5-MS capillary column (60 m × 0.32 mm i.d.).

2.5. GC-isotope ratio mass spectrometry (IRMS) analysis

$\delta^{13}\text{C}$ values of individual long-chain *n*-alkanes were determined with a GC-IRMS system consisting of a HP 6890 GC connected to a Finnigan MAT delta Plus mass spectrometer via a combustion interface. Determination of the $\delta^{13}\text{C}$ of *n*-alkanes was obtained with a DB-5 fused silica capillary column (30 m x 0.32 mm i.d.) with on-column injector. The GC oven programme was 50 °C to 120 °C at 30 °C min⁻¹, then 120 °C to 310 °C at 5 °C min⁻¹. The separated compounds from the GC were introduced to the combustion reactor (850 °C), with contained a fine CuO wire and a fine Pt wire as a catalysts. Analytical errors for $\delta^{13}\text{C}$ of *n*-alkanes were within 0.5 ‰.

3. Results and discussion

3.1. Bulk analysis of organic matter

Fig. 2 shows seasonal variation of TOC flux, C/N ratio, $\delta^{13}\text{C}_{\text{org}}$ and highly unsaturated C₂₁ hydrocarbon (C₂₁HUH) flux in M4 and M6 sediment traps between August 1998 and June 2000. The fluxes of TOC ranged from 0.6 to 33 mg m⁻² d⁻¹ during the period. The fluxes of TOC were generally high in early summer (June) and autumn (August-October) and much less during winter. According to the previous study of bulk elemental analyses, the enhanced TOC flux is attributed to increases in export production from phytoplankton blooms in early summer and autumn (Nakatsuka et al., 2004b). This result agrees well with a previous experiment of sediment traps in the central Sea of Okhotsk (Honda et al., 1997). Episodic increases in the flux were also observed for the M4 lower trap in December 1999. The M6 upper trap samples showed two TOC peaks in April 1999 and February 2000, whereas the M6 lower traps showed two peaks in December 1999 and February 2000.

The C/N ratios ranged from 4.1 to 8.0 and from 5.4 to 9.1 in M4 and M6, respectively. It has been reported that micro algae typically have C/N ratios between 4 and 10, whereas C/N ratios of terrestrial land plants are greater than 20 (Meyers, 1994). Therefore, the lower C/N

ratios observed in the organic matter in settling particles suggests a predominance of marine organic matter.

The $\delta^{13}\text{C}_{\text{org}}$ in settling particles showed large fluctuations (from -27.0 to -20.4 ‰), with relatively heavier values in the lower traps compared to the upper traps. The lighter isotopic values (~ -27 ‰) in settling particles are probably due to higher CO_2 concentration in the Sea of Okhotsk compared to that of the temperate ocean. The observed seasonal variation of $\delta^{13}\text{C}$ in settling particles was probably related to seasonal changes in algal growth rate and phytoplankton species rather than varying contribution of marine vs terrestrial organic matter. In high latitude oceans, seasonal and spatial variations of the growth rate strongly affect the $\delta^{13}\text{C}$ of phytoplankton (Rau et al., 1992; Francois et al., 1993). In fact, the $\delta^{13}\text{C}_{\text{org}}$ of suspended particles collected from the chlorophyll-*a* maximum depth in the Sea of Okhotsk shows a large variation (from -27 to -19 ‰), decreasing offshore from northwestern Sakhalin Island (Nakatsuka et al., 2004a). This is probably explained by spatial variability in the phytoplankton growth rate, with increased growth rate in coastal regions. The $\delta^{13}\text{C}$ of phytoplankton also differs among species, with diatoms tending to have heavier $\delta^{13}\text{C}_{\text{org}}$ than nanophytoplankton (Wu et al., 1999). Biogenic component analyses of settling particles clearly showed a seasonal succession of phytoplankton species from siliceous plankton in early summer to calcareous plankton in autumn in the Sea of Okhotsk (Honda et al., 1997; Nakatsuka et al., 2004b). The increases of $\delta^{13}\text{C}_{\text{org}}$ in late spring at M4 in 2000 and at M6 in 1999 might reflect a diatom dominance or an increase in growth rates of diatoms. The lighter isotopic shift in July 1999 in M4 might result from lower growth rates or a change in plankton species composition. Therefore, the observed seasonal changes in $\delta^{13}\text{C}_{\text{org}}$ in the upper traps probably reflect differences in planktonic species composition and/or growth rates (Bidigare et al., 1997) rather than a simple varying mass balance of marine and terrestrial organic matter.

$\delta^{13}\text{C}_{\text{org}}$ measurements in lower sediment traps reinforced the previous idea of lateral transport of resuspended organic matter from the northwestern continental shelf by the DSW flow (Nakatsuka et al., 2004b). A previous study indicated that DSW flow plays the dominant role in the transport of resuspended particles from the northwestern continental shelf to the

deeper basin of the Sea of Okhotsk (Nakatsuka et al., 2004b). Lower traps showed heavier isotopic compositions compared to the upper traps, indicating additional input of organic matter having relatively heavier $\delta^{13}\text{C}$ in the lower traps as well as *in situ* export flux. The $\delta^{13}\text{C}_{\text{org}}$ of sediments and suspended particulate organic matter on the northwestern continental shelf have heavier isotopic values (-20 ~ -22 ‰) in the Sea of Okhotsk (Table 2). Hence, heavier $\delta^{13}\text{C}_{\text{org}}$ values in the lower traps are likely explained by either input of resuspended organic matter from bottom sediments near the trap sites or lateral transport of particulate organic matter from the northwestern continental shelf. Several peaks of $\delta^{13}\text{C}_{\text{org}}$ in the lower traps clearly correlated with the intrusion events of DSW into the trap sites determined by CTD measurements (dashed lines in Figs 2c and 2d). This indicates lateral transport of the resuspended organic matter deposited on the northwestern continental shelf to the area off Sakhalin by the DSW flow (Nakatsuka et al., 2004b).

3.2. Hydrocarbons in surface sediments

n-Alkanes are major components of aliphatic hydrocarbons in the Okhotsk Sea sediments. C_{14} - C_{35} *n*-alkanes were detected in the surface sediments (0-1 cm) in the western and southern Okhotsk Sea. Their concentrations range from 1.4 to 3.0 $\mu\text{g g}^{-1}$ dry sediment (see Table 2). Their molecular distributions showed an odd-carbon-number predominance with peaks at C_{27} , C_{29} and C_{31} (see Fig. 3). On the other hand, lower molecular weight *n*-alkanes (C_{14} - C_{23}) have low concentrations with no odd/even predominance. Some hopanoid hydrocarbons (17 β (H), 21 α (H)-30-norhopane, neohop-13(18)-ene, 17 β (H), 21 β (H)-30-hopane, 22R-17 α (H), 21 β (H)-hopane, 17 β (H), 21 β (H)-hopane, diploptene and 22R-17 β (H), 21 β (H)-hopane), which are often used as bacterial biomarkers (e.g., Ourisson et al., 1987; Elvert et al., 2001), were detected in sediment samples. Unresolved complex mixture (UCM), which is a bacterial reworking product, is also slightly detected in the sediments. This indicates the presence of bacteria and bacterial reworking of organic compounds in surface sediments. The molecular distributions of *n*-alkanes in the surface sediments from the western region of the Sea of

Okhotsk agree well with previous results from sediments in the southern Sea of Okhotsk (Ternois et al., 2001; Seki et al., 2003). The odd carbon number *n*-alkanes (C₂₅-C₃₅) are major components of terrestrial-plant epicuticular waxes (Eglinton and Hamilton, 1967; Meyers and Ishiwatari, 1993). We calculate the carbon preference index (CPI) of *n*-alkanes, using the following equation (Bray and Evans, 1961):

$$\text{CPI} = 2\sum_{\text{odd}} (\text{C}_{25}\text{-C}_{35}) / [\sum_{\text{even}} (\text{C}_{24}\text{-C}_{34}) + \sum_{\text{even}} (\text{C}_{26}\text{-C}_{36})]$$

The CPI of the *n*-alkanes varied between 5.0 and 6.4 with an average of 5.5 (see Table 2). The CPI values in the Sea of Okhotsk sediments are close to those of the Japan Sea sediments (Yamada and Ishiwatari, 1999), and slightly lower than those (6-9) of the pelagic sediments from the northern North Pacific (Ohkouchi et al., 1997). The $\delta^{13}\text{C}$ values of *n*-alkanes ranged from -32.9 to -28.6 ‰ among the C₂₁-C₃₃ *n*-alkanes (Table 3). $\delta^{13}\text{C}$ values of the *n*-alkanes in all samples are characterized by a decreasing trend with increasing molecular weight up to C₃₂. The $\delta^{13}\text{C}$ values in the Okhotsk Sea coincide well with those in the sediments collected from the Sea of Japan (Yamada and Ishiwatari, 1999), Bering Sea (Ratnayake et al., 2005) and Lake Baikal, which is located in eastern Siberia (Brincat et al., 2000).

The $\delta^{13}\text{C}$ values of plants reflect their photosynthetic pathways, and thus, each biosynthetic type has its own isotopic composition. The long-chain lipids of C3 plants show isotopically lighter values (-39 ~ -30 ‰) than those of C4 plant (-25 ~ -18 ‰), and the $\delta^{13}\text{C}$ of lipids in CAM plants fall in the range between C3 and C4 plants (-29 ~ -20 ‰) (Rieley et al., 1991; Collister et al., 1994; Lockheart et al., 1997). The $\delta^{13}\text{C}$ values of *n*-C₂₉ and *n*-C₃₁ alkanes in Sea of Okhotsk sediments fall within the range expected of C3 terrestrial-plant leaf waxes. For C3 plants, gymnosperms tend to have heavier values (-34 ~ -30 ‰) compared to angiosperms (-39 ~ -32 ‰) (Chikaraishi and Naraoka, 2003). The dominant source of *n*-alkanes in the Okhotsk Sea sediments should be C3 gymnosperm rather than a mixture of C4, CAM and C3 angiosperm plants, because the dominant vegetation in the catchment area (Sakhalin Island and East Siberia) is pine, which is a C3-gymnosperm.

However, despite a general acceptance of using *n*-alkanes as terrestrial biomarkers, some studies suggested possibility of marine sources for the long-chain odd *n*-alkanes in certain regions (Lighthouse et al., 1994; Naraoka and Ishiwatari, 1999). Hence, use of the long-chain lipids as terrestrial biomarkers must be carried out with caution in marine environments. However, the $\delta^{13}\text{C}$ values of pristane, which is an algal biomarker, are heavier (about -28‰) than those of long-chain odd *n*-alkanes in the Sea of Okhotsk, indicating that the long-chain *n*-alkanes are terrestrial-plant origin (Table 3). Comparison of $\delta^{13}\text{C}$ between bulk organic matter and long-chain *n*-alkanes also supports that the main source of long-chain odd *n*-alkanes is terrestrial plants in the Sea of Okhotsk. The $\delta^{13}\text{C}$ results from surface sediments and POC collected from surface waters clearly showed large spatial variability of phytoplankton $\delta^{13}\text{C}$, with heavier values on the northwestern continental shelf (-20‰) and lighter values off Sakhalin ($-27 \sim -22\text{‰}$) (Nakatsuka et al., 2004a). Hence, if the main sources of *n*-alkanes are marine organisms in the Sea of Okhotsk, same spatial difference must be observed in $\delta^{13}\text{C}$ of *n*-alkanes. However, such a difference in the bulk isotopic measurement is not recognized for the $\delta^{13}\text{C}$ of $\text{C}_{25}\text{-C}_{31}$ *n*-alkanes in surface sediments (Table 3). These results indicate that $\text{C}_{25}\text{-C}_{35}$ *n*-alkanes in the sediments are derived mainly from C3 terrestrial-plant rather than marine sources.

3.3. Hydrocarbons in settling particles

Some branched and unsaturated hydrocarbons as well as *n*-alkanes were abundant in settling particles collected from the Sea of Okhotsk. It has been reported that some hydrocarbons are biosynthesized by micro-algae (Volkman et al., 1988). Fig. 4 shows a capillary gas chromatogram of aliphatic hydrocarbons in the settling particles (M4 upper trap) collected from 30 October to 12 November 2000. In the Sea of Okhotsk, the most abundant marine hydrocarbons are C_{21}HUH and pristane. C_{21}HUH is often the most abundant hydrocarbon in diatoms, but dinoflagellates and other algal groups also produce it (Blumer et al., 1971; Nichols et al., 1988). Hence, C_{21}HUH is a generic phytoplankton biomarker. Pristane is a

well known biomarker of zooplankton, particularly of calanoid copepods, which produce it from phytol in chlorophyll-*a* from their diet (Volkman and Maxwell, 1986).

The fluxes of C₂₁HUH are markedly higher in the upper traps than in the lower traps (Fig. 2g and 2h). Enhanced fluxes of C₂₁HUH coincide with all of the spring and autumn blooms. This supports the conclusion that the increased TOC fluxes in the upper traps during these periods are caused by enhanced *in situ* export production. The lower flux values for the lower traps suggest that organic matter captured at depth is more degraded than that collected in the upper traps. The pristane flux (data not shown) is also higher in the upper traps than in the lower traps, with a seasonal change similar to that of C₂₁HUH. This suggests that fecal pellets are an important component of sinking particles. Some diatoms biosynthesize highly branched C₂₀, C₂₅ and C₃₀ alkenes (Volkman et al., 1998). However, highly branched alkenes were not detected in the settling particles of the Sea of Okhotsk.

Table 4 displays $\delta^{13}\text{C}$ of pristane and individual *n*-alkanes in sinking particles. Molecular distribution and $\delta^{13}\text{C}$ values of *n*-alkanes in sinking particles clearly indicate two different source categories: terrestrial plants and other sources. Fig. 5 shows the molecular distribution of the *n*-alkanes in some settling particles with their $\delta^{13}\text{C}$ values as a function of carbon number. Molecular distributions (CPI) and $\delta^{13}\text{C}$ values of *n*-alkanes in settling particles differ largely between these samples, ranging from 1.0 to 7.1 and from -32.9 to -26.0 ‰, respectively. *n*-Alkanes having quite different molecular distributions and $\delta^{13}\text{C}$ values from those expected of C3 terrestrial plants were observed in some of the settling particles (for example *n*-alkanes characterized by low CPI values of 1.1 and heavier $\delta^{13}\text{C}$ values of -26.5 ‰). The $\delta^{13}\text{C}$ values of these *n*-alkanes show a zigzag pattern, where *n*-alkanes with even carbon number are more positive in $\delta^{13}\text{C}$ values than those with odd numbers. Moreover, the $\delta^{13}\text{C}$ values for *n*-alkanes are systematically shifted to negative values with increasing CPI value. This systematic trend is easily explained by a varying mass balance of terrestrial-plant and other sources.

The most likely source of the *n*-alkanes with the lowest CPI and highest $\delta^{13}\text{C}$ values is petroleum. In general, *n*-alkanes of oil origin are characterized by lower CPI values, close to 1.0,

they are also isotopically heavier than *n*-alkanes of terrestrial-plant wax, and are often associated with a high content of UCM due to bacterial degradation of *n*-alkanes and production of UCM. The Sea of Okhotsk, especially near Sakhalin Island, is known as a region of significant oil reservoirs. Currently, operations for oil production have started near the northeastern coast of Sakhalin Island. Quite low quantities of UCM in the Okhotsk Sea samples suggest non-biodegraded oil source or crude and refined product sources for the *n*-alkanes. It has been reported that non-biodegraded oil has no UCM (Spiro et al., 1983; Sun et al., 2005) and that *n*-alkanes with very low CPI but no UCM in the Arabian Sea derive from petroleum based on ^{14}C age determined by radiocarbon analysis (Eglinton et al., 1997). In fact, hopanoid hydrocarbons were quite low (mostly under detection limit) in the upper traps, suggesting that bacterial biodegradation is not important. However, the *n*-alkanes in the settling particles are characterized by lack of shorter chain *n*-alkane below about C_{21} *n*-alkane. In general, natural oil and sheep spilled crude oil have a much greater range of chain length, and more variable molecular distribution. This suggests that refined products such as high-boiling diesel are likely source of the *n*-alkanes with heavy $\delta^{13}\text{C}$ and low CPI in the Sea of Okhotsk.

Alternatively, marine organisms are also possible sources of *n*-alkanes with low CPI values. *n*-Alkane distributions without any odd carbon predominance have been detected in non-polluted regions (Volkman et al., 1983; Nichols et al., 1988; Cripps, 1995; Harada et al., 1995; Bieger et al., 1997) and in a mixed diatom culture experiment (Volkman et al., 1980), suggesting that these *n*-alkanes originated from microalgae or bacterial recycled material. However, the $\delta^{13}\text{C}$ values of pristane (-29 ~ -28 ‰) are different from that of the low CPI *n*-alkanes (-27 ~ -26 ‰) in the sea, indicating that the long-chain *n*-alkanes are not marine origin in the Sea of Okhotsk (Table 3 and 4).

3.4. Reconstruction of the terrestrial-plant source signatures

We estimated distributions of the terrestrial-plant sources using an approach based on the stable carbon isotopes of individual source areas as proposed by Lichtfouse and Eglinton (1995).

According to them, the contribution of petroleum to each n -alkane in the sample can be calculated from:

$$x = (\delta_p - \delta_U) / (\delta_F - \delta_U)$$

where x is the carbon fraction derived from petroleum, δ_p is the $\delta^{13}\text{C}$ values of the n -alkanes from polluted settling particles, δ_U is the $\delta^{13}\text{C}$ value of the same n -alkane in unpolluted sediment, and δ_F is the $\delta^{13}\text{C}$ value of an n -alkane from petroleum. The δ_U value is obtained from the mean $\delta^{13}\text{C}$ values of sedimentary n -alkanes. Values for x have been calculated for n -alkanes in the range (C_{21} - C_{35}). The δ_F value is defined as -26.5‰ , which is the average isotopic value of CPI=1.1 n -alkanes. The relative concentration of n -alkanes in the petroleum is calculated from:

$$A_p = x \cdot A_T$$

where A_T is the relative concentration of an n -alkane in the petroleum and A_p is the relative concentration in a polluted sinking particle.

Fig. 6 displays relative abundances of terrestrial-plant and petroleum derived n -alkanes in settling particles estimated from the Lichtfouse and Eglinton (1995) equation. Some $\delta^{13}\text{C}$ values of n -alkanes (C_{24} and C_{31} n -alkanes) are slightly beyond the range between the two end members. Such terrestrial and petroleum n -alkanes are slightly over- or under-estimated. The CPI values of the estimated unknown sources are close to 1 (from 0.7 to 1.1). On the other hand, the CPI of terrestrial-plant n -alkanes shows higher values (from 2.6 to 17.2). We estimate the fluxes of petroleum and terrestrial-plant n -alkanes by subtracting n -alkanes of other sources from total n -alkanes on the basis of an assumption that the CPIs of terrestrial-plant and petroleum sources of n -alkanes are 7.0 (maximum CPI value in Okhotsk Sea samples) and 1, respectively. In this study, the subtracted C_{25} - C_{31} odd n -alkanes ($\Sigma_{\text{odd}}\text{C}_{25-31}$) were defined as terrestrial-plant n -alkanes. Abundance of calculated terrestrial-plant n -alkanes is underestimated with this assumption (1~20% lighter than $\delta^{13}\text{C}$ estimation). On the other hand, unknown n -alkanes are somewhat overestimated. The fluxes of terrestrial-plant n -alkanes in the settling

particles were calculated from this model, and below we discuss the sources and transport processes of terrestrial organic matter in the western Sea of Okhotsk from the reconstructed terrestrial-plant *n*-alkane fluxes.

3.5. Source and transport

3.5.1. Seasonal changes in the fluxes of long-chain *n*-alkanes (source and transport pathways)

Fig. 7 shows the seasonal variations of long-chain *n*-alkane fluxes in the M4 and M6 sediment traps. The flux of total *n*-alkanes varied seasonally from 0.5 to 17 $\mu\text{g m}^{-2} \text{day}^{-1}$. The fluxes in the upper traps are larger than those in the lower traps during the higher flux periods (Figs 7a and 7b). Estimated terrestrial *n*-alkane fluxes varied from 0 to 6.1 $\mu\text{g m}^{-2} \text{day}^{-1}$ (Figs 7e and 7f). Maximum fluxes are observed in autumn 1998 as well as total *n*-alkane flux. The CPI of long-chain *n*-alkanes ranged from 1 to 7 (Figs 7c and 7d). The CPI values in both upper and lower traps varied simultaneously, with lower values (1.0-4.2) during the period before June 1999, but the CPI of the lower traps increased significantly after December 1999 in M4 and October 1999 in M6. This suggests that the main source of *n*-alkanes captured in the lower traps is almost the same as that of the upper traps during the former period but different during the latter period. It should be noted that enhanced *n*-alkane flux consistently increased when export fluxes were enhanced, suggesting that scavenging by sinking particles, such as fecal pellets, or aggregation of phytoplankton play an important role in downward transport of terrestrial *n*-alkanes.

3.5.2. Lateral transport of terrestrial plant *n*-alkanes

Fig. 8 shows the relationships of long-chain *n*-alkanes and lithogenic material in M4 and M6 sediment traps. Relatively good correlation is observed in the lower traps. As described before, the several intermittent increases in lithogenic fluxes were caused by lateral transport of resuspended sediments via DSW flow (Nakatsuka et al., 2004b). In general, the abundance and preservation of particulate organic matter is related to mineral grain size (Keil et al., 1994).

Most particulate organic matter of suspended particles and sediments is adsorbed to the surfaces of clay mineral grains and is protected against microbial degradation (Keil et al., 1997; Mayer, 1994; Ramson et al., 1998; Hedges and Keil, 1999). A good positive relationship between fluxes of terrestrial-plant *n*-alkanes and lithogenic matter has been reported in sinking particles with no vertical difference from the Arabian Sea (Prahel et al., 2000). Hence, the relatively good correlation in the lower traps suggests a lateral transport of terrestrial *n*-alkanes together with lithogenic material by DSW flow. In particular, during the period from autumn 1999 to Spring 2000, the main source of terrestrial *n*-alkanes captured in the lower traps must be the resuspended particles derived from the northwestern continental shelf. Because the river runoff from the Amur River transports large amounts of terrigenous materials into the western region of the sea, most of the terrestrial plant *n*-alkanes in DSW may be of Amur River origin.

A recent study in the Pacific Ocean suggested inputs of terrestrial organic matter into the Sea of Okhotsk as a major source of dissolved and particulate terrestrial organic matter to the North Pacific Ocean organic carbon reservoir (Hernes and Benner, 2002). According to the study, concentrations of dissolved and particulate lignin phenol, which is a unique biomarker of terrestrial plants, were significant at the depth of the NPIW, suggesting the export of large amount of terrestrial organic matter from the Sea of Okhotsk to the North Pacific through the OSIW. Our results and interpretation are consistent with their idea.

3.5.3. Vertical transport of terrestrial-plant n-alkanes

The fluxes of terrestrial *n*-alkanes in samples collected in Aug-Nov 1998 are the largest of all periods. Good synchronicity of temporal variations of CPI in the upper and lower traps during the period from autumn 1998 to autumn 1999 indicates a vertical transport of *n*-alkanes during the period. No correlation was observed between lithogenic material and terrestrial *n*-alkane concentrations in the upper traps. This result indicates that transport of terrestrial *n*-alkanes to the Sea of Okhotsk is independent from the transport of lithogenic materials. Emission of plant leaf waxes into the atmosphere and their long-range transport is an important

pathway for terrestrial organic matter to the ocean, especially the remote open ocean (Simoneit et al., 1977; Gagosian and Peltzer, 1986; Kawamura et al., 2003; Conte and Weber, 2002a, 2002b). Especially, biomass combustion is an important primary source of organic aerosols in the global atmosphere (Simoneit et al., 2002), because biomass burning directly releases organic compounds, including long-chain *n*-alkanes, into the atmosphere (Simoneit et al., 2002). Because wind direction is normally eastward in eastern Siberia, smoke particles could be transported over the Sea of Okhotsk. Southeastern Russia, which is an important drainage basin of the Amur River, is one of the most extensive regions of wildfire in Siberia. In fact, intense and widespread forest fires occurred over far eastern Siberia in July-October 1998 (Tanimoto et al., 2000; Kajii et al., 2002). Satellite images (NOAA-AVHRR) clearly showed the transport of smoke particles to the Sea of Okhotsk in 1998 (Kudoh, personal communication). Although we not yet have data supporting the atmospheric transport of biomass burning products over the Sea of Okhotsk in 1998, this transport pathway is potentially important in the offshore region such as M4 and M6 stations. In fact, during strong forest fires in Siberia and subsequent outflow to Hokkaido Island in May 2003, enhanced concentrations of *n*-alkanes, waxes and biomass burning products (e.g., levoglucosan) were detected in the aerosol samples collected in Sapporo, Hokkaido Island (Mochida et al., 2004).

Alternatively, an adsorption of DOM to sinking particles is another possible cause for the increase in terrestrial *n*-alkane flux in autumn 1998. Hedges and Keil (1999) predicted the presence of hydrophobic and adsorptive DOM in river waters. When such DOM from the Amur River contacts a large amount of suspended particles in an estuary, especially under the flocculating influence of sea salts, extensive sorptive uptake might be expected, relative to that exhibited in the turbid river (Hedges and Keil, 1999). Coagulation of hydrophobic humic acid has been recognized in rivers (Ertel et al., 1986) and numerous estuaries (Fox, 1991). It was reported that the leaf-wax lipids are contained in dissolved fractions as well as the particulate fraction in waters from river (Jaffé et al., 1995), estuary (Mannino and Harvey, 1999) and lake (Berdié et al., 1995) environments. Coagulation commonly occurs as salinity increases in an estuary. However, coagulation of terrestrial organic matter may rarely occurs in offshore

regions such as M4 and M6.

Sea ice is also a possible transport pathway of terrigenous material to marine sediments in the semi-polar regions. Terrigenous material is incorporated into ice when grounded sea ice forms in coastal regions of shallow water depth. However, the expected increase in $\Sigma\text{oddC}_{25-31}$ flux was not observed during enhanced periods of IRD events. Sea ice formed at the northwestern continental shelf drifts and extends to the south during the winter (carrying with it incorporated terrigenous material) because of strong northwesterly winds and the East Sakhalin Current (Kimura and Wakatsuchi, 1999). Grain size analyses of terrigenous material in the sediment traps (Sakamoto et al., 2001) should enhanced fluxes of coarse grain particles were observed when the sea ice was melting (May), suggesting the discharge of terrigenous grains by sea ice at this time.

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Figure captions

Figure 1 a) Map of the Sea of Okhotsk with location of the surface sediments (solid circles) and sediment traps (solid square) used in this study. Wedged lines show sea ice front in February and May 1999. b) Schematic of near surface circulation in the Sea of Okhotsk as derived from satellite tracked drifter data (Ohshima et al., 2002).

Figure 2 Seasonal change in TOC flux, C/N ratio, $\delta^{13}\text{C}$ of total organic matter ($\delta^{13}\text{C}_{\text{org}}$) and highly unsaturated C_{21} hydrocarbon (C_{21}HUH) in the M4 and M6 sediment traps from August 1998 to June 2000. Solid circles and open squares represent the results of upper and lower traps, respectively. Dashed lines in c and d represent the intrusion events of dense shelf water from the northwestern continental shelf into each trap site estimated from CTD temperature and lithogenic flux data (Nakatsuka et al., 2004b).

Figure 3 $\delta^{13}\text{C}$ and Molecular distribution of individual *n*-alkanes in the surface sediments from the Sea of Okhotsk. Open squares represent $\delta^{13}\text{C}$ of individual *n*-alkanes. Bar graphs represent molecular distribution of *n*-alkanes.

Figure 4 Capillary gas chromatogram of the aliphatic hydrocarbons from the settling particle (XP00-M4U5) in the Sea of Okhotsk. C_{21}HUH is highly unsaturated C_{21} hydrocarbon. C_{number} represents *n*-alkanes.

Figure 5 $\delta^{13}\text{C}$ and Molecular distributions of *n*-alkanes in settling particles from the Sea of Okhotsk. Open squares represent $\delta^{13}\text{C}$ of individual *n*-alkanes. Bar graphs represent molecular distribution of *n*-alkanes. Collection periods of sinking particles are (a) XP99-M4L10 (January 3 2000 to January 16, 2000), (b) XP98-M4L4 (September 28 1998 to October 15 1998) and (c) XP98-M4U4 (September 28 1998 to October 15 1998), (d) XP98-M4L20 (July 3 1999 to July 20 1999) and (e) XP98-M4U18 (May 29 1999 to June 15 1999) and (f) XP98-M4U20 (July 3 1999 to July 20 1999).

Figure 6 Relative contributions of two end members to the settling particles in the Sea of Okhotsk calculated from isotopic mean.

Figure 7 Seasonal changes in (a & b) total *n*-alkane flux and (c & d) carbon preference index (CPI) of *n*-alkanes with the fluxes of (e & f) unknown and (g & h) terrestrial-plant *n*-alkanes ($\Sigma\text{oddC}_{25-31}$) in M4 and M6 sediment traps during the period from August 1998 to June 2000. Gray lines represent the change in sea ice concentration (%) at the trap sites. Dashed lines in g and h represent the intrusion events of dense shelf water from the northwestern continental shelf into each trap site (Nakatsuka et al., 2004b).

Figure 8 Scatter plots of $\Sigma\text{oddC}_{25-31}$ flux vs. lithogenic flux in (a) M4 and (b) M6 sediment traps.

Table captions

Table 1 Station data for the sediment trap moorings

Site	Sample cups	Latitude (N)	Longitude (E)	Collection period	Trap depth (m)	Water depth (m)
XP98-M4 Upper	21	52°58'	145°29'	Aug 7, 1998-Aug 7, 1999	300	1754
XP-98 M4 Lower	21	53°00'	145°29'	Aug 7, 1998-Aug 7, 1999	1550	1754
XP99 M4 Upper	21	53°01'	145°30'	Sep 8, 1999-Jun 7, 2000	300	1756
Xp99 M4 Lower	21	53°01'	145°30'	Sep 8, 1999-Jun 7, 2000	1550	1756
XP98- M6 Upper	21	49°31'	146°29'	Aug 7, 1998-Aug 7, 1999	300	812
XP98- M6 Lower	21	49°31'	146°29'	Aug 7, 1998-Aug 7, 1999	700	812
XP99- M6 Upper	21	49°31'	146°29'	Sep 27, 1999-Jun 7, 2000	300	804
XP99- M6 Lower	21	49°31'	146°29'	Sep 27, 1999-Jun 7, 2000	700	804

Table 2. Analytical results of surface sediments collected from the Okhotsk Sea

Sample	Latitude (N)	Longitude (E)	Water depth (m)	TOC (%)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Total n-alkanes ($\mu\text{g/g}$ dry sed.)	CPI
XP99-MC50	55°35.28'	140°50.76'	184	2.20	-20.82	2.44	5.2
XP99-MC63	54°59.35'	141°00.14'	134	1.07	-20.96	1.80	6.4
XP99-MC5	51°27.87'	145°03.09'	787	2.18	-21.33	2.84	5.7
XP99-MC85	52°21.10'	146°17.59'	1440	1.82	-21.72	1.37	5.3
XP99-MC22	49°31.38'	145°40.39'	490	2.41	-21.46	3.01	5.2
XP99-MC19	48°35.77'	149°41.68'	1613	0.63	-21.89	1.72	5.2

$\text{CPI} = 2\sum(\text{C}_{25}\text{-C}_{33} \text{ odd } n\text{-alkanes}) / \{\sum(\text{C}_{24}\text{-C}_{32} \text{ even } n\text{-alkanes}) + \sum(\text{C}_{26}\text{-C}_{34} \text{ even } n\text{-alkanes})\}$

$\delta^{13}\text{C}_{\text{org}}$ represents $\delta^{13}\text{C}$ of total organic carbon

Table 3 stable carbon isotope composition of pristane and individual n-alkanes in surface sediments from the Sea of Okhotsk

Sample	Pristane	Carbon Number of n-alkanes														
		C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34	C35
XP99-MC50	-27.8	-28.6	-29.5	-30.0	-30.0	-30.4	-31.0	-30.7	-30.9	-31.3	-32.0	-31.8	-32.0	-32.2		
XP99-MC63						-30.7		-30.3		-31.5		-32.1				
XP99-MC5		-30.0	-30.4	-31.1	-31.2	-31.3	-31.4	-31.1	-31.5	-31.8	-32.1	-32.0	-32.6	-32.3		
XP00-MC85		-30.1	-31.8	-30.8	-31.8	-30.9	-30.8	-30.9	-30.6	-31.4		-31.8	-33.0	-31.4		
XP00-MC22	-28.1	-30.4	-30.2	-31.1	-31.1	-31.5	-31.6	-31.2	-32.0	-32.2	-32.9	-32.6	-32.4	-31.6		-29.6
XP99-MC19				-29.7	-30.2	-30.6	-31.1	-30.6	-31.0	-31.4	-31.1	-31.9		-31.3		
Average		-29.8	-30.5	-30.5	-30.9	-30.9	-31.2	-30.8	-31.2	-31.6	-32.0	-32.0	-32.5	-31.7		-29.6

Table 4 Stable carbon isotope composition of priatane and individual n-alkanes in sinking particles from the Sea of Okhotsk.

Sample	Pristane	Carbon Number of n-alkanes														
		C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34	C35
XP98-M4U4	-29.1	-28.2	-29.1	-29.1	-28.2	-29.7	-28.6	-29.8	-28.2	-31.3	-29.6	-32.9	-29.5	-31.4		
XP98-M4L4		-29.1	-29.1	-29.3	-29.7	-30.3	-30.7	-30.4	-29.3	-31.3	-31.2	-32.3	-30.3	-31.7		-27.2
XP98-M4U18	-29.6			-28.6	-27.0	-28.7	-27.3	-29.2	-27.2	-29.0	-27.2	-29.0	-26.7	-27.8	-27.0	
XP98-M4U20	-28.5				-26.8	-26.6	-26.8	-27.0	-26.8	-27.2	-26.0	-26.4	-26.5	-26.8		
XP98-M4L20				-27.5	-25.2	-27.6	-26.6	-28.4	-26.8	-28.9	-26.9	-29.5	-27.7	-28.4	-26.7	

Fig. 1 (Seki et al.)

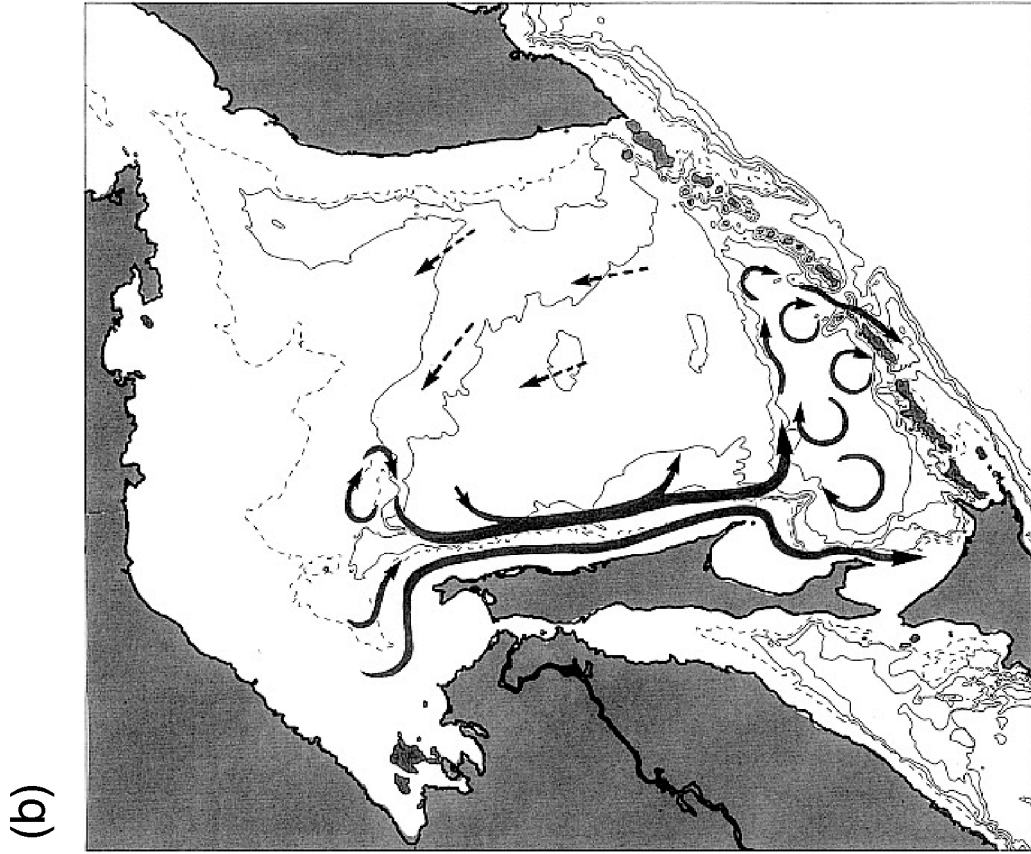
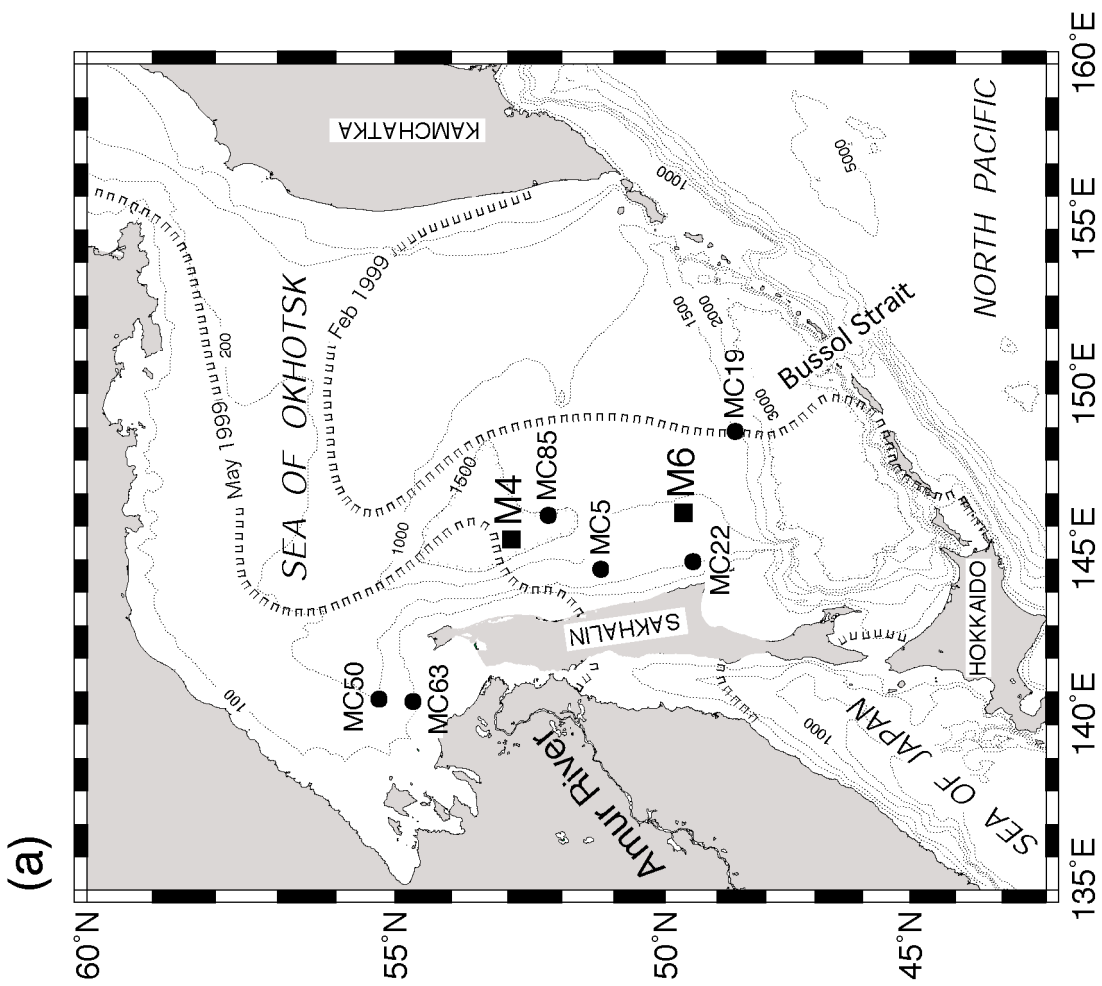


Fig. 2 (Seki et al.)

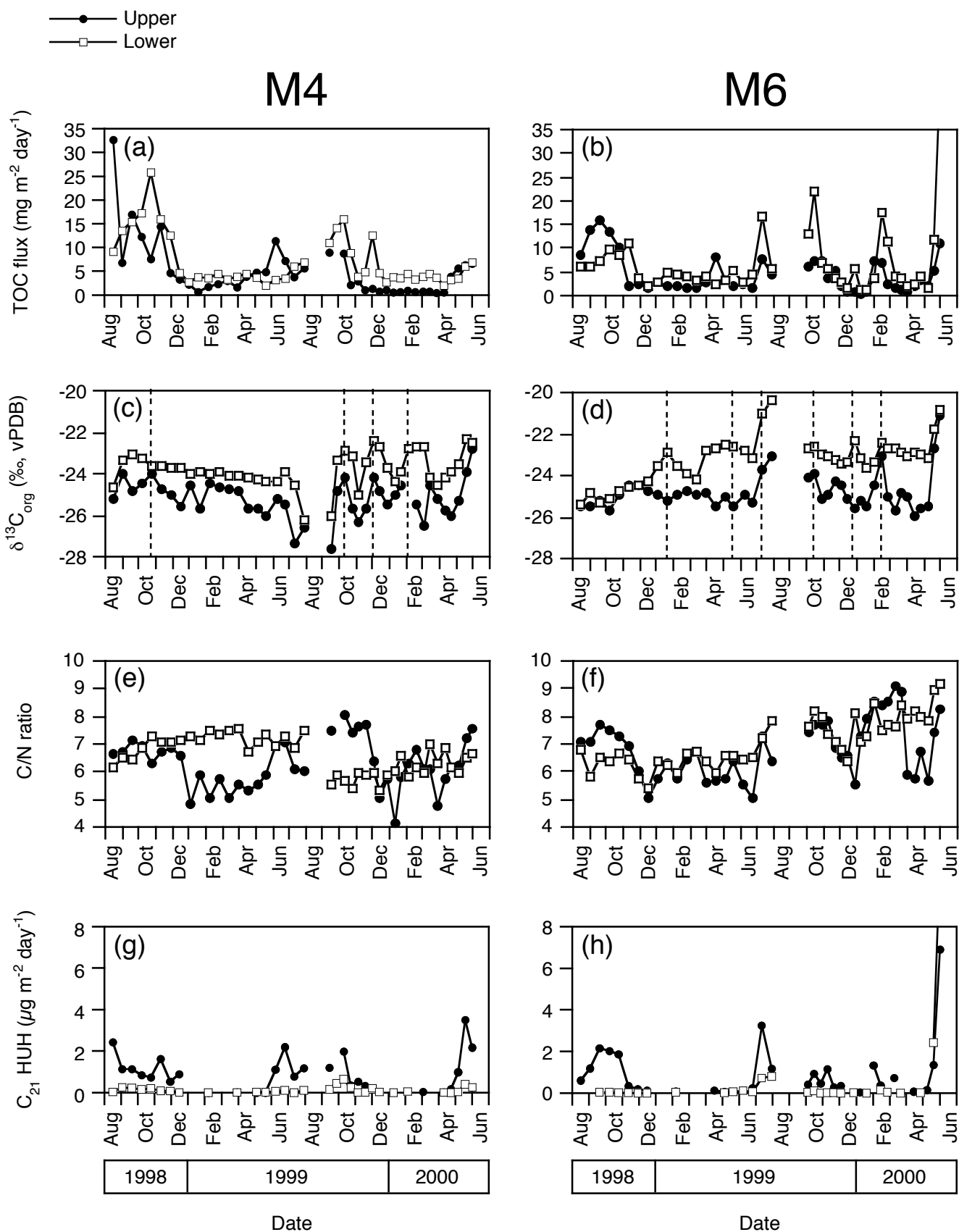


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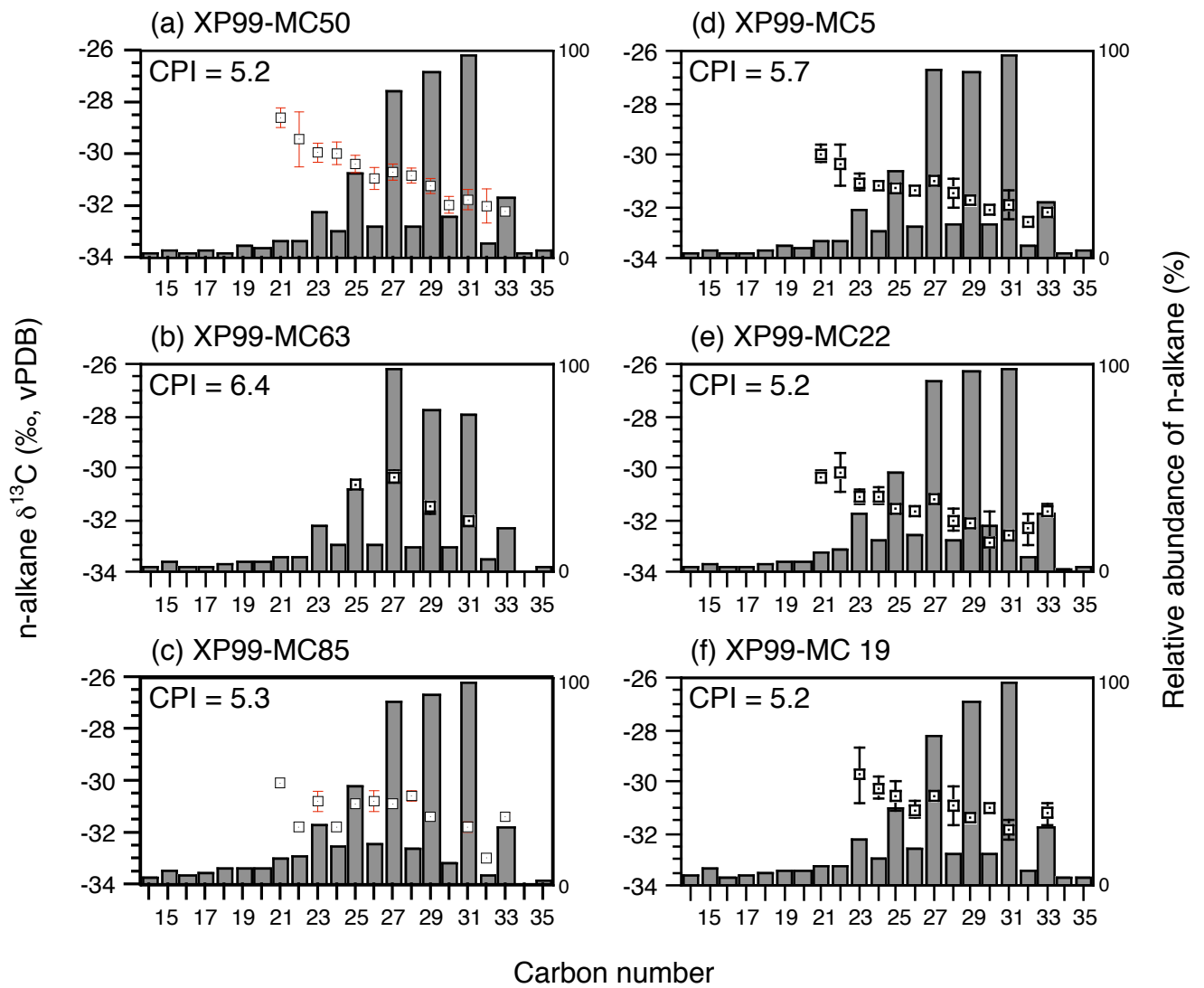


Figure 4 (Seki et al.)

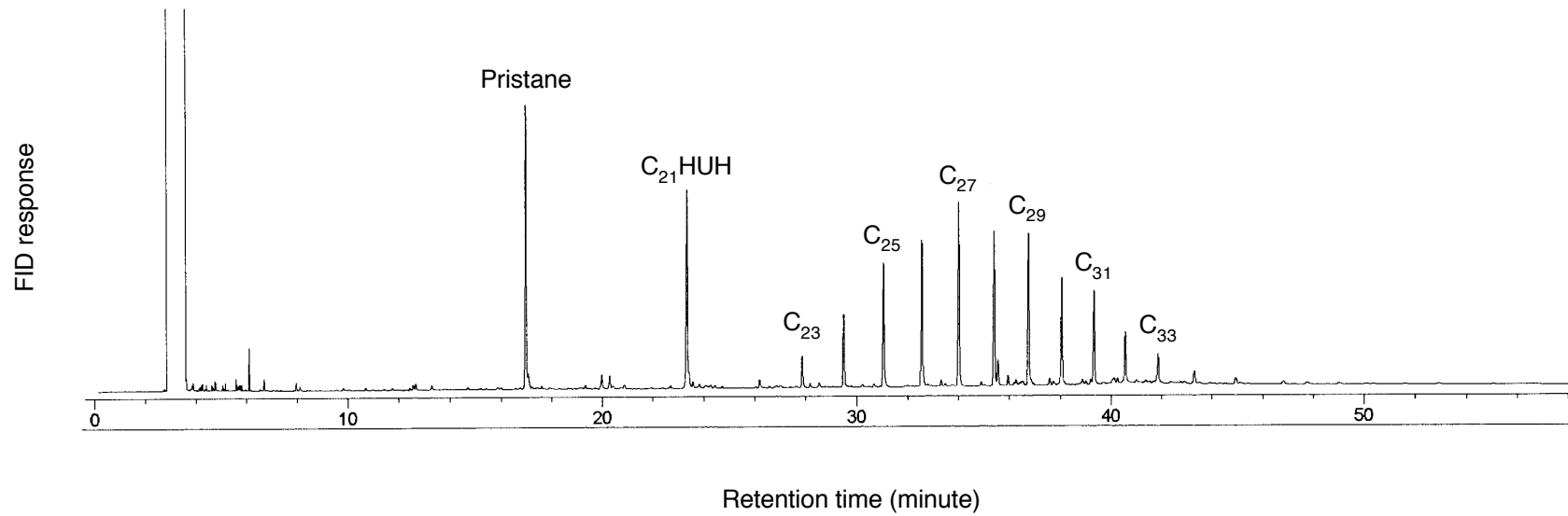


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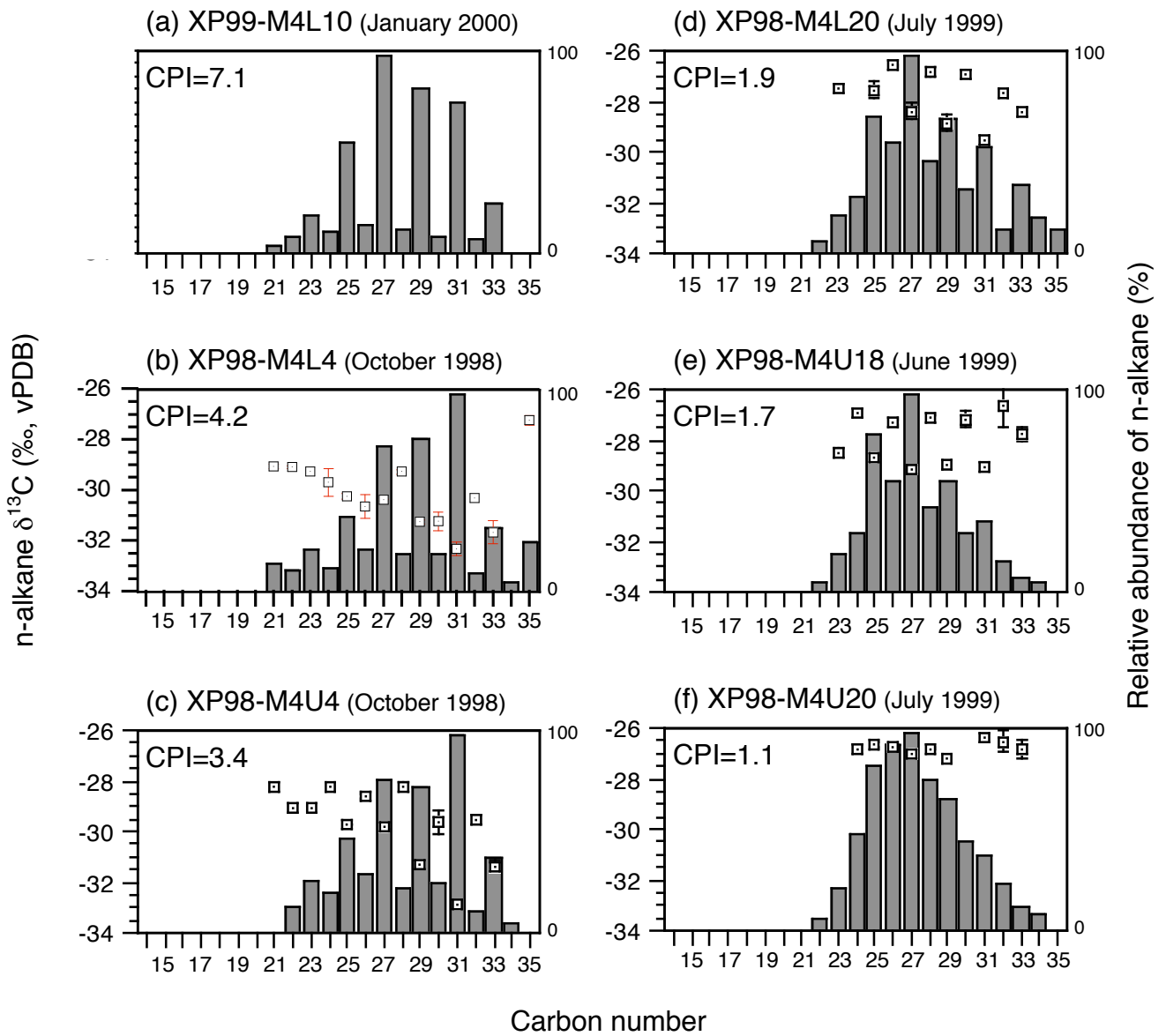


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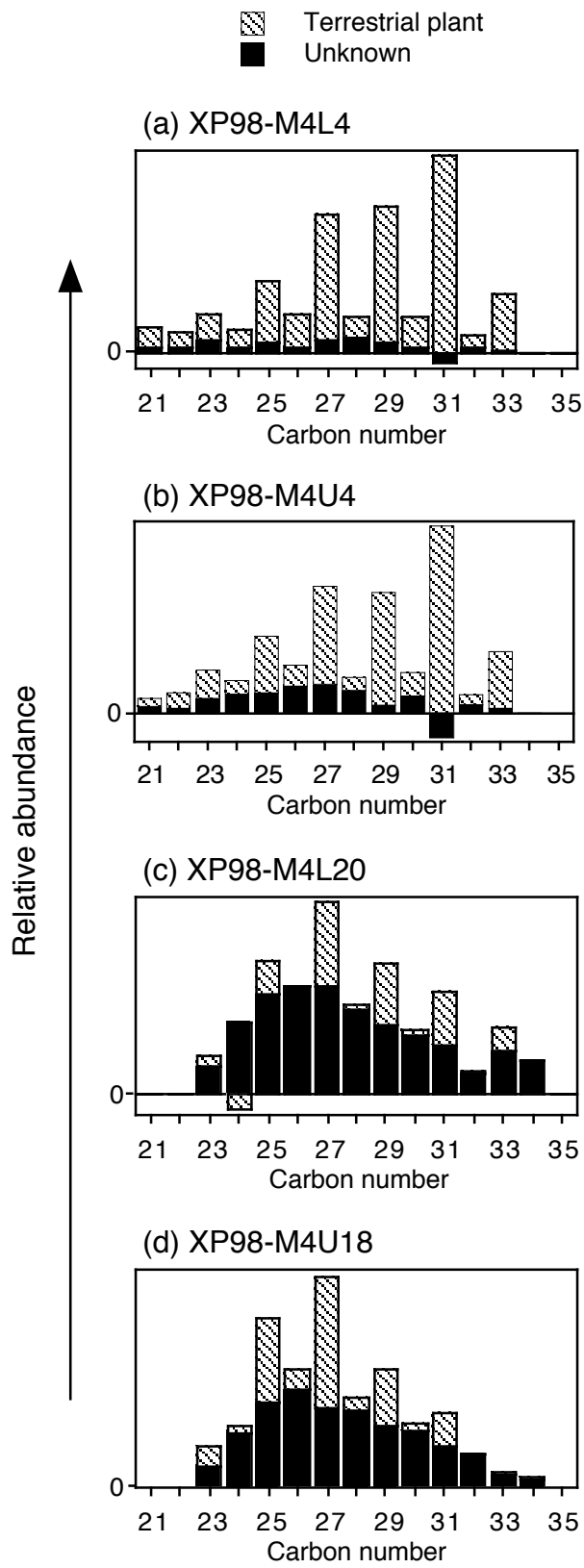


Fig. 7 (Seki et al.)

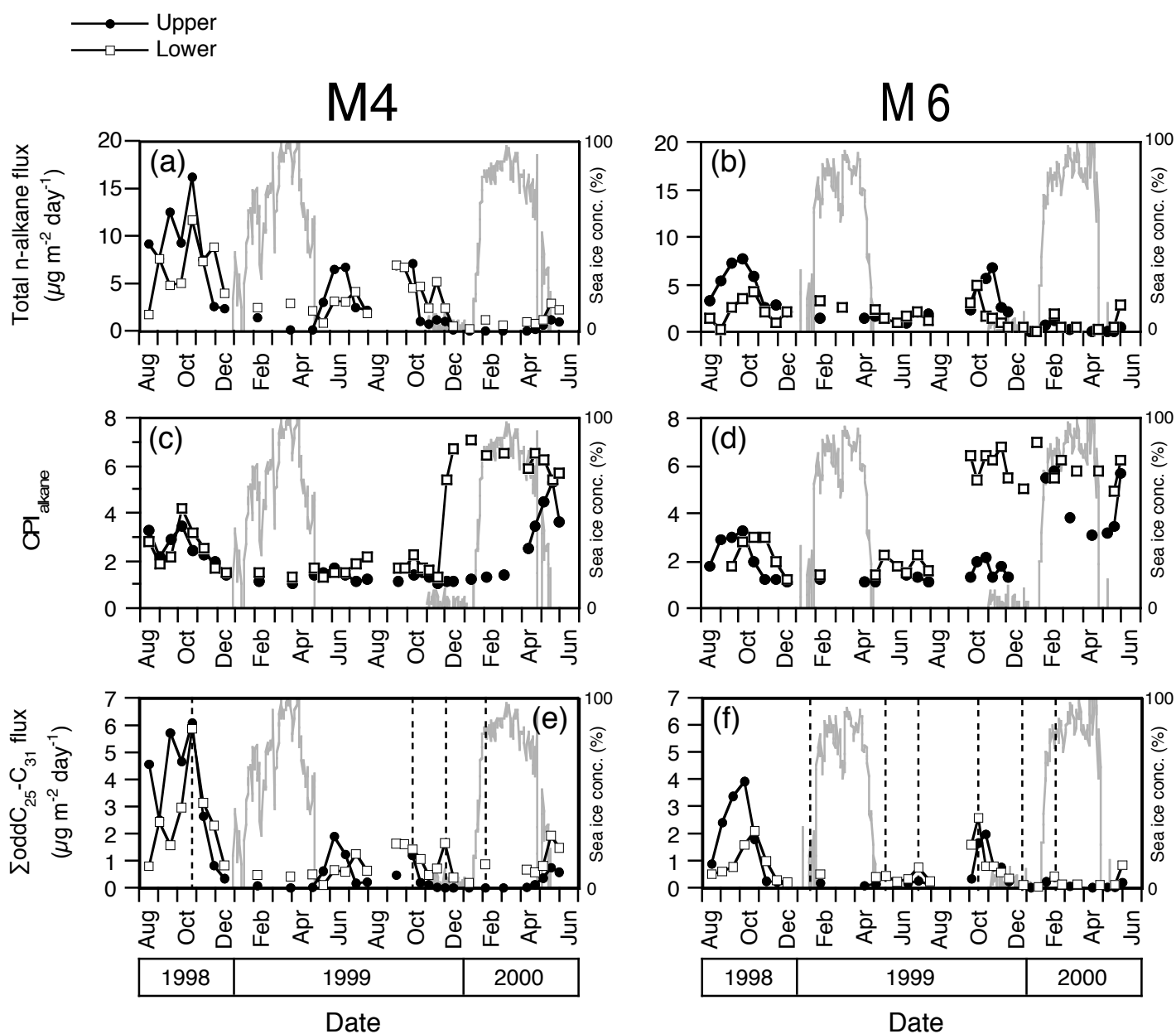


Fig. 8 (Seki et al.)

