Deep-Sea Research II 61–64 (2012) 85–92

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Assessment for paleoclimatic utility of terrestrial biomarker records in the Okhotsk Sea sediments

Osamu Seki [a,*], Naomi Harada [b], Miyako Sato [b], Kimitaka Kawamura [a], Akira Ijiri [c], Takeshi Nakatsuka [d]

[a] *Institute of Low Temperature Science, Hokkaido University, N19W8, Kita-ku, Sapporo 060-0819, Japan*
[b] *Institute of Observational Research for Global Change, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan*
[c] *Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan*
[d] *Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan*

ARTICLE INFO

Available online 29 March 2011

Keywords:
Sea of Okhotsk
Paleoclimate
Long-chain *n*-alkanes
Sediments

ABSTRACT

We measured terrestrial plant biomarker (long-chain *n*-alkanes) in the sediment cores taken from the Sea of Okhotsk to examine paleoclimatic utility of long-chain *n*-alkanes in marine sediments. This study demonstrates that sedimentary record of *n*-alkane in the sea has a high potential to provide important complementary paleo-climate/paleo-environmental information. Molecular distributions of long-chain *n*-alkanes in marine sediments show a typical signature of terrestrial plant wax derived *n*-alkanes with strong odd carbon number predominance from the last glacial to the present, suggesting a source of long-chain *n*-alkanes in the Okhotsk Sea sediments has been terrestrial higher plants throughout the time. The down core profiles of concentrations of C25–C35 *n*-alkanes in XP07-C9 collected from the northwestern site revealed three events of enhanced terrestrial organic matter input during the last deglaciation. The two pronounced events correspond to Melt Water Pulse (MWP) events 1A (14.5–12.5 ka) and 1B (11–6.5 ka). These events possibly linked to increases in river discharge and erosion of submerged continental shelf due to drastic rise in sea level. Down core profiles of molecular distributions of *n*-alkanes in the Okhotsk Sea sediments significantly vary over the last 25 kyr, and are similar to that of a peat core sequence in the East Russia and essentially consistent with pollen data from marine and peat core sequences.

1. Introduction

One of the major goals in the paleoclimate study is to understand climatic linkage between ocean circulation and climate changes in continental regions. Paleoceanographic records are obtained from marine sediments from which high-resolution, continuous and geographically widespread records can be collected from a significant portion of geologic history. On the other hand, reconstruction of paleoclimate in continental region is largely derived from sedimentary records in lacustrine and peat bog. However, in contrast to marine sedimentary sequences, terrestrial records are largely limited to Pleistocene interval with older deposits lacking the temporal and spatial resolution necessary for many paleoenvironmental investigations. In particular, terrestrial records are significantly restricted the postglacial period at the high latitude (e.g., Velichko et al., 1997; Bazarova et al., 2008). Therefore, in high latitudinal regions, significant portions of Earth history, terrestrial environmental records are less developed than marine ones. Also achieving the goal for paleoclimate study relies on the ability to correlate oceanic and continental climate change records accurately.

One way to overcome the issues described above is to utilize terrestrial biomarkers and pollens deposited in marine sediments. This approach also allows direct comparison between marine and terrestrial climate records on the same sediment sequence. Biomarkers have increasingly become more common tool in the reconstruction of past environmental conditions in both continental and marine areas. Molecular analyses of terrestrial biomarker lipids extracted from ocean and lake sediments have been used for reconstructions of paleovegetation and associated paleoclimate histories (e.g., Zhou et al., 2005; Zheng et al., 2007; Seki et al., 2009; Horikawa et al., 2010). In particular, long-chain *n*-alkanes have been extensively studied for the paleclimatic purposes. Molecular distribution and stable carbon and hydrogen isotopic compositions of long-chain *n*-alkanes provide powerful paleoclimate information of terrestrial vegetation and climate. For instance, molecular distribution of *n*-alkanes such as average chain length (ACL), C_{27}–C_{31} *n*-alkane ratio (C_{27}/C_{31}) and P_{aq} index could be used as conventional proxies of continental climate (Vogts et al., 2009) and source input of plants (Ficken et al., 2000). Stable carbon

---

* Corresponding author. Tel.: +81 11 706 5504.
E-mail address: seki@pop.lowtem.hokudai.ac.jp (O. Seki).

0967-0645/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dsr2.2011.03.008

isotopic composition of *n*-alkanes has been used to infer the changes in C3/C4 vegetation where distributions are directly related to climatic conditions (e.g., Bird et al., 1995; Yamada and Ishiwatari, 1999; Huang et al., 2001; Bendle et al., 2007). Hydrogen isotope composition of *n*-alkanes has a potential as more direct proxy of temperature, precipitation, relative humidity and hydrological cycles in the past (e.g., Xie et al., 2000; Liu and Huang, 2005; Hou et al., 2006; Shuman et al., 2006; Seki et al., 2009).

Terrestrial materials deposited in coastal sediments are mainly supplied by river inflows and coastal erosions whereas atmospheric transport of terrestrial materials is more important delivery pathway to the pelagic sediments in the open ocean (Hedges et al., 1997). Thus, terrestrial plant-derived biomarkers deposited in coastal sediments would integrate information about changes in terrestrial ecosystems of catchment in the past. Transport mechanisms of organic matter to the sediments are highly variable depending on their modes of occurrence, i.e., suspended or dissolved forms. Therefore, it is important to understand how fluvial organic materials accumulate in a catchment basin and how climate records are imprinted in sedimentary deposits for better application of terrestrial biomarkers in the paleoenvironmental studies of marine sediments. Here, we discuss an applicability of long-chain *n*-alkanes deposited in sediments from the Sea of Okhotsk as complementary tool for reconstructing terrestrial paleoclimate/paleoenvironment in the high latitudinal East Eurasia.

2. Materials and methods

The piston core XP07-C9 (location 52°24′N 146°00′E, water depth 1431 m) was obtained off Sakhalin during XP07 cruise by the R/V *Professor Khromov* (Fig. 1). This site is closer to a mouth of Amur River than other sites (XP98-PC1, PC2 and PC4) used in this study. Three piston cores: XP98-PC1 (location 51°00′N 152°00′E, water depth 1107 m), PC2 (location 50°24′N 148°20′E, water depth 1258 m) and PC4 (location 49°30′N 146°07′E, water depth 664 m) were obtained along an east–west transect in the central Sea of Okhotsk during XP98 cruise by the R/V *Professor Khromov* as part of a joint Japanese–Russian–US program.

Age models for XP07-C9 were determined by accelerator mass spectrometer-radiocarbon (AMS-^{14}C) dates using shells of planktonic foraminifera. Foraminiferal shells were gently crashed in the 1.5 ml micro tube using homogenizer pestle to open all chambers. Fragments were rinsed by the ultrapure water (Milli-Q water > 18.2 M) five times and ultrasonicated. After the rinse by Milli-Q water, fragments were treated twice by methanol (analytical grade). Subsequently fragments were treated with 250 μl alkali-buffered 1% H_2O_2 (ultrapure) oxidation solution in a hot bath (> 90 °C) in 10 min to remove diagenetic calcite and metal oxides. After that, samples were rinsed by Milli-Q water three times. Finally all fragments were transferred to the chemically cleaned micro tubes with Milli-Q water, and were stocked for ^{14}C analysis. Age model in XP98-PC1, PC2 and PC4 are described by Seki et al. (2004).

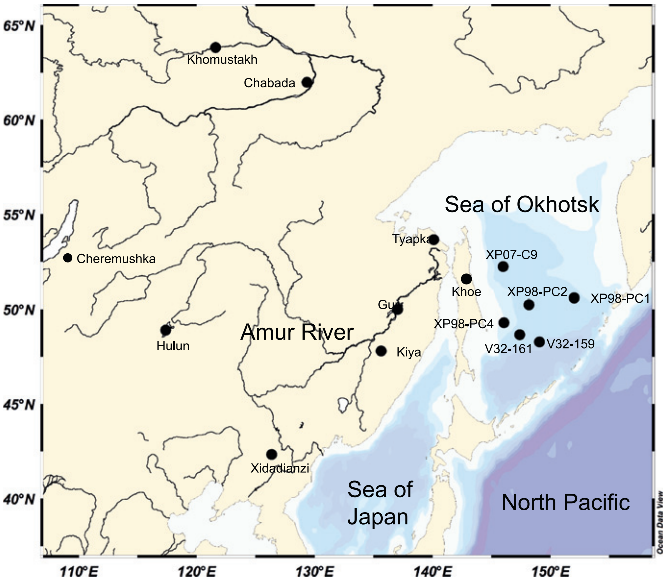

Fig. 1. Map of the Okhotsk Sea and Amur River basin showing the locations of marine and lacustrine sediment cores and peat cores. Arrows show the directions of major surface currents.

Lipid class compounds were extracted from the dry sediment samples (0.5–3.0 g) with dichloromethane/methanol (9:1) using an accelerated solvent extractor (Dionex: ASE 200) at 100 °C and 1500 psi (=10,343 kPa) for 15 min × 2. The extracts were saponified with 0.5 M potassium hydroxide/methanol at 80 °C for 2 h. Neutral components were isolated by extraction with *n*-hexane. Neutral compounds were further separated into 4 subfractions (aliphatic hydrocarbons, aromatic hydrocarbons, ketones and alcohols) by silica gel column chromatography using an automatic solid preparation system (Rapid Trace SPE Workstation, Zymark Center, Hopkinton, Massachusetts, United States). The solvents used were 4 ml of hexane for fraction 1; a mixture of 2 ml of a hexane–toluene mixture (3:1 v/v), 2 ml of hexane–toluene (1:1 v/v), 2 ml of hexane–ethyl acetate (95:5 v/v) and 2 ml of hexane–ethyl acetate (9:1 v/v) for fraction 2; 2 ml of hexane–ethyl acetate (85:15 v/v) followed by 2 ml of hexane–ethyl acetate (4:1 v/v) for fraction 3, and 2 ml of hexane–ethyl acetate (4:1 v/v) followed by 2 ml of ethyl acetate for fraction 4. As for leaf samples, solvent extractable lipids were extracted from dry leaves with *n*-hexane with under ultrasonification. Aliphatic hydrocarbons were separated from other compounds by silica gel column chromatography.

n-Alkanes were analyzed using an HP6890 GC equipped with an on-column injector, CPSIL-5 CB fused silica capillary column (60 m × 0.32 mm i.d., film thickness 0.25 μm) and flame ionization detector. Helium was used as carrier gas. Flow rate is constant at 1.5 ml/min. The GC oven temperature was programmed from 50 to 120 °C at 30 °C/min and then 120–310 °C at 5 °C/min. Each compound was identified by GC/mass spectrometry based on retention times and mass spectra. Semi-quantification of lipid compounds was achieved by GC/FID using an authentic 5α-cholestane standard as internal standard.

3. Oceanographic settings

The Sea of Okhotsk, which is located in the northwestern Pacific rim, is one of the largest marginal sea in the world. There is an anticlockwise cyclonic current system with peculiar conditions of water exchange with the North Pacific. Northward water transport (West Kamchatka Current) dominates to the west of the Kamchatka Peninsula, whereas southward transport (East Sakhalin Current) does so to the east of Sakhalin. This sea is characterized as southern boundary region of seasonal sea ice in the Northern Hemisphere (Kimura and Wakatsuchi, 2000) and the source region of the North Pacific Intermediate Water (NPIW) (Talley, 1991; Wong et al., 1998). Formation of the intermediate water is associated with a generation of seasonal sea ice in the northern area. When sea ice is formed on the northwestern continental shelf during winter, 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 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 (Fig. 1). Area of the Amur River drainage basin is 10^6 km^2. Annual fluxes of fresh waters from the Amur River are estimated to be 345 km^3 yr^{-1}. Estimated annual discharge of dissolved organic matter is 4845×10^3 t and that of suspended organic matter is 808×10^3 t (Levshina, 2008). Thus, the total amount of organic matter annually exported by the Amur River water is 5653×10^3 t, which is comparable to that of largest rivers in the world (Spitzy and Leenheer, 1991; Telang et al., 1991). In the Amur River water, the maximum concentration of organic matter was observed in summer, especially during floods (Levshina, 2008).

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, 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 organic matter, including long-chain *n*-alkanes are exported from the northwestern area to the southern region by the intermediate water flow (Seki et al., 2006). Estimated transports of DOC and particulate organic carbon (POC) by the DSW flow are 13.6 and 0.9 Tg C yr^{-1}, respectively (Nakatsuka et al., 2004a). These fluxes are much higher than those of the sinking POC fluxes from proximal surface waters, suggesting that the supply of organic carbon by the DSW plays an important role in biogeochemical cycles in the sea. Therefore, large amount of terrestrial organic matter supplied by Amur River to the northwestern area of the sea is further transported to the southern region by the intermediate water flow along east coast of Sakhalin Island. This suggests importance of fluvial organic matter supplied from Amur River as major source of terrestrial biomarkers deposited in sediments in the Sea of Okhotsk.

4. Results

Fig. 2 shows carbon preference index (CPI), ACL, C_{27}/C_{31} and P_{aq} index of *n*-alkanes in XP07-C9 together with typical molecular distributions of the late Holocene (1.4 ka), deglaciation (10.3 ka) and last glacial (23.8 ka) samples. Molecular distributions of C_{25}–C_{35} *n*-alkanes in Okhotsk Sea sediments show an odd to even carbon number predominance with a maximum at C_{27}, C_{29} or C_{31}. CPI values of *n*-alkanes (Bray and Evans, 1961) varied between 2.2 and 6.7. These characteristics demonstrate that *n*-alkanes in the soils and sediments are largely originated from vascular higher plants and thus concentration and flux of C_{25}–C_{35} *n*-alkane can be used as indicative of terrestrial organic matter input to the ocean in the Sea of Okhotsk. As shown in Fig. 2, the distribution of *n*-alkanes in the glacial and late Holocene sediments is significantly dominated by C_{31} homolog whereas C_{27} component is the predominant *n*-alkane in the early Holocene and deglacial sediments. The degalcial samples are characterized by relatively large amount of C_{23} *n*-alkane compared to other intervals. Reflecting these characteristics, C_{27}/C_{31} ratio and P_{aq} reach their maxima during the deglaciation while ACL shows an opposite trend with minima during the deglaciation.

Fig. 3 shows down core profiles of concentration of C_{25}–C_{35} *n*-alkanes in marine sediment cores over the last 30 kyr together with global meltwater discharge and lake level records in eastern Eurasia (Yu et al., 2001). Concentration of C_{25}–C_{35} *n*-alkanes in XP07-C9 ranges from 2 to 8 μg/g during the past 25 kyr. As with the previous studies (Ternois et al., 2001; Seki et al., 2003), remarkable increases in the concentration are also recognized in the XP07-C9 during the last deglaciation (from 15 to 6 ka). The profile of XP07-C9 is similar to XP98-PC2, being characterized by the two pronounced deglacial peaks. The two peaks are probably corresponds to Melt Water Pulse (MWP) events 1A (about 14. 5–12.5 ka) and 1B (about 11–6.5 ka) when massive volume of meltwater was discharged to ocean and sea level drastically rose (Fairbanks, 1989). Comparison among all sites revealed that the concentrations are relatively higher in the western region (XP98-PC4, XP98-PC2 and XP07-C9) and lower in the eastern area (XP98-PC1).

Fig. 4 shows changes in ACL of *n*-alkanes over the past 30 kyr. The ACL varies from 28.7 to 29.4 over the past 30 kyr. Variation

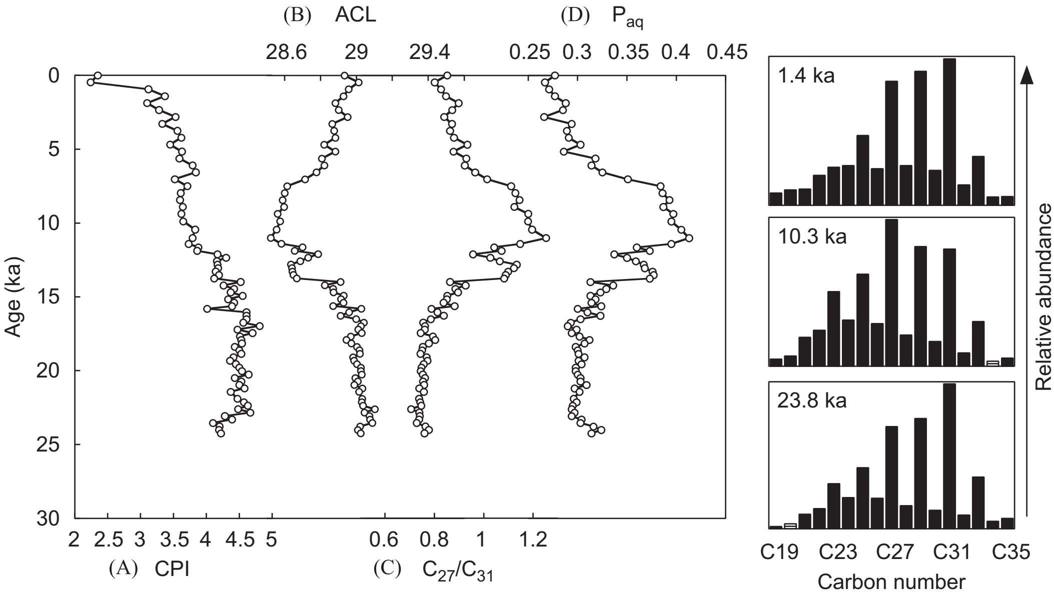

Fig. 2. Down core profiles of (A) CPI, (B) ACL, (C) C_{27}/C_{31} and (D) P_{aq} in XP07-C9 over the past 30 ka together with molecular distributions of *n*-alkanes in sediment core XP07-C9 at (A) 1.4 ka, (B) 10.3 ka and (C) 23.8 ka. $\mathrm{ACL}=(25[C_{25}]+27[C_{27}]+29[C_{29}]+31[C_{31}]+33[C_{33}]+35[C_{35}])/([C_{25}]+[C_{27}]+[C_{29}]+[C_{31}]+[C_{33}]+[C_{35}])$. P_{aq} is defined as $P_{aq}=(C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$ (Ficken et al., 2000).

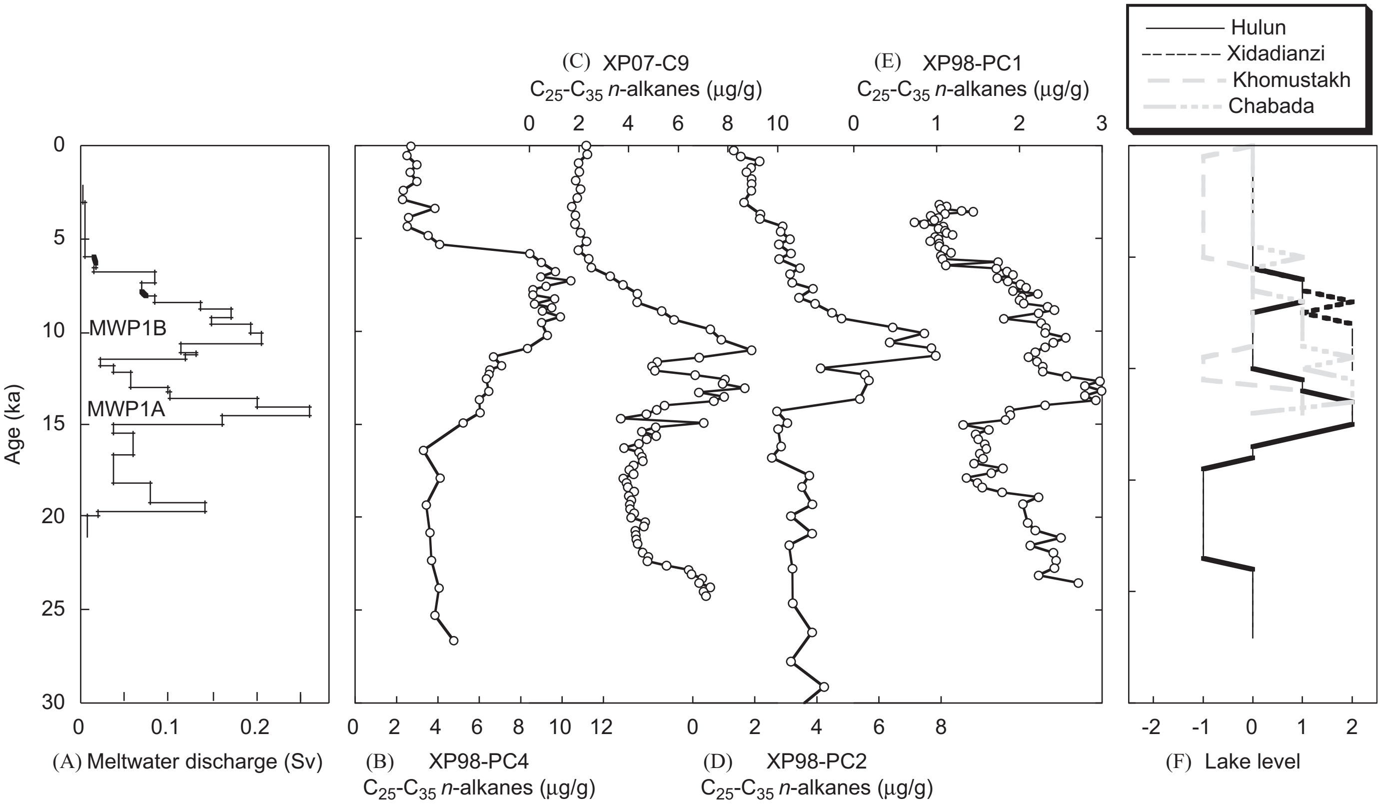

Fig. 3. Down core profiles of C_{25}–C_{35} *n*-alkane concentration over the past 30 ka together with meltwater discharge and lake level records: (A) Melwater discharge (B) XP98-PC4 (Seki et al., 2003), (C) XP07-C9 (this study), (D) XP98-PC2 (Seki et al., 2003), (E) XP98-PC1 (Seki et al., 2003) and (F) Lake level records in Hulun, Xidadianzi, Khomustakh and Chabara (Yu et al., 2001). MWP = Meltwater Pulse events 1A and 1B.

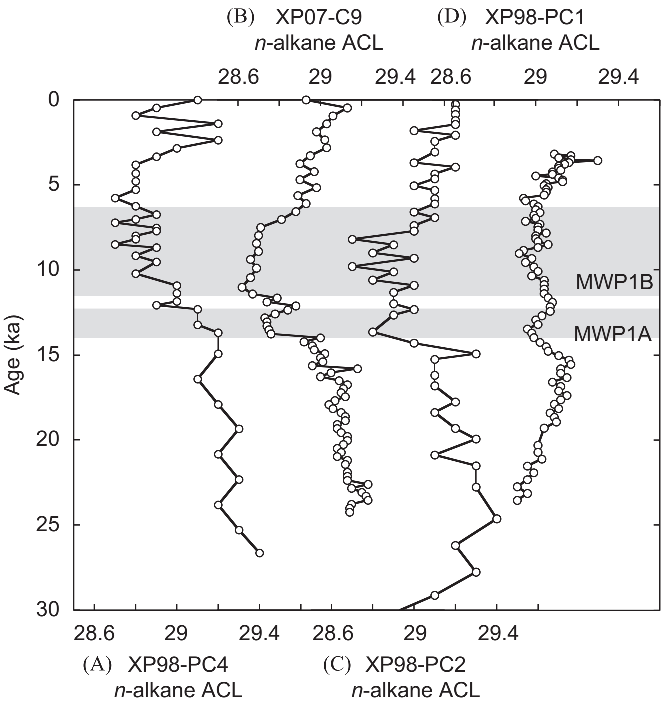

Fig. 4. Down core profiles of average chain length (ACL) of odd C_{25}–C_{35} *n*-alkanes over the past 30 ka: (A) XP98-PC4, (B) XP07-C9, (C) XP98-PC2 and (D) XP98-PC1. $ACL = (25[C_{25}]+27[C_{27}]+29[C_{29}]+31[C_{31}]+33[C_{33}]+35[C_{35}])/([C_{25}]+[C_{27}]+[C_{29}]+[C_{31}]+[C_{33}]+[C_{35}])$. Shaded areas represent periods of Meltwater Pulse (MWP) events 1A and 1B.

pattern of ACL in the all sediments are similar; the highest values during the last glacial period, began to decrease at the early deglaciation and reached its minimum level during the deglaciation, and increase again at the early-mid Holocene. A range of fluctuation is relatively larger in the western sites than the eastern sites. C_{27}/C_{31} ratio and P_{aq} records (data are not shown in this paper) in XP98-PC1, PC2 and PC4 are also similar to that of XP07-C9.

5. Discussion

5.1. Variability of terrestrial biomarker input during the deglaciation

According to previous study (Seki et al., 2003), an increase in the input of terrestrial biomarkers found in western Okhotsk Sea cores during the MWP 1A and 1B can be interpreted to link to a flooding of the shelf owing to the rise of sea level. Sea level was lower in the last glacial period owing to the development of continental ice sheets (Fairbanks, 1989). Estimated sea level during the LGM was −135 to −140 m in the Bonaparte Gulf, Australia (Yokoyama et al., 2000). Thus, significant portion of the modern northwestern continental shelf was exposed to the air during the late glacial period. The enhanced inputs of terrestrial organic matter during deglaciation were probably initiated by resuspension of materials over the submerged land shelf in the northwestern sea through tidal current and subsequently transported to the central Sea of Okhotsk by the East Sakhalin Current as well as in intermediate water (Seki et al., 2003). Distinct MWP signals in XP07-C9, which is more close to northwestern continental shelf than other sites reinforces previous hypothesis that submerged continental shelf and subsequent formation of intermediate water on the submerged continental shelf was major cause of the enhanced terrestrial organic matter input at the MWP events.

However, as shown in Fig. 3F, water level records in Amur River catchment (Hulun and Xidadianzi Lakes) and north of Amur River (Chabada and Khomustakh Lakes) show that water level, which is good indicator of effective precipitation and thus river discharge, has reached it's maximum during the deglaciation and has stayed relatively higher level during the early Holocene (Yu et al., 2001). Evidence for a significant wetter conditions rise in Amur River basin has been also reported by different proxies such as pollen, sedimentary facies and biomarker isotope records in lake sediment and peat sequences (An et al., 2000; Schettler et al., 2006; Seki et al., 2009). The higher lake level during the deglaciation is probably attributed to intensification of summer monsoon precipitation and, locally, meltwater from thawing permafrost and/or the evaporation rate was low because of relatively low temperatures towards the end of the last glaciation. These results consistently suggest that river discharge was higher in the high latitudinal East Eurasia during the last deglaciation than other intervals. Therefore, it is suggested that in addition to the flooding of land shelf, increase in the supply of terrestrial organic matter from Amur and other rivers to the Sea of Okhotsk has also substantially contributed to the intensified signals of terrestrial plant biomarker at the MWP events.

5.2. *Molecular distribution of long-chain n-alkanes*

A number of studies have reported that the molecular distributions of *n*-alkanes significantly depend on plant species and vegetation cover in the catchment (Cranwell, 1973; Rieley et al., 1991; Dodd et al., 1998; Bi et al., 2005; Sachse et al., 2006; Rommerskirchen et al., 2006; Vogts et al., 2009). Several studies reported that *n*-alkane distributions of trees, shrubs, and emergent water plants tend to show large proportions of the C_{27} *n*-alkane (Rieley et al., 1991; Ficken et al., 2000; Bi et al., 2005; Sachse et al., 2006), whereas those of C_3 grasses are generally dominated by C_{31} *n*-alkane (Cranwell, 1973; Bi et al., 2005; Rommerskirchen et al., 2006). It has been also reported that among trees, conifers tend to produce higher molecular weight *n*-alkanes compared to broad leaf trees (Chikaraishi and Naraoka, 2003; Maffei et al., 2004). Molecular distributions of *n*-alkanes in aquatic plants (submerged and floating) are characterized by a predominance of mid chain lengths such as C_{23} and C_{25} while those of terrestrial plants (sub-aerial) are dominated by long-chain homologs ($>C_{29}$) (Ficken et al., 2000; Nott et al., 2000). Emergent aquatic plants have a distribution pattern midway between those of non-emergent and terrestrial plants (Ficken et al., 2000). Based on modern plant data, Ficken et al. (2000) defined a new proxy, P_{aq} that approximates the proportions of aquatic macrophyte versus emergent and terrestrial plant inputs to lacustrine sediments. It has also been reported that *Sphagnum* species show molecular distributions similar to submerged plants, being characterized by a dominance of C_{23} and/or C_{25} *n*-alkanes (Ficken et al., 1998; Baas et al., 2000; Nott et al. 2000; Nichols et al., 2006).

On the other hand, plants tend to synthesize longer chain length *n*-alkanes under water stress conditions to provide a more efficient wax coating (Dodd et al., 1998; Dodd and Rafii, 2000; Shepherd and Griffiths, 2006). Plants in humid condition exhibit distribution maxima in *n*-C_{29} or *n*-C_{31}, whereas plants in hot and arid conditions exhibit distribution maxima in *n*-C_{31} or *n*-C_{33} (Boom et al., 2002; Rommerskirchen et al., 2006; Vogts et al., 2009). Therefore, sedimentary records of molecular distribution could reflect change in input of vegetation in a past.

We evaluate paleoclimatic utility of terrestrial plant derived *n*-alkanes in the Sea of Okhotsk sediments by a comparison of molecular distributions of *n*-alkane in Okhotsk Sea sediments with reported pollen and biomarker records in marine sediments from the Sea of Okhotsk (Morley et al., 1991) and peat cores in Amur River catchment (Bazarova et al., 2008) and Sakhalin Island (Igarashi et al., 2002). The pollen data from the southern Okhotsk Sea sediments (cores V32-159 and V32-161) shows major changes in late glacial/Holocene vegetations, basically the replacement of herbaceous taxa (i.e., *Cyperaceae*, *Gramineae* and *Compositae*) first by birch and alder (i.e., *Betula*, *Alnus* and *Quercus*) during the deglaciation and subsequently by spruce and conifers (*Pinus* and *Picea*) after the mod Holocene (Morley et al., 1991) (Fig. 6). These pollen records also show a significant increase in relative abundance of *Sphagnum* during the deglaciation.

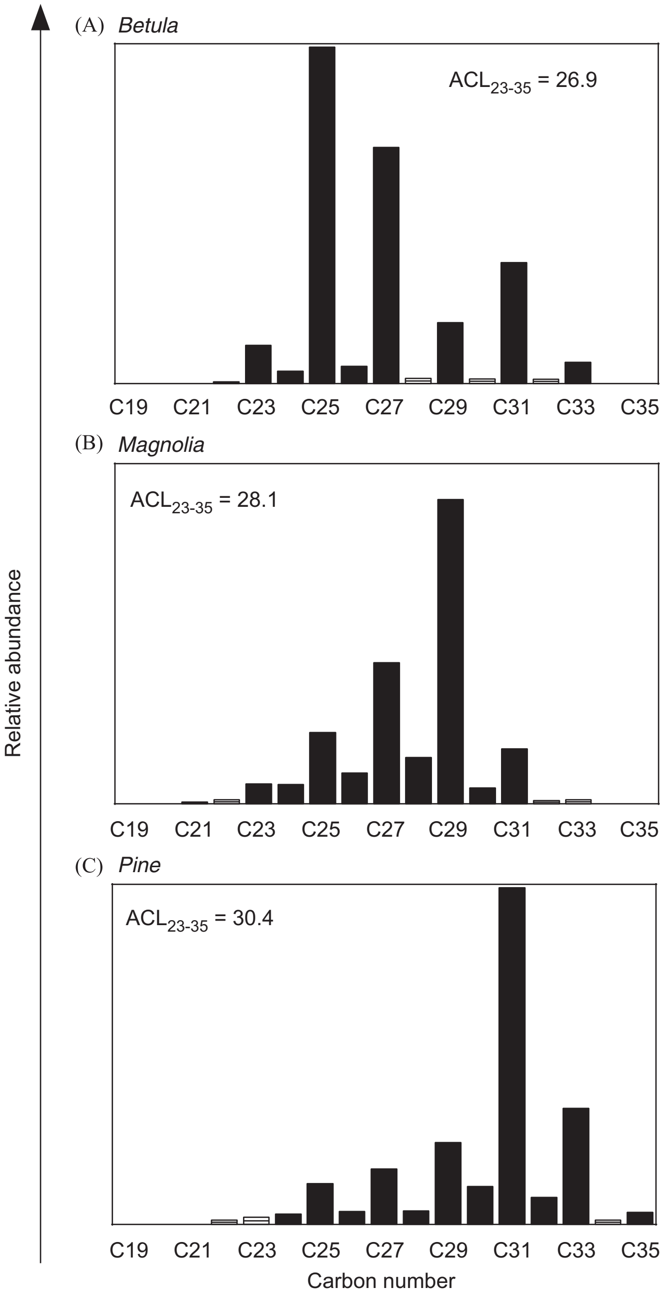

Fig. 5. Chain-length distributions of *n*-alkanes in higher plant leaf wax collected in June from Hokkaido, Japan (43.1°N, 141.3°E): (A) a deciduous broadleaf (*Betula*), (B) a deciduous broadleaf (*Magnolia*) and (C) a conifer (*Pine*). $ACL=(23[C_{23}]+25[C_{25}]+27[C_{27}]+29[C_{29}]+31[C_{31}]+33[C_{33}]+35[C_{35}])/([C_{23}]+[C_{25}]+[C_{27}]+[C_{29}]+[C_{31}]+[C_{33}]+[C_{35}])$.

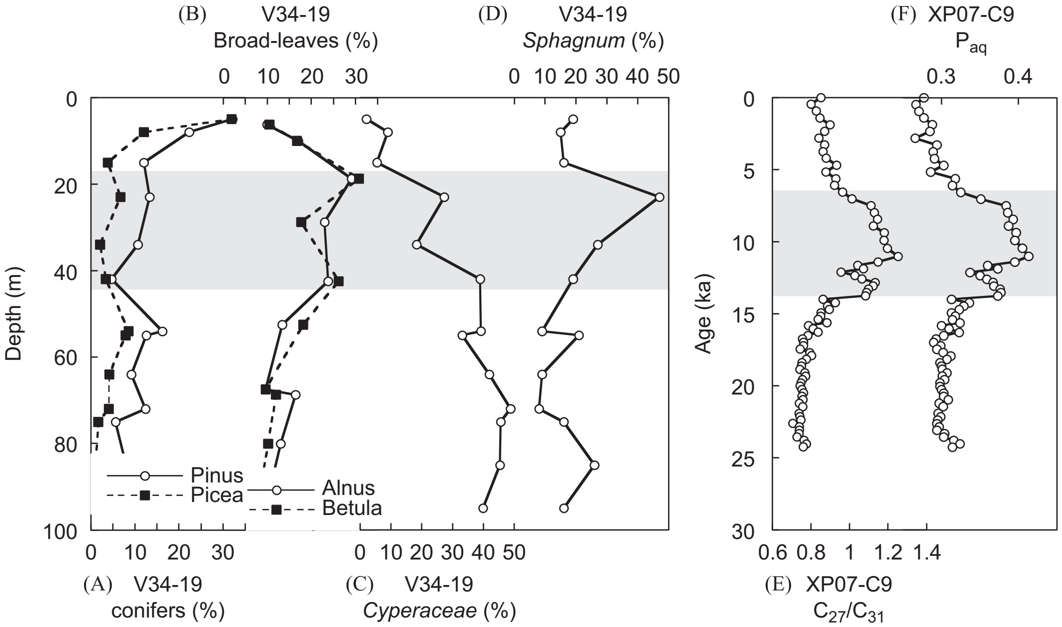

Fig. 6. Comparison of C_{27}/C_{31} ratio and P_{aq} of *n*-alkane in XP07-C9 (E, F) with pollen records in V32-159, Okhotsk Sea (A–D) (Morley et al., 1991). Shaded area represents deglaciation.

Relatively lower ACL and higher C_{27}/C_{31} values in the glacial periods suggests that main source of *n*-alkanes in glacial period has been herbaceous plants and/or conifers. It has been reported that ACL of *n*-alkanes in *Betula* species is especially lower (25–27) than other deciduous trees (Sachse et al., 2006). Thus, the relatively lower ACL values in Okhotsk Sea sediments during the deglaciation and early Holocene are possibly explained by increase in contribution of *Betula* as suggested by the pollen records. Subsequent increase in ACL after the mid Holocene agrees well with replacement of coniferous species, which have relatively higher ACL (Chikaraishi and Naraoka, 2003; Maffei et al., 2004). The P_{aq} record suggests increase in contribution of submerged/floating plants and/or *Sphagnum* in the deglaciation. Based on the pollen record, relatively higher abundances of C_{23} and C_{25} *n*-alkanes during the deglaciation probably reflect an increase in input of *Sphagnum*.

The pollen stratigraphy in the Okhotsk Sea sediments is also similar to that of pollen data from lower Amur River basin (Bazarova et al., 2008), Sakhalin Island (Igarashi et al., 2002), southern area of Amur River basin (An et al., 2000) and a Cheremushka bog sediment core located at eastern coast of the Lake Baikal (Takahara et al., 2000); the predominance of herbaceous plants in the last glacial periods, expansion of *Sphagnum* and broad-leaved trees, including *Betula* in the deglacial and early Holocene and replacement of conifer trees after the mid Holocene (Igarashi et al., 2002; Takahara et al., 2000). In particular, the pollen record in Sakhalin Island (Khoe), which show dramatic vegetation changes at the onset and end of the deglaciation, is well consistent with the C_{27}/C_{31} and P_{aq} profiles in the Okhotsk Sea sediment (Igarashi et al., 2002). Furthermore, the *n*-alkane C_{27}/C_{31} ratio of *n*-alkane in a Cheremushka bog core is very similar to that of the Okhotsk Sea sediments over the last 30 kyr albeit it's resolution is relatively lower than that of Okhotsk Sea sediment core (Ishiwatari et al., 2009). Therefore, the overall variation patterns of the ACL and C_{27}/C_{31} and P_{aq} records in the Okhotsk Sea sediments essentially coincide well with succession pattern of pollen assemblage and biomarker profile in the peat and marine sediments from the last glacial to the present.

To substantiate the above interpretation, we collected plant leaf samples from Sapporo, Hokkaido Island (43.1°N, 141.3°E) where climatic zone is the same as lower Amur River basin. Fig. 5 shows typical chain length distributions of *n*-alkanes extracted from the leaf waxes of *Betula*, *Magnolia* and *Pine*. Normal C_{23}–C_{35} alkanes in the leaf waxes were characterized by a strong odd carbon number predominance with a maximum at C_{27}, C_{29} or C_{31}. The ACL of *n*-alkanes in *Betula* is the lowest of all (26.9), while that of *Pine* show the highest value (30.4). The ACL of *Magnolia*, which is a deciduous broad leaf plant, is medium (28.1) between the other two plants. Although not being conclusive, these results support an idea that the ACL records in the Okhotsk sediments largely reflects vegetation type transported to the marine sediments.

Alternatively, it is also possible that the molecular distribution reflects change in a climate condition. Actually, the variation pattern of the *n*-alkane ACL in the sediments agree well with climate changes in the East Russia; dry condition in the last glacial, wetter climate in the deglaciation and early Holocene, a reversal of dry condition in the late Holocene (Seki et al., 2009). Therefore, despite the presence of a dynamic scale transport system in the Sea of Okhotsk which may potentially disturb sedimentary record, the basis of the sedimentary pollen data and *n*-alkane distributions of modern vegetations, we concluded that the depth variations in the relative abundance of the *n*-alkane homologs in core XP07-C9 largely reflect a change in the types of vegetation in the East Russia as well as climate condition. This study demonstrates terrestrial plant wax *n*-alkane homolog in the Okhotsk Sea sediments is a compartmental tool to reconstruct terrestrial vegetation and climate at high latitudinal region of East Eurasia. Compared to southern sites (XP98-PC4, XP98-PC2 and XP98-PC1), northwestern sites (XP07-C9) obviously show a distinct ACL fluctuation associated with the millennial scale climate changes such as Bølling/Allerød (B/A) and Younger Dryas (YD) oscillations recorded in the northern Greenland ice core (North Greenland Ice Core Project Members, 2004), suggesting more reliable paleoclimate reconstruction in a continent could be obtained from the northwestern site, which is closer to a mouth of Amur River.

Acknowledgments

OS acknowledges the postdoctoral fellowship supported by the Japan Society for the Promotion of Science. This research is also supported by a research Grant (70067K) funded by Institute of Low Temperature Science.

References

An, Z., Porter, S.C., Kutzback, J.E., Wu, X., Wang, S., Liu, X., Li, X., Zhaou, W., 2000. Asynchronous Holocene optimum of the East Asian monsoon. Quaternary Science Reviews 19, 743–762.

Baas, M., Pancost, R., van Geel, B., Sinninghe Damsté, J.S., 2000. A comparative study of lipids in *Sphagnum* species. Organic Geochemistry 31, 535–541.

Bendle, J., Kawamura, K., Yamazaki, K., Niwai, T., 2007. Latitudinal distribution of terrestrial lipid biomarkers and *n*-alkane compound specific stable carbon isotope ratios in the atmosphere over the western Pacific and Southern Ocean. Geochimica et Cosmochimica Acta 71, 5934–5955.

Bi, X., Sheng, G., Liu, X., Li, C., Fu, J., 2005. Molecular and carbon and hydrogen isotopic composition of *n*-alkanes in plant leaf waxes. Organic Geochemistry 36, 1405–1417.

Bird, M.I., Summons, R.E., Gagan, M.K., Roksandic, Z., Dowling, L., Head, J., Fifield, L.K., Cresswell, R.G., Johnson, D.P., 1995. Terrestrial vegetation change inferred from *n*-alkane δ13C analysis in the marine-environment. Geochimica et Cosmochimica Acta 59, 2853–2857.

Boom, A., Marchant, R., Hooghiemstra, H., Sinninghe Damsté, J.S., 2002. CO_2- and temperature-controlled altitudinal shifts of C4- and C3-dominated grasslands allow reconstruction of palaeoatmospheric pCO_2. Palaeogeography, Palaeoclimatology, Palaeoecology 177, 151–168.

Bray, E.E., Evans, E.D., 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. Geochimica et Cosmochimica Acta 36, 1185–1203.

Bazarova, V.B., Klimin, M.A., Mokhova, L.M., Orlova, L.A., 2008. Quaternary International 179, 9–19.

Chikaraishi, Y., Naraoka, H., 2003. Compound-specific δD-δ13C analyses of *n*-alkanes extracted from terrestrial and aquatic plants. Phytochemistry 63, 361–371.

Cranwell, P.A., 1973. Chain-length distribution of *n*-alkanes from lake sediments in relation to post-glacial environmental change. Freshwater Biology 3, 259–265.

Dodd, R.S., Rafii, Z.A., Power, A.B., 1998. Ecotypic adaptation in *Austrocedrus chilensis* in cuticular hydrocarbon composition. New Phytology 138, 699–708.

Dodd, R.S., Rafii, Z.A., 2000. Habitat-related adaptive properties of plant cuticular lipids. Evolution 54, 1438–1444.

Fairbanks, R.G., 1989. A 17,000-year glacio-eustatic sea level record: influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation. Nature 342, 637–642.

Ficken, K.J., Barber, K.E., Eglinton, G., 1998. Lipid biomarker and plant macrofossil stratigraphy of a Scottish montane peat bog over the last two millennia. Organic Geochemistry 28, 217–237.

Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary inputs of submerged/floating freshwater aquatic macrophytes. Organic Geochemistry 31, 745–749.

Gladyshev, S., Martin, S., Riser, S., Figurkin, A., 2000. Dense water production on the northern Okhotsk shelves: comparison of ship-based spring–summer observations for 1996 and 1997 with satellite observations. Journal of Geophysical Research 105, 26281–26299.

Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? Organic Geochemistry 27, 195–212.

Horikawa, K., Murayama, M., Minagawa, M., Kato, Y., Sagawa, T., 2010. Latitudinal and downcore (0–750 ka) changes in *n*-alkane chain lengths in the eastern equatorial Pacific. Quaternary Research 73, 573–582.

Hou, J., Huang, Y., Wang, Y., Shuman, B., Oswald, W.W., Faison, E., Foster, D.R., 2006. Postglacial climate reconstruction based on compound-specific *D/H* ratios of fatty acids from Blood Pond, New England. Geochemistry Geophysics Geosystems, 7. doi:10.1029/2005GC001076.

Huang, Y.S., Freeman, K.H., Eglinton, T.I., Street-Perrott, F.A., 2001. Climate change as the dominant control on glacial–interglacial variations in C3 and C4 plant abundance. Science 293, 1647–1651.

Igarashi, Y., Murayama, M., Igarashi, T., Higake, T., Fukuda, M., 2002. History of Larix forest in Hokkaido and Sakhalin, northeast Asia since the last glacial. Acta Palaeontologica Sinica 41, 524–533.

Ishiwatari, R., Fujino, N., Brincat, D., Yamamoto, S., Takahara, H., Shichi, K., Krivonogov, S.K., 2009. A 35 kyr record of organic matter composition and δ13C of *n*-alkanes in bog sediments close to Lake Baikal: implications for paleoenvironmental studies. Organic Geochemistry 40, 51–60.

Itoh, M., Ohshima, K.I., Wakatsuchi, M., 2003. Distribution and formation of Okhotsk Sea intermediate water: an analysis of isopycnal climatological data. Journal of Geophysical Research, 108. doi:10.1029/2002JC001590.

Kimura, N., Wakatsuchi, M., 2000. Relationship between sea-ice motion and geostrophic wind in the Northern Hemisphere. Geophysical Research Letters 27, 2738–3735.

Kowalik, K., Polyakov, I., 1998. Tides in the Sea of Okhotsk. Journal of Physical Oceanography 28, 1389–1409.

Levshina, S.I., 2008. Dissolved and suspended organic matter in the Amur and Songhua River Water. Water Resources 35, 716–724.

Liu, W., Huang, Y., 2005. Compound specific *D/H* ratios and molecular distributions of higher plant leaf waxes as novel paleoenvironmental indicators in the Chinese Loess Plateau. Organic Geochemistry 36, 851–860.

Maffei, M., Badino, S., Bossi, S., 2004. Chemotaxonomic significance of leaf wax nalkanes in the Pinales (Coniferales). Journal of Biological Research 1, 3–19.

Martin, S., Drucker, R., Yamashita, K., 1998. The production of ice and dense shelf water in the Okhotsk Sea polynyas. Journal of Geophysical Research 103, 27771–27782.

Morley, J.J., Heusser, L.E., Shackleton, N.J., 1991. Late Pleistocene/Holocene radiolarian and pollen records from sediments in the Sea of Okhotsk. Paleoceanography 6, 121–131.

Nakatsuka, T., Yoshikawa, C., Toda, M., Kawamura, K., Wakatsuchi, M., 2002. An extremely turbid intermediate water in the Sea of Okhotsk: implication for the transport of particulate organic carbon in a seasonally ice-bound sea. Geophysical Research Letters, 29. doi:10.1029/2001GL014029.

Nakatsuka, T., Toda, M., Kawamura, K., Wakatsuchi, M., 2004a. Dissolved and particulate organic carbon in the Sea of Okhotsk: their transport from continental shelf to ocean interior. Journal of Geophysical Research 109, C09S14.

Nakatsuka, T., Fujimune, T., Yoshikawa, C., Noriki, S., Kawamura, K., Fukamachi, Y., Genta, M., Ohshima, K.I., Wakatsuchi, M., 2004b. Biogenic and lithogenic particle flux in the western region of the Sea of Okhotsk. Journal of Geophysical Research 109, C09S13.

Nichols, J.E., Booth, R.K., Jackson, S.T., 2006. Paleohydrologic reconstruction based on *n*-alkane distributions in ombrotrophic peat. Organic Geochemistry 37, 1505–1513.

North Greenland Ice Core Project members, 2004. High-resolution record of Northern Hemisphere climate extending into the last interglacial period. Nature 431, 147–151.

Nott, C.J., Xie, S., Avsejs, L.A., Maddy, D., Chambers, F.M., Evershed, R.P., 2000. *n*-Alkane distributions in ombrotrophic mires as indicators of vegetation change related to climatic variations. Organic Geochemistry 31, 231–235.

Rieley, G., Collier, R.J., Jones, D.M., Eglinton, G., Eakin, P.A., Fallick, A.E., 1991. Sources of sedimentary lipids deduced from stable carbon-isotope analyses of individual compounds. Nature 352, 425–427.

Rommerskirchen, F., Plader, A., Eglinton, G., Chikaraishi, Y., Rullkötter, J., 2006. Chemotaxonomic significance of distribution and stable isotopic composition of long-chain alkanes and alkan-1-ols in C4 grass waxes. Organic Geochemistry 37, 1303–1332.

Sachse, D., Radke, J., Gleixner, G., 2006. δ*D* values of individual *n*-alkanes from terrestrial plants along a climatic gradient–implications for the sedimentary biomarker record. Organic Geochemistry 37, 469–483.

Schettler, G., Liu, Q., Mingram, J., Stebich, M., Dulski, P., 2006. East-Asian monsoon variability between 15,000 and 2000 cal. yr BP recorded in varved sediments of Lake Sihailongwan (northeast China, Long Gang volcanic field). Holocene 16, 1043–1057.

Seki, O., Kawamura, K., Nakatsuka, T., Ohnishi, K., Ikehara, M., Wakatsuchi, M., 2003. Sediment core profiles of long-chain *n*-alkanes in the Sea of Okhotsk: enhanced transport of terrestrial organic matter from the last deglaciation to the early Holocene. Geophysical Research Letters 30 2001GL014464.

Seki, O., Ikehara, M., Kawamura, K., Nakatsuka, T., Ohnishi, K., Wakatsuchi, M., Narita, H., Sakamoto, T., 2004. Reconstruction of paleoproductivity in the Sea of Okhotsk over the last 30 kyr. Paleoceanography 19, PA1016. doi:10.1029/2002PA000808.

Seki, O., Yoshikawa, C., Nakatsuka, T., Kawamura, K., Wakatsuchi, M., 2006. Fluxes, source and transport of organic matter in the western Sea of Okhotsk: stable carbon isotopic ratios of *n*-alkanes and total organic carbon. Deep-Sea Research I 53, 253–270.

Seki, O., Meyers, P.A., Kawamura, K., Zheng, Y., Zhou, W., 2009. Hydrogen isotopic ratios of plant–wax *n*-alkanes in a peat bog deposited in northeast China during the last 16 kyr. Organic Geochemistry 40, 671–677.

Shuman, B., Huang, Y., Newby, P., 2006. Compound-specific isotopic analyses track changes in seasonal precipitation regimes in the Northeastern United States. Quaternary Science Reviews 25, 2992–3002.

Shepherd, T., Griffiths, D.W., 2006. The effects of stress on plant cuticular waxes. New Phytologist 171, 469–499. doi:10.1111/j.1469-8137.2006.01826.x.

Spitzy, A., Leenheer, J., 1991. Dissolved organic carbon in rivers. In: Degens, E.T., Kempe, S., Richey, J.E. (Eds.), Biogeochemistry of Major World Rivers. SCOPE, New York, pp. 213–232.

Takahara, H., et al., 2000. Vegetation history of the southeastern and eastern coasts of Lake Baikal from bog sediments since the last interstade. In: Minoura, K. (Ed.), Lake Baikal. A Mirror in Time and Space for Understanding Global Change Processes. Elsevier, Amsterdam, pp. 108–118.

Talley, L.D., 1991. An Okhotsk Sea Water anomaly: implications for ventilation in the North Pacific. Deep-Sea Research I 28, 171–190.

Ternois, Y., Kawamura, K., Keigwin, L., Ohkouchi, N., Nakatsuka, T., 2001. A biomarker approach for assessing marine and terrigenous input to the sediments of Sea of Okhotsk for the last 27,000 years. Geochimica et Cosmochimica Acta 65, 791–802.

Telang, et al., 1991. Carbon and mineral transport in major North American, Russian Arctic, and Siberian rivers: the St. Laurence, the Mackenzie, the Yukon, the Arctic Alaskan rivers, the Arctic basin rivers in the Soviet Union, and the Yenisei. In: Degens, E.T., Kempe, S., Richey, J.E. (Eds.), Biogeochemistry of Major World Rivers. SCOPE, New York, pp. 75–104.

Velichko, A.A., Andrew, A.A., Klimanov, V.A., 1997. Climate and vegetation dynamics in the tundra and forest zone during the late glacial and Holocene. Quaternary International 41/42, 71–96.

Vogts, A., Moossen, H., Rommerskirchen, F., Rullktter, Jr., 2009. Distribution patterns and stable carbon isotopic composition of alkanes and alkan-1-ols from plant waxes of African rain forest and savanna C3 species. Organic Geochemistry 40, 1037–1054.

Wong, C.S., Matear, R.J., Freeland, H.J., Whitney, F.A., Bychkov, A.S., 1998. WOCE line P1W in the Sea of Okhotsk 2. CFCs and the formation rate of intermediate water. Journal of Geophysical Research 103, 15625–15642.

Xie, S., Nott, C.J., Avsejs, L.A., Volders, F., Maddy, D., Chambers, F.M., Gledhill, A., Carter, J.F., Evershed, R.P., 2000. Paleoclimate records in compound-specific δD values pf a lipid biomarker in ombrotrophic peat. Organic Geochemistry 31, 1053–1057.

Yamada, K., Ishiwatari, R., 1999. Carbon isotopic compositions of long-chain *n*-alkanes in the Japan Sea sediments: implications for paleoenvironmental changes over the past 85 kyr. Organic Geochemistry 30, 367–377.

Yokoyama, Y., Lambeck, K., De Deckker, P., Johnston, P., Fifield, L.K., 2000. Timing of the last glacial maximum from observed sea-level minima. Nature 406, 713–716.

Yu, G., Harrison, S.P., Xue, B., 2001. Lake status records from China: data base documentation. Technical Report in Max-Plank-Institute for Biogeochemistry 4, 243.

Zheng, Y., Zhou, W., Meyers, P.A., Xie, S., 2007. Lipid biomarkers in the Zoige-Hongyuan peat deposit; implication of Holocene climate changes in West China. Organic Geochemistry 38, 1927–1940.

Zhou, W., Xie, S., Meyers, P.A., Zheng, Y., 2005. Reconstruction of late glacial and Holocene climate evolution in southern China from geolipids and pollen in the Dingnan peat sequence. Organic Geochemistry 36, 1272–1284.