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# Modern organic carbon deposition in the Laptev Sea and the adjacent continental slope: surface water productivity vs. terrigenous input

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Abstract—Sediment samples from the Laptev Sea, taken during the 1993 RV Polarstern expedition ARK IX/4 and the RV Ivan Kireyev expedition TRANSDRIFT I, were investigated for the amount and composition of their organic carbon fractions. Of major interest was the identification of different processes controlling organic carbon deposition (i.e. terrigenous supply vs. surface water productivity). Long-chain unsaturated alkenones derived from prymnesiophytes, and fatty acids derived from diatoms and dinoflagellates, were analysed by means of gas chromatography and mass spectrometry. First results on the distribution of these biomarkers in surface sediments indicate that the surface water productivity signal is well preserved in the sediment data. This is shown by the distribution of the 16:1(n-7)and 20:5(n-3) fatty acids indicative for diatoms, and the excellent correlation with the chlorophyll aconcentrations in the surface water masses and the biogenic-opal content and increased hydrogen indices of the sediments. The high concentration of these unsaturated fatty acids in shallow water sediments shows the recent deposition of the organic material. In deep-sea sediments, on the other hand, the concentrations are low. This decreased content is typical for phytoplankton material which has been degraded by microorganisms or autoxidation. In general, the alkenone concentrations are very low, suggesting low production rates by prymnesiophytes. Only at one station from the lower continental margin influenced by the inflow of Atlantic water masses, were some higher amounts of alkenones determined. Long-chain n-alkanes as well as high C/N ratios and low hydrogen indices indicate the importance of (fluvial) supply of terrigenous organic matter. © 1997 Elsevier Science Ltd

Key words-fatty acids, alkenones, marine organic matter, terrigenous organic matter, Laptev Sea, Arctic Ocean

## INTRODUCTION

In relation to the world's ocean, the Arctic Ocean is rather less productive due to the permanent icecover (Subba Roa and Platt, 1984); however, regional differences occur. In marginal seas (such as the Laptev Sea) characterized by an increased fluvial nutrient supply, near ice edges, and at local/regional upwelling cells, significantly raised primary production rates are expected. The mapping of sedimentological, geochemical and biological data reflecting the surface water productivity in surface sediments, and the subsequent comparison to recent oceanographic and biological parameters, will allow one to elucidate the most important processes determining primary production in the Arctic Ocean. Besides nutrients, the major Eurasian rivers also transport large amounts of dissolved and particulate material (i.e. chemical elements, siliciclastic and organic matter) onto the shelves where it is accumulated, or further transported, toward the open ocean by different mechanisms (sea-ice, icebergs, turbidity currents, etc.). For example, the annual discharge of suspended sediments by the Lena River is  $17.6 \times 10^6$  tons, and the amount of dissolved organic carbon reaches maximum values of 11 mg/l during summer floods (Martin *et al.*, 1993a). Thus, river-derived (terrigenous) organic material contributes major proportions to the organic carbon in the sediments of the Laptev Sea and its adjacent continental slope.

The major goal of this study is to determine the amount and composition of the organic carbon fraction and to characterize the mechanisms controlling organic carbon deposition in surface sediments from the Laptev Sea and its adjacent continental slope (i.e. surface water productivity vs. terrigenous input).

### FACTORS DETERMINING PRIMARY PRODUCTIVITY AND TERRIGENOUS ORGANIC CARBON FLUX

The most important factors controlling organic carbon enrichment in the marine environment are (1) increased surface water productivity, (2) increased preservation of organic carbon in anoxic and/or high-sedimentation-rate environments, and (3) increased supply of terrigenous organic carbon (e.g. Berger *et al.*, 1989; Stein, 1991). To distinguish between these different mechanisms, more detailed information about the quantity as well as quality of the organic matter is required. To get an estimate of the composition of the organic carbon fraction (i.e. to estimate the terrigenous and marine proportions) Rock-Eval pyrolysis parameters (HI), elemental analysis data (C/N ratio), and  $\partial^{13}C_{org}$ values are useful indicators in organic carbon-rich (TOC > 0.5%), immature sediments (Tissot and Welte, 1984; Stein, 1991). For a more precise determination of the marine and terrigenous proportions of the organic carbon fraction, other methods such as kerogen/coal petrology, gas chromatography (GC), and mass spectrometry (MS) are required. The distribution of n-alkanes determined by GC, for example, allows an identification of contributions of land-derived vascular plant material (characterized by long-chain C<sub>29</sub> and C<sub>31</sub> n-alkanes) and of marine phytoplankton (dominated by C17 and C<sub>19</sub> *n*-alkanes) (e.g. Blumer et al., 1971; Kolattukudy, 1976; Prahl and Muehlhausen, 1989).

For fatty acids, it is generally accepted that marine compounds are mainly represented by shortchain unsaturated fatty acids up to 22:6(n-3) indicating phytoplankton (or zooplankton) productivity, whereas the long-chain saturated fatty acids indicate a terrigenous input. Nearly the same is true for the wax esters. Based on the composition of the "marine" fatty acids it is possible to obtain more information about the productivity-controlling phytoplankton species. Diatoms mainly synthesize 16:1(n-7) and 20:5(n-3) fatty acids (Kates and Volcani, 1966; Ackman et al., 1968; Kattner et al., 1983; Fahl and Kattner, 1993; Graeve et al., 1994), whereas dinoflagellates synthesize the 18:4(n-3) and 22:6(n-3) compounds (Sargent and Henderson, 1986; Graeve, 1993).

At lower latitudes, the alkenones which were produced by prymnesiophytes (Volkman *et al.*, 1980), are used as (paleo-)temperature and (paleo-)productivity markers (Brassell and Eglinton, 1984; Marlowe *et al.*, 1984; Brassell *et al.*, 1986; Prahl and Wakeham, 1987; Prahl *et al.*, 1988).

## METHODS

The surface sediment samples from the Laptev Sea shelf and slope were taken in 1993 during the RV *Polarstern* expedition ARK IX/4 (Fütterer, 1994; Fig. 1) and the Transdrift I expedition with RV *Ivan Kireyev* (Kassens and Karpiy, 1994; Fig. 1). The sampling was carried out with a giant boxcorer.

Total nitrogen and organic carbon contents were determined by means of a Heraeus CHN-analyzer (for details concerning the method see Stein, 1991). C/N ratios were calculated as "total organic carbon/total nitrogen ratios" based on weight percentage. The Rock-Eval parameters hydrogen index (HI) and oxygen index (OI) were determined as described by Espitalié *et al.* (1977).

For the lipid analyses the sediment samples were stored at  $-80^{\circ}$ C or in dichloromethane/methanol (2:1, by vol.) at  $-23^{\circ}$ C until further treatment. The sediment (2 g) was homogenised, extracted and purified as recommended by Folch *et al.* (1957) and Bligh and Dyer (1959). An aliquot of the total extract was used for analyzing *n*-alkanes and alkenones.

### Alkanes

The alkanes were separated from the other fractions by column chromatography with hexane. The composition was analysed with a Hewlett Packard (HP 5890. chromatograph column gas  $30 \text{ m} \times 0.25 \text{ mm}$ ; film thickness  $0.25 \mu \text{m}$ ; liquid phase: HP) using a temperature program as follows:  $60^{\circ}$ C (1 min) to 150°C (rate:  $10^{\circ}$ C/min), then to 300°C (rate: 4°C/min), then 300°C (45 min isothermal). A volume of 1  $\mu$ l was injected (cold injection system:  $60^{\circ}$ C (5 s) to  $300^{\circ}$ C (60 s, rate:  $10^{\circ}$ C/s) using helium as carrier gas. Squalane was added as an internal standard to provide quantitative data.

## Alkenones

The alkenones were separated from the other fractions by column chromatography with hexane/ ethylacetate (95:5 and 90:10, by vol.). A saponification step with 1 M potassium hydroxide in 95% methanol for 2 h at 90°C followed. Fractions were analysed by means of a Hewlett Packard gas chromatograph (as described for the alkane analysis) using a temperature program as follows: 60°C (1 min) to 270°C (rate: 20°C/min), then to 320°C (rate:  $1^{\circ}C/min$ ), then  $320^{\circ}C$  (20 min isothermal). A volume of  $1 \mu l$  was injected (cold injection system:  $60^{\circ}$ C to  $105^{\circ}$ C (rate:  $3^{\circ}$ C/s), then to  $320^{\circ}$ C (rate:  $10^{\circ}C/s$ ), then  $320^{\circ}C$  (60 s isothermal). Identification of the alkenones was achieved from GC retention times and MS fragmentation patterns. For quantification, octacosanoic acid methyl ester was used as an internal standard.

### Fatty acids

An aliquot of the total extract was used for preparing fatty acid methyl esters and free alcohols by transesterification for 4 h at 80°C with 3% concentrated sulfuric acid in methanol. After extraction with hexane the product was analysed by GC (as above) but using DB-FFAP as liquid phase: the temperature program was as follows 160°C to 240°C (rate: 4°C/min), 240°C (15 min isothermal) (modified according to Kattner and Fricke, 1986). The injection volume was 1  $\mu$ l. The fatty acids and alcohols were identified by standard mixtures and quantified using methylnonadecanoate as internal standard.



- RV Polarstern (ARK IX/4, PS24..)
- RV Ivan Kireyev (Transdrift I, IK93..)

Fig. 1. Positions of surface sediments taken during the 1993 RV *Polarstern* and RV *Ivan Kireyev* cruises. Black dots indicate *Polarstern* samples (71 = PS2471, etc.), grey dots indicate *Kireyev* samples (9 = 1K9309, etc.).





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Fig. 3. Long-chain *n*-alkane  $(C_{27} + C_{29} + C_{31})$  concentrations (A), calculated CPI index (B) and ratio of short-chain  $(C_{17} + C_{19})$  to long-chain  $(C_{27} + C_{29} + C_{31})$  *n*-alkanes (C).

## **RESULTS AND DISCUSSION**

The Lena River run-off is of considerable importance to the hydrochemical and depositional structure in the Laptev Sea. The large brackish surface plume extends to about 200 miles northward (Létolle et al., 1993; Cauwet and Sidorov, 1996); approximately 84% of the total outflow is directed to the east and northeast. This is reflected in the total organic carbon (TOC) distribution (Fig. 2). Maximum TOC values of up to 2% occur in the vicinity of the eastern Lena Delta, off the Kotuy river mouth, southwest of the New Siberian Islands, and the central part of the lower Laptev Sea continental slope. Areas of high TOC concentration commonly correspond to low HI values (<100 mg HC/gC) and high C/N ratios (>7) indicating the dominance of terrigenous organic matter (Stein and Nürnberg, 1995; Stein, 1996). However, in the central part of the Laptev Sea and along the upper continental slope, the hydrogen indices reach values > 100 mg HC/gC suggesting the presence of significant concentrations of marine organic matter. The distribution of the bulk parameters is supported by the distribution of the terrigenous biomarkers (Fig. 3, Table 1).

It is generally accepted that long-chain n-alkanes and long-chain wax esters indicate terrigenous input (Yunker et al., 1995; Peulvé et al., 1996). The highest concentrations of these markers (Fig. 3A, Table 1) were found in the vicinity of the eastern Lena Delta. Peulvé et al. (1996) reported the same trends for high molecular weight hydrocarbons  $(C_{23}-C_{35})$ . The concentration decreases in the direction of the shelf and the continental slope. The lowest contents were measured in the deep-sea environment, which is presumably caused by a decreasing terrigenous flux toward the open ocean. The  $C_{42}$  wax ester content decreases from 40 to  $3 \mu g/g$  TOC (Table 1), the long-chain *n*-alkanes from 1.5 to 0.2 mg/g TOC. In general, high contents of terrigenous organic material are shown by high CPI indices (1.9-5.1, Fig. 3B) (Bray and Evans, 1961). Fresh terrigenous organic matter shows a CPI index of 3-10 (Brassell *et al.*, 1978; Hollerbach, 1985), whereas fossil material varies around 1 depending on the state of decomposition. Marine organic material shows no predominance of odd-over-even carbon chain lengths of *n*-alkanes.

The TOC maximum along the lower continental slope characterized by low HI values (Fig. 2) and high C/N ratios (Stein, 1996), and indicative of terrigenous sources, may be related to the inflow of Atlantic water masses laterally transporting (organic carbon-enriched) suspended matter.

The accumulation of marine organic carbon is mainly controlled by primary production and sedimentation rates (e.g. Müller and Suess, 1979; Berger et al., 1989; Stein, 1991). Highly productive environments, such as upwelling areas with values of >250 gC m<sup>-2</sup> yr<sup>-1</sup>, are characterized by accumulation rates of 1 gC cm<sup>-2</sup> kyr<sup>-1</sup>, whereas open-ocean environments with productivity values of about  $50 \text{ gC m}^{-2} \text{ yr}^{-1}$  display accumulation rates of about  $0.005 \text{ gC cm}^{-2} \text{ kyr}^{-1}$  (Stein, 1991). The Laptev Sea, characterized by sedimentation rates of about 40- $60 \text{ cm kyr}^{-1}$ , displays accumulation rates of about  $450 \text{ gC cm}^{-2} \text{ kyr}^{-1}$  (Stein and Schubert, 1996). The maximum rates occur on the shelf. At the ice edge primary productivity values may be significantly increased (e.g. Nelson et al., 1989). This is supported by the marine fatty acid distribution (Fig. 4) in the surface sediments of the Laptev Sea. It is well established that phytoplankton contains particular fatty acids. Thus, the fatty acid composition of cultured diatoms is dominated by 16:1 and 20:5 fatty acids (e.g. Kates and Volcani, 1966; Orcutt and Patterson, 1975; Pohl and Zurheide, 1979; Kattner and Brockmann, 1990). The same result has been found for sea-ice diatoms (Whitaker and Richardson, 1980; Gillan et al., 1981; Nichols et al., 1986) and natural phytoplankton blooms dominated by diatoms (Kattner et al., 1983; Mayzaud et al., 1989). The highest concentrations of the 16:1(n-7) and 20:5(n-3) compounds (0.9 mg/g TOC) which are mainly synthesized by diatoms (Kates and Volcani, 1966; Ackman et al., 1968; Kattner et al., 1983; Fahl and Kattner, 1993; Graeve et al., 1994),

| Location              | Sample | Pos       | ition      | Water depth (m) | C42                   | C37:3*             | C37:2              |  |
|-----------------------|--------|-----------|------------|-----------------|-----------------------|--------------------|--------------------|--|
|                       |        | Latitude  | Longitude  |                 | wax ester μg/g<br>TOC | ketone μg/g<br>TOC | ketone μg/g<br>TOC |  |
| Lena Delta            | IK9306 | 72°00.1'N | 131°00.1'E | 18              | 40.19                 | 0.05               | 0.01               |  |
|                       | IK9316 | 73°00.1'N | 131°50.3'E | 28              |                       |                    |                    |  |
| Shelf                 | IK9365 | 75°48.3'N | 119°91.1'E | 40              | 28.95                 | 0.03               | 0.01               |  |
|                       | IK9368 | 75°41.8′N | 125°86.1'E | 41              | 21.07                 | 0.01               | _                  |  |
|                       | IK9370 | 75°31.3'N | 129°56.8'E | 44              | 24.12                 | 0.01               |                    |  |
| Upper cont.<br>margin | PS2458 | 78°10.0′N | 133°23.9'E | 983             | 3.12                  | -                  | _                  |  |
|                       | PS2467 | 77°05.0'N | 126°13.4'E | 284             | 2.47                  |                    | _                  |  |
|                       | PS2474 | 77°40.2'N | 118°34.5'E | 1497            | 4.21                  |                    |                    |  |
| Lower cont.<br>margin | PS2471 | 79°09.3′N | 119°46.9′E | 3048            | 2.53                  | 0.50               | 0.07               |  |

Table 1. Wax ester and ketone contents of surface sediment samples from the Laptev Sea and the adjacent continental margin

Dash indicates concentrations of less than 0.01 µg/g TOC; IK: RV Ivan Kireyev; PS: RV Polarstern.

\*C37:4 alkenone could not be identified.





Fig. 4. Distribution of the sum of 16:1(n-7) and 20:5(n-3) fatty acids in surface sediments from the Laptev Sea and the adjacent continental margin. Samples were taken during the RV *Palarstern* expedition ARK 1X/4 (Fütterer, 1994) and the RV *Ivan Kireyve* expedition Transdrift 1 (Kassens and Karpiy, 1994). The hatched line symbolizes the ice margin during Sept. 93 (Eicken et al., 1995). Arrow shows the position of maximum chlorophyll a concentration in the surface water (Boctius et al., 1996) and bio-genic opal in the surface sediments (Stein and Nürnberg, 1995).

were obtained near the ice edge, where melting processes induce increasing phytoplankton growth.

These values are well correlated with high concentrations of chlorophyll a and phaeopigments of about 90 mg m<sup>-2</sup> in the surface water masses (Boetius et al., 1996) and biogenic opal of 3-5% (Stein and Nürnberg, 1995) in the surface sediments. Despite the dominance of the terrigenous input in the whole area (up to 99% of total organic material is terrigenous) the high values of the ratio short- to long-chain *n*-alkanes at the ice edge (station PS2458) of about 1 (Fig. 3C) indicate a significant marine influence. Similar to the maximum fatty acid values obtained near the ice edge, high concentrations also occur in the western and northern part of the Lena Delta. In these areas of increasing productivity, the total fatty acid content (the principal marine organic compounds) may reach more than 0.2% of the TOC (Fig. 4, Table 2). We expected such high concentrations in the vicinity of the eastern branch of the Lena Delta, which presents the main outflow of the river, where an enhanced fluvial nutrient supply may cause enhanced phytoplankton productivity. But, because of the low fatty acid concentrations in this area compared to the high contents in the north-western part, this result leads us to assume that there are probably other processes which influence the phytoplankton growth.

It may be that the high concentrations of suspended material act as some kind of "shadow" which decreases the light penetration and reduces photosynthesis. A similar mechanism was described by Palmisano *et al.* (1988) who suggested that com-

munities of algae may enter a "stationary phase" of zero growth due to light limitation by self-shading. The low content of marine biomarkers in this area is well correlated with pigment data according to Heiskanen and Keck (1996). The low chlorophyll a and high phaeopigment concentrations indicate that the pigments have already undergone alteration. In addition to the shadow hypothesis mentioned above there are several possible mechanisms causing the low contents of most of the marine biomarkers. Recycling by microorganisms may be responsible (Saliot et al., 1996) as well as grazing by zooplankton (Volkman and Maxwell, 1986). Our results, and the data obtained within the framework of the international program SPASIBA (Martin et al., 1993b; Heiskanen and Keck, 1996; Peulvé et al., 1996; Saliot et al., 1996), show an insignificant influence of primary productivity in the Lena River and the eastern part of the delta. The high fatty acid content in the north-western part of the Lena Delta is correlated with the position of the Laptev Sea polynya. The winter ice cover of the Laptev Sea is characterized by the occurrence of an approximately 1800 km long, narrow zone of open water on the mid-shelf (Dethleff et al., 1993, 1994; Reimnitz et al., 1994). During winter the polynyas are areas of intensive sea-ice formation, salinity increase, convection, and large heat loss into the atmosphere; springtime is characterized by an accumulation of heat and rapid melting of sea-ice (Zakharov, 1966). These factors may induce increasing primary production especially in this area. The concentrations of the fatty acids in the Laptev Sea

| Fatty acids    | 9307 | 9309 | 9315 | 9316 | 9318 | 9320 | 9323 | 9327 | 9340 | 9349 | 9353 | 9368 | 9370 | 9384 | 9373 A | 93Z2 |
|----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|--------|------|
| 14:0           | 3.3  | 4.8  | 5.7  | 10.2 | 7.4  | 9.1  | 8.2  | 7.6  | 8.5  | 5.8  | 10.6 | 13.6 | 22.2 | 7.3  | 11.1   | 4.3  |
| 15:0           | 16.7 | 1.1  | 12.6 | 2.1  | 1.5  |      |      | 2.2  | 3.2  |      | 2.7  | 2.3  | 4.7  | 1.6  | 1.4    | 4.4  |
| 16:0           | 24.0 | 36.5 | 28.1 | 37.3 | 35.6 | 25.1 | 32.8 | 29.6 | 27.3 | 32.9 | 28.8 | 38.3 | 49.0 | 29.3 | 34.1   | 20.2 |
| 16:1(n-7)      | 39.9 | 38.8 | 33.8 | 23.2 | 35.8 | 42.3 | 39.9 | 44.8 | 37.9 | 37.3 | 38.4 | 22.2 | 16.1 | 24.6 | 34.8   | 48.4 |
| 16:1(n-5)      |      |      |      | _    |      |      |      | 0.7  |      | 3.8  | 1.7  | 6.9  |      | _    | 0.6    | 2.3  |
| 16:2(n-6)      | _    |      |      |      |      |      |      |      |      |      |      | 1.3  |      |      | ·      |      |
| 16:3(n-3)      |      |      |      |      |      |      |      | 1.6  |      | _    |      |      |      |      | 0.7    | -    |
| 16:4(n-?)      |      |      |      | _    |      | _    |      |      | 2.1  | _    |      | _    |      | _    | 0.7    | _    |
| 18:0           |      | 6.0  | 11.1 | 9.6  | 6.5  | 5.1  | 9.2  | 2.9  |      | 9.3  | 5.7  | 3.8  | 6.1  | 10.8 |        | 5.8  |
| 18:1(n-9)      | 5.6  | 6.9  |      | 8.2  | 6.4  | 17.2 | 5.2  | 4.2  | 5.1  | 5.4  | 4.7  | 6.7  |      | 14.0 | 3.2    | 8.6  |
| 18:1(n-7)      | 4.1  | 1.7  | 5.8  | 2.6  | 0.6  |      |      | 3.6  | 6.0  | 4.2  | 3.8  | _    | -    | 10.1 | 8.9    | 1.7  |
| 18:2(n-6)      | 3.5  | 3.3  |      | 5.5  | 3.8  |      |      | 1.6  |      |      | 1.6  |      |      | 2.2  | 1.0    | 3.2  |
| 18:3(n-3)      |      |      |      |      |      |      |      |      |      |      |      |      |      | _    |        |      |
| 18:4(n-3)      | 1.1  | _    |      | 1.5  | 1.3  |      |      | 0.5  | 2.4  |      |      |      |      |      |        | _    |
| 20:1(n-9)      |      |      |      |      |      |      |      |      |      | -    |      |      |      |      |        | 1.3  |
| 20:1(n-7)      |      | _    |      |      |      |      |      |      |      |      |      |      |      |      | 3.6    |      |
| 20:4(n-6)      |      |      |      |      |      |      |      |      |      |      |      | ~    |      |      |        |      |
| 20:5(n-3)      | 5.3  | 4.2  | 2.9  | 5.3  | 4.9  | 1.2  | 4.7  | 3.9  | 7.5  | 1.3  | 3.6  | 6.2  | 1.9  | 2.3  | 1.6    | 2.3  |
| 22:1(n-11)     |      |      |      |      |      |      |      |      |      |      |      |      |      |      |        |      |
| 22:1(n-9)      |      |      |      |      |      |      |      |      |      |      |      |      |      | _    |        |      |
| 22:5(n-3)      |      |      |      |      |      | —    |      |      |      |      |      |      |      |      |        |      |
| 22:6(n-3)      |      | _    |      |      |      | _    |      |      |      |      |      |      |      |      | ·      | 0.7  |
| % Total sats.  | 44.0 | 48.4 | 57.5 | 59.2 | 51.0 | 39.3 | 50.2 | 42.3 | 39.0 | 48.0 | 47.8 | 58.0 | 82.0 | 49.0 | 46.6   | 34.7 |
| % Total monos. | 49.6 | 47.4 | 39.6 | 34.0 | 42.8 | 59.5 | 45.1 | 53.3 | 49.0 | 50.7 | 48.6 | 35.8 | 16.1 | 48.7 | 51.1   | 62.3 |
| % Total PUFA   | 6.4  | 4.2  | 2.9  | 6.8  | 6.2  | 1.2  | 4.7  | 4.4  | 12.0 | 1.3  | 3.6  | 6.2  | 1.9  | 2.3  | 2.3    | 3.0  |

Table 2. Fatty acid composition (weight%) of surface sediments taken during the 1993 RV Kireyev cruise

Dash indicates not detected or trace amounts (<0.1%). Total sats.: Total saturated; Total monous.: Total monounsaturated; Total PUFA: Total polyunsaturated fatty acids.



Fig. 5. Scheme indicating the most important processes controlling the organic carbon flux in the Laptev Sea and the adjacent continental margin and deep-sea areas (fluvial sediment and nutrient supply, gravitational sediment downslope transport, primary production and vertical organic carbon flux, and transport by bottom currents). Additionally, the chemical structures of typical terrigenous (long-chain wax esters, long-chain *n*-alkanes, and lignin phenols) and marine (triaclyglycerols, alkenones, phospholipids, and chlorophyll *a*) biomarkers are shown.

polynya are comparable with the contents of the fatty acids near the ice edge.

The lowest concentrations of marine fatty acids occur in the shallow ice-covered shelf areas as well as in the ice-covered deep-sea environment. On the shelf, the low concentrations can be attributed to low primary productivity due to the sea-ice cover whereas, in the deep sea, the low concentrations may be explained by a combination of low primary productivity and other mechanisms. That is, autoxidation, alteration by grazers and degradation by microorganisms (Saliot *et al.*, 1996) due to the long residence time in the water column, as well as in the surface sediments, may have caused the low concentrations. On the other hand down-slope transport (turbidity currents) might be important (Fig. 5).

The fatty acid composition of various surface sediments are presented in Table 2 and Table 3. In general, the surface sediments are characterized by high proportions of saturated (34-85%) and short-chain monounsaturated fatty acids (14-60%) due to the effect of degradation and autoxidation of the unstable polyunsaturated compounds. The highest proportions of the polyunsaturated fatty acids (around 5% of total fatty acids) occur in the surface sediments from the shallow shelf due to the short residence time in the water column, whereas the surface sediments of the continental slope, and in the deep sea, are characterized by the absence of

the polyunsaturated compounds with the exception of station PS2458 (ice edge). The rather high proportions of the 18:1 fatty acid were found in nearly all surface sediment samples. It is well established that particulate matter in waters of low productivity is deficient in polyunsaturated fatty acids, but it contains high levels of saturated fatty acids and fatty acids with 18 carbon atoms (Goutx and Saliot, 1980; Kattner et al., 1983; Mayzaud et al., 1989; Henderson et al., 1991; Graeve, 1992). In all surface sediment samples no marine fatty alcohols occur, which would indicate zooplankton growth. It is generally accepted that polar copepods accumulate large amounts of lipids in the form of wax esters, or energy-rich long-chain triacylglycerols (Hagen, 1988; Hagen et al., 1993). Moderate amounts of the long-chain marine 22:1(n-11) fatty acid occur in one surface sediment sample from the eastern part of the Laptev Sea (PS2484; 3% of total fatty acid).

It is generally accepted that alkenones are only synthesized by prymnesiophytes (Volkman *et al.*, 1980). At lower latitudes, characterized by temperatures of >10°C, these lipids are used as paleotemperature markers (Brassell and Eglinton, 1984; Marlowe *et al.*, 1984; Brassell *et al.*, 1986; Prahl and Wakeham, 1987; Prahl *et al.*, 1988). In the Arctic Ocean and its marginal seas, where very low surface water temperatures of  $\ll 5^{\circ}$ C are typical,

Table 3. Fatty acid composition (weight%) of surface sediments taken during the 1993 RV Polarstern cruise

| Fatty acids    | 2458 | 2465 | 2469 | 2471 | 2472 | 2473 | 2474 | 2483 | 2484 |
|----------------|------|------|------|------|------|------|------|------|------|
| 14:0           | 7.1  | 8.0  | 14.0 | 10.5 | 3.9  | 7.5  | 11.6 | 5.9  | 3.9  |
| 15:0           | 2.1  | 2.5  |      | 5.2  | 8.2  | 7.5  | 6.2  |      | 0.9  |
| 16:0           | 28.5 | 34.0 | 69.2 | 29.5 | 62.2 | 34.1 | 33.3 | 51.3 | 29.0 |
| 16:1(n-7)      | 32.6 | 17.7 | 16.8 | 20.1 | 14.6 | 32.7 | 24.5 | 37.7 | 25.0 |
| 16:1(n-5)      | 5.8  |      |      | 5.8  | _    |      |      |      | 1.1  |
| 16:2(n-6)      | 0.5  | 2.1  |      |      |      |      |      |      | _    |
| 16:3(n-3)      | _    |      |      |      |      |      |      |      | 3.9  |
| 16:4(n-?)      |      |      |      |      | _    |      | _    |      |      |
| 18:0           | 6.5  | 10.2 |      | 8.5  | 11.1 | 10.9 | 10.5 |      | 10.6 |
| 18:1(n-9)      | 6.8  | 18.1 | _    | 15.0 | _    | 7.3  | 12.3 |      | 7.9  |
| 18:1(n-7)      |      |      |      | 3.7  |      |      | 1.6  | _    | 2.2  |
| 18:2(n-6)      | 1.5  | ·    |      |      |      |      | 2.3  |      | 1.6  |
| 18:3(n-3)      |      |      |      |      |      |      |      |      |      |
| 18:4(n-3)      |      | 3.8  |      | 1.7  |      |      | -    | 5.1  |      |
| 20:1(n-9)      | _    |      |      |      |      |      |      |      | 6.6  |
| 20:1(n-7)      |      | 5.7  |      |      |      | -    |      | -    | 9.7  |
| 20:4(n-6)      |      |      |      |      |      |      |      |      |      |
| 20:5(n-3)      | 7.5  |      |      |      |      |      |      |      |      |
| 22:1(n-11)     | 3.1  |      |      |      |      | _    |      | _    | 3.1  |
| 22:1(n-9)      | _    |      |      |      |      | _    |      | _    |      |
| 22:5(n-3)      |      |      |      |      |      |      |      |      |      |
| 22:6(n-3)      |      |      | —    |      | —    |      | —    |      | _    |
| % Total sats.  | 44.2 | 54.7 | 83.2 | 53.7 | 85.4 | 60.0 | 61.6 | 57.2 | 44.4 |
| % Total monos. | 48.3 | 41.5 | 16.8 | 44.6 | 14.6 | 40.0 | 38.4 | 37.7 | 55.6 |
| % Total PUFA   | 7.5  | 3.8  | _    | 1.7  | _    |      | _    | 5.1  |      |

Dash indicates not detected or trace amounts (<0.1%). Total sats.: Total saturated; Total monos.: Total monounsaturated; Total PUFA: Total polyunsaturated fatty acids.

alkenones cannot be used to estimate temperatures. In this region, the alkenones should only be used as a paleoproductivity indicator. With the exception of one surface sediment sample, which was collected from the lowermost continental slope (water depth of 3047 m, station PS2471), the concentration of alkenones is rather low in the entire Laptev Sea (less than 0.007  $\mu$ g/g TOC) (Table 1). This is probably caused by the low abundance of prymnesiophytes and low temperatures in the Laptev Sea. Therefore, the use of these lipids for reconstructing paleotemperature or paleoproductivity is limited. The rather high concentrations of alkenones in the surface sediment at station PS2471 may be caused by coccolithophorides or other prymnesiophytes which were transported by Atlantic water masses along the continental slope. This assumption may be resolved after our investigation of the corresponding sediment core PS2471 in which high alkenone concentrations occur.

## CONCLUSION

Specific biomarkers can be used to distinguish between marine and terrigenous sources of the organic matter of the Laptev Sea surface sediments. The distribution of the marine biomarkers is well correlated with the sea-ice distribution. The lowest concentrations of the marine fatty acids were found in the ice-covered areas whereas the highest amounts were located in the sediments near the ice margin. The marine fatty acid distribution correlates well with the chlorophyll a and biogenic opal content, indicating an increased surface water productivity near the ice edge. Thus the fatty acids, as relatively unstable organic molecules, can be used as biomarkers for reflecting recent processes. Because of their high concentration in areas of enhanced marine productivity in the Laptev Sea they are significant for the marine organic carbon budget. The terrigenous biomarkers (long-chain *n*alkanes and wax esters) in Laptev Sea surface sediments were mainly supplied by the Siberian rivers. Their concentrations decrease with increasing distance from the source; the lowest concentrations were found in the deep-sea environment.

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#### REFERENCES

- Ackman, R. G., Tocher, C. S. and McLachlan, J. (1968) Marine phytoplankter fatty acid. Journal of the Fisheries Research Board of Canada 25, 1603-1620.
- Berger, W. H., Smetacek, V. and Wefer, G. (Eds.) (1989) Productivity of the Ocean: Past and Present. Life Sciences Research Report 44, Wiley and Sons, New York, 471 pp.
- Bligh, E. G. and Dyer, W. J. (1959) A rapid method of total lipid extraction and purification. *Canadian Journal* of Biochemical Physiology 37, 911-917.

- Blumer, M., Guillard, R. R. L. and Chase, T. (1971) Hydrocarbons of marine phytoplankton. *Marine Biology* 8, 183-189.
- Boetius, A., Nöthig, E., Liebezeit, G. and Kröncke, I. (1996) Distribution of chlorophyll pigments as indicator for marine organic matter input in the Eurasian shelf seas and the central Arctic Ocean. In Surface-Sediment Composition and Sedimentary Processes in the Central Arctic Ocean and Along the Eurasian Continental Margin, eds R. Stein, G. Ivanov, M. Levitan and K. Fahl. Reports of Polar Research 212, 324 pp.
- Brassell, S. C., Eglinton, G., Maxwell, J. R. and Philip, R. P. (1978) Natural background of alkanes in the aquatic environment. In *Aquatic Pollutants: Transformation and Biological Effects*, eds. O. Hutzinger, I. H. Lelyveld and B. C. J. Zoetman, pp. 69–86. Pergamon Press, Oxford.
- Brassell, S. C. and Eglinton, G. (1984) Lipid indicators of microbial activity in marine sediments. In *Heterotrophic Activity in the Sea*, eds. J. E. Hobbie and P. J. Williams, pp. 481-503. Plenum Press, New York.
- Brassell, S. C., Eglinton, G., Marlowe, I. T., Pflaumann, U. and Sarntheim, M. (1986) Molecular stratigraphy: a new tool for climate assessment. *Nature* 320, 129-133.
- Bray, E. E. and Evans, E. D. (1961) Distribution of n-paraffins as a clue to recognition of source beds. *Geochimica et Cosmochimica Acta* 22, 2–15.
- Cauwet, G. and Sidorov, I. (1996) The biogeochemistry of Lena River: organic carbon and nutrients distribution. *Marine Chemistry* 53, 211-227.
- Dethleff, D., Kleine, E. and Loewe, P. (1994) Oceanic heat loss, sea ice formation and sediment dynamics in a turbulent Siberian flaw lead. In *Report Series in Geophysics*, pp. 35-40. Helsinki University Department of Geophysics, Helsinki.
- Dethleff, D., Nürnberg, D., Reimnitz, E., Saarso, M. and Savchenko, Y. P. (1993) East Siberian Arctic Region Expedition '92: The Laptev Sea — its significance for Arctic sea ice formation and Transpolar sediment flux. *Report on Polar Research* **120**, 3–37.
- Eicken, H., Viehoff, T., Martin, T., Kolatschek, J., Alexandrov, V. and Reimnitz, E. (1995) Studies of clean and sediment-laden ice in the Laptev Sea. In Second Workshop on "Russian-German Cooperation in and Around the Laptev Sea", eds H. Kassens et al. St. Petersburg, November 1994. Reports of Polar Research 176, 62-70.
- Espitalié, J., Laporte, J. L., Madec, M., Marquis, F., Leplat, P., Paulet, J. and Boutefeu, A. (1977) Méthode rapide de characterisation des roches-mere de leur potential petrolier et de leur degre d'évolution. *Rev. Inst. Tranc. Petrol.* 32, 23-42.
- Fahl, K. and Kattner, G. (1993) Lipid content and fatty acid composition of algal communities in sea-ice and water from Weddell Sea (Antarctica). *Polar Biology* 13, 405-409.
- Folch, J., Lees, M. and Sloane-Stanley, G. H. (1957) A simple method for the isolation and purification of total lipids from animal tissues. *Journal of Biological Chemistry* 226, 497-509.
- Fütterer, D. K. (1994) The Expedition ARCTIC93 Leg ARK IX/4 of RV "Polarstern" 1993. Report on Polar Research 149, 244.
- Gillan, F. T., McFadden, G. I., Wetherbee, R. and Johns, R. B. (1981) Sterols and fatty acids of an Antarctic sea ice diatom *Stauroneis amphioxys*. *Phytochemistry* 20, 1935-1937.
- Goutx, M. and Saliot, A. (1980) Relationship between dissolved and particulate fatty acids and hydrocarbons, chlorophyll a and zooplankton biomass in Villefranche Bay, Mediterranean Sea. *Marine Chemistry* 8, 299–318.
- Graeve, M. (1992) Umsatz und Verteilung von Lipiden in arktischen marinen Organismen unter besonderer

Berücksichtigung trophischer Stufen. Ph.D. thesis, Universität Bremen, 145 pp.

- Graeve, M. (1993) Turnover and distribution of lipids in Arctic marine organisms with regard to lower trophic levels. *Report on Polar Research* 124, 141.
  Graeve, M., Hagen, W. and Kattner, G. (1994)
- Graeve, M., Hagen, W. and Kattner, G. (1994) Herbivorous or omnivorous? On the significance of lipid composition as trophic markers in Antarctic copepods. *Deep-Sea Research* **41**, 915–924.
- Hagen, W. (1988) Zur Bedeutung der Lipide im antarktischen Zooplankton. Report on Polar Research 49, 129.
- Hagen, W., Kattner, G. and Graeve, M. (1993) Calanoides acutus and Calanus propinguus, Antarctic copepods with different lipid storage modes via wax ester or triacylglycerols. Marine Ecology Progress Series 97, 135-142.
- Heiskanen, A.-S. and Keck, A. (1996) Distribution and sinking rates of phytoplankton, detritus, and particulate biogenic silica in the Laptev Sea and Lena River (Arctic Siberia). *Marine Chemistry* 53, 229–245.
- Henderson, R. J., Olsen, R. E. and Eilertson, H. C. (1991) Lipid composition of phytoplankton from the Barents Sea and environmental influence on the distribution pattern of carbon among photosynthetic end products. *Polar Research* 10, 229–237.
- Hollerbach, A. (1985) Grundlagen der organischen Geochemie. Springer, Berlin, 190 pp.
- Kassens, H. and Karpiy, V. Y. (1994) Russian-German Cooperation: The Transdrift I Expedition to the Laptev Sea. Report on Polar Research 151, 168.
- Kates, K. and Volcani, B. E. (1966) Lipid components of diatoms. *Biochimica et Biophysica Acta* 116, 264-278.
- Kattner, G. and Brockmann, U. H. (1990) Particulate and dissolved fatty acids in an enclosure containing a unialgal Skleletonema costatum (Greve.) Cleve culture. Journal of Experimental Marine Biology and Ecology 114, 1-13.
- Kattner, G. and Fricke, H. S. G. (1986) Simple gas-liquid chromatographic method for simultaneous determination of fatty acids and alcohols in wax esters of marine organisms. *Journal of Chromatography* 361, 313-318.
- Kattner, G., Gercken, G. and Eberlein, K. (1983) Development of lipids during a spring plankton bloom in the Northern North Sea. I. Particulate fatty acids. *Marine Chemistry* 14, 149-162.
- Kolattukudy, P. E. (1976) Chemistry and Biochemistry of Natural Waxes. Elsevier, New York, 459 pp.
- Létolle, R., Martin, J. M., Thomas, A. J., Goordeev, V. V., Gusarova, S. and Sidorov, I. S. (1993) <sup>18</sup>O abundances and dissolved silica in the Lena delta and Laptev Sea (Russia). *Marine Chemistry* 43, 47-64.
- Marlowe, I. T., Brassell, S. C., Eglinton, G. and Green, J. C. (1984) Long chain unsaturated ketones and esters in living algae and marine sediments. Organic Geochemistry 6, 135-141.
- Martin, J. M., Goordeev, V. V. and Emelyanov, E. (1993a) The Arctic Estuaries and Adjacent Seas: Biogeochemical Processes and Interactions with Global Changes. The Third International Symposium, Svletogorsk, Russia, 19-25 April 1993, pp. 1-89.
- Martin, J. M., Guan, D. M., Elbaz-Poulichet, F., Thomas, A. J. and Goordeev, V. V. (1993b) Preliminary assessment of the distributions of some trace elements (As, Cd, Cu, Fe, Ni, Pb and Zn) in a pristine aquatic environment: the Lena River estuary (Russia). Marine Chemistry 43, 185-199.
- Mayzaud, P., Chanut, J. P. and Ackman, R. G. (1989) Seasonal changes of the biochemical composition of marine particulate matter with special reference to fatty acids and sterols. *Marine Ecology Progress Series* 56, 189-204.
- Müller, P. J. and Suess, E. (1979) Productivity, sedimentation rate, and sedimentary organic matter in the

oceans. I. — Organic matter preservation. Deep-Sea Research 26, 1347-1362.

- Nelson, D. M., Smith, W. O., Muench, R. D., Gordon, L. I., Sullivan, C. W. and Husby, D. M. (1989) Particulate matter and nutrient distribution in the ice-edge zone of the Weddell Sea: relationship to hydrography during late summer. *Deep-Sea Research* 36, 191-209.
- Nichols, P. D., Palmisano, A. C., Smith, G. A. and White, D. C. (1986) Lipids of the Antarctic sea-ice diatom Nitzschia cylindrus. Phytochemistry 25, 1649-1653.
- Orcutt, D. M. and Patterson, G. W. (1975) Sterol, fatty acids and elemental composition of diatoms grown in chemical defined media. *Comparative Biochemistry and Physiology* 50B, 579-583.
- Palmisano, A. C., Lizotte, M. P., Smith, G. A., Nichols, P. D., White, D. C. and Sullivan, C. W. (1988) Changes in photosynthetic carbon assimilation in Antarctic seaice diatoms during spring bloom: Variation in synthesis of lipid classes. *Journal of Experimental Marine Biology* and Ecology 16, 1-13.
- Peulvé, S., Sicre, M.-A., Saliot, A., De Leeuw, J. W. and Baas, M. (1996) Molecular characterization of suspended and sedimentary organic matter in an Arctic delta. *Limnology and Oceanography* 41(3), 488-497.
- Pohl, P. and Zurheide, F. (1979) Fatty acids and lipids of marine algae and their control of biosynthesis by environmental factors. In *Marine Algae in Pharmaceutical Science*, eds H. A. Hoppe *et al.*, pp. 473–523. Walter de Gruyter, Berlin.
- Prahl, F. G. and Muehlhausen, L. A. (1989) Lipid biomarkers as geochemical tools for paleoceanographic study. In *Productivity of the Ocean: Past and Present*, eds W. H. Berger et al. Life Science Research Report 44, 271-290.
- Prahl, F. G. and Wakeham, S. G. (1987) Calibration of unsaturation pattern in long-chain ketone compositions for paleotemperature assessment. *Nature* 330, 367–369.
- Prahl, F. G., Muehlhausen, L. A. and Zahnle, D. L. (1988) Further evaluation of long-chain alkenones as indicators of paleoceanographic conditions. *Geochimica et Cosmochimica Acta* 52, 2303–2310.
- Reimnitz, E., Dethleff, D. and Nürnberg (1994) Contrasts in Arctic shelf sea-ice regimes and some implications: Beaufort Sea and Laptev Sea. *Marine Geology* 119, 215-225.
- Saliot, A., Cauwet, G., Cahet, G., Mazaudier, D. and Daumas, R. (1996) Microbial activities in the Lena River delta and Laptev Sea. *Marine Chemistry* 53, 247– 254.

- Sargent, J. R. and Henderson, R. J. (1986) Lipids. In The Biological Chemistry of Marine Copepods, eds E. D. S. Corner and S. C. M. O'Hara, pp. 59-108. Clarendon Press, Oxford.
- Stein, R. and Nürnberg, D. (1995) Productivity proxies: Organic carbon and biogenic opal in surface sediments from the Laptev Sea and the adjacent continental slope. In Second Workshop on "Russian-German Cooperation in and around the Laptev Sea", St. Petersburg, November 1994, eds H. Kassens et al. Reports of Polar Research 176, 286-296.
- Stein, R. and Schubert, C. (1996) Organischer Kohlenstoffeintrag im zentralen Arktischen Ozean während des Spätquartärs. Geowissenschaften 9, 370-375.
- Stein, R. (1996) Organic-carbon and carbonate distribution in Eurasian continental margin and Arctic Ocean deep-sea surface sediments: Sources and pathways. In Surface-Sediment Composition and Sedimentary Processes in the Central Arctic Ocean and Along the Eurasian Continental Margin, eds R. Stein, G. Ivanov, M. Levitan and K. Fahl. Reports of Polar Research 212, 324 pp.
- Stein, R. (1991) Accumulation of organic carbon in marine sediments. In *Lecture Notes in Earth Sciences* 34. Springer, Heidelberg, 217 pp.
- Subba Rao, D. V. and Platt, T. (1984) Primary production of Arctic waters. *Polar Biology* 3, 191–201.
- Tissot, B. P. and Welte, D. H. (1984) Petroleum Formation and Occurrence. Springer, Heidelberg, 699 pp.
- Volkman, J. K., Eglinton, G., Corner, E. D. S. and Forsberg, T. E. V. (1980) Long-chain alkenes and alkenones in the marine coccolithophorid *Emiliania huxleyi*. *Phytochemistry* **19**, 2619–2622.
- Volkman, J. K. and Maxwell, J. R. (1986) Acyclic isoprenoids as biological markers. In *Biological Markers in the Sedimentary Records*, ed. R. B. Johns, pp. 1–42. Elsevier, Amsterdam.
- Whitaker, T. M. and Richardson, M. G. (1980) Morphology and chemical composition of a natural population of an ice-associated Antarctic diatom Navicula glaciei. Journal of Phycology 16, 250-257.
- Yunker, M. B., Macdonald, R. W., Veltkamp, D. J. and Cretney, W. J. (1995) Terrestrial and marine biomarkers in a seasonally ice-covered Arctic estuary — integration of multivariate and biomarker approaches. *Marine Chemistry* 49, 1–50.
- Zakharov, V. F. (1966) The role of flaw leads off the edge of fast ice in the hydrological and ice regime of the Laptev Sea. Academy of Science of the UDSSR 6, 815– 821.