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# Aliphatic lipids in recent sediments of the Fram Strait/Yermak Plateau (Arctic Ocean): composition, sources and transport processes

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## Abstract

Surface sediments ( $n = 39$ ) from the western Fram Strait and across the Yermak Plateau (Arctic Ocean) were investigated by molecular and isotopic organic geochemical methods to determine the composition, distribution and origin of extractable aliphatic lipids ( $n$ -alkanes,  $n$ -alkanols, fatty acids). Bulk geochemical parameters (TOC-content,  $\delta^{13}\text{C}_{\text{org}}$ ) were also determined, including additional samples nearby. Enhanced organic carbon contents of up to 1.6% along the western slope of the Yermak Plateau and north off Spitsbergen, corroborated by an average  $\delta^{13}\text{C}_{\text{org}}$  value of  $-22.3\text{‰}$ , indicated most of the organic material to be of a marine origin, despite ice-cover. The extractable aliphatic lipids contributed up to 1% of the sedimentary organic carbon and were dominated by fatty acids (0.7–9.1 mg/g TOC), whereas  $n$ -alkanes and  $n$ -alkanols contributed only minor amounts (0.1–0.4 mg/g TOC). The detailed molecular and carbon isotopic characterisation of the studied aliphatic compounds enabled assignments of most components to three lipid pools, representing: (a) primary production (marine phytoplankton, sea-ice algae), (b) secondary inputs (by feeding of zooplankton, benthic organisms and bacteria on the former) and (c) terrestrial-derived contributions. The first two compound groups dominated, but varied significantly in relation to the environment and were highest at the MIZ (Marginal Ice Zone), and along the permanently ice-covered western flank of the Yermak Plateau. In contrast, compounds attributable to a terrestrial source were of only minor importance in terms of absolute concentrations and less variable, but showed increasing relative proportions from an average of 8–14% at and southwards of the MIZ up to 27–33% on the Yermak Plateau and towards the central Arctic Ocean as a consequence of the weakening signal of primary and secondary production. This study provides further insights into the Arctic Ocean carbon dynamics, but also an example of the impact of ocean-currents on the deposition and composition of organic matter.

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**Keywords:** Aliphatic lipids; Biomarker; Phytoplankton; Zooplankton; Transport mechanisms; Sediments; Fram Strait; Yermak Plateau; Arctic Ocean

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## 1. Introduction

The Arctic Ocean and the surrounding areas are considered a low productivity environment due to the presence of an almost perennial sea-ice cover, low

availability of light, nutrients and suspended matter (Subba Rao and Platt, 1984). The largely closed sea-ice cover not only has an important influence on the abundance and diversity of marine biota, but also on the oceanic circulation and surface albedo. Despite low annual primary production ( $1\text{--}15\text{ g C m}^{-2}\text{ year}^{-1}$ ; English, 1961; Wheeler et al., 1996; Gosselin et al., 1997) for the ice-covered central parts of the Arctic Ocean, increased seasonal phytoplankton and zooplankton productivity at the Marginal Ice Zone (MIZ) and within the Arctic shelf-seas has been reported. Ramseier et al. (1999, 2001) proposed a high productivity strip close to the mean annual MIZ, termed the BMIZ (Biological Marginal Ice Zone). Maximum concentrations of nutrients, chlorophyll *a*, high production of phytoplankton in surface waters, as well as maximum fluxes of POC and opal were obtained from sediment traps at various depths (Andreassen et al., 1996; Ramseier et al., 1999; Hebbeln, 2000; Owrud et al., 2000), in conjunction with high vertical export and accumulation rates of organic carbon to the surface sediments (Andreassen et al., 1996; Birgel and Stein, 2003). For the Barents Sea, adjacent to the east of the Yermak Plateau, it was assumed that MIZ-associated production sweeping into the Arctic Ocean results in an annual production of  $50\text{--}150\text{ g C m}^{-2}\text{ year}^{-1}$  (Olli et al., 2002 and references therein).

Deep-water exchange between the Arctic and Atlantic Ocean is enabled through the Fram Strait. It is a major driver of global thermohaline circulation, controlling heat transfer and climatically important processes between the Arctic and the world oceans (ARCSS Workshop Steering Committee, 1990; NAD Science Committee, 1992). Up to now knowledge of organic matter composition, in terms of biomarker distributions and concentrations, of recent sediments of the northern Fram Strait has been limited. To improve our understanding of these remote regions, several expeditions were conducted with ice-breaking research vessels to the perennially ice-covered Arctic Ocean (Fütterer, 1992, 1994) and northern Fram Strait/Yermak Plateau (Stein and Fahl, 1997; Jokat, 2000; Krause and Schauer, 2001) in the last decade. Organic carbon contents of surface sediments from the Fram Strait and Arctic Ocean areas were investigated earlier (Hebbeln and Berner, 1993; Stein et al., 1994), but biomarker studies previously con-

centrated only on selected compounds, e.g. on short- ( $n\text{-C}_{17}$ ,  $n\text{-C}_{19}$ ) and long-chain ( $n\text{-C}_{27}$ ,  $n\text{-C}_{29}$ ,  $n\text{-C}_{31}$ ) *n*-alkanes and short-chain fatty acids ( $\text{C}_{16:0}$ ,  $\text{C}_{16:1}$ ,  $\text{C}_{18:0}$  and  $\text{C}_{18:1}$ ) (Schubert, 1995; Schubert and Stein, 1997). To get more detailed information on the sources and composition of extractable organic matter (EOM) in surface sediments, the molecular and carbon isotopic compositions of aliphatic lipids (fatty acids, *n*-alkanols and *n*-alkanes) in recent sediments of the Fram Strait and on the Yermak Plateau have been investigated. The use of biomarker data as proxies reflecting recent environmental conditions and for palaeoenvironmental reconstruction is a well-established geochemical tool. For sediments from open ocean and deep-sea areas of mid- to low-latitude regions, biomarker compositions mainly reflect primary productivity in the water column, whereas the amounts of freshwater and terrestrial-derived compounds generally are low (e.g. Farrimond et al., 1990; Prahl et al., 1994). In contrast, in sediments of the almost perennial ice-covered Arctic Ocean, organic matter composition might be significantly influenced by a “terrestrial overprint” related to sea-ice transport processes (Dethleff et al., 2000). The supply of terrigenous organic matter from melting sea-ice to the seafloor, and by transport within currents is important, as can be seen from previous bulk parameter investigations (e.g. Hebbeln and Berner, 1993; Stein et al., 1994; Schubert and Stein, 1997; Birgel and Stein, 2003). Nonetheless, Wheeler et al. (1996) described a low to moderate primary productivity under permanent sea-ice in the Arctic Ocean, but concluded that it is “less productive than oligotrophic ocean regions not covered by ice”. However, from bulk  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}_{\text{org}}$  data of ice-covered Arctic marine surface sediments, contributions of marine organic matter up to 50% were estimated (Schubert and Calvert, 2001) and circumpolar shelf regions and the MIZ are nowadays considered to belong to the most productive environments on earth, particularly during springtime (Wassmann, 2002).

The major goal of this study was to identify and distinguish processes (i.e. primary and secondary production, allochthonous/terrestrial inputs) and the influence of environmental aspects (e.g. ice-cover, current systems) on the deposition of aliphatic lipids in surface sediments of the eastern Fram Strait and on the Yermak Plateau. A first estimation on the compo-

sition of the organic matter (e.g. the proportions of marine and terrigenous material) was achieved by bulk data analysis (TOC,  $\delta^{13}\text{C}_{\text{org}}$ ).

## 2. Materials and methods

### 2.1. Study area

The surface sediment samples studied cover an area from approximately 76°N to 82.5°N and 5°W to 20°E between Greenland/Spitsbergen and north of Spitsbergen, known as the Fram Strait and Yermak Plateau (Fig. 1). The study area is influenced by a number of environmental conditions, including permanent or temporary sea-ice cover and a system of oceanic currents, which, amongst other things, impact organic matter composition and distribution. Two major currents, the warm West Spitsbergen Current

(WSC,  $T=2-3\text{ }^{\circ}\text{C}$ ;  $S=34.7-34.9$ ) and the ice-infested East Greenland Current (EGC,  $T=-1.5-0\text{ }^{\circ}\text{C}$ ;  $S=30.7-31.0$ ), balance the exchange of Arctic and Atlantic water masses and subdivide Fram Strait in two domains (Schlichtholz and Houssais, 1999a,b; Rudels et al., 2000).

Flowing polewards, the WSC carries warm and saline Atlantic waters along the western coast of Spitsbergen, keeping this region ice-free almost throughout the year (Fig. 1). Here, the WSC is about 100 km wide and is confined over the continental slope. At about 79°N, the WSC divides in sub-branches. The Return Atlantic Current (RAC) recirculates Atlantic water southward to the eastern edge of the EGC (Gascard et al., 1988; Manley, 1995; Schlichtholz and Houssais, 1999a,b). About 22% of the northward flowing Atlantic waters have been estimated to become redirected to the south via the RAC (Manley, 1995). The remaining Atlantic water

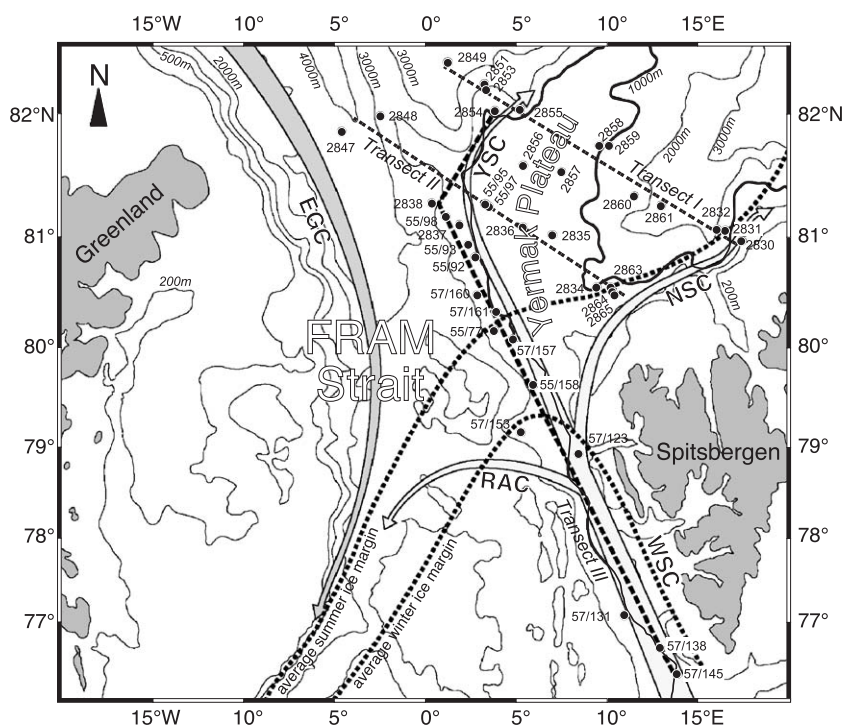


Fig. 1. Map of the study area indicating positions of sampling stations (black dots), locations of Transects I–III, average winter and summer ice margin and major currents. The area of the Yermak Plateau is marked by the bold 1000 m isobath. The position of the summer ice margin crossing the Transects is derived from satellite and shipboard observations during the sampling periods. Light grey arrows track the inflow of warm, saline Atlantic water (WSC=West Spitsbergen Current, RAC=Return Atlantic Current, NSC=North Spitsbergen Current, YSC=Yermak Slope Current), dark grey arrow shows the outflow of cold, fresh Arctic water and sea-ice (EGC=East Greenland Current).

of the WSC then is subdivided into the North Spitsbergen Current (NSC, also referred as Svalbard Branch) and the Yermak Branch at about equal water mass volumes (Manley, 1995). Deflected by coriolis-forcing, the NSC (Svalbard Branch) turns east and stays close to the continental shelf north off Spitsbergen, at a depth of approximately 250 m (Manley, 1995). The Yermak Branch follows the western slope of the Yermak Plateau, but part of it also spreads over the Plateau. Most relevant to our study, an intermediate to deep, bottom-intensified subbranch of the Yermak Branch, named Yermak Slope Current (YSC, Schlichtholz and Houssais, 1999a) has been identified. The YSC, consisting mainly of cold, Norwegian Sea deep-water with low salinity, is topographically forced to follow the western and northern slope of the Yermak Plateau at a water depth of about 1000–1500 m (Fig. 1).

The main outflow of Arctic water masses occurs in the western part of the Fram Strait via the East Greenland Current (EGC). The EGC transports cold, fresh water and sea-ice southwards out of the Arctic (Saloranta and Svendsen, 2001), resulting in a permanent ice-cover throughout the year reaching far to the south.

Current velocities of the WSC were measured west of Svalbard with 9–16 cm/s in water depths between 500 and 1500 m (Fahrbach et al., 2001), whereas YSC velocities are reduced to 1–3 cm/s (Schlichtholz and Houssais, 1999a,b). Although no data are available for the NSC, average velocities are supposed to be similar or even lower than those of the YSC.

## 2.2. Samples, lipid extraction and analysis

The surface sediment samples (0–1 cm) were recovered during the expeditions ARK XIII/2 (Stein and Fahl, 1997), ARK XV/2 (Jokat, 2000) and ARK XVI/1 and 2 (Krause and Schauer, 2001) on RV *Polarstern*. The sampling was carried out either with a giant box corer or a multicorer.

All samples were stored at  $-30\text{ }^{\circ}\text{C}$  until further treatment. Sediment samples were freeze-dried, homogenised, and partitioned into subsamples. TOC was determined by means of a LECO CS analyser. Subsamples analysed for total organic carbon isotopic composition ( $\delta^{13}\text{C}_{\text{org}}$ ) were acidified with 0.1 N HCl prior to measurement and dried at  $60\text{ }^{\circ}\text{C}$  for 12 h.

$\delta^{13}\text{C}_{\text{org}}$ -measurements were performed in duplicate on an ANCA-SL 20-20 mass spectrometer (Europa Scientific). Subsamples for lipid analysis were extracted and purified by a modified method based on Folch et al. (1957) and Bligh and Dyer (1959). Prior to extraction and fractionation, internal standards were added for quantification of the respective compound class including squalane, nonadecanoic acid methyl ester and cholest-5-en-3 $\beta$ -ol-D<sub>6</sub>. Sediment samples were extracted in three steps using 40 ml each of methanol, methanol:dichloromethane (1:1, v/v) and dichloromethane. The combined total extract was transesterified with 1 ml of 5% concentrated hydrochloric acid in methanol for 12 h at  $50\text{ }^{\circ}\text{C}$ . Silica gel column chromatography was used to separate *n*-alkanes by elution with hexane and a combined FAME (Fatty Acid Methyl Ester) and *n*-alkanol/sterol fraction, eluted with hexane/ethylacetate (4:1, v/v), by volume. Sterols/*n*-alkanols were silylated with 500  $\mu\text{l}$  BSTFA (*N*, *O*-Bis trimethylsilyltrifluoroacetamide with 1-% trimethyl-chlorosilane) for 2 hours at  $60\text{ }^{\circ}\text{C}$ .

All biomarkers were analysed with a Hewlett Packard gas chromatograph (HP 6890) on a 30-m DB5-MS capillary column (J&W Scientific, 0.25 mm i.d.; film thickness 0.25  $\mu\text{m}$ ), using Helium as carrier gas and a temperature program as follows:  $60\text{ }^{\circ}\text{C}$  (2 min),  $150\text{ }^{\circ}\text{C}$  (rate:  $15\text{ }^{\circ}\text{C}/\text{min}$ ),  $320\text{ }^{\circ}\text{C}$  (rate:  $3\text{ }^{\circ}\text{C}/\text{min}$ ),  $320\text{ }^{\circ}\text{C}$  (10 min isothermal). The injection volume was 1  $\mu\text{l}$  (Gerstel Cold Injection System;  $60\text{ }^{\circ}\text{C}$  (10s),  $300\text{ }^{\circ}\text{C}$  (60s), rate  $12\text{ }^{\circ}\text{C}/\text{s}$ ).

Identification of compounds was achieved by GC retention times compared to authentic reference compounds and additionally confirmed by MS fragmentation patterns on a Hewlett Packard 5890 GC/MSD 5972A using identical conditions as described above for GC analysis.

Compound-specific carbon isotope analysis (irm-GC/MS) of selected samples was carried out with a HP 6890 GC coupled via a Finnigan GCC-II-interface to a Finnigan Delta<sup>plus</sup> XL mass spectrometer. Samples were injected in pulsed-splitless mode and compound separation was achieved on a J&W DB1-MS capillary column (length = 60 m, i.d. = 0.32 mm, film thickness = 0.25  $\mu\text{m}$ , carrier gas = helium). The GC-temperature was programmed from  $30\text{ }^{\circ}\text{C}$  (5 min) to  $150\text{ }^{\circ}\text{C}$  ( $15\text{ }^{\circ}/\text{min}$ ) and then to  $320\text{ }^{\circ}\text{C}$  (20 min) at a rate of  $3\text{ }^{\circ}\text{C}/\text{min}$ . Carbon isotope ratios are notated as  $\delta$ -values ( $\delta^{13}\text{C}$  [‰]) relative to the PDB-standard and

have been corrected for the addition of carbon during derivatisation. Several CO<sub>2</sub>-pulses of known  $\delta^{13}\text{C}$  value at the beginning of each run were used for calibration. Reported  $\delta^{13}\text{C}$  values were obtained by two to three replicate analyses of each sample to calculate the average carbon isotopic composition. Instrumental precision was checked regularly with standard mixtures of *n*-alkanes (C<sub>16</sub>–C<sub>30</sub>), fatty acid methyl esters (C<sub>19</sub>, C<sub>31</sub>) and cholesterol-d<sub>6</sub>, all of known carbon isotopic composition and resulted in standard deviations < 0.4‰.

### 2.3. Data presentation and subgrouping of samples

The isolines presented in the distribution map of TOC (Fig. 2) are based on the VG Gridding Algorithm supplied by the ODV-software package (Schlitzer, 2002), allowing construction of a variable resolution, rectangular grid, where grid-spacing along X and Y directions varies according to data density.

Based on the organic carbon contents and distribution and the geographical, hydrographical and en-

vironmental settings, the samples originating from the eastern part of the Fram Strait and covering the area and surrounding of the Yermak Plateau have been either arranged onto different *Transects* (I–III, indicated in Fig. 1) or into groups characterising different regions of the investigation area.

The approximately longitudinal *Transects I and II* are both located >80°N and run across the Yermak Plateau (Fig. 1). Most stations underlie permanent ice-cover. However, both *Transects* include eastern stations seasonally influenced by the MIZ and stations with temporary open water conditions. *Transect III* runs from approximately 76.5°N in the south (open water) across the MIZ towards the north (permanently ice-covered) and follows the inflow of Atlantic water from the WSC along the western flank of the Yermak Plateau within the YSC (Fig. 1). Besides our study, oceanographic and biological investigations were recently performed on similar stations or adjacent *Transects* and stations (Andreassen et al., 1996; Owrud et al., 2000; Soltwedel et al., 2000; Rudels et al., 2000; Rutgers van der Loeff et al., 2002; Schewe and

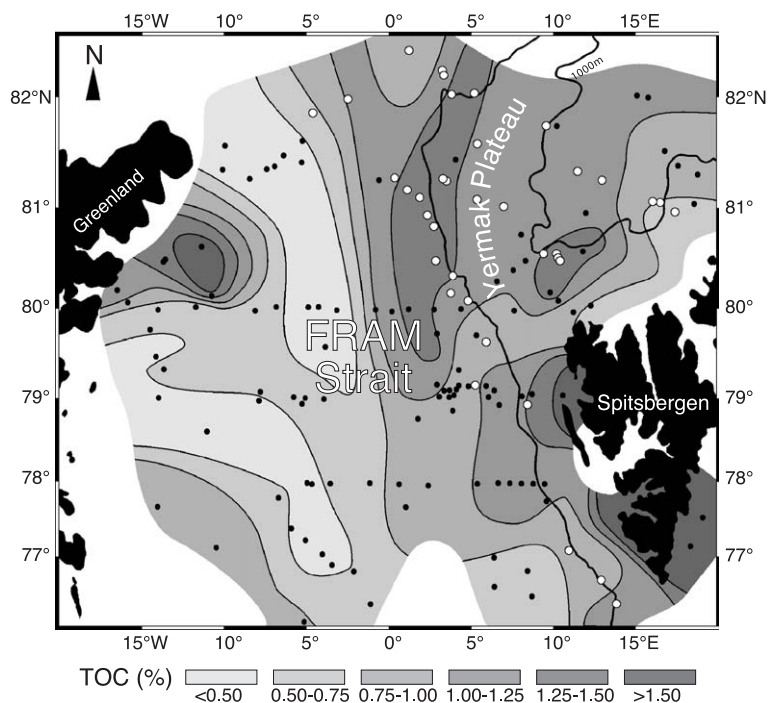


Fig. 2. TOC-content (%) of surface sediments in the Fram Strait (Hebbeln and Berner, 1993; Stein et al., 1994; Notholt, 1998; Kierdorf, 2001; and on [www.pangaea.de](http://www.pangaea.de)). Samples used for lipid analysis are indicated by white dots. The TOC values of these samples can be found in Table 1.

Soltwedel, 2003). Despite presenting data of individual stations along the above mentioned *Transects*, stations have also been arranged in groups representative of the following subareas: Open Water (OW), the Marginal Ice Zone (MIZ), the Yermak Plateau (YP; water depth of about 1000 m), the deep (>2000 m) Arctic Ocean (AO) and stations on the western flank of the Yermak Plateau (YSC, Yermak slope current).

### 3. Results and discussion

#### 3.1. Total organic carbon (TOC) content

The distribution of total organic carbon (TOC) contents in the Fram Strait is shown in Fig. 2. To improve data density, additional data from stations nearby and from previous studies have been included (Hebbeln and Berner, 1993; Stein et al., 1994; Notholt, 1998; accessible through <http://www.pangaea.de>; Kierdorf, 2001, Birgel and Stein, 2003). TOC values ranged from <0.5% to >1.5%. In general, TOC-contents divide the Fram Strait along 0° longitude into two regions, with lower values (<0.75%) to the west and higher (>0.75%) TOC-contents toward the east. The lower TOC contents in the western part correspond to the permanently ice-covered area influenced by the cold and less productive Arctic waters of the EGC. However, a local maximum with TOC-values >1.25% appears east of Greenland in an area between ca. 80/81°N and 10/15°W, corresponding to the region of open water (ice-free) conditions of the NE Greenland polynya. According to Hebbeln and Berner (1993), this is related to enhanced primary productivity caused by the open water conditions of the polynya, providing light and nutrients that favour phytoplankton growth.

Towards the eastern part of the Fram Strait, surface sediments are generally characterised by higher TOC-values (>0.75%). Towards the shallow western Spitsbergen shelf, TOC-values increase to >1%. Higher biological productivity, caused by open water conditions and the “warm” surface waters of the WSC seems to be the most reasonable explanation for enhanced TOC-contents on the slope west of Spitsbergen. In addition, an input of terrigenous organic matter across the slope (mainly via gravity-driven,

near-bottom downslope transport, Hebbeln and Berner, 1993) towards the deeper central Fram Strait is supplied by the fjords of Spitsbergen, where TOC is >1.5%. Increased TOC values in the fjord areas might potentially also result from input of reworked organic material (coals) from Spitsbergen (Hebbeln and Berner, 1993). However, Rock-Eval data from samples of this area indicate only minor contributions of coal-derived organic material (Birgel and Stein, 2003 and references therein).

Most interesting, locally enhanced TOC contents (>1.25%) are further recorded in the surface sediments situated on the western flank of the Yermak Plateau and north off Spitsbergen. For stations located close to 80°N, these elevated TOC values can be explained by enhanced seasonal productivity in the vicinity of the ice-edge, where melting processes locally supply nutrients. North of Spitsbergen, productivity might be additionally triggered by relatively warm Atlantic water transported via the NSC resulting in open water areas in summer (e.g. Owrud et al., 2000). However, most of the stations on the western flank of the Yermak Plateau up to approximately 82°N, where TOC-contents also reach >1.25%, are ice-covered throughout the year. For these stations, enhanced organic carbon contents cannot be explained by overlying surface water productivity. As described above, this part of the Yermak Plateau is influenced by the Yermak Slope Current (YSC, cf. Fig. 1). Therefore, high TOC-values at these stations might result from the northward transport of organic carbon along the western part of the Yermak Plateau within the YSC. This is in good agreement with recent studies describing resuspension and particle transport occurring especially on the western flank of the Yermak Plateau (Rutgers van der Loeff et al., 2002). Such a transport mechanism from south to north was also proposed by Soltwedel et al. (2000) based on pigment distributions.

#### 3.2. Concentrations and distribution of compound classes and $\delta^{13}C_{org}$

Total concentrations of aliphatic lipids vary by approximately one order of magnitude, from 1149  $\mu\text{g/g}$  TOC (PS2851) in the northernmost part of the Fram Strait up to 9549  $\mu\text{g/g}$  TOC (PS55/77) in the

vicinity of the MIZ at 80°N, 5°E (Table 1). Total fatty acids clearly dominated the aliphatic lipids, but also showed a high variability from 744 (PS2851) up to 9077 µg/g TOC (PS55/77). Total *n*-alkanes ranged from 167 (PS2865) to 393 µg/g TOC (PS57/131), and comparable concentrations were found for *n*-alkanols

(85–431 µg/g TOC, PS57/138 and PS55/95, respectively). At all stations, the concentrations of fatty acids exceeded those of *n*-alkanes and *n*-alkanols by factors of >5–10.

Despite the large variations observed in the concentrations of the lipid classes,  $\delta^{13}\text{C}_{\text{ORG}}$  values remained

Table 1  
Concentrations of aliphatic lipid classes (µg/g TOC),  $\delta^{13}\text{C}_{\text{ORG}}$  and %-TOC of surface sediments in northeastern Fram Strait

Sample	Transect (subregion <sup>a</sup> )	<i>n</i> -Alkanes <sup>b</sup>	<i>n</i> -Alkanols <sup>b</sup>	Fatty acids <sup>b</sup>	Total	$\delta^{13}\text{C}_{\text{ORG}}$ (‰ vs. PDB)	TOC (%)
		µg/g TOC					
PS2830	I	331	268	1577	2176	−22.6	<b>0.58</b>
PS2831	I (MIZ)	266	190	2781	3237	−22.3	0.71
PS2832	I	252	187	1581	2020	−21.9	0.78
PS2834	II (YP)	262	181	1356	1799	−21.9	1.04
PS2835	II (YP)	223	207	1383	1813	−22.0	1.00
PS2836	II (YP)	242	201	1260	1703	−22.2	1.00
PS2837	III (YSC)	258	142	1415	1815	−22.4	1.51
PS2838	III	228	151	1407	1786	−22.1	1.39
PS2847	II (AO)	242	190	1095	1527	−21.9	0.75
PS2848	II (AO)	265	199	1379	1843	−22.0	1.20
PS2849	I (AO)	249	226	952	1427	− <b>21.5</b>	0.67
PS2851	I (AO)	235	170	<b>744</b>	<b>1149</b>	−22.1	1.16
PS2853	I (AO)	218	184	1162	1564	−22.2	0.73
PS2854	I/III (YSC)	180	313	2287	2780	−22.3	1.33
PS2855	I (YP)	257	147	1117	1521	−22.0	1.27
PS2856	I (YP)	265	173	1255	1693	−21.9	1.17
PS2857	I (YP)	252	227	1259	1738	−21.8	1.04
PS2858	I (YP)	235	160	1530	1925	−22.5	1.23
PS2859	I (YP)	246	193	1247	1686	−22.4	1.11
PS2860	I	239	144	1063	1446	−22.0	1.22
PS2861	I	251	191	1196	1638	−22.2	1.25
PS2863	II (MIZ)	267	191	1490	1948	−22.1	1.21
PS2864	II (MIZ)	242	225	2222	2689	−22.1	1.42
PS2865	II	<b>167</b>	122	1263	1552	−22.9	<b>1.58</b>
PS55/77	III (MIZ)	261	211	<b>9077</b>	<b>9549</b>	−22.4	1.32
PS55/92	III (YSC)	278	172	3840	4290	−22.5	1.45
PS55/93	III (YSC)	289	286	5231	5806	−22.4	1.38
PS55/95	II (YSC)	274	<b>431</b>	3224	3929	−22.3	1.38
PS55/97	II (YP)	261	191	1580	2032	−22.3	1.25
PS55/98	III (YSC)	292	182	4053	4527	−22.2	0.79
PS55/158	III (OW)	245	120	3261	3626	−22.3	0.95
PS57/123	III (OW)	209	97	2134	2440	−22.6	1.26
PS57/131	III (OW)	<b>393</b>	131	1866	2390	− <b>23.9</b>	0.83
PS57/138	III (OW)	n.d.	<b>85</b>	1530	1615	−23.5	0.87
PS57/145	III (OW)	n.d.	93	1761	1854	n.d.	1.19
PS57/153	III (OW)	223	107	3327	3657	−22.0	1.36
PS57/157	III (MIZ)	355	195	4137	4687	−22.5	0.86
PS57/160	III (YSC)	266	190	6630	7086	−22.4	1.15
PS57/161	III (YSC)	280	153	3238	3671	−22.4	1.39

Bold numbers indicate minimum and maximum values. n.d. = not determined.

<sup>a</sup> Abbreviations used for subareas: AO = Arctic Ocean (>2000m water depth, >81.5°N); YP = Yermak Plateau (approx. 1000 m water depth); OW = Open water (<80°N); MIZ = Marginal Ice Zone; YSC = Yermak Slope Current.

<sup>b</sup> For individual compounds contributing to the respective lipid classes see Appendix A–C.

relatively constant (average  $-22.3\text{‰} \pm 0.4$  S.D.,  $n=38$ ) and varied from  $-23.9\text{‰}$  (PS 57/131) to  $-21.5\text{‰}$  (PS 2849). Only two out of the 38 samples showed a relative  $^{13}\text{C}$ -depletion corresponding to  $\delta^{13}\text{C}_{\text{org}}$ -values  $< -23\text{‰}$  (Table 1).

Both the carbon isotopic composition and the high abundance of short-chain fatty acids (mainly composed of mono- and polyunsaturated compounds, see below) indicate organic material dominantly derived from a marine source. A marine origin for most of the organic matter, as inferred from the bulk carbon isotope ratios is in accordance with reports from other regions of the Arctic Ocean (e. g. Goñi et al., 2000; Schubert and Calvert, 2001).

The average  $\delta^{13}\text{C}_{\text{org}}$  value of  $-22.3\text{‰}$  ( $\pm 0.4$  S.D) obtained within our study can be compared to the value of  $-21.6\text{‰}$  ( $\pm 0.3$ ) representative of Arctic pelagic primary producers determined by Hobson and Welch (1992) and to the range of  $\delta^{13}\text{C}_{\text{POC}}$  from  $-22.0$  to  $-23.2\text{‰}$  ( $n=3$ ) in surface waters of the North East Water Polynya in the western part of the Fram Strait (Notholt, 1998). Compilations of  $\delta^{13}\text{C}_{\text{org}}$  values from Arctic Amerasian continental shelf sediments (Goñi et al., 2000; Naidu et al., 2000) and the Siberian Laptev Sea shelf (Mueller-Lupp et al., 2000) showed a general cross-shelf increase in  $\delta^{13}\text{C}_{\text{org}}$  due to seawards increasing contributions of marine organic carbon. Depending on the shelf area, values of  $-24\text{‰}$  to  $-21\text{‰}$  were attributed to represent the marine organic carbon source, whereas the terrestrial organic carbon showed a rather uniform  $\delta^{13}\text{C}_{\text{org}}$ -value of approximately  $-27\text{‰}$ . For comparison,  $\delta^{13}\text{C}_{\text{org}}$ -ratios from typical modern Arctic tundra vegetation range from  $-27.2\text{‰}$  to  $-29.2\text{‰}$  (Pfeiffer and Janssen, 1993; Gundelwein, 1998).

The different characteristics for the subareas defined with respect to the occurrence of aliphatic lipids are most obvious from the averaged concentrations given in Table 2. Lowest average amounts of total aliphatic lipids were present in those regions covered permanently by ice, i.e. in surface sediments north of the Yermak Plateau towards the deeper ( $>2000$  m) Central Arctic Ocean (AO,  $1502 \mu\text{g/g}$  TOC, Table 2) and on the shallower ( $<1000$  m) Yermak Plateau itself (YP,  $1768 \mu\text{g/g}$  TOC, Table 2). Total fatty acid concentrations averaged  $1066 \mu\text{g/g}$  TOC for the AO and  $1332 \mu\text{g/g}$  TOC on the YP. As mentioned, both regions are characterised by permanent ice-cover,

Table 2  
Average (aver.), minimum (min.), maximum (max.) and standard deviation (SD) of aliphatic lipid classes ( $\mu\text{g/g}$ TOC),  $\delta^{13}\text{C}_{\text{ORG}}$  (‰ vs. PDB) and  $\% \text{C}_{\text{ORG}}$  for different subregions of northeastern Fram Strait

	AO ( $n=5$ )			YP ( $n=9$ )			YSC ( $n=8$ )			MIZ ( $n=5$ )			OW ( $n=4/6^a$ )							
	aver.	min.	max.	aver.	min.	max.	aver.	min.	max.	aver.	min.	max.	aver.	min.	max.	SD				
<i>n</i> -alkanes	242	218	265	249	223	265	14	265	180	292	36	242	355	44	267	209	393	85		
<i>n</i> -alkanols	194	170	226	21	187	227	25	234	142	431	101	202	190	225	15	106	85	131	17	
fatty acids	1066	744	1379	237	1332	1117	1580	147	3740	1415	6630	1635	3941	1490	9077	3030	2313	1530	3327	784
total	1502	1148	1844	251	1768	1520	2033	148	4238	1815	7086	1651	4422	1948	9548	3036	2597*	1615	3657	868
$\delta^{13}\text{C}_{\text{ORG}}$	-21.9	-22.2	-21.5	0.3	-22.1	-22.5	-21.8	0.2	-22.4	-22.5	-22.2	0.1	-22.3	-22.5	-22.1	0.2	-22.9	-23.9	-22.0	0.8
$\% \text{C}_{\text{ORG}}$	0.90	0.67	1.20	0.26	1.12	1.00	1.27	0.11	1.30	0.79	1.51	0.23	1.10	0.71	1.42	0.31	1.08	0.83	1.36	0.22

For definition of subregions and abbreviations used see text and Table 1.

<sup>a</sup> Average of *n*-alkanes determined on only four out of six samples, total average thus slightly underestimated.



increasing in thickness to the north. Thus, the somewhat reduced total fatty acid concentrations towards the north in the AO compared to the YP might reflect an influence of the thickness of the ice-cover on the amounts of fatty acids produced and deposited in the sediments. Maximum average concentrations of total aliphatics (4422  $\mu\text{g/g}$  TOC) and total fatty acids (3941  $\mu\text{g/g}$  TOC) were observed for stations situated under or in the vicinity of the MIZ (Table 2), supposed to represent the zone of highest seasonal primary productivity. Despite maximum average amounts, total fatty acid concentrations of surface sediments close to the MIZ are also characterised by substantial variability, as expressed by the wide range (1490–9077  $\mu\text{g/g}$  TOC, Table 2) and large standard deviation (SD = 3030  $\mu\text{g/g}$  TOC, Table 2). Both, maximum concentration and variation thus might reflect the highly dynamic and productive environmental conditions of the MIZ.

In the open water (OW) areas south of the MIZ, total aliphatic lipids averaged 2597  $\mu\text{g/g}$  TOC and total fatty acids 2313  $\mu\text{g/g}$  TOC, which is lower than at the MIZ but higher than compared to the ice-covered AO and YP. For the YSC region, even though also situated under permanent ice-coverage, concentration levels of aliphatic lipids were found to be surprisingly high (total: 4238  $\mu\text{g/g}$  TOC, fatty acids: 3740  $\mu\text{g/g}$  TOC, Table 2) and better compare to those at the MIZ rather than to the low amounts observed for the YP and AO.

It is noteworthy that the averaged total fatty acid concentrations (and consequently also the sum of total aliphatics) showed a marked difference with respect to the environmental regimes, whereas the average total amounts of *n*-alkanes and *n*-alkanols did not show major variations. This indicates that the fatty acids mostly derive and reflect local environmental conditions and autochthonous sources, whereas *n*-alkanes and *n*-alkanols most probably are allochthonous.

### 3.3. Composition and sources of selected aliphatic lipids

#### 3.3.1. Fatty acids

An overview on the composition of the fatty acids identified in the samples is provided in the following section. Their potential sources are discussed paying special emphasis to the uniqueness of the Arctic

environment. Abbreviations used for unsaturated fatty acids (e. g.  $\text{C}_{16:1n-7}$ ) designate the location of the (first, in case of PUFA) double bond with reference to the end of the chain (opposite to the carboxyl group), following the recommendation of the IUPAC-IUB Commission on Biochemical Nomenclature recommendation (1976). The compositions of the fatty acid fraction for all stations are given in Appendix A and average values for the different subregions are presented in Table 3.

The fatty acids consisted of branched (*iso/ante-iso*- $\text{C}_{15}$  and  $\text{C}_{17}$ ), *n*-saturated, monounsaturated (MUFA) and polyunsaturated (PUFA) compounds. In all samples, even numbered fatty acids (especially those with 14, 16 and 18 carbon atoms) showed a strong predominance. Relative proportions of saturated fatty acids ( $\text{C}_{14}$ – $\text{C}_{28}$ ) ranged from 25% at the MIZ (station PS55/77) up to 56% in the northern, ice-covered part of the Fram Strait (station PS2851). Contributions of MUFA ranged from 29% (PS2851) to 59% (PS55/95) and up to 22% (PS55/77) of the fatty acid fraction consisted of PUFA (Appendix A). Most of the variation in fatty acid concentrations is already explained when looking at the amounts of saturated fatty acids and MUFA, and as both were the principle fatty acid subfractions, their proportions covaried and showed a significant negative correlation ( $r = -0.929$ ).

Branched fatty acids showed less variability and were of minor relative and absolute abundance. Overall, they contributed only 2–9% to the total fatty acids, whereby on average this proportion was lower at MIZ-stations (4%) than for AO- and YP-samples (8%) (Table 3). The short-chain  $\text{C}_{16}$  and  $\text{C}_{18}$  fatty acids were most abundant throughout all samples, with (a) a general predominance of the respective monounsaturated compounds (i.e. the ratios 16:1/16:0 and 18:1/18:0 being  $>1$ , Appendix A) and (b) a higher abundance of  $\text{C}_{16}$  than  $\text{C}_{18}$  structures. Compared to  $\text{C}_{16}$  and  $\text{C}_{18}$  MUFA,  $\text{C}_{20:1}$  and  $\text{C}_{22:1}$  were present at lower levels.  $\text{C}_{20:4}$  and  $\text{C}_{20:5}$  clearly dominated the PUFA-fraction, and were often found at higher amounts than  $\text{C}_{18:1}$  and the long-chain saturates ( $>n\text{-C}_{22}$ ). When comparing the amounts of individual fatty acids among all stations, significant differences in the extent of the respective concentration ranges (i.e. the ratio of maximum/minimum concentrations) became obvious, depending on the fatty acid type. As a

Table 3

Average concentrations ( $\mu\text{g/g}$  TOC) of fatty acids, percentual composition and ratios in surface sediments for subregions of northeastern Fram Strait

Compound	Assigned lipid pool	AO ( $n=5$ )		YP ( $n=9$ )		YSC ( $n=8$ )		MIZ ( $n=5$ )		OW ( $n=6$ )	
		Aver.	SD	Aver.	SD	Aver.	SD	Aver.	SD	Aver.	SD
<i>n-Saturates</i>											
14	A	47	12	51	7	183	94	221	215	111	58
15	B	13	3	15	2	30	12	28	14	23	5
16		167	38	197	27	553	303	605	441	361	150
17	B	7	2	8	2	17	8	18	10	15	7
18		42	5	39	4	65	24	61	14	49	11
20		23	4	20	5	26	10	26	5	20	10
21		6	1	6	1	7	2	7	2	4	1
22		31	5	31	5	34	9	29	3	18	5
23		9	3	12	1	15	5	10	1	6	2
24	A+C	60	5	65	8	77	20	66	9	43	11
25		14	3	16	4	17	5	16	3	9	3
26	A+C	61	5	60	8	73	18	62	5	41	14
27		15	2	14	2	32	27	18	6	14	7
28	A+C	45	16	38	9	46	32	27	25	18	23
<i>Monounsaturates</i>											
16:1 <i>n</i> -7	A	170	64	256	45	1058	545	1257	1372	657	404
16:1 <i>n</i> -5	A	31	6	56	43	228	313	81	40	128	98
18:1 <i>n</i> -9	B	48	16	70	15	312	315	181	62	104	34
18:1 <i>n</i> -7	B	80	38	111	19	181	121	285	231	194	120
20:1 <i>n</i> -9	B	11	10	15	7	22	11	27	14	15	2
20:1 <i>n</i> -7	B	6	4	7	5	39	25	25	18	34	14
22:1 <i>n</i> -11, 22:1 <i>n</i> -9 <sup>a</sup>	B	25	9	31	7	48	23	42	28	18	12
<i>Polyunsaturates</i>											
18:2		11	6	25	13	68	45	69	42	47	30
18:4 <i>n</i> -3	A	28	11	21	9	50	27	81	86	37	19
20:2		7	4	7	4	24	31	27	21	21	12
20:4 <i>n</i> -6	A	9	7	21	13	110	92	224	323	69	36
20:5 <i>n</i> -3	A	9	6	23	16	230	169	280	284	128	85
20:4 <i>n</i> -3	A	5	3	5	3	12	14	18	26	5	9
22:6 <i>n</i> -3	A	4	1	6	3	9	3	11	4	10	4
<i>Branched</i>											
i-15	B	29	9	39	4	58	12	49	7	39	8
ai-15	B	39	13	47	4	70	19	58	9	47	13
i-17	B	7	2	9	1	28	30	18	4	16	4
ai-17	B	8	1	10	1	21	20	15	3	15	5
Total ( $\mu\text{g/g}$ TOC)		1066	237	1332	147	3740	1635	3941	3030	2313	784
% Assigned		70	3	72	2	78	4	78	5	76	3
% Saturated		51	5	43	3	31	6	30	7	32	2
% MUFA		35	4	41	4	50	6	48	7	50	1
% PUFA		7	1	8	2	13	4	18	4	14	2
% Branched		8	1	8	1	5	2	4	2	5	1
<i>Ratios</i>											
16:1/16:0		1.2	0.2	1.6	0.5	2.3	0.8	2.2	0.6	2.2	0.3
18:1/18:0		3.0	1.0	4.7	0.8	7.6	2.4	7.7	3.8	6.1	1.6

general rule, this variability increased in magnitude from even numbered LCFA ~ branched < saturates < MUFA < PUFA. Thus, the concentrations of branched and even numbered LCFA varied only by a factor of about 5–10, whereas those of the MUFA and PUFA varied by factors of up to ~ 60 and ~ 270, respectively. In terms of absolute amounts, the concentrations of the two major C<sub>16</sub>-fatty acids varied from 119 to 1353 µg/g TOC (C<sub>16:0</sub>) and 97 to 3612 µg/g TOC (C<sub>16:1n-7</sub>), respectively. The highest variability was observed for C<sub>20:5n-3</sub>, ranging over two orders of magnitude from 3 up to 773 µg/g TOC (Appendix A).

Though averaging smoothes much of this variability, clear differences in the fatty acid compositions remained obvious when comparing the different subregions of the study area (Table 3). On average, stations positioned close to or at the MIZ contained highest total fatty acid amounts (3941 µg/g TOC), the highest fraction of PUFA (18%) and the lowest proportions of saturated (30%) and branched (4%) compounds. This situation is reversed for surface sediments deposited under permanent ice-cover, (with the exception of YSC-stations, see below) where saturated (51% and 43%) and branched fatty acids (8%) are of greater relative importance, while PUFA (7–8%) but also total fatty acid concentrations are lowest (1066 µg/g TOC, AO and 1332 µg/g TOC, YP).

Surface sediments from the area of open water conditions (OW) compare in fatty acid distribution to those of the MIZ, but comprise only about half the amount (OW: 2313 µg/g TOC, MIZ: 3941 µg/g TOC). Though under comparable permanent ice-cover to the AO- and YP-stations, surface sediments on the western Yermak slope (YSC, Table 3) contained fatty acids similar in concentration and distribution as stations at the MIZ.

The marginal ice zones (MIZ) in the Fram Strait are known to provide favourable environmental conditions for enhanced seasonal productivity and indeed,

most of the major fatty acids described above can reliably be attributed to primary production. The dominant fatty acid within these samples, C<sub>16:1n-7</sub>, is a common lipid-constituent in microalgae of diverse taxa, such as diatoms, dinoflagellates, prymnesiophytes and haptophytes. C<sub>16:1n-7</sub> accounts for >30% to the fatty acids of diatoms whilst other algae, e.g. green algae, contain lower or trace levels of this component (Volkman et al., 1989; Viso and Marty, 1993).

Other fatty acids, such as C<sub>14:0</sub>, C<sub>16:0</sub>, C<sub>18:1n-9</sub>, C<sub>20:1n-9</sub>, C<sub>20:5n-3</sub>, and C<sub>22:6n-3</sub> are frequently encountered in the aquatic environment. Being common constituents of the lipid fraction from diverse phytoplankton species (Volkman et al., 1989; Viso and Marty, 1993; Pond et al., 1998; Volkman et al., 1998), their occurrence in water, particulate and sediment samples is therefore usually related to surface water productivity, although neither restricted to a marine nor to an exclusive phytoplankton origin (as discussed below for zooplankton contributions). In estuaries, shelf regions and marginal seas, (i.e. areas influenced by riverine inputs) these compounds, if derived from plankton, more likely result from contributions of freshwater/lacustrine species. For the Arctic, this has been shown e.g. for the Siberian Laptev Sea (Fahl and Stein, 1999). In addition, in polar regions sea-ice algae (living in the ice, meltwater-ponds on the ice, in the water column close to the underside of the ice, or close to the ice-edge) provide another plausible source for the above-mentioned fatty acids. Several studies (e.g. Henderson et al., 1998; Falk-Petersen et al., 1998) have investigated the fatty acid distributions of ice-algal assemblages and phytoplankton from the MIZ in the Barents Sea, adjacent to the east of our investigation area. From these studies it is known that the ice-algal assemblages found under the ice and close to the MIZ are dominated by diatoms such as *Nitzschia frigida* and *Melosira arctica*, consistent

#### Notes to Table 3:

SD=standard deviation. *n*=number of samples included. % Assigned=total fraction of fatty acids assigned to distinct sources. MUFA=monounsaturated fatty acids. PUFA=polyunsaturated fatty acids. For definition of subregions and abbreviations (AO, YP, YSC, MIZ, OW) see text and Table 1. Letters A, B, C indicate assignment of fatty acids to the lipid pools explained in Section 4.3. Notice that the amounts of long chain *n*-saturates represent a mixture of lipid pools A and C, as revealed by their stable carbon isotopic composition (see Section 3.3.3). Individual fatty acid amounts contributing to the averages are provided in Appendix A.

<sup>a</sup> Sum of both isomers.

with the universal predominance of diatoms in assemblages of sea-ice algae (e.g. Kirst and Wiencke, 1995). The fatty acids of the mentioned sea-ice diatoms also consist mainly of  $C_{14:0}$ ,  $C_{16:0}$ ,  $C_{16:1n-7}$  and  $C_{20:5n-3}$ , similar to diatoms from temperate environments (Volkman et al., 1989; Viso and Marty, 1993).

The ratio of  $\Sigma C_{16:1}/C_{16:0}$  as a general diatom indicator was proposed by Claustre et al. (1988–89) and values  $>1.6$  have been used as evidence for diatom-derived fatty acid contributions in diverse aquatic systems, including the cold environment (Budge and Parrish, 1998; Parrish et al., 2000; Budge et al., 2001; Ramos et al., 2003). This is supported by comparisons of  $C_{16:1}/C_{16:0}$  ratios among different taxonomic classes of marine microalgae (Viso and Marty, 1993; Zhukova and Aizdaicher, 1995). According to the fatty acid distributions provided by Falk-Petersen et al. (1998) and Henderson et al. (1998)  $\Sigma C_{16:1}/C_{16:0}$ -ratios range from 1 to 2.5 for *N. frigida* and *M. arctica* associations from the MIZ in the Barents Sea. However, it should be noted that this ratio (a) also varies with growth rate (e.g. Mayzaud et al., 1989), and (b) can also significantly decrease during sedimentation of living phytoplankton due to the higher susceptibility of unsaturated fatty acids to the biological and/or chemical degradation (e.g. Tanoue and Handa, 1980 and references therein). Thus, the ratio of  $C_{16:1}/C_{16:0}$  in surface sediments is rarely  $>1$  and more typically well below 1. Given the values from Belicka et al. (2002), surface sediments of various Arctic Ocean basins have  $C_{16:1}/C_{16:0}$  ratios from 0.1 to 0.7, whereas in surface sediments and particles collected on the Chukchi Shelf this ratio varies from 1.1–2.1. Constrained by these complementary data, we argue that these higher ratios are related to diatom-dominated phytoplankton blooms.

Among our samples, this ratio ranged from 1.0 to 3.8 (Appendix A). Throughout our samples this ratio is surprisingly high. However, it was markedly lower in Arctic Ocean and Yermak Plateau samples under permanent ice-cover (AO, YP: average 1.2–1.6, Table 3) compared to stations derived from the MIZ, OW, or the YSC (average 2.2–2.3, Table 3).

Diatoms are known to be a primary source of PUFA such as  $C_{18:4n-3}$ ,  $C_{20:5n-3}$ , and  $C_{20:4n-3}$  (Volk-

man et al., 1989; Zhukova and Aizdaicher, 1995). In major, we suggest that diatoms also account for the sedimentary occurrence of PUFA in the eastern Fram Strait and on the Yermak Plateau (Appendix A), whereby  $C_{20:5n-3}$  is usually the most prominent single PUFA. As could be seen for the variations in the  $C_{16:1}/C_{16:0}$  ratios, the contribution of PUFA to the total fatty acids is relatively high at the MIZ- (18%), intermediate at YSC- and OW-stations (13–14%) and lower on the YP and in the AO (7–8%, Table 3). For all samples ( $n=39$ ), there is a highly significant correlation of the amounts of  $C_{16:1n-7}$  and  $C_{18:4n-3}$  ( $r=0.911$ ),  $C_{20:5n-3}$  ( $r=0.915$ ) and  $C_{20:4n-3}$  ( $r=0.908$ ), respectively. Together, therefore, these results indicate that significant proportions of the fatty acids derive from diatom-dominated phytoplankton and ice-algae. This organic matter is delivered to the sediment surface in a good state of preservation, as indicated by the resemblance of the major fatty acid distribution not only to that published for cultured diatoms, but also to nearby upper water column diatom samples. Compared to surface sediments from the central Arctic Ocean (AO) and on the Yermak Plateau (YP), a higher proportion of this relatively fresh and undegraded material is especially well preserved in the sediments originating from the area of the MIZ, but also from the YSC. This is further confirmed by comparable variations in relative proportions of intact chlorophyll-*a* to the total sedimentary chloroplast pigments, an independent indicator of the “freshness” of primary organic matter at the seafloor, as reported by Soltwedel et al. (2000) for the same samples.

Common to organisms of all taxa, saturated  $C_{14}$ ,  $C_{16}$ , and  $C_{18}$  fatty acids are less source-specific than mono- and polyunsaturated fatty acids. Their ubiquity and their probable additional derivation from (bio-) geochemical reduction of unsaturated fatty acids generally limit their biomarker potential in marine geochemical investigations, especially in deeper sediments. As stated above, the  $C_{16}$  saturated fatty acid was consistently present in lower abundance than the corresponding MUFA, and this is even more obvious for the  $C_{18:1}/C_{18:0}$ -ratios (1.9–12.6, Appendix A). Both ratios are unique of a mixed fresh phyto-/zooplankton source rather than a geochemical degradation product for  $C_{16:0}$  and

C<sub>18:0</sub> seems most likely. However, we infer that the saturated *n*-fatty acid C<sub>14:0</sub> is reliably derived from primary production, consistent with a high general abundance of this compound within diatoms (Volkman et al., 1989; Viso and Marty, 1993), Arctic ice algae and phytoplankton from the MIZ (Falk-Petersen et al., 1998). It is noteworthy that the concentrations of C<sub>14:0</sub> in our samples are even more strongly correlated ( $r=0.992$ ) to those of C<sub>16:1*n-7*</sub> than the various PUFA and C<sub>16:1*n-7*</sub>.

Arctic and Antarctic zooplankton (copepods) and a variety of Arctic benthic organisms contain significant levels of C<sub>18:1</sub> as well, at comparable or even higher contents than C<sub>16:1</sub> (Albers et al., 1996; Graeve et al., 1997). C<sub>18:1*n-7*</sub> is a known chain elongation product from dietary uptake of a C<sub>16:1*n-7*</sub> fatty acid (Sargent and Henderson, 1986). A similar synthetic pathway has been proposed for benthic organisms collected on the shelves off northeast Greenland, Spitsbergen and the western Barents Sea (Graeve et al., 1997). A chain elongation pathway of C<sub>18:1*n-9*</sub> to C<sub>22:1*n-11*</sub> via the intermediate C<sub>20:1*n-9*</sub> is known for copepods of both Polar Oceans (Kattner and Hagen, 1995). As an energetic adaptation to the cold, copepods from high-latitudes are known for their extensive accumulation of wax-esters (>70% of total lipids) as storage lipids, and these waxes are dominated by fatty acids such as C<sub>20:1*n-9*</sub> and C<sub>22:1*n-11*</sub>, as well as C<sub>18:1</sub> (Kattner and Hagen, 1995; Albers et al., 1996; Graeve et al., 1997). These typical fatty acid constituents of wax-esters are also known from copepods of the Fram Strait (Kattner et al., 1989), at the MIZ, and from open waters of Spitsbergen (Scott et al., 2001). PUFA such as C<sub>20:5*n-3*</sub> and C<sub>20:4*n-6*</sub> are essential fatty acids for most of the higher marine organisms, including zooplankton. Their variable amounts within Arctic copepods and various benthic organisms are considered to reflect different feeding behaviours (Graeve et al., 1997; Scott et al., 2002).

A variety of organisms other than zooplankton are known to have the capacity to synthesise C<sub>18</sub> mono-unsaturated fatty acids. C<sub>18:1*n-7*</sub> has been considered to be a bacteria-specific fatty acid marker (Parkes and Taylor, 1983; Gillan and Sandstrom, 1985), but a compilation of fatty acid compositions of some representative marine bacteria (Russel and Nichols, 1999) shows C<sub>18:1*n-7*</sub> only to account for 1–3.6

wt.% of total fatty acids. The odd-numbered *n*-fatty acids with 15 and 17 carbon atoms as well as their *iso*- and *anteiso*-homologues identified in the samples investigated also point towards a bacterial origin (Leo and Parker, 1966; Cooper and Blumer, 1968; Boon et al., 1979; Perry et al., 1979; Sicre et al., 1988; Kaneda, 1991). Compared to the higher relative abundances of *n*-, *i*- and *ai*-C<sub>15</sub> and C<sub>17</sub> acids (8.4–17.5%) given for marine bacteria by Russel and Nichols (1999), C<sub>18:1*n-7*</sub> (1–3.6%) is of only minor importance. Conversely, the higher amounts of C<sub>18:1*n-7*</sub> compared to *n*-, *i*-, and *ai*-C<sub>15</sub> and C<sub>17</sub> fatty acids within our samples (cf. Appendix A; Table 3) point towards a source of C<sub>18:1*n-7*</sub> other than bacteria, most likely zooplankton.

Long-chain saturated fatty acids (C<sub>24</sub>–C<sub>30</sub>) with a strong predominance of even-numbered carbon chains are typical constituents of higher land plant leaf waxes (Eglinton et al., 1968; Simoneit, 1978; Naraoka and Ishiwatari, 2000). Their occurrence in marine sediments is usually attributed to terrestrial inputs via riverine or eolian transport. More important for the Arctic is entrainment by ice of river-discharged terrestrial organic carbon supplied to the large Amerasian shelf areas. Ice formation over these shelf areas accompanied by sediment inclusion is a proven mechanism for example for the removal and export of sediment from the Laptev Sea shelf to the interior basins of the Arctic Ocean (Eicken et al., 2000; Schoster et al., 2000). The occurrence of LCFA within surface sediment samples of the central Arctic Eurasian Basin and the Greenland Sea, north of our investigation area, has been likewise documented (Belicka et al., 2002).

Previously (Volkman et al., 1998 and herein), however, it has been noted that microalgae and bacteria may also produce these fatty acids, but in trace amounts (<2%) relative to C<sub>14</sub>–C<sub>20</sub> fatty acids. The occurrence of long-chain saturated fatty acids, e.g. C<sub>24</sub>, has been noted also for Arctic phytoplankton and ice algae (Henderson et al., 1998). Moreover, based on stable carbon isotopic evidence (see also Section 3.3.3), Naraoka and Ishiwatari (2000) attributed significant contributions of long-chain, even numbered saturated fatty acids (e.g. 63–80% for *n*-C<sub>26</sub>, in marine sediments to a “non-terrestrial” source.

In summary, the fatty acid compositions of the sediments from the Fram Strait and on the Yermak Plateau are dominated by products derived from primary production, most likely of a (sea-ice) diatom origin, as indicated by high amounts of  $C_{16:1n-7}$ ,  $C_{20:5n-3}$ ,  $C_{20:4n-6}$  and  $C_{14:0}$ . Another suite of fatty acids, attributable most likely to bacteria (branched fatty acids) and zooplankton (mainly copepods,  $C_{20:1}$ ,  $C_{22:1}$  and  $C_{18:1}$  fatty acids) reflects the transfer of the initially produced organic carbon through different trophic levels. Compared to the before mentioned fatty acids of primary and secondary origin, long-chain fatty acids of a probable, but not exclusive (see Section 3.3.3) higher land plant origin are of minor importance. The overall composition of the fatty acid fractions, dominated by high amounts of MUFA and PUFA indicates a “fresh” status of the organic material accumulating in surface sediments and points to a rapid export to the seafloor.

### 3.3.2. *n*-Alkanes and *n*-alkanols

*n*-Alkanes and *n*-alkanols were investigated for their supposed higher land plant origin and to provide additional measures for terrestrial-derived contributions besides the long-chain fatty acids. The *n*-alkanes from cuticular waxes of higher land plants typically range from  $C_{23}$ – $C_{35}$  with a distinct predominance of odd-carbon chain lengths and a concentration maximum at  $C_{27}$ ,  $C_{29}$  or  $C_{31}$  (Eglinton et al., 1962; Eglinton and Hamilton, 1967; Rieley et al., 1991; Kunst and Samuels, 2003). The carbon Preference Index (CPI, Bray and Evans, 1961 and others) is an expression of this odd-numbered *n*-alkane predominance, and *n*-alkane mixtures from natural vegetation waxes have high (>5) CPI (e.g. Eglinton and Hamilton, 1963). Analogous, sedimentary *n*-alkanes in the aquatic environment, when also showing a pronounced preference of long-chain (> $C_{25}$ ) odd-numbered homologues (and high CPI) are interpreted to derive from terrestrial organic inputs.

Within all samples investigated, the hydrocarbon fractions (Appendix B) contained *n*-alkanes from  $C_{15}$  to  $C_{32}$ , usually dominated by higher homologues. Total *n*-alkanes ranged from 167 to 393  $\mu\text{g/g}$  TOC, revealed no major variation amongst individual stations or averages for the different sub-regions and were generally low compared to fatty

acids (cf. Tables 1 and 2). The noticeable predominance of odd-numbered *n*-alkanes (> $n$ - $C_{22}$ ) is well expressed in the corresponding CPI, ranging from 1.2 (PS57/131) to 3.0 (PS2849), whereby the CPI for 20 of the 37 samples is >2 (Appendix B). The sum of long-chain, odd-numbered *n*-alkanes ( $C_{25}$ – $C_{31}$ ) of supposed higher land plant origin varied from 43–116  $\mu\text{g/g}$  TOC and contributed 20–47% to the total *n*-alkanes (Appendix B). Total *n*-alkane concentrations obtained within this study compare to the values from Belicka et al. (2002) for their stations 36 (114  $\mu\text{g/g}$  TOC) and 37 (146  $\mu\text{g/g}$  TOC) located in the Eurasian Basin north of our investigation area. In addition, calculation of the CPI from the *n*-alkane distributions provided by Belicka et al. (2002) gives comparable values (2.9 and 2.5) than above.

The *n*-alkanols detected in surface sediments from the Fram Strait and on the Yermak Plateau (Appendix C) consisted of even numbered compounds, ranging from  $C_{16}$  to  $C_{28}$ . In most samples, the concentrations of *n*-alkanols > $C_{22}$  are higher than those of short chain homologues and typically maximised in  $C_{26}$ . Concentrations of total *n*-alkanols (85–431  $\mu\text{g/g}$  TOC, Table 1) were in the same order of magnitude than those of total *n*-alkanes and also compare to total *n*-alkanols (104 and 144  $\mu\text{g/g}$  TOC) from surface sediments of the Eurasian Basin (Belicka et al., 2002). In accordance with their known dominance in plant waxes, we assumed the  $n$ - $C_{22}$  to  $n$ - $C_{28}$  alkanols also to reflect terrestrial contributions.

### 3.3.3. Carbon isotopic composition of selected compounds

When possible (in terms of concentrations and sufficient chromatographic resolution), compound specific stable carbon isotopic ratios were determined for fatty acids, *n*-alkanes and *n*-alkanols for 11 samples selected out of the total of 39. Instead of reporting these  $\delta^{13}\text{C}$  values for each station and compound investigated separately, we show the range and average carbon isotopic ratio for the different compounds in Fig. 3. For comparison, the figure also includes the range and average of  $\delta^{13}\text{C}_{\text{org}}$  as reported in Table 1. Although the samples investigated cover a large area, there is only a small ( $\sim 3\%$ ) overall variability with respect to the  $^{13}\text{C}$ -

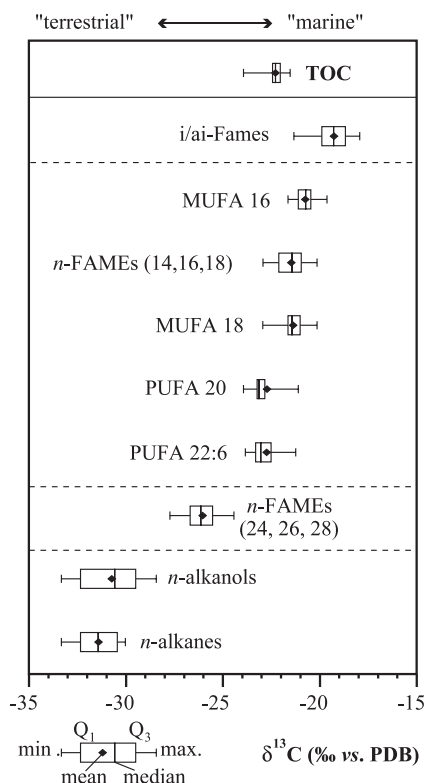


Fig. 3.  $\delta^{13}\text{C}$ -values (range and average) of Corg and aliphatic lipids in surface sediments of the Fram Strait and on the Yermak Plateau. *i/ai*-fatty acids: *iso*- and *anteiso*- $\text{C}_{15}$  fatty acids; MUFA 16:  $\text{C}_{16:1n-7}$  and  $\text{C}_{16:1n-5}$  fatty acids; MUFA 18:  $\text{C}_{18:1n-9}$  and  $\text{C}_{18:1n-7}$  fatty acids; PUFA 20:  $\text{C}_{20:4n-6}$  and  $\text{C}_{20:5n-3}$  fatty acids; PUFA 22:  $\text{C}_{22:6n-3}$  fatty acid; *n*-alkanols: long-chain ( $\text{C}_{22}$ – $\text{C}_{26}$ ) even carbon numbers; *n*-alkanes: long-chain ( $\text{C}_{25}$ – $\text{C}_{31}$ ) odd carbon numbers. Given values cover 38 samples for  $\delta^{13}\text{C}_{\text{org}}$  and 11 samples for compound specific  $\delta^{13}\text{C}$ -values, distributed over the entire investigation area. The standard error is shown by the box, whereas the diamond represents the mean value. The lines extending from the box are indicating the minimum/maximum values.

content of both TOC and of distinct compounds. On the other hand,  $\delta^{13}\text{C}$ -values for the suite of compounds measured range from  $-33\text{‰}$  up to  $-19\text{‰}$ .

*n*-Alkanes ( $\text{C}_{25,27,29,31}$ ) and *n*-alkanols ( $\text{C}_{22,24,26}$ ) are most depleted in  $^{13}\text{C}$ , ranging from  $-33\text{‰}$  to  $-29\text{‰}$  (Fig. 3). Such a carbon isotopic depletion is commonly attributed and in accordance with inputs derived from a terrestrial (higher land plant) source possessing a  $\text{C}_3$  biosynthetic pathway (Collister et al., 1994). Collister et al. (1994) and others (e.g. Huang et al., 1996; Ficken et al., 1998) also showed

that biosynthetically related *n*-alkyl lipids (e.g. *n*-alkanes, *n*-alkanols, *n*-fatty acids) in epicuticular waxes of the same plant have similar carbon isotopic compositions. Therefore, the similarity in the carbon isotopic composition of the long-chain *n*-alkanols and of the long-chain *n*-alkanes in our samples (Fig. 3) most likely points to a common  $\text{C}_3$  land plant source.

The fatty acids contributing the highest proportions to the sedimentary organic carbon contents (i.e. saturated, monounsaturated, and polyunsaturated fatty acids up to  $\text{C}_{22}$ ) are relatively enriched in  $^{13}\text{C}$  (Fig. 3) compared to the terrestrial *n*-alkanes and *n*-alkanols. Within the suite of fatty acids, the PUFA structures ranged from about  $-24\text{‰}$  to  $-21\text{‰}$ , saturated  $\text{C}_{14}$ – $\text{C}_{18}$  compounds and  $\text{C}_{18}$  monounsaturates from  $-23\text{‰}$  to  $-20\text{‰}$ , and  $\text{C}_{16}$  monounsaturates from about  $-22\text{‰}$  to  $-19\text{‰}$ . Branched fatty acids (*i/ai*- $\text{C}_{15}$ ) were the most  $^{13}\text{C}$ -enriched, ranging from approximately  $-21\text{‰}$  up to  $-18\text{‰}$  (Fig. 3). The carbon isotopic compositions of all these lipids, i.e. of all  $\text{C}_{14}$ – $\text{C}_{22}$  fatty acids, are consistent with a marine source and are typical for lipids derived from marine organisms (e.g. Freeman et al., 1995; Pancost et al., 1997; van Dongen et al., 2002). It is known that the carbon isotopic composition of a consumer closely reflects its diet and this basic principle has been used to trace organic carbon flows through food webs (e.g. Peterson, 1999; Boschker and Middelburg, 2002). Following this concept, the carbon isotopic composition of fatty acids presumed to derive from zooplankton and bacterial sources (e.g. MUFA 18, *i/ai*- $\text{C}_{15}$ , cf. preceding section and Fig. 3) imply that organic carbon derived from primary production is their principle organic carbon source.

Long-chain fatty acids (LCFA) with even carbon atom numbers, also of a probable plant wax origin, are  $^{13}\text{C}$  enriched by an average of  $5\text{‰}$  compared to *n*-alkanes and *n*-alkanols (Fig. 3). Their average carbon isotopic composition ( $-26\text{‰}$ ) is intermediate between that observed for *n*-alkanes and *n*-alkanols ( $-33\text{‰}$  to  $-29\text{‰}$ , see above) and compounds of "marine" origin ( $-26\text{‰}$  up to  $-19\text{‰}$ , see below), and points towards a mixed origin for LCFA. Naraoka and Ishiwatari (2000) observed a gradual increase in  $^{13}\text{C}$  of up to  $+6\text{‰}$  for LCFA in a section from riverine to estuarine to open ocean surface sediments and attributed this to seawards increasing contributions of

LCFA derived from marine primary productivity. The same was concluded upon the stable carbon isotopic composition of LCFA in a recent study of the Altamaha river mouth (Shi et al., 2001).

We estimated the proportions of LCFA originating from terrestrial and marine derived sources using a simple two-endmember carbon isotopic mixing calculation, and assuming that *n*-alkyl lipids from a common source possess the same carbon isotopic composition. This is at least valid for biosynthetically related *n*-alkyl lipids in epicuticular waxes of terrestrial plants (Collister et al., 1994; Huang et al., 1996; Ficken et al., 1998). Consequently, the  $\delta^{13}\text{C}$  value for the higher land plant derived proportions of LCFA within the samples should be reflected by the carbon isotopic composition of the plant-derived *n*-alkanes and *n*-alkanols. As shown above, their similar carbon isotopic composition indeed indicates a common plant wax origin. As the  $\text{C}_{26}$  *n*-alkanol was the most abundant plant-derived alkyl-lipid within the samples (Appendix B, C), its  $\delta^{13}\text{C}$ -value was chosen to reflect the terrestrial derived endmember within the mixing calculation. The second (“marine”) endmember was then defined by the respective  $\delta^{13}\text{C}$  value of the  $\text{C}_{16:1n-7}$  fatty acid from the same sample. The measured  $\delta^{13}\text{C}$  value of the LCFA ( $\delta_{\text{LCFA}}$ ) then originates from:

$$\delta_{\text{LCFA}} = (1 - f_{\text{terr}})\delta_{16:1n-7} + f_{\text{terr}}\delta_{\text{C}_{26n}\text{-alkanol}} \quad (1)$$

where  $f_{\text{terr}}$  ( $0 < f_{\text{terr}} < 1$ ) is the terrestrial fraction of the LCFA. The %-proportion of terrestrial derived LCFA was then calculated by rearranging Eq. (1) into:

$$\begin{aligned} \% \text{LCFA}_{\text{terr}} &= 100 f_{\text{terr}} \\ &= 100 \frac{(\delta_{\text{LCFA}} - \delta_{16:1n-7})}{(\delta_{\text{C}_{26n}\text{-alkanol}} - \delta_{16:1n-7})} \end{aligned} \quad (2)$$

For the available number of samples ( $n=11$ ), the calculated proportions of terrestrially-derived LCFA ranged from 45% to 57% and averaged 51.5% (S.D.=4.8). Given this low variability and to include those samples where compound specific carbon isotopic ratios were not measurable, a constant proportion of 51.5% (i. e. the determined mean) of the LCFA were assumed to derive from a higher land plant

origin, whereas the remaining fraction is attributed to primary production.

#### 3.4. Processes controlling extractable organic matter composition

Among the numerous individual aliphatic lipids detected, some must be considered to be rather unspecific with respect to a distinct source, but others have the potential to trace and differentiate at least between a “marine” and “terrestrial” origin, respectively to indicate autochthonous and allochthonous contributions. Rather than attempting to separate distinct organism groups (e.g. diatoms, dinoflagellates, sea-ice algae) contributing in varying proportions to the organic fraction of the sediments, we defined three general “lipid pools” reflecting organic carbon derived from:

- (A) Primary production (marine phytoplankton, sea-ice algae);
- (B) Secondary inputs (either by feeding of zooplankton, benthic organisms and bacteria on marine phytoplankton);
- (C) Terrestrial sources (higher land plants).

The assignment of each compound to these lipid pools is based upon their structure and known occurrence within specific organisms (see Sections 3.3.1. and 3.3.2.) and was, where possible, verified by compound specific carbon isotope measurements (Section 3.3.3.). The reduction to these groups nonetheless retains all information relevant for an interpretation of the dataset with respect to the major sources and processes leading to the deposition of sedimentary lipids for the area of investigation.

The first group (A) includes compounds derived from photoautotrophic carbon fixation. In contrast to the temperate marine environment, however, in polar seas the habitat of potential primary producers is extended and includes some algae living within, on, or under the ice.

The following fatty acids identified within our sediments have been included in the pool of compounds representing primary production:  $\text{C}_{14:0}$ ,  $\text{C}_{16:1n-7}$ ,  $\text{C}_{16:1n-5}$ ,  $\text{C}_{18:4n-3}$ ,  $\text{C}_{20:4n-6}$ ,  $\text{C}_{20:4n-3}$ ,  $\text{C}_{20:5n-3}$ , and  $\text{C}_{22:6n-3}$ . As revealed by their stable carbon isotopic composition, a portion of the LCFA most



probably also derives from primary production and this fraction is included in the sum of lipids from primary production.

Compounds reflecting secondary inputs (B) comprise those lipids typical of bacteria (odd numbered straight chain, *iso*- and *anteiso*-C<sub>15</sub> and C<sub>17</sub>-fatty acids) and zooplankton (C<sub>18:1n-9</sub>, C<sub>18:1n-7</sub>, C<sub>20:1n-9</sub>, C<sub>20:1n-7</sub>, C<sub>22:1n-11/n-9</sub>).

Terrestrial organic carbon (lipid pool “C”) was traced by the summed amounts of long chain, even numbered *n*-alkanols (C<sub>22</sub>, C<sub>24</sub>, C<sub>26</sub>, C<sub>28</sub>) and long chain, odd numbered *n*-alkanes (C<sub>25</sub>, C<sub>27</sub>, C<sub>29</sub>, C<sub>31</sub>). In addition, the higher land plant derived proportions of LCFA are also included.

Table 4 summarises the amounts of aliphatic lipids for the respective lipid pools, the percentages thereof as well as the fraction of total lipids assigned.

Table 4

Distribution of aliphatic lipids (µg/g TOC) attributed to different lipid pools in surface sediments of northeastern Fram Strait, percentages (normalized to 100%) thereof and fraction of assigned lipids

Lipid pool	Transect	I	I	I	I+III	I	I	I	I	I	I	I	I	I
	Area	AO	AO	AO	YSC	YP	YP	YP	YP	YP	YP	YP	YP	MIZ
	Station	2849	2851	2853	2854	2855	2856	2857	2858	2859	2860	2861	2832	2831
Primary		316	261	443	912	406	442	453	563	461	391	467	587	1331
Secondary		227	168	326	642	342	366	325	451	342	282	304	437	711
Terrestrial		372	276	292	445	258	298	382	302	332	278	316	314	307
% Primary		35	37	42	46	40	40	39	43	41	41	43	44	57
% Secondary		25	24	31	32	34	33	28	34	30	30	28	33	30
% Terrestrial		41	39	28	22	26	27	33	23	29	29	29	23	13
% Assigned lipids		64	61	68	72	66	65	67	68	67	66	66	66	73

Lipid pool	Transect	I	II	II	II	II	II	II	II	II	II	II	III	III
	Area		AO	AO	YSC	YP	YP	YP	YP	YP	MIZ	MIZ		YSC
	Station	2830	2847	2848	55/95	55/97	2836	2835	2834	2863	2864	2865	2838	55/98
Primary		622	398	498	1723	654	469	554	653	607	917	575	553	2576
Secondary		356	271	374	837	379	379	398	291	374	522	329	396	550
Terrestrial		429	335	327	328	334	314	324	305	324	318	199	274	296
% Primary		44	40	42	60	48	40	43	52	47	52	52	45	75
% Secondary		25	27	31	29	28	33	31	23	29	30	30	32	16
% Terrestrial		30	33	27	11	24	27	25	24	25	18	18	22	9
% assigned lipids		65	66	65	74	67	68	70	69	67	65	71	68	76

Lipid Pool	Transect	III	III	III	III	III	III	III	III	III	III	III	III	III
	Area	YSC	YSC	YSC	YSC	YSC	MIZ	MIZ	OW	OW	OW	OW	OW	OW
	Station	2837	55/93	55/92	57/160	57/161	55/77	57/157	55/158	57/153	57/123	57/131	57/138	57/145
Primary		595	2928	2236	3039	1781	6198	2190	1663	1921	1094	898	766	821
Secondary		352	1189	689	1714	632	1129	990	803	512	507	496	403	390
Terrestrial		255	288	286	363	265	286	281	186	214	118	189	77	108
% Primary		50	66	70	59	67	81	63	63	73	64	57	61	62
% Secondary		29	27	21	34	24	15	29	30	19	29	31	32	30
% Terrestrial		21	7	9	7	10	4	8	7	8	7	12	6	8
% assigned lipids		66	76	75	72	73	80	74	73	72	70	66	77	71

Station locations are given in Fig. 1, for area abbreviations (AO, YP, MIZ, OW, YSC) see Table 1 and text. For definition of lipid pools see text. Notice that to account for their mixed source, amounts of LCFA as given in Appendix A have been partitioned into lipids of primary and terrestrial origin upon their carbon isotopic composition as explained in the text. % assigned lipids is the fraction of the sum of primary, secondary and terrestrial lipids out of the total lipids (as given in Table 1).

The relative proportions of assignable lipids varied from 61% at AO-station PS2849 to 80% at the MIZ (PS55/77) and on average comprised about 70%.

In the subsequent sections of this paper, aliphatic lipids derived from lipid pools (A) and (B) will be also referred to as primary and secondary products, lipids or compounds. Notice however, that more generally both are also termed “marine”, in contrast to compounds of a “terrestrial” origin.

### 3.4.1. Distribution of lipid pools in perennially ice-covered areas (Transects I and II)

Fig. 4 gives an overview on the distribution of primary, secondary, and terrestrial derived aliphatics

and the fraction of assignable lipids in two transects across the northern Yermak Plateau. Individual numbers of the respective fractions are provided in Table 4. Most of the stations in *Transects I and II* derive from an area with a permanent sea-ice cover, providing a permanent shade of the upper water column, even in those times of the year when light is available in the high Arctic. While in general primary productivity is supposed to be low under such conditions (Wheeler et al., 1996), adapted algal communities growing in the bottom of the ice, at the ice-water interface, as well as phytoplankton, accounts for average primary production rates of  $275 \text{ mg C m}^{-2} \text{ day}^{-1}$  in the Nansen Basin (Gosselin et al., 1997), north of the Yermak

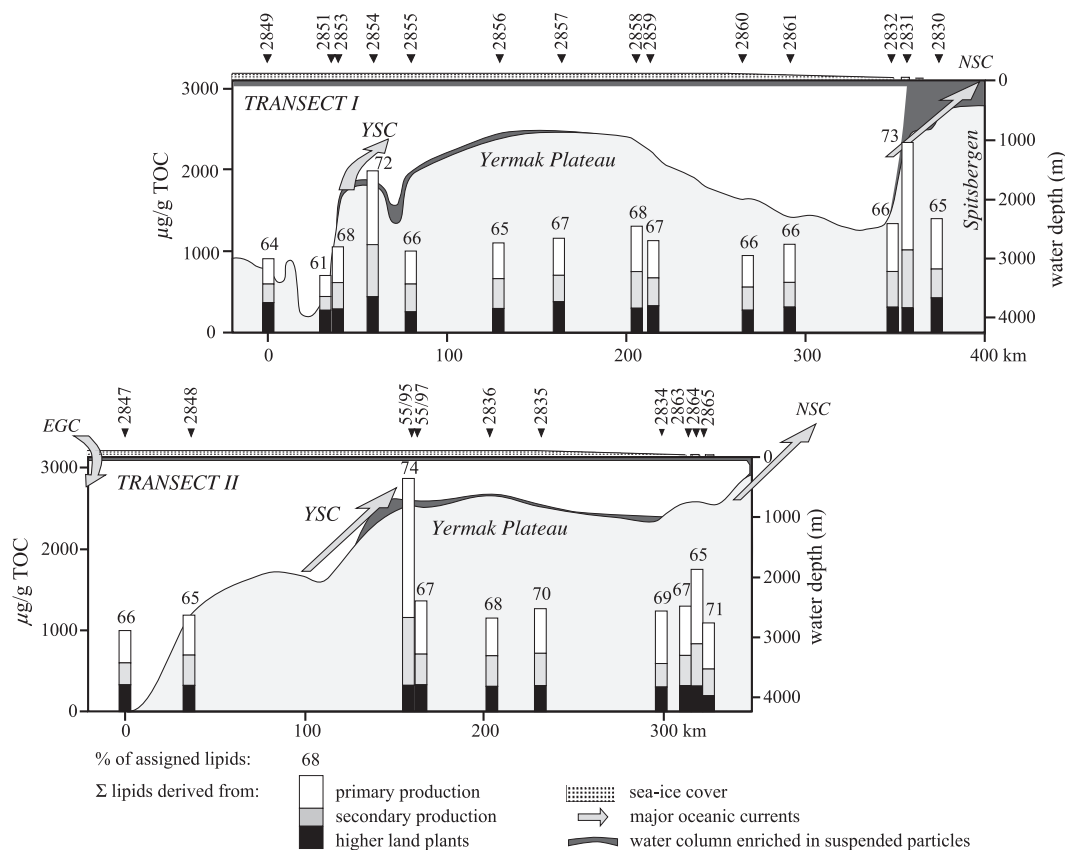


Fig. 4. Total lipids of different sources in surface sediments across the Yermak Plateau. For locations of Transects I and II see Fig. 1. The thickness of ice-cover and water column parts enriched in suspension (adapted from Rutgers van der Loeff et al., 2002) is shown schematically and not scaled in vertical extension. For individual amounts of lipid pools at the respective stations see Table 4. The numbers given to the columns represent percentages of lipid pools A, B, and C of the total lipid amounts.

Plateau. Approximately double this amount of carbon is produced at the MIZ of Fram Strait according to the range of values published ( $426 \text{ mg C m}^{-2} \text{ day}^{-1}$ , Smith et al., 1987;  $7\text{--}720 \text{ mg C m}^{-2} \text{ day}^{-1}$ , Hirche et al., 1991).

With respect to our data, lowest amounts of primary lipids were contained in surface sediments from the northernmost deep-sea stations of *Transects I and II* (261–498  $\mu\text{g/g}$  TOC; PS2849–PS2953, PS2847, PS2848, Fig. 4, Table 4). In contrast, the amounts of primary produced lipids approximately doubled (917–1331  $\mu\text{g/g}$  TOC) in surface sediments close to the MIZ (Stations PS2864 *Transect II*; PS2831, *Transect I*; respectively, Fig. 4; Table 4). As this mirrors the differences in primary production rates when comparing ice-covered deep-sea areas and MIZ (see above), we thus can conclude that the sedimentary contents of lipids attributed to primary productivity are correlated with the surface water productivity. On the Yermak Plateau, the sum of lipids representing primary production ranged from 406–563  $\mu\text{g/g}$  TOC (Stations 2854–2832) in *Transect I* and 469–654  $\mu\text{g/g}$  TOC (Stations PS55/97–PS2863) in *Transect II*. This compares to the amounts detected for stations under seasonally open water conditions on the shallow Spitsbergen shelf (Stations PS2830, PS2865, 622 and 575  $\mu\text{g/g}$  TOC, respectively, Fig. 4, Table 4). On the Yermak Plateau, the concentrations of lipids recording primary production did not vary systematically, i.e. no distinct trend with increasing northwards distance from the ice-edge was observed. Except for this observation, Stations PS2854 (*Transect I*) and PS55/95 (*Transect II*), both situated on the western flank of the Yermak Plateau at comparable water depth, showed enhanced contents (912 and 1723  $\mu\text{g/g}$  TOC) of lipids reflecting primary production, and in the case of Station PS55/95, even exceeding the amounts at the MIZ. These elevated amounts must reflect contributions from an additional source other than surface water productivity and we discuss this aspect later. Independent to our study, the above described characteristics of water and sea-ice related primary productivity recorded in surface sediments, including the anomaly on the western flank of the Yermak Plateau, have been described by means of chloroplast pigments determined at identical stations (Soltwedel et al., 2000).

The second lipid pool contained in surface sediments on the Yermak Plateau comprises compounds derived of secondary production, mainly from zooplankton and bacterial activity. Based upon traditional views on food web structures, the organic carbon source of these organisms originates from primary production, and this is supported by the similarity in the carbon isotopic composition of the fatty acids from bacteria and zooplankton compared to the fatty acids derived from primary production (see Fig. 3). However, comparison at the amounts of primary lipids and those of secondary origin (Fig. 4, Table 4) revealed an overall positive correlation, and indeed, this can be expressed by a linear relationship in the form of  $\Sigma \text{ secondary lipids} = 0.599 * \Sigma \text{ lipids primary production}$  ( $R^2 = 0.73$ ). Thus, at all stations of *Transects I and II* the amounts of zooplankton and bacterial derived lipids are at about 60% of the lipids attributed to primary production. This positive correlation is surprising, as normally one would expect an inverse relationship between primary and secondary producers, i.e. a higher consumption should lower the amounts of primary produced organic carbon. As this is not observed in our case, we hypothesise that most of the primary produced lipids in surface sediments must have rapidly escaped the water column without being significantly impacted by microbial degradation and zooplankton grazing. This was already mentioned with respect to the fatty acid compositions at all stations (e.g. high ratios of  $\text{C}_{16:1}/\text{C}_{16:0}$ , high relative proportions of PUFA, see Section 3.3.1.). The expressed relationship of primary and secondary lipids in the surface sediments might thus be regarded as a result of effective export of a distinctive part of primary produced organic matter (aggregated phytodetritus, faster sinking and larger species, e.g. diatoms, ballasted by lithogenic matter). In contrast, another part of primary producers remains suspended in the upper water column and is available for utilisation in the bacterial and zooplankton food loop and thus reaches the seafloor as secondary lipids. Additionally, fecal pellets might provide another ballast effect leading to the rapid export of primary produced organic matter. It is known that the abundance of distinct phytoplankton species blooming at the ice-edge changes seasonally in species composition and is usually dominated by diatoms in spring (e.g. Andreassen et al., 1996). In

summer and early autumn (September) phytoplankton is composed primarily of flagellates (Rat'kova and Wassmann, 2002). The grazing pressure of calanoid copepods in summer and autumn is much higher than in spring, because they have to accumulate large lipid reserves for overwintering. Therefore zooplankton feeding and the vertical export via zooplankton fecal pellets might be more important towards the end of the phytoplankton bloom. Diatoms can be rapidly exported from the upper water column and reach great depths, with aggregation playing a prominent role in this process (Alldredge and Jackson, 1995), whilst most flagellates remain suspended.

Although we observe distinctively lower amounts of both primary and secondary lipids over the Yermak Plateau compared to the ice-edge of both *Transects* (Fig. 4), this is not correlated with distance from the ice-edge in northwards direction. Rather, concentration levels remain relatively uniform up to a distance of ca. 200 km north of the MIZ and also compare to the levels in seasonally open waters south of the MIZ. Schlichtholz and Houssais (1999a) identified a weak influence of Atlantic water from a southern direction over the Yermak Plateau, called the Yermak Plateau Current (YPC). This Atlantic water, however was found to be denser, colder and fresher, i.e. more admixed, than the Atlantic water on the western side of the Plateau (Rudels et al., 2000), likely due to upwelling of colder waters caused by cyclonic surface circulation (Muench et al., 1992) and an intensified tidal mixing (Hunkins, 1986) over the Yermak Plateau. Though weak, this inflow leads to advection of phyto- and zooplankton (or organic matter thereof) from the more productive open waters and/or from the MIZ over the Plateau, as indicated by the presence of Atlantic diatom species and copepods (e.g. *Calanus finmarchicus*) from sediment traps under sea-ice (Falk-Petersen et al., 2000). In summary with admixing of the water-column by upwelling and tidal motion (see above), the overall comparable amounts of primary and secondary lipids in surface sediments on the Yermak Plateau are likewise explained. Benthic activity might serve as further explanation for the uniform and lower lipid contents on the Yermak Plateau compared to the ice-edge. We cannot evaluate reworking of organic matter by benthic meio-

and macrofauna due to the lack of appropriate marker compounds. Nevertheless, reworking by benthic bacteria seems to be only of subordinate importance for the lipid distribution on the Yermak Plateau, as indicated by sedimentary bacterial fatty acids comparable in amounts to the other regions of the investigation area (Table 3). However, in relative terms, branched fatty acids are slightly enhanced (8%) on the Yermak Plateau and Arctic Ocean stations compared to the other areas (4–5%, Table 3). The same was noted by Soltwedel et al. (2000), as their data only showed a weak trend for higher proportions of bacterial biomass at stations with lower organic matter availability at the seafloor (i.e. on the Yermak Plateau and the northern, permanently ice-covered areas), whereby bacterial biomass was approximately 10% higher at northern stations.

Compared to marine primary and secondary lipids, the amounts contributed by higher land plants are low overall in *Transects I and II* (Fig. 4), ranging from 258–445 and 199–335  $\mu\text{g/g}$  TOC, respectively (Table 4). Higher concentrations in *Transect I* found at the southernmost station PS2830 on the shallow Spitsbergen shelf are probably derived from coastal inputs, as suggested by enhanced suspended load in this part of the *Transect* (see Fig. 4, Rutgers van der Loeff et al., 2002). However, compared to the amounts of terrestrial-derived compounds in sediments nearby, this supply seems to be only of local importance. In the southern part and shallow shelf region of *Transect II*, no signs of such a local supply of terrestrial-derived lipids were observed, in fact, concentrations of higher land plant compounds were lowest at station PS2865. Therefore, the nearby landmass seems not to be a significant source explaining the amounts of higher land plant lipids on the Yermak Plateau. Rather we presume that they derive from sea-ice transport of terrestrial derived organic matter on the Eurasian shelf areas via the Transpolar Drift. CPI values of suspended matter transported from the Ob and Yenisei rivers to the Kara Sea are up to 6.5 (Hefter, unpublished data) and range from three to four in surface sediments of the northern Kara Sea (Fernandes and Sicre, 2000). Ice exiting the Kara Sea to the north will influence the Fram Strait, Svalbard, and Barents Sea regions and was proposed as a potential transport agent of

contaminants entrained from atmospheric, marine, and riverine sources with a mean travel time of 2–3 years for a piece of ice from the Kara Sea to Fram Strait (Pfirman et al., 1997 and references therein). In the Fram Strait, no direct riverine input of fresh terrestrially derived material is expected due to the lack of major rivers nearby. The CPI values in surface sediment samples of the ice-covered Fram Strait and on the Yermak Plateau range from 1.8 to 3.0 (Appendix B). The somewhat reduced CPI, compared to values of the proposed Kara Sea source area, might thus result from (microbial) reworking during sea-ice transport lasting several years. Based on the sedimentary CPI values, we also suspect the atmospheric transport and direct deposition of terrestrial organic matter to the Fram Strait is of minor importance, as atmospheric input of land-derived compounds to the ocean takes place in a matter of days (Gagosian and Peltzer, 1985), whereby higher CPI values (e.g. up to 7.6 in dust samples over the central eastern Atlantic; Schefuß et al., 2003) are normally preserved.

In both *Transects*, stations on the western flank of the Yermak Plateau differed from the general trends of lipid distribution and from stations nearby. At station PS2854 (*Transect I*), the amounts of lipids derived from primary and secondary produc-

tion were enhanced (912 and 642  $\mu\text{g/gTOC}$ , respectively) and comparable to the amounts found at the MIZ (albeit in a distance of 250 km) than surrounding stations. This was even more obvious for station PS55/95 of *Transect II* (Fig. 4), as there the concentrations of primary and secondary lipids even exceeded those of the MIZ (stations PS2863, PS2864). These locally enhanced abundances of marine lipids cannot be easily explained by a supply exclusively from the upper water column, and likely are sourced elsewhere.

### 3.4.2. Distribution of lipid pools tracking the WSC/YSC inflow (*Transect III*)

Samples included in *Transect III* were chosen at about a constant water depth (1000–2000 m) to follow the Atlantic water inflow from the WSC at the southern tip of Spitsbergen (77°N) and the YSC up to 82°N at the northwestern flank of the Yermak Plateau. Fig. 5 shows the distribution of the respective lipid pools along this *Transect* in conjunction with intermediate to deep currents. Compared to *Transects I and II* (Fig. 4), it is obvious that, with the exception of terrestrial inputs, the distribution of lipid classes behaves differently. The overall variability is greater, but also lipids reflecting primary production reach higher amounts.

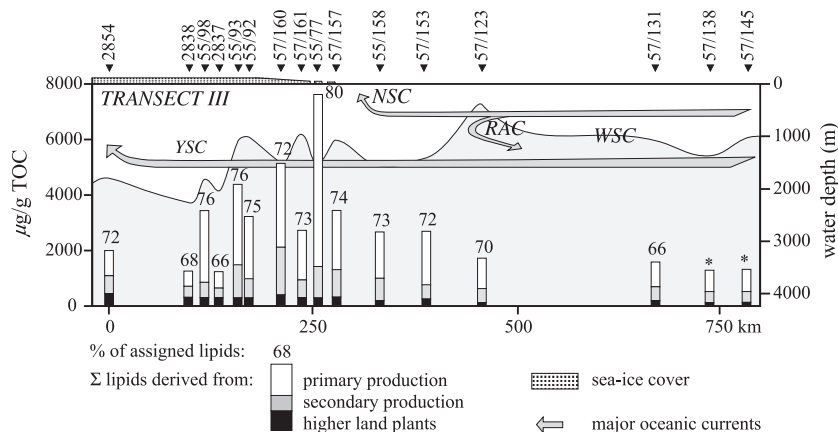


Fig. 5. Total lipids of different sources in surface sediments following the inflow of Atlantic water in eastern Fram Strait from 76°N to 82°N to the western flank of the Yermak Plateau. For locations of stations see Fig. 1. The thickness of the ice-cover is schematically and not scaled in vertical extension. For individual amounts of lipid pools at the respective stations see Table 4. The numbers given to the columns represent percentages of lipid pools A, B, and C of the total lipid amounts. \*Amounts of higher land plant lipids slightly underrepresented, as *n*-alkanes were not determined.

Station PS2854, which was discussed in the *Transect I* survey, is also included in *Transect III* and can be used for direct comparison. Relative to most other stations in *Transect III* this station has lower amounts of primary and secondary lipids. The northernmost station PS2854 nonetheless contains primary and secondary lipids in contents equal or even slightly higher than open water stations in the south on the western Spitsbergen shelf (57/131; 57/138, 57/145, Fig. 5). From sediment traps deployed north and west of Spitsbergen (Andreassen et al., 1996; Owrud et al., 2000) it was found, that vertical export of marine phytoplankton and fecal pellet aggregations are (a) higher in open water areas than under sea-ice, (b) lower than at the MIZ and (c) that the highest variability occurs at the MIZ. This can be seen as a basic conceptual model with respect to the distribution of primary productivity and associated vertical fluxes in sections from permanent ice-cover to the MIZ to open water conditions, as also proposed for the Greenland Sea (Peinert et al., 2001). In line with this model, highest total lipid concentrations of primary production at station PS55/77 argue for a direct benthic–pelagic coupling, i.e. the surface sedimentary lipid record at this station reflects enhanced primary production and export from the MIZ. This also seems to be true for the southern, open water part of *Transect III*. The increase in surface sedimentary lipids derived from primary production (comparing open water stations PS57/145–PS57/123 (766–1094  $\mu\text{g/g}$  TOC) with open-water stations close to the MIZ PS57/157–PS57/153 (1663–1921  $\mu\text{g/g}$  TOC) might thus indicate a higher productivity at northern open water stations. This could be explained by a higher availability of nutrients closer to the MIZ due to upwelling and ice-melt. However, examination of the contents of marine lipids in surface sediments starting from the MIZ in northwards direction under the ice, the whole region on the western flank of the Yermak Plateau behaves, for at least a distance of about 200 km, different than expected. Starting from the ice-edge at station PS55/77, the surface sedimentary amounts of primary lipids are (a) comparable and even higher than at the open water stations, (b) highly variable and (c) show a distinct decrease in concentration with increasing distance from the MIZ. Thus, in contrast to the MIZ and the open water stations and also in

contrast to most stations of *Transects I and II*, the distribution of primary lipids is clearly unrelated to upper water column productivity. Rather, their distribution on the western slope of the Yermak Plateau seems to be primarily coupled to the Yermak Slope Current. Recently it was described that this current causes a distinct benthic nepheloid layer (BNL) along the western flank of the Yermak Plateau (Rutgers van der Loeff et al., 2002, see also Fig. 4). By measuring  $^{234}\text{Th}$  depletion in the bottom water mass of the Yermak slope, these authors also provided evidence for the existing of a settling-resuspension loop in the order of 80–120  $\text{mg suspension m}^{-2} \text{ day}^{-1}$  and with an average particle residence time of 1–2 months within the BNL. In the surface sediments  $^{234}\text{Th}$  is enriched, indicating removal of particulate matter from the BNL. Elevated numbers of suspension feeders in the Yermak slope and high amounts of fresh organic matter (chlorophyll-*a*) in the surface sediments indicate a major lateral advection of primary produced matter (Soltwedel et al., 2000; Rutgers van der Loeff et al., 2002). At stations north of the sea-ice cover, primary produced material concentrations (2000–4000  $\mu\text{g/g}$  TOC) exceeded those from neighbouring Yermak Plateau stations. The influence of the YSC, however, monotonically decreases with increasing distance from the MIZ, suggesting a gradually weakening velocity of the YSC. Nevertheless the lateral advection of allochthonous particulate organic matter via the WSC/YSC appears to be the major process controlling deposition of primary and secondary produced organic matter in surface sediments of this permanently ice-covered and low productive zone of the northern Fram Strait (Figs. 4 and 5).

#### 3.4.3. “Marine” vs. “terrigenous” organic matter

The proportions of marine and terrestrial organic carbon in the Arctic shelf, adjacent continental slope and also central Arctic basin sediments have been estimated using a variety of organic-geochemical approaches. These studies generally indicate that organic carbon in most of these settings is dominated (i.e. >50%) by allochthonous, river-supplied terrestrial organic carbon (Schubert and Stein, 1997; Macdonald et al., 1998; Stein and Fahl, 2000; Mueller-Lupp et al., 2000; Goñi et al., 2000; Belicka et al., 2002, amongst others). Based on

bulk stable carbon isotopic evidence, however, Schubert and Calvert (2001) calculated that the terrestrial fraction in eastern central Arctic surface sediments and on the Yermak Plateau could be as low as 30%, although the same authors calculated terrestrial organic carbon contributions as high as 48% (using  $C_{org}/N_{org}$  ratios).

The average proportions for the three distinctive lipid pools are summarised for the different regions of the study area (Fig. 6). Overall, primary and secondary marine lipids dominate relative to terrestrial-derived lipids in the surface sediments. Surface sediments in the northernmost, permanently ice-covered areas (AO, Arctic Ocean >2000 m water depth; YP, Yermak Plateau <1000 m water depth) exhibited highest contributions of terrestrial-derived compounds (27–33%) (Fig. 6). Apart of this, the region influenced by the Yermak Slope Current (YSC), compa-

rable in ice-cover and positioning to the YP, on average contained only 11% terrestrial lipids. Similarly, areas located further south, (MIZ, OW, Fig. 6) also contained only about 8–9% terrestrial-derived compounds, despite their proximity to the Spitsbergen shelf.

The subdivision of marine-derived compounds into those of primary and secondary origin revealed a relative constant percentage (26–30%) of secondary lipids for all areas. Highest absolute amounts of total lipids but also from primary production (see numbers on top of Fig. 6) are from open water and Atlantic water influenced regions. This might indicate that the zooplankton and bacterial community is not able to utilize the locally enhanced primary productivity at the eastern Fram Strait and especially at the MIZ with similar efficiency than in heterotrophic communities in areas of lower productivity.

It is interesting to note that assignment of both, primary and secondary lipids as marine-derived compounds, results in terrestrial contributions for the northernmost part of the study area (27–33%) similar in proportion to that obtained from bulk organic carbon isotopic compositions in the adjacent central Arctic Ocean. Additionally, we also observed a gradual increase in the terrestrial proportions towards the Central Arctic Ocean (also expressed in the 27% vs. 33% difference between YP and AO, Fig. 6). It is also notable that if the fraction of secondary lipids was not accounted for it would enhance the estimated terrestrial proportions for some samples to >50% (cf. Table 4). For the deeper parts of the investigation area and also for most parts of the northeastern Yermak Plateau, our data are thus consistent with previous estimates. However, enhanced marine contributions (mean 60–64%, max. 81%, Fig. 6, Table 4) at the MIZs and open waters northwest and north off Spitsbergen clearly differentiates this Arctic Ocean shelf region from the Siberian shelves.

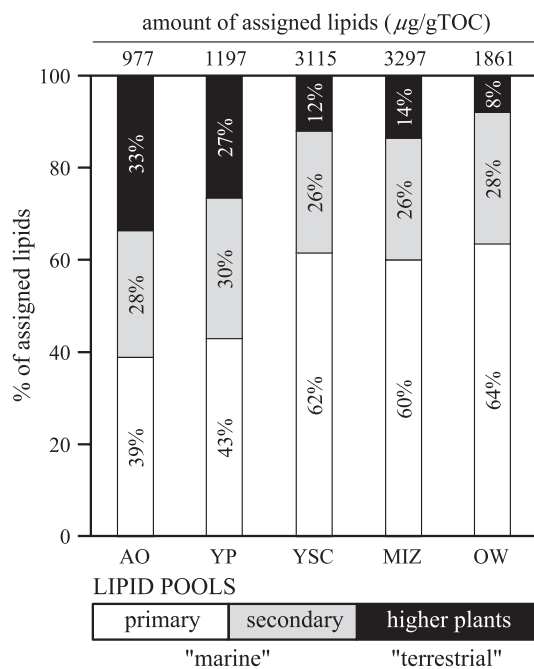


Fig. 6. Relative mean proportions of lipid pools for different areas in northeastern Fram Strait. Numbers on top represent mean total amount of the summed fractions. AO: Arctic Ocean (>2000 m), YP: Yermak Plateau (1000–1500 m), MIZ: Marginal Ice Zone, OW: Open water, YSC: Yermak Slope Current. Individual percentages for all stations are given in Table 4.

#### 4. Conclusions

Spatial variations in the molecular and carbon isotopic composition of the aliphatic lipid fraction in surface sediments from the northeastern Fram Strait

and on the Yermak Plateau provide important information about organic carbon depositional processes. About 80% of the identified lipids could be assigned to one of three lipid pools, based on chemical structure and carbon isotopic composition: (a) primary production, (b) secondary origin (zooplankton, bacteria) and (c) terrestrial-derived compounds. Most of the inferred origins of specific lipids were supported by their carbon isotopic composition, however LCFA of supposed higher land plant origin appeared to reflect a mixture of marine and terrestrial inputs. The northeastern Fram Strait and the Yermak Plateau is dominated by considerable amounts of autochthonous marine carbon from both, primary (mainly diatoms) and secondary (zooplankton, bacteria) producers. A significant fraction of lipids derived from primary production successfully escapes degradation in the water column and dominates over secondary lipids, suggesting an important surface water-benthic coupling. Maximum marine biomarker concentrations in surface sediments close to, or at the ice-edge northwest and north off Spitsbergen reflected the development of large phytoplankton blooms associated with the MIZ. Sediments from the western Yermak Slope are outstanding from the organic matter record of the MIZ, but also in contrast to stations nearby on the shallower Yermak Plateau of equivalent ice-conditions and low productivity. This specific area on the western flank of the Yermak Slope is influenced by a current-driven lateral advection of particulate organic matter in a northwards direction. We found a lipid signature characteristic of the MIZ over distances up to 200 km from the MIZ. We suggest a qualitative and quantitative effective transport in a suspension–resuspension settling-loop. With increasing distance from the MIZ, however, the transport and deposition of marine organic matter decreases towards north, indicating a gradual weakening of the current velocity.

Terrestrial lipids are also supplied to this area, but provide only a minor fraction because of the overall strong imprint of primary and secondary lipids. The presence of these terrestrial compounds indicates the export from plant wax derived material to the Yermak Plateau and eastern Fram Strait. As the absolute concentrations of terrestrial lipids are roughly constant throughout the region, the terrestrial contribution represents a diffuse background signal, most probably as a result of long range sea-ice transport from the north, with minor contributions of the nearby Spitsbergen landmass. The imposed signal of primary and secondary production is notably weaker downslope the northern Yermak Plateau towards the deeper (>2000 m) central Arctic Ocean. As a consequence, the proportion of terrestrial lipids increases up to about 40% towards values previously recognised in the deep central Arctic basins.

This study shows that organic-geochemical molecular and isotopic measurements can provide an enhanced insight in organic carbon dynamics, but also pinpoint the influence of ocean-currents for the preservation and long-range redistribution of marine organic matter in sediments.

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## Appendix A

Concentrations ( $\mu\text{g/g}$  TOC), percentual composition and ratios of fatty acids in surface sediments from the eastern Fram Strait and on the Yermak Plateau

Compound	assigned lipid pool	Transect													
		Area	I AO	I AO	I AO	I+III YSC	I YP	I YP	I YP	I YP	I YP	I YP	I YP	I YP	I MIZ
	Station	2849	2851	2853	2854	2855	2856	2857	2858	2859	2860	2861	2832	2831	
<i>n-Saturates</i>															
14	A	40	32	48	98	44	54	46	57	48	43	54	78	113	
15	B	13	10	15	28	13	16	13	17	15	13	13	19	24	
16		153	119	169	339	161	190	185	230	189	157	183	263	436	
17	B	4	6	9	23	10	10	6	9	8	9	5	7	30	
18		47	34	41	70	31	37	43	40	37	34	34	41	72	
20		28	19	19	33	16	20	29	23	22	20	21	24	22	
21		7	5	4	6	7	6	5	6	4	7	6	6	11	
22		35	25	26	47	27	30	36	36	32	31	28	37	32	
23		11	4	9	19	12	12	14	13	13	10	14	12	11	
24	A+C	54	55	59	115	62	68	70	72	75	65	58	62	71	
25		12	12	12	18	11	14	20	15	17	15	17	19	14	
26	A+C	57	56	59	104	55	60	63	68	67	63	60	61	60	
27		13	15	13	20	13	13	16	15	14	16	15	12	11	
28	A+C	45	23	43	83	25	45	41	39	38	33	31	34	45	
<i>Monounsaturates</i>															
16:1 <i>n</i> -7	A	119	97	202	470	206	223	231	270	219	174	243	318	625	
16:1 <i>n</i> -5	A	27	24	39	86	36	14	57	56	43	39	60	31	108	
18:1 <i>n</i> -9	B	51	24	52	103	64	62	63	103	64	45	50	71	159	
18:1 <i>n</i> -7	B	43	41	108	226	99	111	89	131	102	89	101	152	266	
20:1 <i>n</i> -9	B	8	3	28	9	27	21	10	20	12	14	5	7	36	
20:1 <i>n</i> -7	B	5	4	3	17	3	4	10	9	3	4	14	10	9	
22:1 <i>n</i> -11, 22:1 <i>n</i> -9*	B	38	24	15	40	31	32	31	47	28	25	27	34	33	
<i>Polyunsaturates</i>															
18:2		13	5	9	13	11	27	30	38	16	9	25	48	30	
18:4 <i>n</i> -3	A	34	26	36	47	22	18	6	26	29	24	9	24	38	
20:2		10	8	8	12	7	9	13	8	7	8	5	14	9	
20:4 <i>n</i> -6	A	4	4	15	20	8	17	15	24	12	12	12	27	112	
20:5 <i>n</i> -3	A	5	3	15	23	14	20	12	29	10	8	14	28	222	
20:4 <i>n</i> -3	A	6	4	6	11	4	7	0	7	5	6			13	
22:6 <i>n</i> -3	A	5	6	4	11	3	5	2	7	8	7	3	5	15	
<i>Branched</i>															
i-15	B	23	19	36	70	35	41	40	42	42	31	31	50	53	
ai-15	B	29	25	44	95	42	49	46	51	51	38	42	65	64	
i-17	B	5	5	7	16	9	10	8	11	8	7	7	9	21	
ai-17	B	8	7	9	15	9	10	9	11	9	7	9	13	16	
Total ( $\mu\text{g/g}$ TOC)		952	744	1162	2287	1117	1255	1259	1530	1247	1063	1196	1581	2781	
% assigned		65	67	73	75	74	71	69	72	72	71	71	70	77	
% saturated		55	56	45	44	44	46	47	42	46	49	45	43	34	
% MUFA		31	29	38	42	42	37	39	42	38	37	42	39	44	
% PUFA		8	8	8	6	6	8	6	9	7	7	6	9	16	
% branched		7	8	8	9	9	9	8	8	9	8	7	9	6	
<i>Ratios</i>															
16:1/16:0		1.0	1.4	1.6	1.5	1.2	1.6	1.4	1.4	1.4	1.7	1.3	1.7		
18:1/18:0		1.9	3.9	4.7	5.3	4.7	3.5	5.9	4.5	3.9	4.4	5.4	5.9		

(continued on next page)

## Appendix A (continued)

Compound	assigned lipid pool	Transect	I	II	II	II	II	II	II	II	II	II	III	III
		Area	AO	AO	YSC	YP	YP	YP	YP	MIZ	MIZ		YSC	
		Station	2830	2847	2848	55/95	55/97	2836	2835	2834	2863	2864	2865	2838
<i>n-Saturates</i>														
14	A	78	48	65	99	62	49	55	42	68	110	55	66	200
15	B	20	12	17	19	14	14	17	13	14	22	11	19	29
16		276	171	225	349	250	186	203	177	242	366	186	215	521
17	B	21	8	7	15	7	9	8	5	6	12	6	12	11
18		51	43	47	59	41	38	41	40	40	66	29	45	56
20		27	23	25	21	9	22	20	20	22	30	13	18	25
21		5	7	6	4	6	7	7	6	6	7	3	7	7
22		40	32	35	33	38	30	29	23	28	33	19	26	27
23		12	8	11	20	13	10	13	10	11	10	6	13	12
24	A+C	82	65	65	69	68	63	58	48	65	62	35	68	60
25		19	17	17	15	22	12	12	18	21	17	8	14	20
26	A+C	81	64	69	65	72	54	49	54	70	62	32	65	61
27		16	18	16	14	18	11	14	11	26	19	14	13	19
28	A+C	70	68	46	72	54	27	36	33		39	38	40	38
<i>Monounsaturates</i>														
16:1 <i>n</i> -7	A	269	175	257	815	309	227	286	332	312	429	261	247	1012
16:1 <i>n</i> -5	A	28	29	34	408	44	39	52	165	38	40	44	68	947
18:1 <i>n</i> -9	B	61	44	67	323	89	67	67	55	90	232	64	58	198
18:1 <i>n</i> -7	B	99	83	125	178	115	128	140	86	99	34	114	143	28
20:1 <i>n</i> -9	B	23	9	7	19	14	9	15	7	9	16	21	15	24
20:1 <i>n</i> -7	B	5	6	13	67	15	7	2	14	15	12	9	2	44
22:1 <i>n</i> -11, 22:1 <i>n</i> -9*	B	33	30	19	93	23	38	29	23	33	32	21	28	75
<i>Polyunsaturates</i>														
18:2		20	6	21	36	50	13	13	28	28	125	22	10	145
18:4 <i>n</i> -3	A	41	36	10	28	25	27	28	7	14	49	18	24	47
20:2		13		11	7		9	5	9	15	26	5	8	13
20:4 <i>n</i> -6	A	18	4	18	85	53	24	19	16	30	93	65	17	61
20:5 <i>n</i> -3	A	62	7	16	165	62	18	27	16	74	107	62	26	227
20:4 <i>n</i> -3	A	6		7	11		7	5	7			7	8	
22:6 <i>n</i> -3	A	7	3	4	12	5	8	13	3	6	10	12	13	5
<i>Branched</i>														
i-15	B	30	28	41	47	36	42	45	32	39	57	29	43	48
ai-15	B	41	37	59	51	44	47	54	41	49	71	33	55	65
i-17	B	11	7	9	16	11	10	10	7	11	18	11	10	15
ai-17	B	12	7	10	9	11	8	11	8	9	16	10	11	13
Total (µg/g TOC)		1577	1095	1379	3224	1580	1260	1383	1356	1490	2222	1263	1407	4053
% assigned		70	70	70	83	72	73	74	75	71	69	76	74	79
% saturated		51	53	47	26	43	42	41	37	42	38	36	44	27
% MUFA		33	34	38	59	39	41	43	50	40	36	42	40	57
% PUFA		11	5	6	11	12	8	8	6	11	18	15	8	12
% branched		6	7	9	4	6	8	9	6	7	7	7	8	3
<i>Ratios</i>														
16:1/16:0		1.1	1.2	1.3	3.5	1.4	1.4	1.7	2.8	1.4	1.3	1.6	1.5	3.8
18:1/18:0		3.1	3.0	4.1	8.5	5.0	5.1	5.0	3.5	4.7	4.0	6.1	4.5	4.0

(continued on next page)

## Appendix A (continued)

Compound	assigned lipid pool	Transect	III	III	III	III	III	III	III	III	III	III	III	III	III
		Area Station	YSC 2837	YSC 55/93	YSC 55/92	YSC 57/160	YSC 57/161	MIZ 55/77	MIZ 57/157	OW 55/158	OW 57/153	OW 57/123	OW 57/131	OW 57/138	OW 57/145
<i>n-Saturates</i>															
14	A		62	262	223	340	177	591	221	164	188	122	95	63	36
15	B		16	35	31	57	28	51	30	26	28	25	23	19	16
16			218	719	572	1194	512	1353	627	485	582	375	291	192	242
17	B		15	30	10	25	8	13	27	12	9	27	17	13	11
18			34	85	53	112	49	72	54	65	49	50	46	30	51
20			15	22	21	48	20	23	31	39	19	12	16	11	22
21			7	5	8	10	6	7	5	3	6	2	4	3	5
22			25	38	28	47	27	27	25	22	24	14	20	10	17
23			10	19	10	19	10	10	9	8	8	5	7	4	6
24	A+C		64	91	64	95	61	78	54	54	55	36	48	26	40
25			11	10	18	27	14	14	15	10	13	5	6	7	10
26	A+C		61	70	62	99	58	61	57	52	57	25	45	22	46
27			8	89	29	54	24	12	20	11	26	10	7	12	20
28	A+C		20		33	88	33		51		46			49	15
<i>Monounsaturates</i>															
16:1 <i>n</i> -7	A		309	1575	1256	1956	1068	3612	1307	940	1309	640	488	248	318
16:1 <i>n</i> -5	A		64	81	90	86	61	93	125	58	65	66	72	235	273
18:1 <i>n</i> -9	B		129	406	150	1047	136	176	246	126	105	73	84	76	159
18:1 <i>n</i> -7	B		22	380	264	125	227	591	435	399	159	236	184	151	35
20:1 <i>n</i> -9	B		17	25	16	46	17	31	42	16	13	13	18	14	15
20:1 <i>n</i> -7	B		6	80	28	39	31	36	51	51	25	13	44	28	41
22:1 <i>n</i> -11, 22:1 <i>n</i> -9*	B		31	44	33	36	31	92	22	29	27	5	11	6	28
<i>Polyunsaturates</i>															
18:2			58	38	70	123	63	97	67	59	63	15	23	26	93
18:4 <i>n</i> -3	A		11	96	36	76	59	231	74	19	72	40	36	27	26
20:2			7	6	24	98	22	63	21	38	23	14	4	16	32
20:4 <i>n</i> -6	A		31	288	111	208	78	800	87	140	53	59	48	66	47
20:5 <i>n</i> -3	A		36	500	432	197	256	773	224	282	150	129	94	65	45
20:4 <i>n</i> -3	A		6	38		28		15	64				7		22
22:6 <i>n</i> -3	A		6	10	11	11	8	16	9	9	7	8	13	15	5
<i>Branched</i>															
i-15	B		44	71	53	74	57	49	47	43	50	37	41	33	28
ai-15	B		48	79	56	96	67	51	54	55	66	51	47	32	32
i-17	B		13	23	24	101	18	21	20	24	16	14	16	11	17
ai-17	B		11	16	24	68	12	18	16	22	14	13	11	20	8
Total (µg/g TOC)			1415	5231	3840	6630	3238	9077	4137	3261	3327	2134	1866	1530	1761
% assigned			72	80	78	74	77	82	79	77	76	76	77	80	72
% saturated			40	28	30	33	32	25	30	29	33	33	33	30	30
% MUFA			41	50	48	50	49	51	54	50	51	49	48	50	49
% PUFA			11	19	18	11	15	22	13	17	11	12	12	14	15
% branched			8	4	4	5	5	2	3	4	4	5	6	6	5
<i>Ratios</i>															
16:1/16:0			1.7	2.3	2.4	1.7	2.2	2.7	2.3	2.1	2.4	1.9	1.9	2.5	2.4
18:1/18:0			4.4	9.2	7.8	10.5	7.4	10.7	12.6	8.1	5.4	6.2	5.8	7.6	3.8

Station locations are given in Fig. 1, for area abbreviations (AO, YP, YSC, MIZ, OW) see text and Table 1. \*=sum of both isomers, MUFA=monounsaturated fatty acids, PUFA=polyunsaturated fatty acids. Letters A, B, C indicate assignment of fatty acids to the lipid pools explained in Section 3.4, % assigned is the fraction of the sum thereof to the total fatty acids. Notice that the amounts of long chain *n*-saturates represent a mixture of lipid pools A and C, as revealed by their stable carbon isotopic composition (see Section 3.3.3).

## Appendix B

Concentrations ( $\mu\text{g/g}$  TOC) of *n*-alkanes and CPI in surface sediments from the eastern Fram Strait and on the Yermak Plateau

<i>n</i> -Alkane	assigned lipid pool	Transect													
		Area	I	I	I	I+III	I	I	I	I	I	I	I	I	I
		Station	2849	2851	2853	2854	2855	2856	2857	2858	2859	2860	2861	2832	2831
15			0.5	1.1	0.9	1.6	5.0	4.0		1.4	1.1	0.7	2.3	1.4	1.6
16			2.5	4.9	4.0	5.4	11.5	9.9	1.3	5.7	4.9	4.1	6.4	4.8	7.2
17			6.7	9.5	8.9	8.0	15.2	15.0	6.6	10.3	10.5	9.0	11.4	10.7	11.9
18			8.6	12.3	10.7	10.6	15.2	15.1	9.9	11.7	12.3	12.1	13.0	11.7	15.9
19			12.2	16.0	13.9	14.6	20.0	20.3	14.6	15.9	16.3	16.3	16.0	14.5	23.2
20			11.6	14.4	13.0	11.4	15.7	16.1	13.6	13.0	14.2	14.8	14.8	14.0	17.2
21			15.1	15.8	14.6	12.5	16.5	17.2	15.9	14.8	15.8	16.6	16.5	15.9	18.4
22			14.3	15.0	13.7	11.6	16.0	16.3	15.0	14.3	15.2	15.3	15.2	15.0	17.8
23			20.8	18.1	17.0	13.2	18.0	18.9	19.7	17.3	18.5	19.0	19.5	19.8	19.6
24			13.4	13.1	12.5	10.0	13.4	13.8	13.9	12.3	13.5	13.6	13.7	14.0	14.8
25	C		22.5	18.1	17.3	12.8	17.6	18.6	21.2	18.0	19.1	18.9	19.6	20.5	19.0
26			11.0	10.9	10.7	8.5	11.6	11.9	11.8	10.6	11.4	11.2	11.2	11.7	12.2
27	C		29.5	21.8	20.5	14.5	20.3	21.9	27.4	22.9	23.5	22.5	24.1	25.4	21.7
28			8.5	9.6	9.1	7.5	10.2	10.4	10.3	9.6	10.2	9.8	9.4	10.3	11.0
29	C		33.1	23.2	22.0	15.4	21.2	23.5	31.0	24.8	25.4	23.9	25.5	26.7	23.1
30			5.0	6.4	5.9	5.1	6.8	7.2	7.1	6.7	7.0	6.4	6.4	7.0	7.6
31	C		31.1	20.9	19.7	14.0	18.3	20.4	28.8	22.0	22.9	21.2	22.6	24.1	19.3
32			2.8	3.7	3.6	3.1	4.3	4.4	4.0	3.9	4.0	3.7	3.6	4.0	4.8
Total ( $\mu\text{g/g}$ TOC)			249.2	234.8	218.0	179.8	256.8	264.9	252.1	235.2	245.8	239.1	251.2	251.5	266.3
$\Sigma$ assigned to Q ( $\mu\text{g/g}$ TOC)			116.2	84.0	79.5	56.7	77.4	84.4	108.4	87.7	90.9	86.5	91.8	96.7	83.1
% assigned to C			47	36	36	32	30	32	43	37	37	36	37	38	31
CPI (22–32)			3.0	2.1	2.1	1.8	1.9	1.9	2.5	2.2	2.1	2.1	2.3	2.2	1.8

<i>n</i> -Alkane	assigned lipid pool	Transect													
		Area	I	II	II	II	II	II	II	II	II	II	II	III	III
		Station	2830	2847	2848	55/95	55/97	2836	2835	2834	2863	2864	2865	2838	55/98
15			3.8	1.1	2.7	3.2	2.8	0.2	1.7	2.5	2.8	0.9	2.1	2.4	4.7
16			11.9	4.3	8.1	9.6	7.4	2.9	5.1	7.7	6.8	4.3	6.0	6.7	11.4
17			18.3	7.1	13.0	14.4	9.9	8.2	8.5	10.8	9.8	9.3	7.8	11.3	14.8
18			19.4	10.3	14.4	15.4	14.4	11.4	9.9	12.6	13.6	12.2	8.9	12.4	17.6
19			26.3	14.1	19.9	23.4	18.4	15.4	13.3	17.8	19.0	16.4	13.3	16.1	22.3
20			20.3	13.2	16.0	16.2	16.6	14.1	11.4	13.8	15.2	14.6	9.3	13.8	18.3
21			21.9	15.3	17.6	17.4	17.9	16.0	12.9	15.7	17.1	16.1	10.3	15.0	19.9
22			21.1	14.6	16.4	19.4	16.4	15.0	12.0	15.5	16.1	14.8	11.4	14.0	18.0
23			24.1	19.4	19.4	19.1	19.8	18.7	16.4	19.3	19.9	18.3	11.8	17.1	21.4
24			17.1	13.7	14.2	14.0	14.7	13.6	11.5	13.6	14.2	13.3	8.5	12.5	16.3
25	C		22.8	20.5	19.1	18.5	19.6	19.2	17.9	20.1	20.3	18.7	11.8	16.9	21.1
26			13.8	11.8	12.1	12.4	12.5	11.7	10.0	11.5	12.1	11.6	7.6	10.6	13.7
27	C		27.1	24.8	22.7	21.9	23.2	24.2	23.4	25.6	25.4	23.0	14.5	20.0	23.9
28			12.1	10.0	10.7	10.6	10.8	10.2	8.8	10.1	10.5	9.9	6.3	9.5	11.9
29	C		29.6	27.6	24.5	23.7	24.1	26.6	26.4	28.1	27.4	25.0	15.9	21.1	24.4

## Appendix B (continued)

	assigned	Transect													
		I	II	II	II	II	II	II	II	II	II	II	III	III	
	lipid pool	Area	AO	AO	YSC	YP	YP	YP	YP	MIZ	MIZ			YSC	
<i>n</i> -Alkane		Station	2830	2847	2848	55/95	55/97	2836	2835	2834	2863	2864	2865	2838	55/98
30			8.6	7.1	7.4	7.3	7.4	7.2	5.6	7.0	7.3	6.9	4.2	6.5	7.6
31	C		27.3	23.4	22.4	21.3	21.3	23.6	24.5	26.1	25.3	22.1	13.6	18.0	20.4
32			5.2	3.7	4.6	5.7	4.2	4.0	3.3	4.2	4.2	4.2	3.4	3.8	4.7
Total (μg/gTOC)			330.7	242.0	265.2	273.5	261.4	242.2	222.6	262.0	267.0	241.6	166.7	227.7	292.4
Σ assigned to C(μg/gTOC)			106.8	96.3	88.7	85.4	88.2	93.6	92.2	99.9	98.4	88.8	55.8	76.0	89.8
% assigned to C			32	40	33	31	34	39	41	38	37	37	33	33	31
CPI (22–32)			2.1	2.3	2.0	1.9	2.0	2.2	2.5	2.3	2.2	2.1	2.0	2.0	1.8

	assigned	Transect													
		III	III	III	III	III	III	III	III	III	III	III	III	III	III
	lipid pool	Area	YSC	YSC	YSC	YSC	YSC	MIZ	MIZ	OW	OW	OW	OW	OW	OW
<i>n</i> -Alkane		Station	2837	55/93	55/92	57/160	57/161	55/77	57/157	55/158	57/153	57/123	57/131	57/138	57/145
15			6.4	5.7	4.7	2.1	4.3	5.9	19.9	1.9	3.4	7.4	1.6	n.d.	n.d.
16			11.8	13.6	9.9	6.5	10.2	12.8	23.5	7.9	8.3	13.4	9.8	n.d.	n.d.
17			17.2	15.3	17.3	11.5	13.7	19.2	23.6	11.9	12.4	15.5	21.4	n.d.	n.d.
18			16.0	18.0	16.7	15.0	17.6	16.7	23.4	15.4	14.3	16.1	28.6	n.d.	n.d.
19			19.0	27.3	22.1	19.5	21.3	24.9	28.1	23.8	19.8	19.2	35.7	n.d.	n.d.
20			16.2	18.0	17.8	17.2	18.8	16.7	22.3	18.0	15.0	15.3	34.2	n.d.	n.d.
21			17.0	19.2	18.9	18.7	19.8	17.5	22.8	18.8	15.7	15.0	33.7	n.d.	n.d.
22			15.4	18.8	17.9	17.2	18.1	15.6	21.2	20.3	15.3	13.8	31.3	n.d.	n.d.
23			18.1	20.0	20.0	20.8	20.9	17.7	23.2	18.4	15.4	13.5	30.3	n.d.	n.d.
24			13.6	14.9	15.0	15.2	15.8	13.8	18.2	14.5	12.2	11.1	25.6	n.d.	n.d.
25	C		17.3	18.9	19.0	20.0	20.0	16.7	21.7	15.7	14.6	11.5	25.4	n.d.	n.d.
26			11.4	12.5	12.6	12.8	13.1	11.5	15.1	11.5	10.4	9.0	20.6	n.d.	n.d.
27	C		19.5	21.6	21.4	22.9	21.9	18.2	23.0	15.8	15.7	11.2	23.2	n.d.	n.d.
28			10.0	11.1	11.0	11.0	11.4	10.3	13.0	9.8	9.1	8.4	17.2	n.d.	n.d.
29	C		20.4	22.5	22.3	23.4	22.2	18.8	23.5	15.8	16.9	11.1	21.1	n.d.	n.d.
30			7.0	7.9	7.6	7.4	8.1	5.9	7.8	6.7	6.5	5.3	11.6	n.d.	n.d.
31	C		17.7	19.2	19.2	20.5	18.3	14.6	19.4	13.1	14.4	8.7	14.8	n.d.	n.d.
32			4.1	4.9	4.4	4.3	4.4	4.0	5.2	5.2	4.0	3.1	6.4	n.d.	n.d.
Total (μg/gTOC)			258.1	289.4	277.8	266.0	279.9	260.8	354.9	244.5	223.4	208.6	392.5	n.d.	n.d.
Σ assigned to C(μg/gTOC)			74.9	82.2	81.9	86.8	82.4	68.3	87.6	60.4	61.6	42.5	84.5	n.d.	n.d.
% assigned to C			29	28	29	33	29	26	25	25	28	20	22	n.d.	n.d.
CPI (22–32)			1.8	1.8	1.8	1.9	1.8	1.7	1.7	1.5	1.6	1.3	1.2	n.d.	n.d.

Station locations are given in Fig. 1, for area abbreviations see text and Table 1. CPI=carbon preference index according to Bray and Evans (1961) calculated for the carbon atom number range from 22 to 32. Compounds of lipid pool C are attributed to a higher land plant origin. n.d.=not determined.

## Appendix C

Concentrations ( $\mu\text{g/g}$  TOC) of *n*-alkanes and CPI in surface sediments from the eastern Fram Strait and on the Yermak Plateau

	assigned	Transect I													
		Area	AO	AO	AO	I+III	I	I	I	I	I	I	I	I	I
<i>n</i> -Alkanol	lipid pool	Station	2849	2851	2853	2854	2855	2856	2857	2858	2859	2860	2861	2832	2831
16			12.0	15.3	16.8	28.3	16.1	17.5	15.5	15.1	15.3	11.6	17.2	18.1	17.4
18			38.8	31.3	38.1	52.4	23.5	30.4	27.6	22.7	29.4	24.2	26.7	32.5	39.1
22	C		40.1	32.6	32.4	51.2	29.7	33.3	41.8	32.6	38.1	30.8	36.2	37.2	36.8
24	C		31.2	24.7	26.2	97.9	21.4	27.3	33.0	24.0	30.3	22.7	28.0	26.7	29.2
26	C		66.8	37.5	42.0	50.3	34.3	38.5	67.8	39.9	48.1	33.6	50.7	46.6	36.2
28	C		36.9	28.2	28.8	33.2	21.6	25.6	41.4	25.2	31.8	21.1	32.5	26.2	31.2
Total ( $\mu\text{g/gTOC}$ )			225.8	169.6	184.3	313.3	146.6	172.6	227.1	159.5	193.0	144.0	191.3	187.3	189.9
$\Sigma$ assigned to C ( $\mu\text{g/gTOC}$ )			175.0	123.0	129.4	232.6	107.0	124.7	184.0	121.7	148.3	108.2	147.4	136.7	133.4
% assigned to C			78	73	70	74	73	72	81	76	77	75	77	73	70

	assigned	Transect II													
		Area	AO	AO	YSC	YP	YP	YP	YP	YP	MIZ	MIZ			YSC
<i>n</i> -Alkanol	lipid pool	Station	2830	2847	2848	55/95	55/97	2836	2835	2834	2863	2864	2865	2838	55/98
16			19.6	14.0	22.7	260.5	20.4	18.9	15.2	14.3	15.5	20.1	11.9	17.5	21.3
18			46.0	38.8	31.3	33.9	24.6	35.7	33.2	30.7	18.5	59.5	21.3	24.4	37.0
22	C		44.4	31.8	41.3	35.9	40.1	38.9	40.1	29.0	37.9	41.4	24.9	30.5	35.0
24	C		42.4	26.5	29.0	27.4	29.9	29.2	29.2	24.3	29.5	29.6	17.1	20.9	25.0
26	C		67.2	46.8	45.7	43.4	46.8	48.3	54.3	49.1	54.1	45.1	26.7	34.7	38.3
28	C		48.5	32.2	29.3	29.9	29.5	30.1	35.0	33.3	35.0	29.5	20.0	22.7	25.8
Total ( $\mu\text{g/gTOC}$ )			268.1	190.1	199.3	431.0	191.3	201.1	207.0	180.7	190.5	225.2	121.9	150.7	182.4
$\Sigma$ assigned to C ( $\mu\text{g/gTOC}$ )			202.5	137.3	145.3	136.6	146.3	146.5	158.6	135.7	156.5	145.6	88.7	108.8	124.1
% assigned to C			76	72	73	32	76	73	77	75	82	65	73	72	68

	assigned	Transect III													
		Area	YSC	YSC	YSC	YSC	YSC	MIZ	MIZ	OW	OW	OW	OW	OW	OW
<i>n</i> -Alkanol	lipid pool	Station	2837	55/93	55/92	57/160	57/161	55/77	57/157	55/158	57/153	57/123	57/131	57/138	57/145
16			18.8	136.8	25.9	31.8	22.6	27.1	45.6	17.6	17.7	30.4	39.5	25.1	15.1
18			18.0	26.3	23.3	27.2	26.2	37.3	39.8	31.2	17.9	22.2	34.7	33.3	22.4
22	C		30.9	38.8	37.3	41.6	34.5	45.3	34.4	23.7	24.8	15.0	19.0	9.7	16.9
24	C		23.6	26.6	25.8	29.8	22.7	31.5	24.8	16.7	17.6	11.2	12.2	6.5	12.0
26	C		31.8	36.7	37.2	39.8	25.8	44.9	30.7	18.7	20.0	11.5	16.4	6.2	16.1
28	C		19.0	21.2	22.2	19.5	21.1	24.4	19.8	12.1	8.9	6.3	9.4	4.2	10.9
Total ( $\mu\text{g/gTOC}$ )			142.1	286.4	171.7	189.7	152.9	210.5	195.1	120.0	106.9	96.6	131.2	85.0	93.4
$\Sigma$ assigned to C ( $\mu\text{g/gTOC}$ )			105.3	123.3	122.5	130.7	104.1	146.1	109.7	71.2	71.3	44.0	57.0	26.6	55.9
% assigned to C			74	43	71	69	68	69	56	59	67	46	43	31	60

Station locations are given in Fig. 1, for area abbreviations see Table 1 and text. Compounds of lipid pool C are attributed to a higher land plant origin.

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