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Carbon sources in suspended particles and surface sediments from the Beaufort Sea revealed by molecular lipid biomarkers and compound-specific isotope analysis

I. Tolosa[1], **S. Fiorini**[1,*], **B. Gasser**[1], **J. Martín**[1,2], **and J. C. Miquel**[1]

[1]International Atomic Energy Agency – Environment Laboratories, 4, quai Antoine 1er, MC 98000, Monaco
[2]Instituto de Ciencias del Mar, CSIC, Paseo Marítimo de la Barceloneta, 37–49, 08003 Barcelona, Spain
[*]now at: Ecole Normale Supérieure, CEREEP ECOTRON-Ile de France, CNRS-ENS UMS 3194, 78 rue du chateau, 77140, Saint-Pierre les Nemours, France

Correspondence to: I. Tolosa (i.Tolosa@iaea.org)

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Abstract. Molecular lipid biomarkers (hydrocarbons, alcohols, sterols and fatty acids) and compound-specific isotope analysis of suspended particulate organic matter (SPM) and surface sediments of the Mackenzie Shelf and slope (southeast Beaufort Sea, Arctic Ocean) were studied in summer 2009. The concentrations of the molecular lipid markers, characteristic of known organic matter sources, were grouped and used as proxies to evaluate the relative importance of fresh algal, detrital algal, fossil, C_3 terrestrial plants, bacterial and zooplankton material in the organic matter (OM) of this area. Fossil and detrital algal contributions were the major fractions of the freshwater SPM from the Mackenzie River with $\sim$ 34 % each of the total molecular biomarkers. Fresh algal, C_3 terrestrial, bacterial and zooplanktonic components represented much lower percentages, 17, 10, 4 and $<$ 1 %, respectively. In marine SPM from the Mackenzie slope, the major contributions were fresh and detrital algal components ($>$ 80 %), with a minor contribution of fossil and C_3 terrestrial biomarkers. Characterization of the sediments revealed a major sink of refractory algal material mixed with some fresh algal material, fossil hydrocarbons and a small input of C_3 terrestrial sources. In particular, the sediments from the shelf and at the mouth of the Amundsen Gulf presented the highest contribution of detrital algal material (60–75 %), whereas those from the slope contained the highest proportion of fossil (40 %) and C_3 terrestrial plant material (10 %). Overall, considering that the detrital algal material is marine derived, autochthonous sources contributed more than allochthonous sources to the OM lipid pool. Using the ratio of an allochthonous biomarker (normalized to total organic carbon, TOC) found in the sediments to those measured at the river mouth water, we estimated that the fraction of terrestrial material preserved in the sediments accounted for 30–40 % of the total carbon in the inner shelf sediments, 17 % in the outer shelf and Amundsen Gulf and up to 25 % in the slope sediments. These estimates are low compared to other studies conducted 5–20 yr earlier, and they support the increase in primary production during the last decade mainly because of the increase in the number of ice-free days and due to the strength and persistence of winds favouring upwelling.

1 Introduction

The Arctic Ocean is known to be very sensitive to climate change. Some consequences of global warning on the Arctic environment are reduction of the ice cover and thawing of the carbon-rich permafrost. This leads to an increase of the surface exposed to solar radiation and of the input of carbon into the ocean, both favourable to phytoplankton growth (Arrigo et al., 2008; Barber and Hanesiak, 2004; Johannessen et al., 2004). Therefore a better knowledge of this precarious environment is crucial. A major contribution of terrigenous particulate organic carbon (POC) to continental shelves is the discharge from large Arctic rivers which is further amplified

by the input resulting from coastal erosion (Stein and Macdonald, 2004). The Mackenzie River, with a freshwater discharge of 281 $km^3\,yr^{-1}$ into the Beaufort Sea, is the most important in terms of POC contribution to the Arctic Ocean (Rachold et al., 2004) and dominates sediment supply to the Canadian Beaufort Sea (Macdonald et al., 1998; Rachold et al., 2000). Available estimations specify that about 50 % of the 127 Mt of the terrigenous sediments annually provided by the Mackenzie River are rapidly accumulated in the delta front area, 40 % stays on the shelf, and 10 % escapes to the slope and farther (Macdonald et al., 1998). Marine organic carbon from primary and secondary production has been estimated at ~ 3.3 Mt C yr^{-1} for the Mackenzie Shelf and delta, but a large fraction of this marine carbon seems to be rapidly recycled in both the water column and the sediment/water interface (Macdonald et al., 1998).

Based on $\delta^{13}C$ bulk values, previous studies have estimated the total volume and the offshore extent of terrigenous organic matter preserved in the sediments of this region (Goñi et al., 2005; Magen et al., 2010). The issue of $\delta^{13}C$ end-member determination is particularly problematic in this area (Amiel and Cochran, 2008; Belt et al., 2008; Forest et al., 2007), because there are other sources of POC than those derived from terrestrial vegetation and marine productivity. In particular, the fossil contribution from the river drainage basins may represent a significant source of POC with intermediate $\delta^{13}C$ values, and the algal productivity in the rivers could be a source of $\delta^{13}C$-depleted POC (Goñi et al., 2005). Mass balance studies using lipid $\delta^{13}C$ and ^{14}C signatures indicated that 40–50 % of the carbon buried in the Beaufort Sea was derived from the weathering of ancient sedimentary rock (Drenzek et al., 2007).

Compared to bulk geochemical analyses, where the issue of the $\delta^{13}C$ marine end-member determination is particularly delicate, the examination of organic matter at molecular level can provide more specific information related to the carbon cycle, source identification and apportionment in the Beaufort Sea. Several studies from the 1980s have partially characterized the Mackenzie–Beaufort sea system using specific molecular compounds (Yunker et al., 1995, 2002, 2005, 2011; Belicka et al., 2004; Goñi et al., 2000, 2005; Drenzek et al., 2007). In particular, these studies all reported data on lipid biomarkers, which are well suited to evaluate the supply of terrigenous organic matter (Bouloubassi et al., 1997; Saliot et al., 2002), but only a few have combined these analyses with compound-specific isotope determinations (Drenzek et al., 2007; Goñi et al., 2005). The approach using the $\delta^{13}C$ values of individual compounds is relevant since the isotope data provide additional evidence supporting the proposed origins of the biomarkers, and in certain cases this combination is essential for an accurate determination of the origin of the biomarkers. The present study combines a comprehensive list of biomarkers and compound-specific carbon isotope analysis on suspended particulate matter (SPM) and surface sediments collected in summer 2009. Here, the coupled data were used in the southeast Beaufort Sea to better understand the sources of carbon, the transport and the fate of organic matter from the Mackenzie River to the marine off-shore waters and surface sediments. Based on the contribution of different molecular markers (hydrocarbons, alcohols, sterols and fatty acids) characteristic of known organic matter sources and taking into account the different lability of the molecules, we evaluate and compare the relative importance of different organic pools, such as fresh algal, refractory algal, fossil, C_3 terrestrial plants, bacterial and zooplankton material between the river SPM, marine offshore SPM and surface sediments. Additionally, a quantitative approach comparing the concentrations of allochthonous biomarkers normalized to the total organic carbon between marine sediments and river SPM allowed the reassessment of the fraction of allochthonous material preserved in the sediments of the Beaufort Sea.

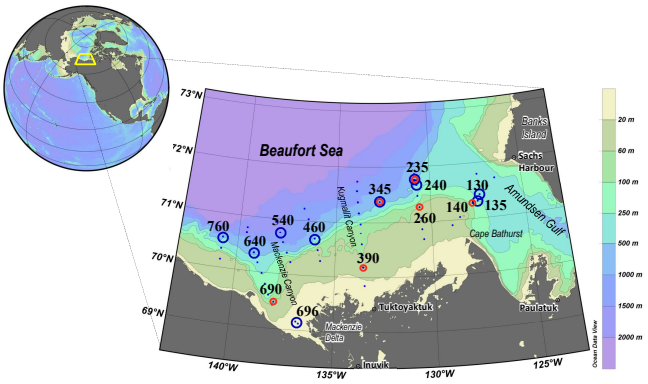

Fig. 1. Map of the Malina survey area. Sites of suspended particulate matter sampling: blue circles. Sites of sediment sampling: red circles.

2 Material and methods

2.1 Study area and sampling

This study was conducted in the southeast Beaufort Sea during summer 2009 (1 to 24 August 2009) on board the Canadian research icebreaker CCGS *Amundsen* from approximately latitudes 69 to 72° N and longitudes 125 to 145° W (Table 1, Fig. 1). The study was organized within the framework of the Malina project.

The Arctic Ocean, including the Beaufort Sea, is strongly structured in several vertical layers and is filled with water from the Atlantic and Pacific oceans as well as superficial waters influenced by river discharge and ice melting (Stein and Macdonald, 2004). The water masses comprise the polar mixed layer (PML, salinity < 31, 0–50 m depth), which is influenced by fresh waters from the rivers and melting sea ice, the upper Pacific halocline (salinity: 31–33, 50–200 m depth) associated with a prominent nutrient maximum at salinities

Table 1. List of stations where sampling of suspended particulate matter (SPM) and sediments were conducted. For sediment samples, total organic carbon (TOC) is also indicated.

Station	Latitude (N)	Longitude (W)	Bottom depth (m)	Date	TOC ($mg\,g^{-1}$)
SPM					
760	70.55	140.8	560	12 Aug 2009	
640	70.34	139.14	570	12 Aug 2009	
540	70.75	137.89	1514	18 Aug 2009	
460	70.68	136.05	470	19 Aug 2009	
345	71.36	132.61	540	15 Aug 2009	
240	71.67	130.74	459	6 Aug 2009	
235	71.76	130.83	600	24 Aug 2009	
135	71.31	127.46	227	21 Aug 2009	
130	71.43	127.36	311	7 Aug 2009	
Mackenzie River (696/697)	69.16	136.81	2.7/1.7	13 Aug 2009	
Sediments					
690	69.49	137.94	55	1 Aug 2009	16.5
390	70.18	133.57	47	1 Aug 2009	17.5
345	71.40	132.64	577	16 Aug 2009	13.8
235	71.76	130.77	576	22 Aug 2009	13.7
260	71.27	130.61	60	5 Aug 2009	13.2
140	71.28	127.78	154	7 Aug 2009	16.8

of ∼ 33, the lower Atlantic halocline (200–275 m depth) and the relatively warm (> 0 °C) and salty deep waters of Atlantic origin (salinity > 34.5, > 275 m depth). The main hydrodynamic and trophic features for the different zones are described in more detail by Codispoti et al. (2005) and by Matsuoka et al. (2012). A particularly important feature of the Arctic Ocean is the strong perennial cold halocline, which isolates surface waters (and sea ice) from warm and salty Atlantic waters.

The sample set of the present study includes the following: (1) suspended particulate material (SPM) from the slope waters (200–1500 m bottom depth) and from the Mackenzie River and (2) superficial sediments from the Mackenzie Shelf (< 100 m), the slope and from the mouth of the Amundsen Gulf. The Mackenzie Shelf is ∼ 150 km wide and is crossed by two submarine canyons: the broad, deep Mackenzie Canyon at about 138° W, and the narrow, relatively shallow Kugmallit Canyon at about 134° W. SPM samples were collected at the chlorophyll *a* maximum depth, determined by a CTD probe equipped with a fluorometer, at the Pacific halocline layer (∼ 130 m depth) and at 200 and/or 300 m depth. One sample at site 130 was taken in the upper PML (3 m depth) in waters showing a salinity of 28.2.

For sampling suspended particles, Challenger Oceanics in situ pumps were used to filter large volumes (400 to 900 L) of water, through a Nitex screen of 70 µm and a precombusted (550 °C) microquartz filter (QMF, Sartorius) of 1 µm pore size. Only the size fraction collected on the microquartz filter (1–70 µm) was analysed. SPM from the Mackenzie River was obtained by collection of freshwater with a Zodiac and filtering on GF/F filters.

Sediments were sampled by means of a box corer. The top 5 mm of sediment were sampled with a metallic spatula and collected in a Teflon tube. Filters and sediments were stored frozen at −80 °C until analysis in the laboratory.

Organic carbon was measured with a Vario EL elemental analyser (Elementar Analysensysteme GmbH©) after acidification of the filter aliquots and sediments with 1M H3PO4 (Miquel et al., 1994; Martin et al., 2009). Several runs of blanks (pre-combusted QMA filters) and standards (Acetanilide Merck pro analysis) were performed for calibration of carbon measurements.

The other auxiliary parameters corresponding to the suspended particulate matter samples (Table 2) were obtained from the Malina database, where data and methods are fully described. Briefly, temperature, pressure and salinity were measured using a Seabird Fastcast SBE-49. Suspended particulate matter (SPM) was obtained following the method described in Doxaran et al. (2012). Total Chl *a* was obtained by using the method described in Ras et al. (2008). Nutrient concentrations (nitrate, phosphate and silicate) were determined onboard using the methods described in Raimbault et al. (2008). The dissolved CO_2 concentration was derived from alkalinity, pH, temperature, salinity and the concentrations of silicate and phosphate using the CO2SYS program developed for CO_2 system (Lewis and Wallace, 1998). Total alkalinity (A_T) of water samples was measured by open-cell potentiometric titration (Mucci et al., 2010), and pH measurements on board were measured as described in Lansard et al. (2012).

Table 2. Bulk biochemical parameters corresponding to the suspended particulate matter (SPM) samples in the Beaufort Sea and Mackenzie River. Stations are identified by their number (e.g. 130) followed by the sampling depth (e.g. 3).

Locations-Depth (m)	Depth (m)	Temperature (°C)	Salinity	C_{org} ($\mu g\,L^{-1}$)	SPM ($mg\,L^{-1}$)	Total Chl *a* ($mg\,m^{-3}$)	NO_3 (μM)	PO_4 (μM)	$SiOH_4$ (μM)	$[CO_{2_{aq}}]$ ($\mu mol\,kg^{-1}$)
130-3	3	4.63	28.22	42.45	0.20	0.14	0.01	0.60	3.12	20.6
130-130	130	−1.39	33.07	5.84		0.03	5.45	1.27	1.92	40.3
130-200	200	−0.99	33.99	6.25		0.01	12.89	1.44	25.21	34.1
135-40	40	−0.82	31.26	11.17	0.07	0.10	0.01	0.79	3.71	17.3
135-70	70	−1.26	31.75	11.10	0.07	0.21	6.67	1.29	15.49	20.8
135-85	85	−1.27	32.21	7.58		0.15	8.12	1.50	18.67	33.3
135-145	145	−1.41	33.07	5.92		< 0.042	15.17	1.82	33.08	38.6
235-70	70	−1.12	31.89	12.33	0.07	0.27				25
235-85	85	−1.30	32.37	7.69		0.13				34
235-145	145	−1.37	32.75	3.81		< 0.0087				39.4
235-200	200	−0.07	34.55	3.18						24.5
240-70	70	−1.20	32.11	8.37	0.60	0.12	9.62	1.40	23.61	28.6
240-130	130	−1.41	33.03	6.44		0.03	13.20	1.59	33.41	40.3
240-200	200	−0.71	34.24	9.34		0.02				28.1
345-60	60	−1.15	31.33	18.81	0.15	0.52	2.80	1.01	9.15	18.7
345-85	85	−1.24	32.19	5.39		0.16	9.91	1.54	23.40	30.4
345-145	145	−1.40	33.16	1.10						38.3
345-200	200	−0.62	34.28	2.77						27.1
460-70	70	−1.14	31.85	12.93	0.07	0.53				26.3
460-130	130	−1.43	33.09	4.36		0.01				40.9
460-200	200	−0.75	34.19	8.14						27.7
460-300	300			6.07						
540-70	70	−1.15	31.82	6.61	0.06	0.44	6.06	2.20	14.04	24.8
540-90	90	−1.36	32.26	7.48		0.06	10.22	2.75	22.43	33.5
540-200	200	−0.43	34.38	2.76		< 0.0054	12.26	1.74	12.71	24.9
640-70	70	−1.09	30.48	11.71	0.05	0.15				∼ 21.7
640-130	130			6.19		< 0.048				
640-200	200			3.97		< 0.0136				
760-130	130	−1.43	33.01	3.82		0.01	15.65	1.93	37.19	39.2
760-200	200			4.28						
760-300	300	0.29	34.67	3.24						24.4
Mackenzie River	0.5	10.08	0.23	1210	111.50	3.16	3.31	0.02	64.17	

2.2 Lipid extraction

Filters containing the suspended particles and freeze-dried sediments were spiked with internal standards (n-$C_{24}D_{50}$, friedeline, 5α-androstan-3β-ol and cholanic acid), and lipids extracted with 40 mL of a mixture of CH_2Cl_2/MeOH (3 : 1) in a microwave oven at 70 °C for 15 min. Isolation of the neutral and acid lipid fractions was performed following the method of Tolosa and de Mora (2004a). Extractable lipids were saponified using 1 mL of KOH 6 % in methanol/water (80 : 20) plus 1 mL of Milli-Q water (80 °C, 1 h). The neutral fraction was then recovered with n-hexane and subjected to fractionation by HPLC on a normal phase column (Nucleosil column, 20 cm × 0.4 cm i.d. 5 µm) to isolate aliphatic hydrocarbons (F1), polycyclic aromatic hydrocarbons (F2), ketone compounds (F3) and sterol and alcohol fraction (F4). F1 and F2 were combined for the total hydrocarbon analysis. Saponified solutions were acidified with 1 mL of HCl 6 N to pH 2, and the fatty acids were extracted with hexane : ethyl acetate (9:1).

2.3 Gas chromatography

The sterol fraction was treated with *bis*-(trimethylsilyl)-trifluoroacetamide (BSTFA) (200 µL, 70 °C, 1 h) to convert the alcohols and sterols to their corresponding trimethylsilyl ethers. The acid fraction was derivatized by transesterifying

the lipid extract with 500 µL of 20 % BF_3 in methanol at 80 °C for 1 h.

Quantification of neutral compounds was performed on a Hewlett-Packard HP 7890 A with a flame ionisation detector (FID) and a splitless injector. The column was a HP-5 (30 m × 0.25 mm i.d. × 0.25 µm film thickness), and injector and detector temperatures were 270 °C and 320 °C, respectively. The oven temperature was programmed at 4 °C min^{-1} from 60 °C to 310 °C, then held 20 min.

Quantification of the acidic compounds was carried out with a Hewlett-Packard HP 5890 series II equipped with a FID and on-column injector. The DB-23 (30 m × 0.32 mm × 0.25 µm) column was pre-connected with a press-fit connector to a 0.32 mm i.d., deactivated, fused silica capillary. Helium was the carrier gas (1.2 mL min^{-1}). The GC oven for the DB-23 column was programmed from 60 °C (0.5 min hold) to 250 °C at 6 °C min^{-1}.

Aliphatic hydrocarbons, sterols and fatty acids were quantified by internal standards ($C_{24}D_{50}$, 5α-androstan-3β-ol, and cholanic acid, respectively). Confirmation of peak identity was obtained using GC with mass spectrometric detection (GC-MS) (Hewlett-Packard 5889B MS "Engine") operated in the electron impact at 70 eV. It was equipped with a HP5-MS column (30 m × 0.25 mm i.d., 0.25 µm thick). Helium was the carrier gas. The oven temperature was programmed from 60 °C to 290 °C at 4 °C min^{-1}. Compound identification was made according to their mass spectra and the retention times of standards.

2.4 Compound-specific isotope analysis

The lipid biomarkers were analysed for their stable carbon isotope composition using an HP 5890 GC equipped with a HP 7673 autoinjector and interfaced through a combustion furnace with a Finnigan MAT Delta C isotope ratio mass spectrometer (GC/C/IRMS).

The GC/C/IRMS was equipped with a 100 % methylpolysiloxane fused silica column (Ultra-1, 50 m × 0.32 mm i.d.; 0.5 µm film thickness) pre-connected with a press-fit connector (Supelco, France) to a 0.32 mm i.d., deactivated, fused silica capillary retention gap of 5 m. Injections of 2 µL in isooctane were made via an on-column injector. The GC oven was programmed from 60 to 100 °C at 10 °C min^{-1}, then to 310 °C at 4 °C min^{-1} and maintained at 310 °C for 40 min. Values reported were determined at least from triplicates to calculate the average and standard deviation. All $\delta^{13}C$ values are reported in the delta notation relative to the Pee Dee Belemnite (PDB) standard as follows:

$$\delta^{13}C\,‰ = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB} - 1] \times 10^3. \quad (1)$$

Corrections for the isotopic change introduced in the derivatization of sterols, fatty alcohols, and fatty acids were determined through derivatization of standards of known isotopic composition applying the equation of Jones et al. (1991). Cholesterol, $C_{18:0}$ fatty acid and $C_{18:0}$ FAME, methanol (with BF_3) and BSTFA of known isotopic carbon composition (measured by elemental analyser coupled to isotope ratio mass spectrometer) were used to calibrate the GC/C/IRMS and correct the isotopic change introduced by the derivatization. The surrogate standards, 5α-androstan-3β-ol, cholanic acid and the GC internal standard friedeline of known isotopic composition served as internal isotopic standards.

Most of the values reported here correspond to the $\delta^{13}C$ values of peak abundances higher than 0.5 V (m/z 44) where the standard deviation (S.D) was comparable to the instrument specifications (0.5 ‰). We also present some $\delta^{13}C$ values of peak abundances $\geq$0.3 V and $\leq$ 0.5 V with slightly higher variability (S.D. $<$ 2 ‰), which was validated by standards within this range.

2.5 Background on lipid biomarker origins

Hydrocarbons from both natural and anthropogenic sources are very common in the environment. Among biogenic hydrocarbons, the *n*-alkanes exhibit a strong odd carbon-number predominance in living organisms where the carbon-number distributions vary depending on the source organism. Higher terrestrial plants are dominated by the long-chain (C_{25}–C_{33}) *n*-alkanes, lower terrestrial plants by the medium-chain (C_{23}–C_{25}) *n*-alkanes and aquatic algae by the short-chain *n*-alkanes (C_{17}–C_{21}) (Volkman et al., 1992; Baas et al., 2000). Other biogenic hydrocarbons include the polyunsaturated straight-chain alkenes, *n*-$C_{21:6}$ and related isomers (*n*-$C_{21:5}$, *n*-$C_{21:4}$) derived from autotrophic marine and freshwater plankton (Volkman et al., 1992), the C_{25} monounsaturated hydrocarbon (IP_{25}) used as a sea ice algae proxy (Belt et al., 2007) and retene, a diagenetic polycyclic aromatic hydrocarbon (PAH) from higher plants (Simoneit, 1977). In contrast to these biogenic sources, petroleum sources usually show a wide distribution range of *n*-alkanes with no predominance of odd or even carbon numbers. We use the carbon preference index (CPI) defined as the sum of the odd carbon-numbered alkanes added to the sum of the even carbon-numbered alkanes to characterize the sources of *n*-alkanes (Bray and Evans, 1961). In fact, extant plants typically show CPIs $>$ 5 (Rielley et al., 1991) while petroleum-derived *n*-alkanes have CPI values around 1 (Wang et al., 2003). Whenever both sources are mixed, terrestrial wax *n*-alkanes (C_{25}–C_{31}) are calculated by subtracting the fossil contribution resulting from the average of the next higher and lower even carbon-numbered homologues as follows: wax *n*-$C = [C_n] - 0.5[C_{(n+1)} + C_{(n-1)}]$ (Simoneit et al., 1990). The presence of an unresolved complex mixture (UCM) defined as a hump in the hydrocarbon chromatograms is also a diagnostic tool of petroleum/fossil sources (Volkman et al., 1992).

Among alcohols, phytol is a marker for phototrophic organisms (Baker and Louda, 1983). Short-chain (n-C_{14}–C_{20}) alcohols (SCOH) and short-chain monounsaturated alcohols (SCMUOH) might have multiple microbial sources (Robinson et al., 1984b), and long-chain (n-C_{22}–C_{30}) even carbon-numbered n-alcohols (LCOH) are markers of terrestrial higher plant waxes (Rieley et al., 1991), and long-chain (C_{20}–C_{24}) monounsaturated fatty alcohols (LCMUOH), biomarkers typical of zooplankton (Lee et al., 2006). Finally, α-amyrin (Olean-12-en-3α-ol), is a specific triterpenoid for angiosperms and also present in peat (Hernes and Hedges, 2004).

Sterols occur in all eukaryotic organisms, and the specificity of these compounds for different phytoplankton groups and vascular plants is well known (Volkman, 1986, 2003). The 24-methylcholesta-5, 22(E)-dien-3β-ol ($C_{28}\Delta^{5,22}$, brassicasterol), 24-methylcholesta-5, 24(28)-dien-3β-ol ($C_{28}\Delta^{5,24(28)}$) and 24-ethylcholest-5-en-3β-ol (sitosterol, $C_{29}\Delta^{5}$) are common lipids in diatoms (Barrett et al., 1995, Volkman et al., 1998); $C_{28}\Delta^{5,24(28)}$ and the Z isomer of fucosterol (isofucosterol, 24-ethylcholesta-5, 24(28)(Z)-dien-3β-ol; $C_{29}\Delta^{5,24(28)}$) are typical of prasinophytes (Volkman et al., 1994). Dinosterol (4α-23,24-trimethylcholest-22(E)-en-3β-ol ($C_{30}\Delta^{22}$) is commonly used as a biomarker for dinoflagellates (Robinson et al., 1994a) and 27-nor-24-methylcholesta-5, 22(E)-dien-3β-ol (nor$C_{27}\Delta^{5,22}$) together with $C_{28}\Delta^{5,22}$ predominate in the marine dinoflagellate *Gymnodinium* simplex (Goad and Withers, 1982) and in marine invertebrates (Volkman et al., 1981). Cholest-5-en-3β-ol (cholesterol, $C_{27}\Delta^{5}$) is considered a typical marker for zooplankton-derived organic matter supply, but it is also present in many classes of algae (Harvey et al., 1987). The 24-methylcholesta-5-en-3β-ol ($C_{28}\Delta^{5}$), 24-ethylcholesta-5, 22(E)-dien-3β-ol ($C_{29}\Delta^{5,22}$) and sitosterol have often been considered as terrestrial markers, but they are also produced by both phytoplankton and aquatic plants (e.g. Volkman, 1986, 2003).

Fatty acids (FAs) are among the most abundant lipid biomarkers. Different group classes are distinguishable: the linearly saturated are used to separate marine from terrigenous sources through short-chain C_{14}–C_{18} (SCFA) and long-chain C_{22}–C_{30} (LCFA), respectively (Grimalt and Albaigés, 1990). Branched fatty acids (BrFA), composed of *iso*- and *anteiso*-branched compounds with odd chain lengths (e.g. C_{15}, C_{17}), are used as bacterial markers (Volkman et al., 1980). Vaccenic acid ($C_{18:1\omega7}$) is considered to be an indicator of bacterial input when $18:1\omega9/18:1\omega7 < 1$. However when this isomer ratio > 1, then it suggests a dominant phytoplanktonic source (Thoumelin et al., 1997). Monounsaturated long-chain C_{22}–C_{30} (LCMUFA) are typical of zooplankton (Lee et al., 2006). Polyunsaturated fatty acids (PUFA) are used as plankton biomarkers. Their presence indicates a fresh algal input, because they are not resistant to degradation processes. Among the PUFA, the $C_{18:5\,w3}$ and $C_{18:4\,w3}$ are abundant in flagellates (green algae and cryptomonads), $C_{20:5\,w3}$ predominates in many diatom species and $C_{22:6\,w3}$ dominates in dinoflagellates and flagellates (crytomonads) (Dalsgaard et al., 2003).

We estimated the relative contributions of organic matter (OM) constituents by grouping the different molecular lipid biomarkers into their different sources (fossil, algal, zooplankton, bacterial and terrestrial). We also took into account the different lability of the molecules to discern between fresh/labile and refractory/detrital algae. We assigned PUFA, phytol, IP_{25}, n-$C_{21:6}$, $C_{28}\Delta^{5,24(28),}$ $C_{29}\Delta^{5,24(28)}$ within the fresh/algal component, because these molecules are more labile bearing double bonds or oxygenated functionalities compared to the higher stability of the rest of biomarkers studied. These criteria yielded the following components: fossil (UCM, and petroleum hydrocarbons), fresh/labile algal (PUFA, phytol, IP_{25}, n-$C_{21:6}$, $C_{28}\Delta^{5,24(28)}$, $C_{29}\Delta^{5,24(28)}$), refractory/detrital algal (SCFA, SCMUFA, rest of sterols, biogenic alkanes, SCOH, SCMUOH), zooplankton (LCMUFA, LCMUOH), bacterial (branched FAs) and C_3 terrestrial plants (LCFA, LCOH, wax n-alkanes). We stress that this is an empirical approach because some of the compounds, such as sitosterol, might derive from more than one source (algal and/or terrestrial). Hence, only relative changes among the stations and depths were evaluated.

3 Results

Table 2 describes the biochemical parameters accompanying the SPM samples from the slope waters of the Beaufort Sea and from the Mackenzie River. For clarification, the first number in the codes, e.g. 640-70, refers to the station (640), whereas the second number after the dash indicates the water depth sampled (70 m). The sample 130-3 was the only one obtained in waters, which exhibited clear influence from the rivers and/or melting sea ice (salinity < 29). For samples from the depth of chlorophyll and POC maximum (60–70 m), the seawater showed salinity values $\sim$ 31–32 and nitrate concentrations from 2.8 to 9.6 µM, consistent with the nutrient-replete Pacific halocline water mass. At 130 m depth, salinity values of $\sim$ 33, high concentrations of nitrates ($\sim$ 13–15 µM, except site 130) and CO_2, and very low values of POC and total chlorophyll a were measured. Finally at 200 m and below, salinities were highest ($\geq$ 34) showing a typical Atlantic water origin (Matsuoka et al., 2012).

3.1 Hydrocarbons

Tables 3 and 4 summarize the hydrocarbons found in the SPM and sediments. All marine suspended particulate samples except for the most superficial one at 3 m depth showed traces of n-alkanes from C_{23} to C_{33} with no odd/even predominance (CPI$\sim$ 1). The hydrocarbon fraction of the SPM of the Mackenzie River and that from the surficial sediments (Table 4) showed a wide distribution range of quantifiable

Table 3. Selected hydrocarbon concentrations and diagnostic ratios in suspended particle samples from the Beaufort Sea.

Locations-Depth (m)	n-C_{17} (ng L^{-1})	$\sum$ n-$C_{21:x}$ (ng L^{-1})	Retene (ng L^{-1})	Wax (C_{25}–C_{31}) (ng L^{-1})	n-alkanes (ng L^{-1})	UCM (ng L^{-1})	CPI (C_{23}–C_{35}/C_{22}–C_{34})
130-3	< 0.32	8.46	< 0.02	9.20	28.32	n.d.	2.73
130-130	< 0.14	0.78	< 0.02	< 0.3	1.64	n.d.	1.63
130-200	< 0.14	0.29	< 0.01	< 0.3	2.50	n.d.	1.32
135-40	< 1.14	1.60	< 0.02	< 0.3	2.06	n.d.	0.80
135-70	< 0.81	2.90	< 0.02	< 0.3	1.04	n.d.	1.15
135-85	< 0.73	1.94	< 0.02	< 0.3	1.23	n.d.	1.10
135-145	< 0.85	0.23	< 0.02	< 0.3	1.62	n.d.	1.07
235–70	< 0.93	3.80	< 0.02	< 0.3	0.85	n.d.	1.65
235-85	< 0.79	2.31	< 0.02	< 0.3	1.65	n.d.	1.15
235-145	< 1.67	0.12	< 0.01	< 0.3	2.60	n.d.	1.48
235-200	< 0.73	0.12	< 0.01	< 0.3	1.64	n.d.	1.20
240-70	< 0.58	2.97	< 0.01	< 0.3	2.75	n.d.	1.03
240-130	< 0.70	0.15	< 0.04	< 0.3	12.14	n.d.	1.25
240-200	< 0.65	1.23	< 0.04	0.38	19.16	n.d.	1.11
345-60	< 0.18	10.41	< 0.01	< 0.3	1.14	n.d.	1.39
345-85	< 1.03	1.30	< 0.01	< 0.3	0.45	n.d.	1.09
345-145	< 0.13	0.04	< 0.01	< 0.3	0.28	n.d.	2.69
345-200	< 0.17	0.08	< 0.01	< 0.3	1.10	n.d.	1.21
460-70	< 0.13	4.78	< 0.01	< 0.3	0.29	n.d.	n.d.
460-130	< 0.13	0.14	< 0.01	< 0.3	1.57	n.d.	1.56
460-200	< 0.12	0.19	< 0.01	< 0.3	2.27	n.d.	0.80
460-300	< 0.45	0.00	< 0.01	< 0.3	1.27	n.d.	2.30
540-70	< 0.17	1.91	< 0.01	< 0.3	1.24	n.d.	1.00
540-90	< 0.17	1.39	< 0.01	< 0.3	0.98	n.d.	1.36
540-200	< 0.10	0.11	< 0.01	< 0.3	1.86	n.d.	1.14
640-70	< 0.95	0.81	< 0.04	< 0.3	16.82	n.d.	1.16
640-130	< 0.12	0.48	< 0.01	< 0.3	2.34	n.d.	1.42
640-200	< 0.10	0.23	< 0.01	< 0.3	0.78	n.d.	1.55
760-130	< 0.18	0.12	< 0.01	< 0.3	1.11	n.d.	1.02
760-200	< 0.20	0.23	< 0.01	< 0.3	< 0.5	n.d.	n.d.
760-300	< 0.17	0.04	< 0.01	< 0.3	1.19	n.d.	1.10
Mackenzie	129	50	14	231	1547	8376	2.39

n-C_{12} to n-C_{35} alkanes, which is overlying a moderate unresolved complex mixture (UCM), typical of fossil/petrogenic sources. Algal and photosynthetic bacterial hydrocarbons, characterized by low, odd-numbered carbon n-alkanes (n-C_{17}), were only predominant in the Mackenzie River water and sediments. Similarly, the long-chain homologues (n-C_{27}, n-C_{29}, n-C_{31}) derived from terrestrial higher plant waxes and the mid-chain n-alkanes of odd carbon-numbered (n-C_{23}, n-C_{25}) derived from lower plants were only detected in the sediments, in the superficial suspended particles of site 130-3 and in the freshwater sample of the Mackenzie River.

Other compounds derived from autotrophic marine and freshwater plankton, e.g. the polyunsaturated straight-chain alkenes, n-$C_{21:6}$ and related isomers (n-$C_{21:5}$, n-$C_{21:4}$) (Volkman et al., 1992), were found in all SPM and sediments. Higher concentrations were measured in the deep chlorophyll maxima (DCM) and in the inner shelf sediments.

The C_{25} monounsaturated hydrocarbon (IP_{25}) from sea ice diatoms (Belt et al., 2007) was found in all sediment samples with concentrations ranging from 44 to 235 ng g^{-1}, the highest concentration being measured at site 390 of the east and the lowest at site 690 off the west river mouth.

Retene, a diagenetic polycyclic aromatic hydrocarbon (PAH) from higher plants, was only detected in sediments and in the riverine particulate matter (14 ng L^{-1}). Higher concentrations were found in the riverine particulate matter and shelf sediments.

Table 4. Selected hydrocarbon concentrations and diagnostic ratios in sediment samples from the Beaufort Sea

Locations-Depth (m)	n-C_{17} (ng g^{-1})	$\sum n$-$C_{21:x}$ (ng g^{-1})	IP_{25} (ng g^{-1})	Retene (ng g^{-1})	Wax (C_{25}–C_{31}) (ng g^{-1})	n-alkanes (ng g^{-1})	UCM (ng g^{-1})	CPI(C_{23}–C_{35}/C_{22}–C_{34})	UCM/n-alkanes
390-47	466	950	235	57	1031	7131	47 856	2.4	6.7
690-55	392	748	44	52	1166	6259	34 781	3.0	5.6
260-60	141	218	164	41	574	2658	15 486	3.1	5.8
140-154	163	418	185	21	645	3013	19 684	3.0	6.5
235-576	225	66	127	32	577	3667	24 503	2.7	6.7
345-577	211	50	99	29	701	3762	20 983	2.7	5.6

3.2 Alcohols

Tables 5 and 6 summarize the alcohol concentrations found in the SPM and sediments. Phytol and short-chain n-C_{14}–C_{20} alcohols (SCOH) were the major compounds identified in all marine SPM samples. The concentrations of phytol, a non-specific marker for phototrophic organisms, if compared at the depth of chlorophyll and POC maxima, were highest at sites 345, 460, and 235, and are consistent with the chlorophyll data (Table 2). Phytol concentration also decreased from surface to depth as expected due to degradation. Within the SPM samples, the long-chain n-alcohols (n-C_{22} to n-C_{30}) derived from terrestrial higher plant waxes (LCOH) were only predominant in the Mackenzie River and in the surface water of site 130. In all other samples, they were below detection limit (< 1 ng L^{-1}). Long-chain monounsaturated fatty alcohols (LCMUOH (C_{20}–C_{24}), biomarkers typical of zooplankton, were found at high concentration levels in the deeper water of site 240 and in the river freshwater; their percentage composition relative to total alcohols increased with water column depth.

In sediment samples, the highest concentrations of phytol were measured in the shallow sediments close to the river mouth (sites 390 and 690), and the lowest values observed in the deeper sediments of the slope (235 and 345). LCOH exhibited higher concentrations at the nearshore stations (3 µg g^{-1}, constituting 53 to 70 % of n-alcohols) than at sediments offshore (1.4–2.2 µg g^{-1}), but the contribution of the latter to the n-alcohols was higher (> 70 %). The sediment at site 140, located in the Cape Bathurst polynya region at the mouth of the Amundsen Gulf, showed intermediate concentration values of terrestrial n-alcohols (1.8 µg g^{-1}), with contributions to n-alcohols similar to those of the inshore stations (59 %).

3.3 Sterols

Tables 7 and 8 summarize, respectively, the percentage composition of the major sterols and total sterol concentrations found in the SPM and in the sediments. Sterol distribution in suspended particles from the deep chlorophyll maximum was dominated by 27-nor-24-methylcholesta-5, 22(E)-dien-3β-ol (nor$C_{27}\Delta^{5,22}$), 24-methylcholesta-5, 22(E)-dien-3β-ol ($C_{28}\Delta^{5,22}$, brassicasterol), 24-methylcholesta-5, 24(28)-dien-3β-ol ($C_{28}\Delta^{5,24(28)}$) and the Z isomer of fucosterol (isofucosterol, 24-ethylcholesta-5, 24(28)(Z)-dien-3β-ol; $C_{29}\Delta^{5,24(28)}$). Other minor sterols included cholesta-5, 22(E)-dien-3β-ol ($C_{27}\Delta^{5,22}$), cholest-5-en-3β-ol (cholesterol, $C_{27}\Delta^{5}$), 24-methylcholesta-5-en-3β-ol ($C_{28}\Delta^{5}$); 24-ethylcholesta-5, 22(E)−dien-3β-ol ($C_{29}\Delta^{5,22}$), 24-ethylcholest-5-en-3β-ol (sitosterol, $C_{29}\Delta^{5}$), the 4α-23,24-trimethylcholest-22(E)-en-3β-ol ($C_{30}\Delta^{22}$) and the 24(Z)-propylcholesta-5, 24(28)-dien-3β-ol ($C_{30}\Delta^{5,24(28)}$). In contrast to the marine samples, the freshwater sample from the Mackenzie River was dominated by $C_{29}\Delta^{5}$ and $C_{27}\Delta^{5}$.

The nor$C_{27}\Delta^{5,22}$ sterol was the most abundant sterol at sites 345-60, 235-70, 135-70 with percentage values higher than 20 % of the total sterols.

In sediments, the sterol distribution was dominated by $C_{29}\Delta^{5}$, $C_{28}\Delta^{5,22}$, $C_{27}\Delta^{5}$ and $C_{28}\Delta^{5,24(28)}$. The α-amyrin (Olean-12-en-3α-ol), a specific triterpenoid for angiosperms and also present in peat, was only measured in the sediments and its concentration was higher in the slope than in the shelf sediments.

3.4 Fatty acids

Concentrations of the total fatty acids and selected biomarkers in SPM and sediments are summarized in Tables 9 and 10.

Polyunsaturated fatty acids (PUFA) and short-chain fatty acids (SCFA) were the major FA classes in the SPM with values from 11 to 61 % and from 25 to 77 % of the total FAs, respectively. In sediments, the major component was the short-chain monounsaturated FA (SCMUFA (14–18) with percentages higher than 40 %, while PUFA and SCFA exhibited lower contributions with values ranging from 12 to 22 % and from 21 to 26 % of the total FAs, respectively. Typical molecular distributions are shown in Figs. 3c, 4 and 6. At molecular level, marine suspended particles from the deep chlorophyll maximum of sites 130, 135, 235, 240, 345 and 460 were generally dominated by $C_{16:0}$, $C_{14:0}$, $C_{18:4\omega3}$, $C_{18:5\omega3}$, $C_{22:6\omega3}$ and $C_{20:5\omega3}$. In contrast, suspended particles of the freshwater site, the superficial water of site 130 (130–3) and all the sediments exhibited distributions dominated by $C_{16:0}$, $C_{16:1\omega7}$, $C_{14:0}$ and $C_{20:5\omega3}$. Suspended particles of the deep chlorophyll maximum of sites 540 and 670 showed

Table 5. Alcohol concentrations in the suspended particles from the Beaufort Sea (ng L^{-1}). Percentage of total alcohols is given in brackets.

Locations-Depth (m)	SCOH (n-C_{14}–C_{20})	LCOH (n-C_{22}–C_{30})	n-alcohols	SCMUOH (C_{14}–C_{18})	LCMUOH (C_{20}–C_{24})	Phytol compounds	Total alcohols
130-3	4.4 (7.2)	24.5 (40)	28.9 (47)	1.6 (2.6)	5.9 (9.7)	25 (40)	61
130-130	4.0 (25)	0.0 (0)	4.0 (25)	1.2 (7.5)	3.8 (24)	6.7 (43)	16
130-200	1.0 (9.2)	0.0 (0)	1.0(9.2)	1.0 (8.9)	4.1 (37)	4.9 (44)	11
135-40	0.0 (0.0)	0.0 (0)	0.0 (0)	0.3 (5.3)	1.5 (29)	3.5 (66)	5
135-70	6.7 (20)	0.0 (0)	6.7 (20)	1.4 (4.3)	7.7 (23)	17 (52)	33
135-85	0.6 (3.8)	0.0 (0)	0.6 (4)	0.5 (2.9)	2.8 (18)	12 (76)	16
135-145	0.0 (0.0)	0.0 (0)	0.0 (0)	0.2 (7.2)	0.3 (14)	1.9 (79)	2
235-70	4.7 (24)	0.0 (0)	4.7 (11)	1.6 (3.7)	11.2 (26)	26 (59)	43
235-85	2.3 (28)	0.0 (0)	2.3 (12)	0.4 (2.2)	1.0 (5.1)	16 (81)	20
235-145	0.0 (0.0)	0.0 (0)	0.0 (0)	0.0 (0)	0.2 (16)	1.0 (84)	1
235-200	0.0 (0.0)	0.0 (0)	0.0 (0)	1.0 (15)	3.2 (48)	2.4 (36)	7
240-70	6.0 (24)	1.0 (4.2)	7.1 (28)	1.0 (4.1)	3.0 (12)	13.7 (55)	25
240-130	2.9 (28)	0.0 (0)	2.9 (28)	1.6 (16)	4.3 (41)	1.6 (15)	10
240-200	53 (38)	0.0 (0)	53 (38)	30 (21)	57 (40)	1.8 (1.3)	142
345-60	4.2 (6.7)	0.9 (1.5)	5.1 (8.2)	1.4 (2.3)	7.0 (11)	48 (78)	62
345-85	0.0 (0.0)	0.0 (0)	0.0 (0)	0.3 (3.1)	0.8 (9)	7.7 (88)	9
345-145	0.0 (0.0)	0.0 (0)	0.0 (0)	0.0 (0)	0.3 (38)	0.5 (63)	1
345-200	1.5 (26)	0.7 (12.6)	2.2 (38)	0.2 (3.1)	2.2 (38)	1.1 (20)	6
460-70	8.5 (16)	0.0 (0)	8.5 (16)	1.4 (2.7)	6.6 (13)	36 (69)	53
460-130	0.0 (0.0)	0.0 (00	0.0 (0)	0.2 (9.3)	0.3 (16)	1.4 (75)	2
460-200	0.0 (0.0)	0.0 (0)	0.0 (0)	0.0 (0)	0.2 (8)	2.6 (92)	3
460-300	6.4 (41)	0.0 (0)	6.4 (41)	2.9 (18)	3.3 (21)	3.0 (19)	16
540-70	6.8 (31)	0.0 (0)	6.8 (30)	1.4 (6.1)	4.0 (18)	10.1 (45)	22
540-90	1.7 (16)	0.5 (4.9)	2.3 (20)	0.5 (4.7)	0.6 (5)	7.8 (70)	11
540-200	0.6 (15)	0.5 (12.5)	1.1(27)	0.1 (2.8)	1.1 (28)	1.7 (42)	4
640-70	0.0 (0.0)	0.0 (0)	0.0 (0)	0.5 (6.6)	0.0 (0)	7.0 (93)	8
640-130	3.1 (24)	0.0 (0)	3.1 (24)	1.5 (12)	2.8 (22)	5.2 (41)	13
640-200	0.0 (0.0)	0.0 (0)	0.0 (0)	0.4 (11)	1.3 (32)	2.3 (57)	4
760-130	0.7 (21)	0.6 (19.2)	1.3 (40)	0.1 (3.2)	0.4 (12)	1.5 (45)	3
760-200	0.6 (14)	0.4 (8.1)	1.0 (22)	0.2 (3.5)	1.0 (23)	2.2 (51)	4
760-300	2.9 (40)	0.7 (9.9)	3.7 (49)	0.7 (8.8)	1.8 (25)	1.3 (17)	7
Mackenzie	697 (27)	886 (35)	1583 (62)	93 (3.6)	124 (5)	755 (30)	2555

Table 6. Alcohol concentrations in the sediments from the Beaufort Sea (µg g^{-1}). Percentage of total alcohols is given in brackets.

Locations-Depth (m)	SCOH (n-C_{14}–C_{20})	LCOH (n-C_{22}–C_{30})	n-alcohols	SCMUOH (C_{14}–C_{18})	LCMUOH (C_{20}–C_{24})	Branched alcohols	Phytol compounds	Total alcohols
390-47	2.61 (15)	3.02 (18)	5.63 (33)	1.71 (10)	0.54 (3)	0.19 (1)	9.0 (53)	17.1
690-55	1.29 (11)	3.12 (27)	4.41 (38)	1.57 (13)	0.37 (3)	0.09(1)	5.3 (45)	11.7
260-60	0.53 (10)	1.36 (25)	1.89 (35)	0.26 (5)	0.18 (3)	0.05 (1)	2.9 (55)	5.3
140-154	1.26 (16)	1.86 (23)	3.13 (39)	0.95 (12)	0.34 (4)	0.04 (0.5)	3.5 (44)	8.0
235-576	0.58 (17)	1.64 (47)	2.22 (64)	0. 20 (6)	0.25 (7)	0.04 (1)	0.77 (22)	3.5
345-577	0.74 (16)	2.23 (48)	2.97 (64)	0.20 (4)	0.40 (9)	0.05 (1)	0.99 (21)	4.6

Table 7. Concentrations of sterols in suspended particulate matter (SPM) from the Beaufort Sea (ng L^{-1}). Percentage of total sterols is given in brackets.

Locations-Depth (m)	nor$C_{27}\Delta^{5,22}$	$C_{27}\Delta^{5,22}$	$C_{27}\Delta^{5}$	$C_{28}\Delta^{5,22}$	$C_{28}\Delta^{5,24(28)}$	$C_{28}\Delta^{5}$	$C_{29}\Delta^{5,22}$	$C_{29}\Delta^{5}$	$C_{29}\Delta^{5,24(28)}$	$C_{30}\Delta^{22}$	$C_{30}\Delta^{5,24(28)}$	Sum sterols
130-3	5.2 (3)	10.2 (7)	7.0 (4)	10.8 (7)	48.1 (31)	1.0 (1)	3.6 (2)	18.7 (12)	19.1 (12)	3.8 (2)	2.2 (1)	156
130-130	0.9 (4)	1.8 (8)	3.1 (14)	2.4 (10)	2.1 (9)	0.4 (2)	1.1 (5)	2.8 (12)	1.7 (7)	1.0 (5)	0.5 (2)	22.8
130-200	0.8 (4)	1.6 (7)	2.6 (12)	3.6 (16)	2. (9)	0.5 (2)	0.8 (3)	2.4 (11)	1.7 (8)	0.6 (2)	0.4 (2)	22.0
135-40	2.2 (11)	1.4 (7)	< 2.4	2.5 (13)	1.7 (9)	0.4 (2)	0.3 (2)	1.7 (9)	3.3 (17)	0.5 (3)	0.7 (3)	19.3
135-70	7.3 (22)	2.1 (6)	2.2 (7)	3.5 (11)	2.9 (9)	0.6 (2)	0.7 (2)	2.4 (7)	3.5 (11)	0.5 (1)	1.5 (4)	32.9
135-85	2.7 (12)	1.3 (6)	1.9 (9)	2.2 (10)	2.1 (10)	0.7 (3)	0.7 (3)	1.7 (8)	3.4 (16)	0.2 (1)	0.8 (4)	21.7
135-145	0.3 (4)	0.6 (9)	< 1.8	0.8 (11)	0.9 (13)	0.4 (6)	0.3 (5)	1.0 (14)	0.6 (9)	0.1 (1)	0.1 (2)	7.09
235-70	10.9 (28)	2.3 (6)	2.2 (9)	5.1 (13)	3.1 (8)	0.8 (2)	0.7 (2)	2.4 (6)	4.0 (10)	0.5 (1)	1.1 (3)	39.5
235-85	3.3 (17)	1.2 (6)	< 1.7	2.2 (11)	2.3 (12)	1.2 (6)	0.6 (3)	1.6 (8)	2.9 (15)	0.2 (1)	0.9 (5)	19.6
235-145	0.4 (6)	0.6 (9)	< 2.4	1.0 (14)	0.5 (7)	0.03 (0.4)	0.4 (6)	1.6 (23)	0.8 (12)	0.1 (1)	0.1 (2)	6.96
235-200	0.8 (6)	1.3 (9)	< 2.2	2.3 (16)	1.2 (9)	0.5 (3)	0.7 (5)	2.2 (15)	1.5 (10)	0.3 (2)	0.3 (2)	14.5
240-70	2.5 (10)	2.3 (10)	2.2 (9)	2.7 (11)	3.3 (14)	0.8 (3)	0.4 (2)	1.7 (7)	3.0 (13)	0.1 (0.3)	1.0 (4)	23.8
240-130	0.7 (4)	1.4 (9)	3.2 (19)	1.7 (10)	1.0 (6)	0.4 (2)	0.8 (5)	2.4 (14)	1.2 (8)	0.3 (2)	0.2 (1)	16.4
240-200	0.7 (4)	1.6 (9)	2.3 (14)	2.1 (13)	1.2 (7)	0.4 (2)	0.6 (4)	1.9 (11)	1.5 (9)	0.3 (2)	0.3 (2)	16.4
345-60	11.3 (26)	2.3 (5)	2.4 (6)	5.8 (13)	3.6 (8)	0.6 (2)	0.7 (2)	2.1 (5)	5.2 (12)	0.5 (1)	2.1 (5)	43.2
345-85	0.8 (9)	0.7 (8)	< 2.2	1.2 (14)	1.2 (13)	0.07 (1)	0.3 (3)	0.7 (8)	2.4 (26)	0.1 (1)	0.4 (5)	9.14
345-145	0.2 (5)	0.4 (9)	0.6 (15)	0.5 (13)	0.3 (6)	0.03 (1)	0.2 (5)	0.5 (12)	0.4 (10)	0.04 (1)	0.1 (3)	4.00
345-200	0.5 (4)	0.9 (7)	1.8 (15)	1.6 (13)	0.8 (7)	0.4 (3)	0.6 (5)	1.5 (13)	1.2 (10)	0.2 (2)	0.3 (2)	11.9
460-70	5.8 (13)	2.5 (6)	2.3 (5)	5.2 (12)	4.4 (10)	0.4 (1)	0.9 (2)	2.7 (6)	8.8 (20)	0.4 (1)	3.5 (8)	43.5
460-130	0.3 (5)	0.5 (10)	< 1.0	0.9 (17)	0.5 (9)	0.03 (1)	0.3 (5)	0.7 (14)	0.7 (12)	0.1 (1)	0.1 (2)	5.26
460-200	0.3 (3)	0.6 (7)	1.6 (19)	1.0 (12)	0.8 (10)	0.4 (5)	0.4 (5)	0.9 (11)	0.6 (7)	0.1 (1)	0.2 (2)	8.25
460-300	0.5 (3)	1.3 (8)	1.8 (11)	1.9 (12)	1.7 (10)	1.1 (7)	0.6 (4)	1.9 (12)	1.2 (7)	0.3 (2)	0.2 (1)	16.4
540-70	1.1 (6)	1.1 (6)	1.4 (8)	1.3 (8)	1.9 (11)	0.8 (5)	0.6 (4)	3.1 (18)	2.2 (13)	0.1 (0.3)	0.9 (5)	17.4
540-90	1.2 (12)	0.7 (8)	1.0 (10)	1.7 (18)	0.7 (7)	0.1 (1)	0.3 (3)	0.7 (7)	1.0 (10)	0.1 (1)	0.1 (1)	9.60
540-200	0.3 (4)	0.6 (8)	1.1 (15)	1.1 (15)	0.6 (9)	0.3 (4)	0.3 (4)	0.6 (9)	0.6 (8)	0.1 (1)	0.1 (2)	7.25
640-70	0.9 (5)	1.1 (6)	< 7.7	1.2 (6)	2.0 (11)	1.3 (7)	1.5 (8)	5.4 (28)	2.9 (15)	0.1 (1)	0.4 (2)	19.1
640-130	0.6 (3)	1.4 (8)	2.7 (15)	2.3 (12)	1.7 (9)	0.9 (5)	0.7 (4)	2.2 (12)	1.4 (8)	0.3 (1)	0.3 (1)	18.1
640-200	0.4 (3)	0.9 (8)	1.2 (11)	1.4 (13)	1.2 (11)	0.5 (5)	0.5 (4)	1.2 (11)	1.1 (10)	0.3(3)	0.2 (2)	10.9
760-130	0.3 (4)	0.5 (7)	0.9 (13)	1.1 (14)	1.1 (15)	0.3 (4)	0.3 (4)	0.6 (9)	0.6 (8)	0.1 (1)	0.1 (1)	7.38
760-200	0.4 (4)	0.9 (9)	1.2 (13)	1.2 (12)	1.2 (13)	0.4 (4)	0.3 (3)	0.7 (7)	0.8 (8)	0.4 (4)	0.2 (2)	9.92
760-300	0.3 (4)	0.7 (10)	1.1 (16)	0.9 (13)	0.7 (9)	0.3 (4)	0.3 (4)	0.7 (9)	0.7 (9)	0.1 (2)	0.1 (1)	7.24
Mackenzie	11.4 (1)	207 (8)	450 (18)	274 (11)	131 (5)	156 (6)	135 (6)	654 (26)	< 1.27	< 1.27	< 1.27	2473

Table 8. Concentrations of sterols in sediments from the Beaufort Sea (µg g^{-1}). Percentage of total sterols is given in brackets.

Locations-Depth (m)	nor$C_{27}\Delta^{5,22}$	$C_{27}\Delta^{5,22}$	$C_{27}\Delta^{5}$	$C_{28}\Delta^{5,22}$	$C_{28}\Delta^{5,24(28)}$	$C_{28}\Delta^{5}$	$C_{29}\Delta^{5,22}$	$C_{29}\Delta^{5}$	$C_{29}\Delta^{5,24(28)}$	$C_{30}\Delta^{22}$	$C_{30}\Delta^{5,24(28)}$	Sum sterols	α -amyrin
390-47	0.35 (0.9)	1.96 (5)	3.37 (9)	5.02 (14)	3.64 (10)	3.71 (10)	2.42 (7)	8.81 (24)	1.88 (5)	0.25 (1)	1.31 (3)	36.8	0.044
690-55	0.18 (1.2)	1.01(6)	2.03 (13)	1.04 (7)	2.23 (14)	1.15 (7)	0.52 (3)	2.42 (15)	0.64 (4)	0.13 (1)	0.82 (5)	15.6	0.073
260-60	0.12 (1.6)	0.46 (6)	1.52 (19)	0.76 (10)	0.63 (8)	0.37 (5)	0.31 (4)	1.11 (14)	0.41 (5)	0.15 (2)	0.18 (2)	7.80	0.080
140-154	0.23 (1.9)	0.87 (7)	1.58 (13)	1.99 (16)	1.08 (9)	0.56 (5)	0.47 (4)	1.62 (13)	0.78 (6)	0.36 (3)	0.29 (2)	12.2	0.104
235-576	0.09 (1.6)	0.27 (5)	0.63 (12)	0.61 (11)	0.34 (7)	0.24 (4)	0.27 (5)	1.06 (19)	0.43 (8)	0.19 (3)	0.16 (3)	5.43	0.077
345-577	0.19 (2.0)	0.58 (6)	0.98 (10)	1.11 (12)	0.61 (6)	0.34 (3)	0.39 (4)	1.99 (21)	0.92 (10)	0.27 (3)	0.32 (3)	9.42	0.086

intermediate distributions between the two previously described, suggesting a mixed contribution of flagellates and diatoms at these sites.

Similar to the LCOH, only the sediments, the superficial water of site 130 and the Mackenzie River sample contained the homologous series of long-chain C_{22}–C_{30} *n*-alkanoic acids (LCFA), typical of higher plants, with the C_{24} member being the most abundant.

The branched FA of known bacterial origin (BrFA), e.g. *iso*- and *anteiso*-C_{15} and C_{17} FAs, were minor components (< 5 % of total FAs). Highest concentrations were measured in the river sample and sediments, and the lowest values in the off-shore waters where they decreased from the DCM towards higher depths. At some sites (345, 240, 460, 640, 760), relatively high percentages were observed in the upper Pacific halocline at ∼ 130 m depth.

3.5 Principal component analysis (PCA)

Principal component analysis (PCA) was performed on a dataset from SPM consisting of weight ratios of individual fatty alcohols to total fatty alcohols, individual sterols to total sterols, and of FA groups and selected FA compounds to total FAs. The analysis was done with STATISTICA package for Windows (version 6.1).

Table 9. Concentrations and diagnostic ratios of selected fatty acids (FAs) in SPM from the Beaufort Sea (ng L^{-1}). Percentage of total FAs is given in brackets.

Locations-Depth (m)	Total FAs	SCFA (C_{14}–C_{20})	LCFA (C_{22}–C_{28})	SCMUFA (C_{14}–C_{18})	LCMUFA (C_{20}–C_{24})	Br FA	PUFA	C_{18}PUFA	$C_{20:5\omega3}$	$C_{22:6\omega3}$	18:1ω9/18:1ω7
130-3	2297	754 (33)	47 (2.1)	496 (22)	7.2 (0.3)	29 (1.3)	907 (39)	293 (13)	326 (14)	212 (9)	4.9
130-130	311	105 (34)	0.7 (0.2)	89 (28)	1.2 (0.4)	4.3 (1.4)	108 (35)	43 (14)	25 (8)	31 (10)	9.0
130-200	372	120 (32)	0.9 (0.2)	138 (37)	1.6 (0.4)	6.6 (1.8)	99 (27)	30 (8)	34 (9)	27 (7)	4.8
135-40	266	104 (39)	0.5 (0.2)	29 (11)	0.7 (0.3)	0.6 (0.2)	132 (49)	65 (24)	22 (8)	30 (11)	8.3
135-70	446	134 (30)	0.5 (0.1)	48 (11)	1.2 (0.3)	2.8 (0.6)	260 (58)	142 (32)	32 (7)	57 (13)	8.3
135–85	250	80 (32)	0.5 (0.2)	33 (13)	0.6 (0.2)	2.1 (0.8)	132 (53)	73 (29)	18 (7)	21 (8)	7.4
135-145	133	61 (46)	0.1 (0.1)	31 (23)	1.0 (0.8)	0.9 (0.7)	38 (28)	12 (9)	14 (11)	7.8 (6)	5.5
235-70	408	116 (28)	0.8 (0.2)	58 (14)	1.3 (0.3)	3.4 (0.8)	225 (55)	120 (29)	33 (8)	44 (11)	8.6
235-85	287	93 (32)	0.0 (0.0)	50 (17)	0.0 (0.0)	0.0 (0.0)	141 (49)	76 (27)	28 (10)	22 (8)	6.6
235-145	114	65 (57)	1.2 (1)	20 (17)	0.1 (0.1)	0.0 (0.0)	27 (24)	12 (10)	6.4 (6)	6.7 (6)	7.4
235-200	110	42 (38)	0.5 (0.4)	30 (27)	1.1 (1)	1.0 (0.9)	36 (32)	14 (13)	9.2 (8)	9.3 (8)	5.4
240-70	331	113 (34)	1.8 (0.5)	42 (13)	0.8 (0.2)	4.6 (1.4)	166 (50)	94 (28)	25 (7)	31 (9)	5.4
240-130	151	100 (66)	0.3 (0.2)	25 (17)	1.0 (0.7)	2.7 (1.8)	21 (14)	9.0 (6)	5.0 (3)	5.0 (3)	3.2
240-200	234	59 (25)	0.4 (0.2)	100 (42)	1.3 (0.6)	2.3 (1.0)	64 (27)	19 (8)	24 (10)	13 (5)	2.6
345-60	903	212 (23)	0.8 (0.1)	94 (10)	2.1 (0.2)	3.2 (0.3)	586 (65)	327 (36)	69 (8)	118 (13)	14.1
345-85	166	57 (35)	0.2 (0.1)	22 (13)	0.1 (0.0)	1.0 (0.6)	83 (50)	48 (29)	10 (6)	11 (6)	6.7
345-145	26	7.3 (28)	0.0 (0.0)	5 (20)	0.0 (0.0)	0.6 (2.3)	12 (48)	5 (20)	2.4 (9)	3.7 (14)	10.3
345-200	133	73 (55)	0.3 (0.2)	25 (19)	0.8 (0.6)	1.1 (0.8)	32 (24)	13 (10)	7.2 (5)	8.2 (6)	9.8
460-70	721	179 (25)	1.8 (0.2)	87 (12)	1.1 (0.2)	3.7 (0.5)	444 (61)	246 (34)	63 (9)	86 (12)	6.5
460-130	68	28 (41)	0.1 (0.1)	15 (21)	0.0 (0.0)	0.8 (1.1)	24 (35)	9.4 (14)	6.2 (9)	6.2 (9)	5.1
460-200	252	106 (42)	0.7 (0.3)	73 (29)	0.5 (0.2)	1.1 (0.4)	67 (26)	16 (6)	30 (12)	15 (6)	6.8
460-300	286	97 (34)	0.4 (0.1)	101 (35)	4.1 (1)	2.2 (0.8)	80 (28)	15 (5)	40 (14)	20 (7)	4.3
540-70	315	81 (26)	0.9 (0.3)	71 (22)	0.8 (0.3)	1.6 (0.5)	155 (49)	75 (24)	40 (13)	25 (8)	8.0
540-90	175	45 (26)	0.5 (0.3)	34 (20)	0.2 (0.1)	1.2 (0.7)	92 (52)	55 (31)	12 (7)	15 (9)	11.0
540-200	129	44 (34)	0.5 (0.4)	37 (29)	0.5 (0.4)	1.3 (1.0)	44 (34)	18 (14)	12 (9)	10 (8)	8.1
640-70	922	716 (77)	4.3 (0.5)	90 (10)	0.0 (0.0)	0.0 (0.0)	103 (11)	42 (5)	33 (4)	12 (1)	14.8
640-130	354	112 (32)	1.7 (0.5)	124 (35)	1.1 (0.3)	2.9 (0.8)	106 (30)	30 (9)	43 (12)	24 (7)	8.7
640-200	237	80 (34)	0.5 (0.2)	77 (32)	0.8 (0.3)	1.4 (0.6)	76 (32)	32 (14)	24 (10)	14 (6)	7.1
760-130	76	30 (40)	0.2 (0.3)	16 (21)	0.2 (0.3)	1.1 (1.4)	27 (36)	14 (18)	4.3 (6)	6.9 (9)	8.8
760-200	158	39 (25)	0.8 (0.5)	60 (38)	0.6 (0.4)	1.9 (1.2)	53 (33)	22 (14)	16 (10)	11 (7)	12.2
760-300	146	41 (28)	0.4 (0.3)	59 (40)	0.8 (0.6)	1.4 (0.9)	41 (28)	15 (11)	14 (10)	7.2 (5)	9.5
Mackenzie	13 590	4249 (31)	910 (7)	3473 (26)	67 (0.5)	518 (4)	3896 (29)	1405 (10)	1022 (7)	130 (1)	0.8

Table 10. Concentrations and diagnostic ratios of selected fatty acids (FAs) in sediments from the Beaufort Sea (µg g^{-1}). Percentage of total FAs is given in brackets.

Locations-Depth (m)	Total FAs	SCFA (C_{14}–C_{20})	LCFA (C_{22}–C_{28})	SCMUFA (C_{14}–C_{18})	LCMUFA (C_{20}–C_{24})	Br FA	PUFA	C_{18} PUFA	$C_{20:5\omega3}$	$C_{22:6\omega3}$	18:1ω9/18:1ω7
390-47	572	147 (26)	6.2 (1.1)	281 (49)	2.6 (0.5)	6.9 (1.2)	125 (22)	13.8 (2.4)	75 (13)	6.1 (1.1)	1.0
690-55	250	55 (22)	5.1 (2.0)	131 (52)	1.0 (0.4)	3.1 (1.2)	53.7 (21)	8.91 (3.6)	32 (13)	2.8 (1.1)	3.1
260-60	90.8	20 (22)	1.5 (1.6)	50.6 (56)	0.5 (0.6)	1.3 (1.5)	16.0 (18)	2.02 (2.2)	9.8 (11)	1.0 (1.1)	0.4
140-154	252	53 (21)	2.3 (0.9)	153 (61)	0.8 (0.3)	2.3 (0.9)	38.4 (15)	5.27 (2.3)	23 (9)	2.6 (1.0)	0.6
235-576	28.6	6.7 (23)	2.2 (7.5)	14.4 (50)	0.6 (1.9)	1.1 (3.8)	3.45 (12)	0.62 (2.2)	1.8 (6)	0.2 (0.8)	0.5
345-577	30.3	7.4 (25)	2.5 (8.2)	12.5 (41)	0.7 (2.2)	1.5 (5.0)	5.37 (18)	0.76 (2.5)	2.6 (8)	0.5 (1.6)	0.4

Figure 2 summarizes the PCA results. The plot (2A) distinguishes two groups which are characterized by typical factor loadings of their variables (2B). Phytol, nor$C_{27}\Delta^{5,22}$ sterol, C_{18} PUFA and $C_{22:6\omega3}$, representing fresh phytoplankton dominated by flagellates and dinoflagellates, showed all negative factor loadings for PC1. The rest of sterols together with the short-chain monounsaturated fatty acids (SCMUFA), the branched FAs, the long-chain *n*-alcohols and FAs, indicating refractory material from both marine and terrestrial sources, showed all positive loadings. Similarly, the loadings for PC2 were positive for long-chain *n*-alcohols and *n*-fatty acids, branched FAs, LCMUOH (C_{20}–C_{24}), $C_{16:4\omega1}$ and phytanic acid, indicating zooplanktonic, terrestrial, diatom and bacterial sources. From these loadings the two clusters in the

Table 11. Stable carbon isotopic composition (δ^{13}C (‰) average of three replicate injections with S.D. < 0.8) of selected lipid biomarkers in SPM from Beaufort Sea.

Locations-Depth (m)	*n*-$C_{21:6}$	phytol	nor$C_{27}\Delta^{5,22}$	$C_{27}\Delta^5$	$C28\Delta^{5,24(28)}$	$C29\Delta^5$	$C29\Delta^{5,24(28)}$	*i*-C_{15} FA	C_{16} FA	$C_{20:5\omega3}$	$C_{22:6\omega3}$
130-3	−32.9	−30.0	−32.3	−29.8	−26.4	−32.5	−32.9	−24.5	−30.4	−31.9	−32.3
130-130								−24.0	−28.6	−32.4	−31.8
130-200									−29.2	−32.6	−32.9
135-40								−29.3*	−31.1	−37.2	−36.0
135-70		−36.1	−28.1	−28.6	−31.8	−31.7	−33.2				
135-85								−28.5	−30.4	−33.1	−33.5
135–145								−26.3	−28.6	−30.8	−32.6
235-70		−40.6	−33.5		−29.8	−32.1*	−34.2	−29.2*	−30.7	−33.2	−34.8
235-145									−27.7	−33.5	−32.6
235-200								−27.0	−29.3	−32.7	−32.7
240-70	−36.6	−36.5	−26.6	−26.9	−33.7	−31.3	−34.5	−28.9	−30.2	−35.0	−35.5
240-200	−33.5				−28.0	−29.6	−32.5*		−29.5	−31.9	−32.1
345-60	−35.6	−30.9	−23.6	−27.3	−32.0	−31.9	−33.9	−27.4*	−31.2	−33.2	−31.9
345-85		−37.9	−27.9		−34.0		−36.1				
345-145										−32.9	−32.2
345-200								−26.7	−29.6	−33.3	−33.2
460-70	−37.2								−32.9	−34.2	−34.7
460-300									−29.1	−32.4	−32.3
540–70	−36.1							−27.0*	−30.5	−32.5	−33.4
540-200								−26.5	−30.2	−32.9	−32.9
640-70									−29.4	−30.6	−32.4
640-200								−26.2	−31.1	−32.9	−32.7
760-200								−29.1	−29.7	−32.8	−32.9
Mackenzie	−35.2	−35.9		−31.1	−29.4	−30.7		−29.6	−31.0	−36.0	−34.5

* Values with 1 < S.D. < 2.

Table 12. Stable carbon isotopic composition (δ^{13}C (‰) average of three replicate injections with S.D. < 0.8) of selected lipid biomarkers in sediments from Beaufort Sea.

Locations-Depth (m)	C_{23}	C_{29}	IP_{25}	*n*-$C_{21:6}$	Phytol	C_{26}-OH	$C_{28}\Delta^{5,24(28)}$	$C_{29}\Delta^5$	*i*-C_{15}	C_{16}FA	$C_{20:5\omega3}$	C_{26}-FA
390-47	−30.1	−30.2	−20.6	−29.5	−27.4	−31.2	−24.3	−24.0	−28.4*	−28.2	−29.6	−30.5
690-55	−30.1	−30.9		−31.5	−29.1	−31.5	−25.5	−28.6	−29.3*	−31.1	−31.8	−32.1
260-60	−30.4	−29.8	−18.7	−29.2	−28.4	−31.9	−24.2	−26.7	−27.6	−28.5	−29.8	−30.7*
140-154	−29.8	−30.3	−17.5	−31.5	−27.9	−30.5	−24.6	−27.2		−30.0	−32.3	−30.9
235-576	−30.2	−30.3	−19.9		−28.3	−31.1	−25.4*	−27.2	−27.5*	−29.4	−31.6	−30.6*
345-577	−29.7	−30.9	−20.3		−29.1	−30.9	−26.6	−27.2	−26.3	−28.0	−30.1	−30.0

* Values with 1 < S.D. < 2.

plot represent a group with high negative PC1 loadings (fresh phytoplankton component) and a group with a high positive PC1 contribution (marine and terrestrial refractory material). The first group represents suspended particles from the DCM (60–85 m), except for the station 640-70 and the second group all the deeper suspended particles (≥ 100 m) and the superficial 640-70. Other scattered and particular samples included the Mackenzie River, with high contribution of terrestrial and refractory material, the 240-200 with high contribution of zooplankton material, the 130-3 with some refractory and diatom material, and the 135-40 with very low phytoplankton marker concentrations.

3.6 Compound-specific isotope analysis

Tables 11 and 12 summarize the stable carbon isotopic composition δ^{13}C (‰) of selected lipid biomarkers in SPM and sediments. Values are given as mean of triplicate injections with s.d. Additional δ^{13}C data are also displayed together with their molecular abundances in Figs. 3, 4, 6 and 9.

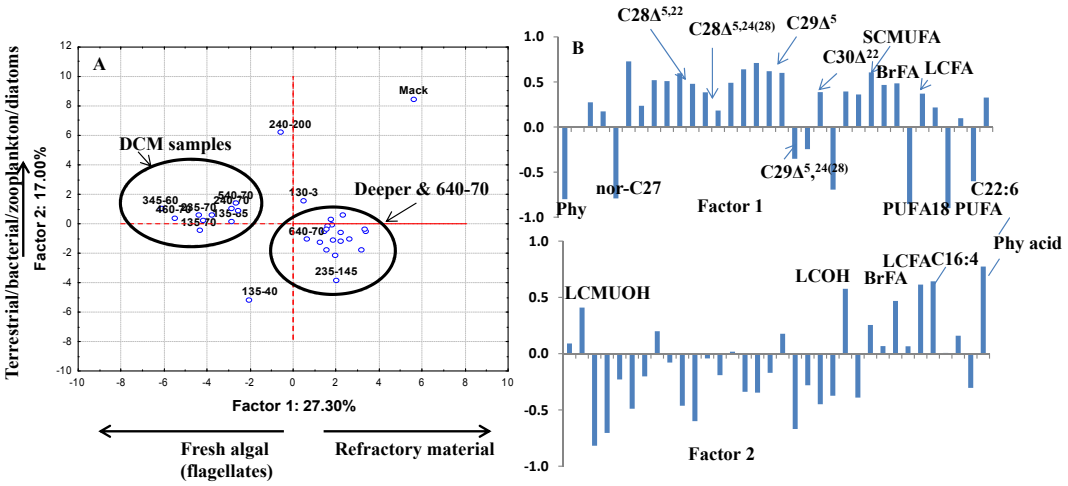

Fig. 2. Principal component score plot for each suspended particulate matter sample **(A)**, showing 44 % of the variance and **(B)** factor loadings for the variables.

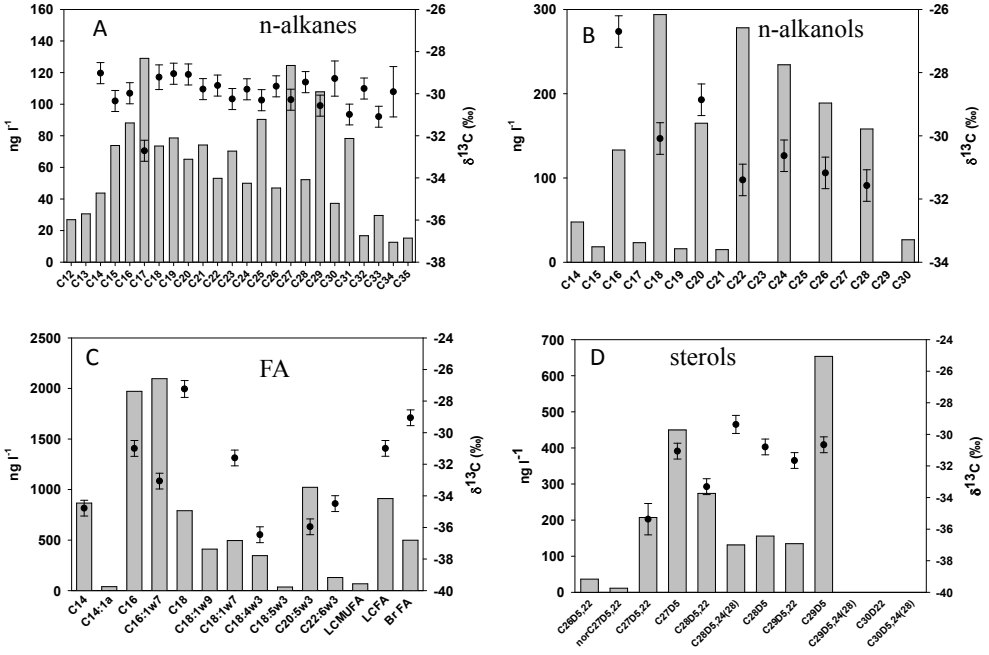

Fig. 3. Concentrations (bars) and carbon isotopic ratios (mean ± SD, $n = 3$) of selected molecular biomarkers in the suspended particulate matter from the Mackenzie River: **(A)** *n*-alkanes; **(B)** *n*-alkanols; **(C)** selected fatty acid (FA) compounds; and **(D)** sterol compounds.

Carbon isotope ratios of phytol in SPM showed a large range of values, from −31 ‰ at site 345-60 , where a bloom of flagellates/dinoflagellates occurred, to values as low as −40 ‰ at site 235-70, where dinoflagellates were predominant. At site 345, a −7 ‰ depletion between samples at 60 and 85 m was observed. The most depleted values were even more depleted than the one measured in the freshwater sample (−36 ‰). In contrast to the SPM, carbon isotope composition of phytol in sediments was quite homogeneous with values from −27 to −29 ‰.

Isotope values of the algal planktonic *n*-$C_{21:6}$ in the marine SPM (−33 to −37 ‰) were not different from the value obtained in the Mackenzie River (−35 ‰), and more enriched values were obtained in the sediment samples (−29 to −31 ‰).

The $\delta^{13}C$ signatures of the FAs in our SPM and sediments from the shelf are more depleted than those of previous studies (Goñi et al., 2000, 2005) that report values of −19 to −24 ‰ using the methodology of alkaline CuO.

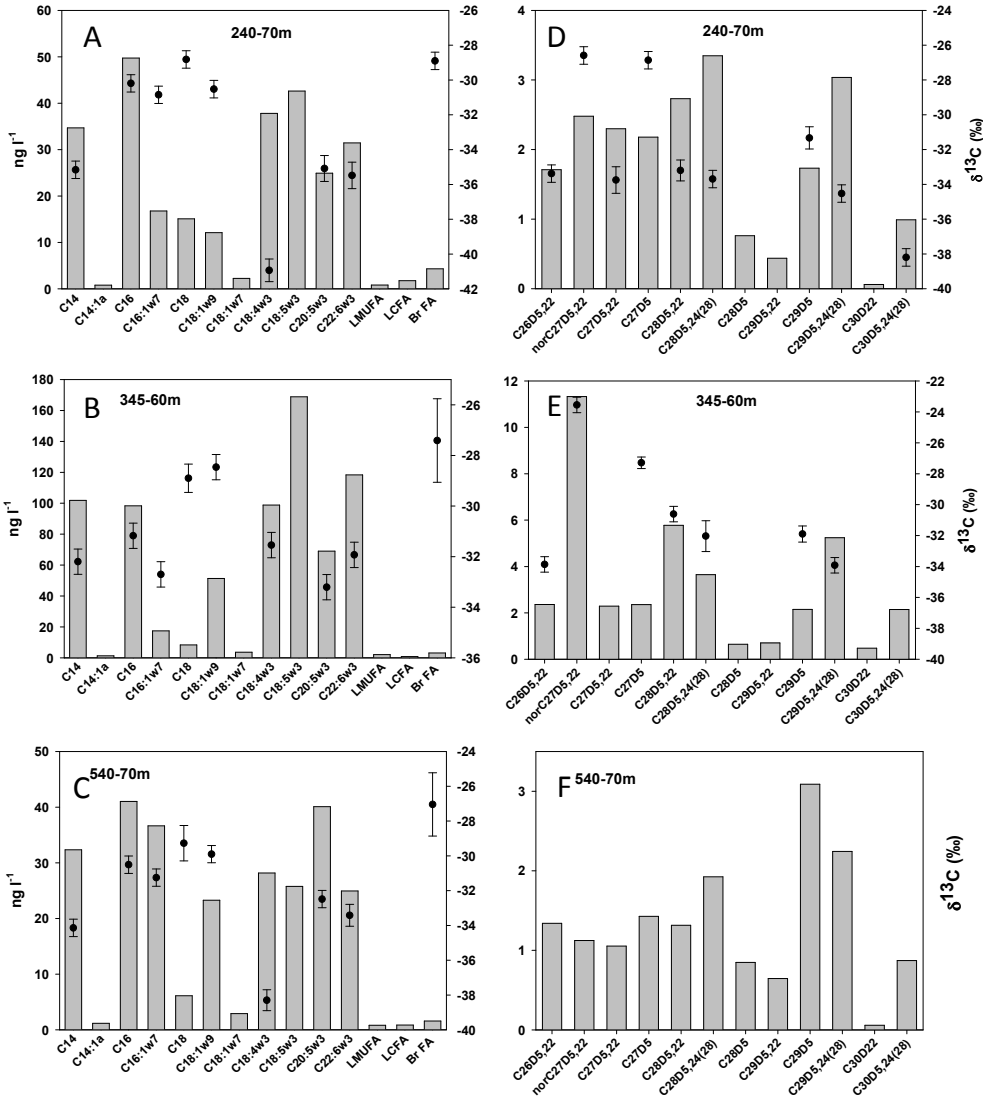

Fig. 4. Concentrations (bars) and carbon isotopic ratios (mean ± SD, $n = 3$) of selected fatty acids **(A–C)** and sterols **(D–F)** in selected SPM from the Mackenzie slope.

The δ^{13}C values for the *n*-alkanes in sediments averaged −29.5 ‰. The C_{27} and C_{29} homologues were slightly lighter showing mean δ^{13}C values of −30 and −30.5 ‰, respectively, which fell into the high range of C_3 vascular plants (−29 to −39 ‰; Collister et al., 1994; Chikaraishi and Naraoka, 2003; Bi et al., 2005). Similar δ^{13}C-depleted values were obtained for the odd mid-chain alkanes (C_{23}–C_{25}), giving no evidence for input of C_4 plants or aquatic plants (Chikaraishi and Naraoka, 2005).

Isotopic values of the marker for sea ice algae with 25 carbon atom skeleton (ice proxy, IP_{25}) in sediments ranged between −17 and −21 ‰.

4 Discussion

4.1 Sources of organic carbon in the suspended particlesof the Mackenzie River

The Mackenzie River flows through various types of land including Arctic tundra, boreal forest, peatland and mountains (Dyke and Brooks, 2000). The tundra is an ecosystem rather decoupled from the river system and is likely to make a small contribution to the total OM. In contrast, the boreal forest, mostly conifers, is certainly an important source of terrigenous organic matter of higher plant origin (Carrie et al., 2009; Solomon et al., 2000). The Mackenzie River is also the likely source of fossil material, such as coal fragments, to the Beaufort Sea (Dyke and Brooks, 2000; Yunker et al., 2011).

As it is shown in Fig. 3a, the algae-related n-C_{17} alkane predominates over the short-chain n-alkanes in the Mackenzie River giving evidence of the importance of freshwater algae or photosynthetical bacteria (Han and Calvin, 1969). Its $\delta^{13}C$ value of -32.7‰ contrasts with those measured for the even n-alkanes, which are fossil derived ($\delta^{13}C$ of ~ -30‰). A higher abundance and lower $\delta^{13}C$ values of the odd-chain alkanes compared to the even alkanes can also be observed. This highlights the terrestrial contribution of the odd n-alkanes (n-C_{27}, n-C_{29}, n-C_{31}, with $\delta^{13}C$ values of -31‰), overlapping the petroleum-derived alkanes. This latter fossil signature is enhanced by the presence of a considerable amount of UCM, typical of fossil/petrogenic sources (Table 3). A confirmation of the fossil source was also obtained by mass fragmentograms (m/z 191, not presented here), which exhibited a series of extended C_{32}–C_{35} hopanes characteristic of oil-derived hydrocarbons. The contribution of n-C_{23} and n-C_{25} homologues relative to the other long-chained n-alkanes, with a n-C_{23} to n-C_{23} plus n-C_{29} ratio ~ 0.4–0.5, indicates an additional contribution of C_3-lower plants, such as mosses. Similar ratios were reported for the Eurasian Arctic rivers, where *Sphagnum*-rich peats were the major source of OM (Vonk et al., 2008). The distribution of n-alkanols with even carbon (Fig. 3b) showed maximum values at n-C_{18} and n-C_{22}, and a decreasing trend from n-C_{22} to n-C_{28}. This distribution which was already found in SPM from the Mackenzie River in 1987 (Yunker et al., 1995) indicates a mixing of bacterial, algal and vascular land plants. The $\delta^{13}C$ values for the alcohols n-C_{22} to n-C_{28} were around -31‰, typical of gymnosperms C_3 plants (Chikaraishi and Naraoka, 2003, 2007). More enriched values were obtained for the short-chain n-alkanols (-26 to -30‰), which are likely to derive from bacterial sources. As expected, the compound-specific isotope values for lipids are depleted by ~ 5–6‰ compared to the $\delta^{13}C$ reported for bulk samples of the Mackenzie River (-26 to -27‰) (Goñi et al., 2005). Although lignin and $\delta^{13}C$ data indicated that the major source of terrigenous material in this area consists of non-woody, C_3 angiosperm vascular plant vegetation derived from the tussock vegetation (sedges, cotton grass) (Goñi et al., 2000; Naidu et al., 2000), our relatively enriched n-alkanes and n-alkanols $\delta^{13}C$ values suggest that they might be derived from gymnosperms. Angiosperms usually have long-chain n-alkyl compounds depleted in ^{13}C compared to gymnosperms, with n-alkane $\delta^{13}C$ values of -36‰ for angiosperms and -31.6‰ for gymnosperms (Chikaraishi and Naraoka, 2003, 2007).

The fatty acid signature exhibited by the Mackenzie River (Fig. 3c) shows a typical profile of diatoms with relatively depleted $\delta^{13}C$ values (-36‰), typical of freshwater phytoplankton. In addition to this aquatic production, the terrestrial component represented by the LCFA (n-C_{22} to n-C_{28}) with $\delta^{13}C$ values of -31‰ confirms again the C_3 higher plant contribution. The bacterial lipids represented by the branched FAs and $C_{18:1\omega7}$ were among the less important groups of FAs, and the $18:1\omega9/18:1\omega7 < 1$ indicates a major bacteria-derived source for the $C_{18:1\omega7}$ in the river SPM.

Sterol distribution in suspended particles from the Mackenzie River (Fig. 3d) was dominated by $C_{29}\Delta^5$, $C_{27}\Delta^5$, $C_{28}\Delta^{5,22}$ and $C_{27}\Delta^{5,22}$. In the river water, it is likely that part of the sterols present are derived from higher plants or macrophytes, e.g. $C_{28}\Delta^5$, $C_{29}\Delta^5$ and $C_{29}\Delta^{5,22}$ sterols, sitosterol ($C_{29}\Delta^5$) being by far the most abundant sterol. Their $\delta^{13}C$ values ranging from -30.6 to -31.6‰ suggest a C_3 terrestrial source, but these values are not distinguishable from those of the diatom-derived $C_{28}\Delta^{5,24(28)}$ (-30‰). In contrast, the other two diatom related sterols, $C_{28}\Delta^{5,22}$ and $C_{27}\Delta^{5,22}$, show more depleted $\delta^{13}C$ values (-34 to -36‰), typical of freshwater phytoplankton. Phytoplankton growing in fresh waters typically have depleted $\delta^{13}C$ values (-25–42‰) in comparison to C_3 land plants (-20 to -32‰) (Boutton, 1991). However, carbon isotopic data in freshwater ecosystems are not always source-specific, because values for freshwater phytoplankton and terrestrial plants can overlap (Cloern et al., 2002). Volkman (1986) suggested that an evaluation of campesterol/stigmasterol/β-sitosterol ratios is necessary in order to determine if these sterols are appropriate to be used as terrestrial biomarkers. For various higher plants, the relative abundance of these plant sterols has been found to be 1/(0.5–1.3)/(11.5–31) (Nishimura, 1977). Hence, the main source of sitosterol in the river water seems to be from terrestrial emergent vascular plants.

Overall, the lipid composition of the Mackenzie River water was characterized by a major fossil component, important amounts of algal material dominated by diatoms and a terrestrial component mainly derived from the C_3 emergent plants.

4.2 Sources of organic matter in the suspended particles of the off-shore marine water column

Total primary productivity in the Beaufort Sea usually ranges from 30 to 70 g C m^{-2} yr^{-1}, indicating oligotrophic conditions (Brugel et al., 2009; Carmack et al., 2006, 2004; Mundy et al., 2009). In summer, nutrients are rapidly drawn from the surface layer, resulting in the formation of a subsurface chlorophyll maximum at 25 to 30 m depth (Carmack et al., 2004). In our samples from summer 2009, Chl *a* concentrations were generally low (< 1 mg m^{-3}) throughout the water column with a subsurface maximum centered around 60–70 m depth. The highest concentrations of marine algal biomarkers and Chl *a* were found on the east side of the main Mackenzie runoff (sites 345 and 460). Typical distributions of the diagnostic fatty acids and sterols are shown in Fig. 4. As it is observed in Fig. 4 and Table 9, the greater concentration of $C_{22:6\omega3}$ over $C_{20:5\omega3}$, together with the high concentrations of $C_{18:4\omega3}$ and $C_{18:5\omega3}$, in the upper 100 m of the eastern part of the study area (sites 130, 135, 235, 240, 345, 460) suggests that flagellates, including Prymnesiophyceae and Prasinophyceae (Dunstan et al., 1992), and

dinoflagellates were the major constituents of the phytoplankton in the surface waters of this area. In contrast, the higher contribution of $C_{20:5\omega3}$ in the offshore waters from the western sector of the study area (sites 540, 640 and 760), and in the lower Atlantic halocline water (> 200 m depth), of all sites sampled indicates a prevalence of diatom remnants. Moreover, the sterol profile dominated by $C_{28}\Delta^{5,24(28)}$ and $C_{29}\Delta^{5,24(28)}$ (Fig. 4d) may indicate that OM derives from prasinophytes (Volkman et al., 1994). These results are consistent with the findings of Balzano et al. (2012) and Lovejoy et al. (2007), where Arctic *Micromonas*, a typical Prasinophyceae was shown to be the dominant picoplankton during the sampling period. Previous studies (autumn 2003–2004) also showed higher abundances of prasinophytes in the Mackenzie Shelf contributing up to 38 % of the total phytoplankton community (Brugel et al., 2009).

The most enriched δ^{13}C values of phytol (Table 11) were measured at 3 and 60 m depths at sites 130 and 345, respectively, suggesting the highest growth rates. The large distribution of δ^{13}C values (Table 11) accounts for differences in light regime and growth rate. These results are consistent with the large range in δ^{13}C bulk values (−27 ‰ to −18 ‰) displayed by biogenic particulate OM in the Arctic Ocean (Goericke and Fry, 1994). The δ^{13}C values observed for the straight-chain polyunsaturated alkene *n*-$C_{21:6}$ ranged from −33 to −37 ‰ (Table 11) and are more depleted than those obtained in the sediment samples (−29 to −31 ‰) and the value reported by Belt et al. (2008) in a sediment trap from the Franklin Bay (−28 ‰). Although δ^{13}C values of −35 to −42.2 ‰ for polyunsaturated highly branched isoprenoid isomers from the Baffin Bay were suggested to result from freshwater diatoms (Belt et al., 2008), the so depleted values obtained in marine waters (sites 240, 345, 460 and 540) suggest that the algal compounds (hydrocarbon *n*-$C_{21:6}$ and $C_{20:5\omega3}$ and $C_{22:6\omega3}$ FAs) are derived from slow-growing phytoplankton (Benthien et al., 2007). Indeed, the isotopic signature of pelagic phytoplankton from high latitudes, with relatively high concentrations of CO_2, can be significantly depleted in ^{13}C, with δ^{13}C values ranging from −18 to −28 ‰ in the Arctic Ocean (Goericke and Fry, 1994; Gradinger, 2009; Iken et al., 2005; Ruttenberg and Goñi, 1997; Schubert and Calvert, 2001; Tremblay et al., 2006). Also, the large isotopic offsets between algal biomass and eukaryotic lipid biomarkers ranging from −2 to 12 ‰ (Schouten et al., 1998; Hayes, 2001) are accounting for the relatively depleted δ^{13}C of the biomarkers.

Alkenones typical of four genera of haptophyte algae of the class of Prymnesiophyceae belonging to the Isochrysidales order (*Emiliania, Gephyrocapsa, Isochrysis* and *Chrysotila*) were not detected in any of the water and sediment samples of the present study. This outcome is consistent with the taxonomic results, which report the absence of coccolithophorids (Coupel, personal communication, 2011). However, *Chrysochromulina* spp. belonging to the order of Prymnesiales was observed by Balzano et al. (2012), and sediment traps intercepted coccolithophorids in summer 2004 in Franklin Bay, west of the Amundsen Gulf (Forest et al., 2008). Generally, the occurrence of this class of algae in the Arctic Ocean and adjacent seas is very controversial. Coccolith production appears to be nearly absent in the North Water Polynya of the Baffin Bay (Hargrave et al., 2002), whereas large blooms of *Emiliania huxleyi* occur on the eastern Bering Shelf area (Murata, 2006). Moreover, alkenones found in surface sediments from the Laptev Sea were likely derived from coccolithophorids or other Prymnesiophyceae transported by Atlantic water masses along the continental slope (Fahl and Stein, 1997). All these findings might be related to the geochemical control on primary productivity. For instance, the silicate-rich Pacific waters versus the carbonate-rich Atlantic waters seem to potentially offer different advantages between diatoms/flagellates and coccolithophorids (Carmack et al., 2006).

As it can be observed in the first component of the PCA (Fig. 2b), the correlation of phytol with nor$C_{27}\Delta^{5,22}$ was better than with the $C_{28}\Delta^{5,22}$, $C_{28}\Delta^{5,24(28)}$ diatom sterols (positive scores), showing that the phytoplankton biomass was dominated by dinoflagellates/flagellates. No correlation was found between dinosterol and nor$C_{27}\Delta^{5,22}$, which indicates that they derive from different organisms. Microscopy counts during the Malina cruise revealed the presence of several dinoflagellate species belonging to the genera *Gymnodinium* and *Gyrodinium* (Balzano et al., 2012). Overall, the specific composition of the particulate matter from off-shore waters indicating the importance of dinoflagellates and prasinophytes, together with the low phytoplankton biomarker concentrations and low δ^{13}C, suggests post-bloom conditions during the survey. The low δ^{13}C (Fig. 4, Table 11) likely results from the reduced growth rates that favour the assimilation of the lighter isotope and also from the repleted concentrations of CO_2 in the cold waters.

The traces of *n*-alkanes from C_{23} to C_{33} with no odd/even predominance (CPI ∼ 1) in all samples, except the most superficial one at 3 m depth, indicate fossil- or microbially derived hydrocarbons (Grimalt et al., 1988; Volkman et al., 1980). However, as UCM was not detected, the fossil component in the marine suspended particles was certainly very low. The suspended particulate sample from the upper PML (3 m) of site 130 stands out among all other SPM samples. It contains biogenic material dominated by diatoms plus terrigenous material (wax *n*-alkanes, LCOH, LCFA). A likely explanation for the presence of this material could be the deposition of aerosols on the ice. Plant waxes readily form aerosols and are subject to atmospheric transport. This together with ice melting and subsequent release of particles results in the transfer of terrigenous material from the shelf and land to the offshore waters (Pfirman et al., 1995). The apparent absence of terrestrial biomarkers in the rest of the suspended particles likely results from a massive dilution by marine-derived biomarkers. These observations are consistent with previous studies with sediment traps in the area,

where the levels of terrigenous flux decreased substantially in summertime (Forest et al., 2007).

Moderate amounts of the LCMUOH fatty alcohols, typical of zooplankton, occurred in the deeper SPM, and in particular at site 240. Moreover, below the euphotic zone of site 240, δ^{13}C values indicated phytoplankton produced at higher growth rates at depth than at the DCM. Growth rates and δ^{13}C values of compounds synthesized before and after a bloom are lower than those of compounds synthesized in the main exponential growth phase. All these parameters point out that post-bloom conditions prevailed in the euphotic layer of site 240, whereas the important signal of zooplankton and diatom markers below the euphotic layer gives evidence of the opportunistic behaviour of predators grazing on the sinking flux of remnants of phytoplankton produced during bloom conditions in the euphotic layer. Herbivorous grazers, particularly copepods, may at times effectively graze on suspended algal material in the slope of the Mackenzie Shelf (Forest et al., 2007).

The bacterial lipids represented by the branched FAs were among the less important groups of FAs, exhibiting the highest abundance in the DCM and decreasing from DCM to deep waters. However, percentage values were highest at $\sim$ 130 m depth of most sites (240, 345, 460, 640, 760), corresponding to waters from the upper Pacific halocline. These results are consistent with those from Ortega-Retuerta (2012), where specific bacterial populations predominated in waters below 100 m, and bacteria abundance decreased from river to offshore waters and from surface to deep waters. Although vaccenic acid ($C_{18:1\omega7}$) is considered to be an indicator of bacterial input, its 18:1ω9/18 : 1ω7 isomer ratio >1 (Table 9) suggests a dominant phytoplanktonic source in the marine offshore SPM, in contrast to the major bacteria-derived source in the river SPM.

The δ^{13}C of sitosterol in off-shore SPM had similar depleted values as sitosterol in the river. But they were also similar to other algal sterols (Table 11), which makes it difficult to discern the source of sitosterol only by the δ^{13}C value. However, the poor correlation between the concentrations of sitosterol and other phytoplanktonic markers (phytol, 24-methylenecholesterol, isofucosterol) (excluding the sample 130–3 m) ($r = 0.29$ to 0.35) seems to indicate the mixing of terrestrially and marine-derived sitosterol. Therefore, the terrestrial input derived from this biomarker in the Arctic Sea should be considered with caution. Still, the high percentages of sitosterol relative to total sterols at stations 540 and 640 point out the influence of the Mackenzie River plume. During Malina, the river plume extended farther offshore in the western channel than in the eastern channel, which was reflected by the spatial distribution of high CDOM absorption in the upper PML (Matsuoka et al., 2012).

In order to evaluate the quality and nature of the lipidic component of the OM, we estimated the relative contributions of OM constituents by grouping the different molecular lipid biomarkers into the following components: fossil (UCM, and petroleum hydrocarbons), fresh/labile algal (PUFA, phytol, IP_{25}, n-$C_{21:6}$, $C_{28}\Delta^{5,24(28)}$, $C_{29}\Delta^{5,24(28)}$), refractory/detrital algal (SCFA, SCMUFA, rest of sterols, biogenic alkanes, SCOH, SCMUOH), zooplankton (LCMUFA, LCMUOH), bacterial (branched FAs) and C_3 terrestrial plants (LCFA, LCOH, wax n-alkanes). Figure 5 shows the relative composition for each SPM sample including the freshwater sample from the Mackenzie River. For the Mackenzie River, $C_{18:1\omega7}$ was included within the bacterial and $C_{29}\Delta^5$ within the terrestrial component. The fossil and refractory algal contributions are the dominant fractions of the freshwater OM from the river with $\sim$ 34 % each of the total molecular lipid biomarkers, whereas the terrestrial contribution derived from the C_3 vascular plants accounted for only 10 % and the bacterial and zooplankton pools hardly reached 4 %. In contrast to the freshwater sample, the major contribution in the offshore SPM was from fresh and refractory algal components. As expected, the fresh/labile algal component dominated in the samples from the DCM, whereas the refractory algal material increased with water column depth. Heterotrophic bacterial biomarkers were relatively low in both marine and river samples. For comparison, the POC in samples collected with traps deployed at $\sim$ 100 m depth in the Mackenzie Shelf and slope in 2003–2004 was found to be predominantly marine, whereas the allochthonous (terrestrial) carbon contribution accounted for only 14 to 38 % of total POC (Magen et al., 2010). Other studies based on the same approach of POC/Al ratio used by Magen et al. (2010) found that carbon fluxes of marine origin were higher than 80 % in sediment traps deployed over the slope during summer 2004 (Forest et al., 2007) and averaged 70 % of the total annual POC flux on the shelf during 1987–1988 (O'Brien et al., 2006). In contrast, using the two-end-member mixing model of the marine and terrestrial δ^{13}C values, marine POC fluxes were as low as $\sim$ 10–15 % of the terrestrial fluxes in the Mackenzie outer shelf (Amiel and Cochran, 2008). However, this percentage is extremely sensitive to the δ^{13}C of the marine end-member. A decrease of one per mill yields an increase of approximately 20 % in the estimated marine component.

4.3 Sources of organic matter in the sediments

All concentrations of biomarkers and total organic carbon (TOC) in surface sediments decreased from the shelf to the slope. Relatively high concentrations of phytol and PUFA, such as $C_{20:5\omega3}$ and $C_{22:6\omega3}$ in the sediments (Fig. 6 and Tables 6 and 10), indicate a contribution of fresh OM, which is likely due to a high rate of algal carbon flux, as these PUFA are quickly degraded in the water column after cells lyse. Since diatoms did not represent the major phytoplankton community in our water column samples, the abundance of $C_{20:5\omega3}$ in sediments reflects a previous dominance of diatoms in the water column. Their enriched δ^{13}C values in sediments compared to those in SPM (Tables 11 and 12)

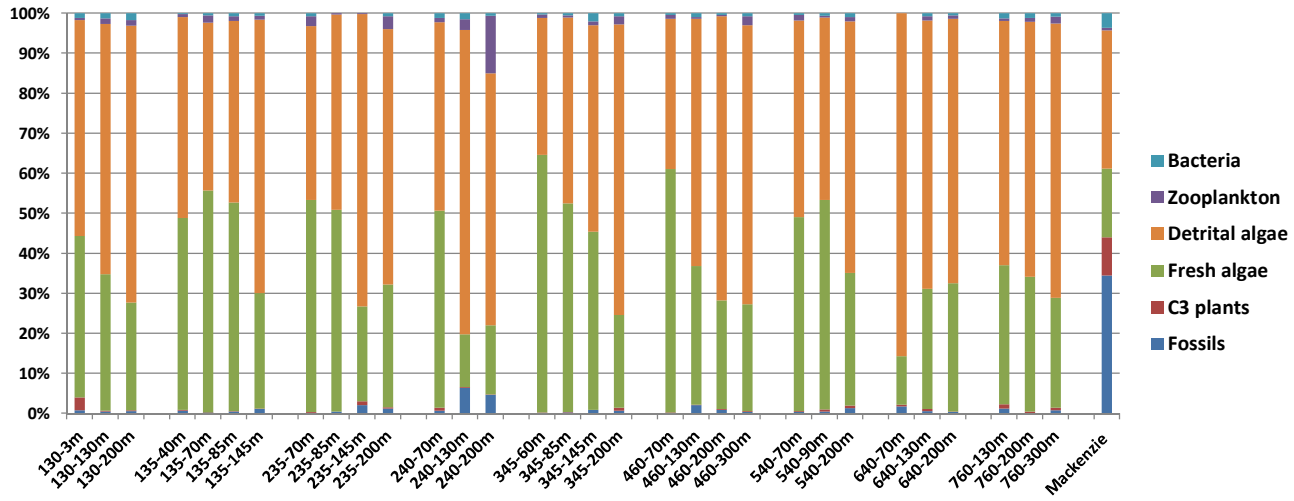

Fig. 5. Relative contributions of OM constituents in the SPM from the Mackenzie River and in the offshore waters from the Mackenzie slope. The molecular biomarkers were separated into the following components: fossil (UCM, and petroleum hydrocarbons), fresh/labile algal (PUFA, phytol, IP_{25}, n-$C_{21:6}$, $C_{28}\Delta^{5,24(28)}$, $C_{29}\Delta^{5,24(28)}$), refractory/detrital algal (SCFA, SCMUFA, rest of sterols, biogenic alkanes, SCOH, SCMUOH), zooplankton (LCMUFA, LCMUOH), bacterial (branched FA) and C_3 terrestrial plants (LCFA, LCOH, wax n-alkanes). For the Mackenzie River, $C_{18:1\omega7}$FA and $C_{29}\Delta5$ were included within respectively the bacterial and terrestrial component.

suggest the sinking of ungrazed diatoms derived from a bloom and/or from ice algae mats released when ice melts. A previous study in the area highlighted that diatoms were important primary producers during the summer, whereas in autumn smaller cells (e.g. flagellates) were dominant (Morata et al., 2008).

The presence of the IP_{25} with highly enriched $\delta^{13}C$ values (Table 12) also confirms the input from ice algae in the sediments. These heavy $\delta^{13}C$ values are well comparable with the data of Belt et al. (2008) from sediments of the Franklin Bay, and are distinguishable from those of OM of planktonic origin (e.g. phytol). Their percentage contribution to total algal hydrocarbons increased from the shelf (5 %) to offshore (48 %) (Fig. 7). Previous studies in this area estimated the production by ice algae to be between 2 and 30 % of the total marine production (O'Brien et al., 2006, and references therein).

Sediment at site 390 showed the highest concentration of lipid biomarkers including the IP_{25} (Table 4), and exhibited the most enriched $\delta^{13}C$ values for all sterols including sitosterol (with values of ~ -24 ‰) (Table 12). These $\delta^{13}C$ values are indicative of marine sources and, together with the distribution of FAs and sterols (Fig. 6), suggest that diatoms (including sea ice diatoms) can be the source of sitosterol at this site. Benthic microalgal production is believed to be small, and the production by macrophytes is not important in the Mackenzie Shelf (Macdonald et al., 1998). We rather believe that these results reflect the annual history of sea ice melting. This means that site 390 was likely to be situated within the flaw polynya (see satellite pictures of the ice cover in Forest et al., 2012) and was subject to a bloom early in the year, which explains the high concentrations of marine and ice algal biomarkers.

Heterotrophic bacteria play an important role in the degradation of the OM during early diagenesis. Branched FAs derived from bacterial biomass were more abundant in the nearshore sediments, and their $\delta^{13}C$ values (i-C_{15}, Table 12) were relatively more enriched than those from terrestrial sources (C_{26} FA) suggesting a predominant utilization of marine-derived OM. The $18:1\omega9/18:1\omega7$ ratios were <1 (Table 10) in all offshore and deeper sediments indicating the predominant bacterial origin of the $C_{18:1\omega7}$ FA in these sediments. All these autochthonous natural inputs overlap with the allochthonous inputs derived from land plants and fossil material. The $\delta^{13}C$ values for the n-alkanes, typical of C_3 vascular plants, were consistent with those previously reported in surface sediments from the Beaufort Sea (Drenzek et al., 2007) and the Franklin Bay (Belt et al., 2008). Higher abundance of terrestrial LCOH and LCFA was measured in the shallow sediments (Tables 6 and 10), but the percentage of terrestrial material was higher in sediments underlying a deeper water column because of the higher lability of marine organic matter. Fossil material was evidenced by the moderate unresolved complex mixture (UCM) and the background of petrogenic n-alkanes. A low biodegradation of petroleum-related inputs in this area was confirmed by the low ratio of UCM/n-alkanes (<7) (Table 4), since values >10 are indicative of chronic/degraded petroleum contamination (Simoneit, 1982).

The correlation found between the long-chain n-alkanols, n-alkanoic acids and n-alkanes ($r > 0.95$) confirms that these three classes of terrigenous biomarkers have a common

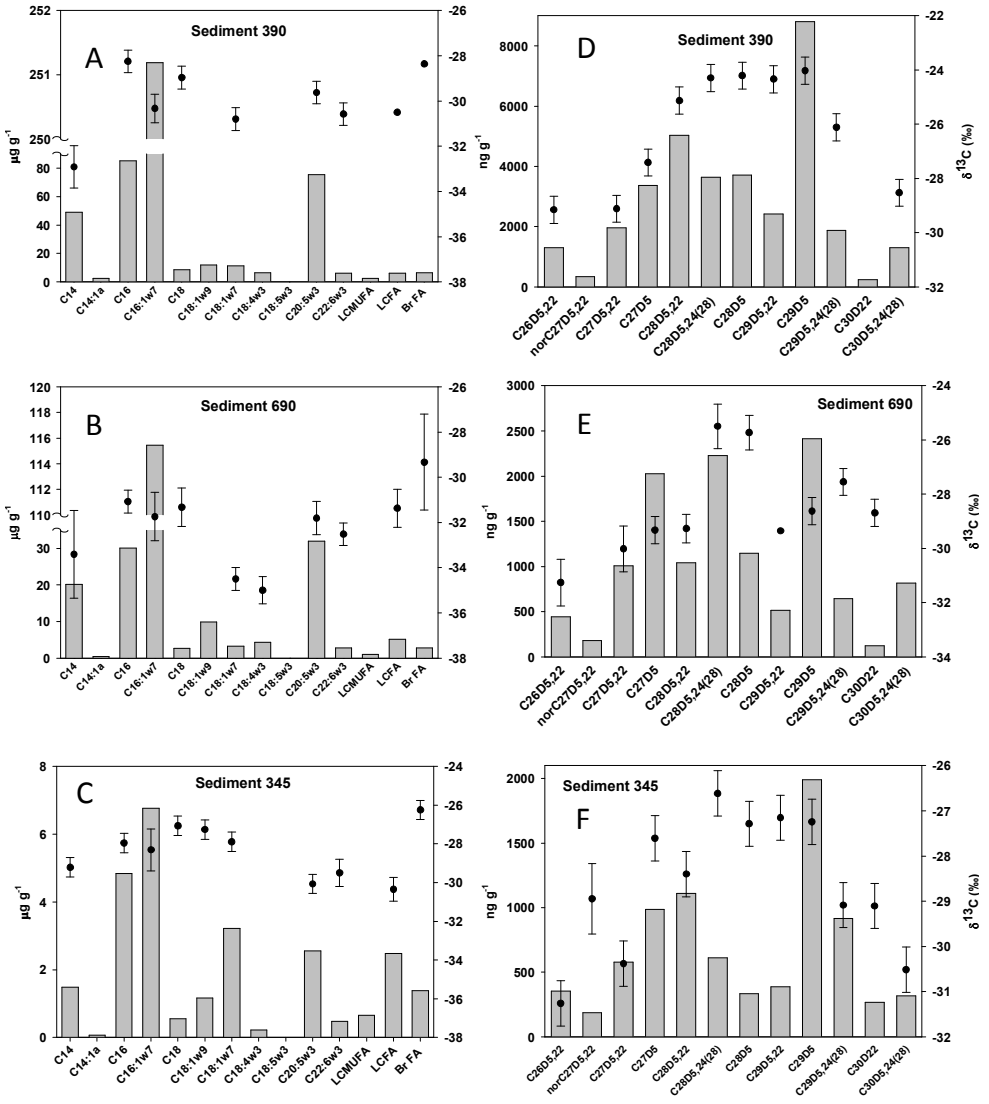

Fig. 6. Concentrations (bars) and carbon isotopic ratios (mean ± SD, $n = 3$) of selected fatty acids **(A–C)** and sterols **(D–F)** in selected sediments from the Mackenzie Shelf and slope.

source, similar transport, deposition and degradation pathway in the area. Other common terrigenous biomarkers, such as α-amyrin, retene and sitosterol exhibit relatively poor correlations with the long-chain terrestrial biomarkers. However, when site 390 is excluded, all other sediment samples showed relatively good correlation between sitosterol and long-chain terrestrial biomarkers, confirming the dominant terrestrial origin of sitosterol in these sediments. Also, the δ^{13}C value of sitosterol in the sediment 390, −24 ‰, typical of marine sources contrasts with the more depleted values of the rest of sediments (∼ 28 ‰) and that of the Mackenzie River (−31 ‰). Assuming the isotope ratio of the Mackenzie River (−31 ‰) as the terrestrial and the value from sediment at site 390 (−24 ‰) as marine end-member, we estimate that 66 % of sitosterol in sediments of the site 690 is terrestrial, whereas it was only 39 % at the site 260, and 45 % in the slope and deeper sediments.

We estimated the relative contribution of the different OM components in the same way as in the SPM (Fig. 8). However, in sediments we included $C_{18:1\omega7}$ within the bacterial markers, sitosterol within the C_3 terrestrial plant markers (except at site 390) and cholesterol within the zooplankton markers. It can be observed that in all sediments the algal component dominates over the fossil and C_3 plant material. In particular, the sediments from the shelf and Amundsen Gulf present the highest contribution of detrital algal material (60–73 %), whereas the slope sediments (235 and 345) contain a higher proportion of fossil (40 %) and C_3 terrestrial plants (10 %). The contribution of zooplankton and bacteria-derived organic material is always minor and hardly

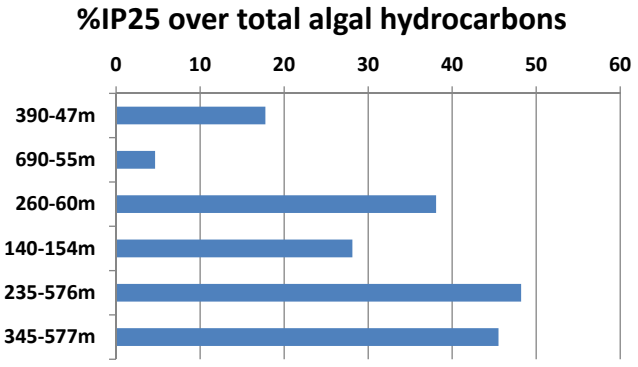

Fig. 7. Percentage contribution of the C_{25} monounsaturated hydrocarbon (sea ice IP_{25} biomarker) to the total algal hydrocarbons in sediments from the Mackenzie Shelf and slope. Total algal hydrocarbons include the IP_{25} *n*-C_{15}, *n*-C_{17}, *n*-C_{19}, *n*-$C_{21:6}$, *n*-$C_{21:5}$ and *n*-$C_{21:4}$.

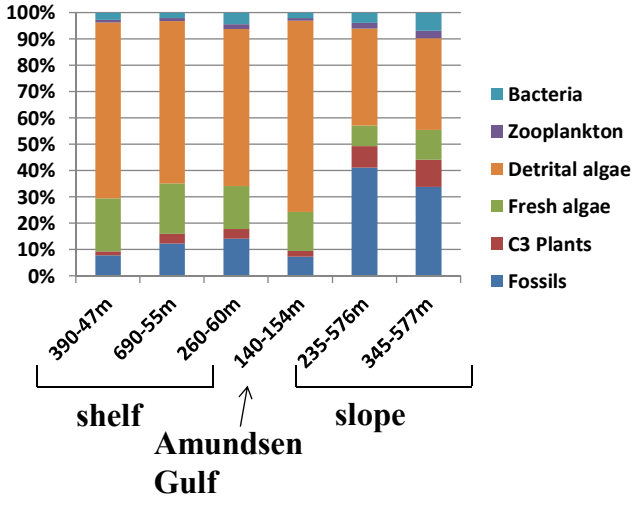

Fig. 8. Relative contributions of OM constituents in the sediments from the Mackenzie Shelf, Amundsen Gulf and slope. The molecular biomarkers were separated into the following components: fossil (UCM, and petroleum hydrocarbons), fresh/labile algal (PUFA, phytol, IP_{25}, *n*-$C_{21:6}$, $C_{28}\Delta^{5,24(28)}$, $C_{29}\Delta^{5,24(28)}$), refractory/detrital algal (SCFA, SCMUFA, rest of sterols, biogenic alkanes, SCOH, SCMUOH), zooplankton (LCMUFA, LCMUOH and cholesterol), bacterial (branched FA, branched alcohols and $C_{18:1\omega7}$FA) and C_3 terrestrial plants (LCFA, LCOH, wax *n*-alkanes and sitosterol (except for site 390)).

reaches respectively 3 % and 7 % of the total quantified lipid molecular biomarkers. If we consider that the fossil and C_3 plant material represent the total allochthonous lipidic component, then autochthonous sources contributed more than allochthonous sources to the OM lipid pool in the sediments of the shelf and Amundsen Gulf. Still, our data show that the relative contribution of fossil and C_3 terrestrial plants increased with water column depth, certainly due to the degradation of the algal components within the water column.

4.4 Transport and fate of particulate matter

Patterns of lipid categories throughout the water column and in the sediment were studied at the slope sites 235 and 345. Figure 9 (site 235) shows dramatically different patterns between the deep chlorophyll maximum (∼ 70 m) in the upper Pacific halocline, the lower Atlantic halocline (∼ 200 m) and the sediment. Flagellates dominated at the depth of maximum chlorophyll, and diatom biomarkers became relatively more important at 200 m and in sediment. This suggests post-bloom conditions within the water column with only larger phytoplankton exported to deeper depths and sediments. This is consistent with the well-known fact that picoplankton are efficiently recycled within the food web and only large phytoplankton are exported (Michaels and Silver, 1988). Moreover, the enriched carbon isotope values obtained for the sedimentary diatom markers imply high rates of primary production. These features of site 235 were also observed at site 345.

Selective loss with water column depth of the more labile organic compounds with respect to organic carbon is related to degradation processes during the transport of particles into deep water (Tolosa et al., 2004b; Wakeham et al., 1997). While maximum values of PUFA and phytol were observed around the DCM, the maxima for the bacterial signatures shifted down to 130–200 m (Fig. 10). As expected, the ratio PUFA/(SCFA + SCMUFA), an index of freshness of organic matter, exhibited the highest values (fresher material) at the deep chlorophyll maximum (∼ 70 m), with the exception of sample 640–70, which seemed to be affected by the Mackenzie River plume. The minimum values were noticed in the samples collected within the Pacific halocline water mass at 130 m depth, coinciding with the highest percentage of bacterial markers. These observations might be explained by the remineralization of organic matter that could produce the nutrient maximum and oxygen minimum in this layer (Cota et al., 1996).

The distribution of TOC-normalized concentration of biomarkers in the surface sediment did not differ from that based on absolute concentrations of lipids. As shown in Fig. 11, the concentrations of fresh/labile algal biomarkers (PUFA, phytol) sharply decreased by ∼ 80 % from the inner to the outer shelf including the Amundsen Gulf site, and to the slope. Concentrations of bacterial (BrFA) and zooplankton (LCMUFA) biomarkers were markedly higher in the inner shelf than at the other sites. Allochthonous biomarkers, e.g. LCFA from C_3 plant and fossil biomarkers, were highest in the inner shelf, lowest in the outer shelf and Amundsen Gulf and increased again in the slope. As expected, the highest index of freshness (PUFA/(SCFA + SCMUFA) was measured in the shallow areas of the inner shelf, and decreased with water column depth (with the exception of site 345). This decrease of lipid concentrations with water column depth suggests that labile algal material is subject to degradation and recycling by bacteria throughout the water

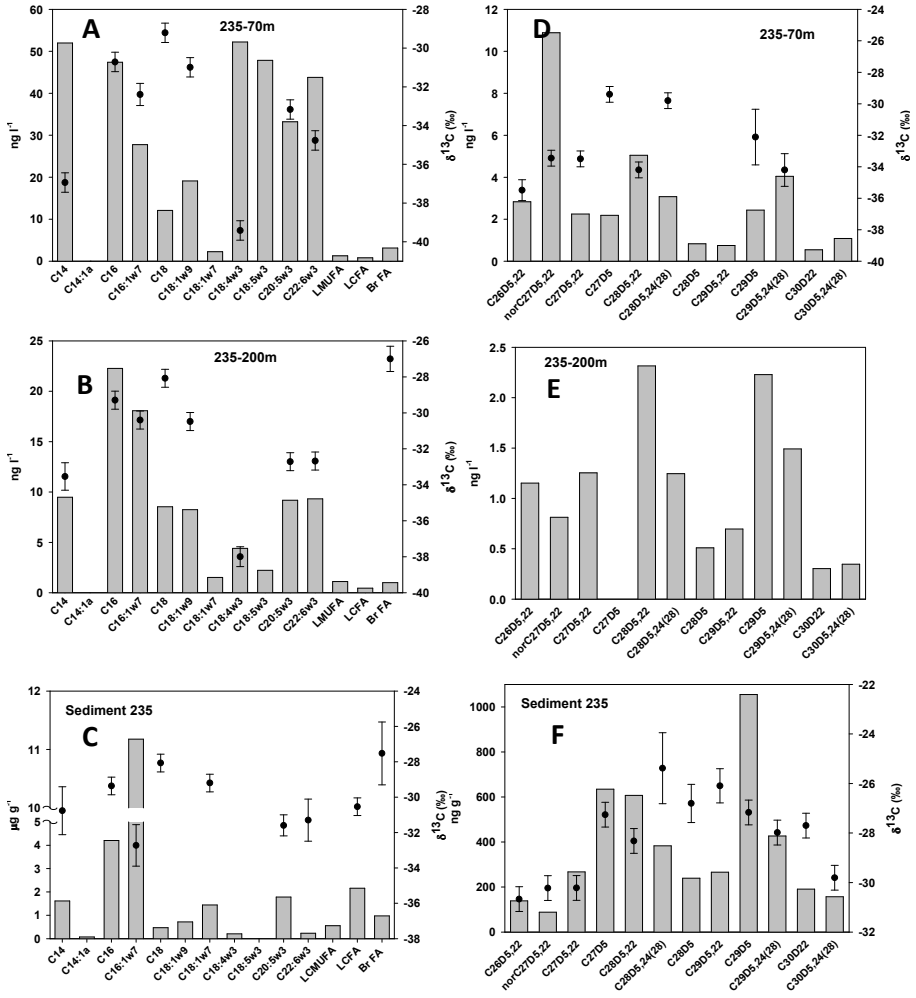

Fig. 9. Concentrations (bars) and carbon isotopic ratios (mean ± SD, $n = 3$) of selected fatty acids **(A–C)** and sterols **(D–F)** in a depth profile from site 235.

column before being stored in the sediment floor. However, the presence of labile compounds in the sediments lying hundreds of meters below the ocean surface is probably due to a rapid sinking of ungrazed phytoplankton from blooms of diatoms or ice algae mats released when ice melts. If these compounds were deposited and resuspended en route to the deep basins, they would be degraded for periods of time long enough to be lost (Yunker et al., 2005). As FAs degrade faster than *n*-alkanes, the ratios of long-chain *n*-alkanoic acids to *n*-alkanes indicated a higher preservation of the terrestrial OM in the inner shelf compared to the outer shelf where more degraded or refractory terrestrial material was found. These terrigenous biomarkers preserved in the sediments might derive from fluvial or eroded shoreline sedimentary organic matter that has been carried out offshore by advective particle transport, e.g. nepheloid layers (Forest et al., 2007; Honjo et al., 2010). Moreover, the inverse distribution between retene and α-amyrin (Fig. 12) might indicate a different transport of these two terrestrial compounds, presumably arising from their precursors and association with particles. α-amyrin, a specific biomarker for angiosperms (Hernes and Hedges, 2004), is linked to bound fractions and associated with low-density, higher plant debris. It might therefore be widely dispersed by the Mackenzie River and be preserved out to the shelf edge and slope. In contrast, retene (which is a dominant component of coals) is preferentially linked to diagenetic PAHs associated with lithic particles that settled out in nearshore sediments (Yunker et al., 1995).

4.5 Estimation of allochthonous organic carbon content in sediments

The organic content of deep surface sediments is anomalously high in the Beaufort Sea (Magen et al., 2010) certainly due to the addition of terrestrial plants and fossil material through river transport to the shelves and basins and to the tight pelagic–benthic coupling. The percentage of allochthonous carbon (% C-terr) in marine sediments may be

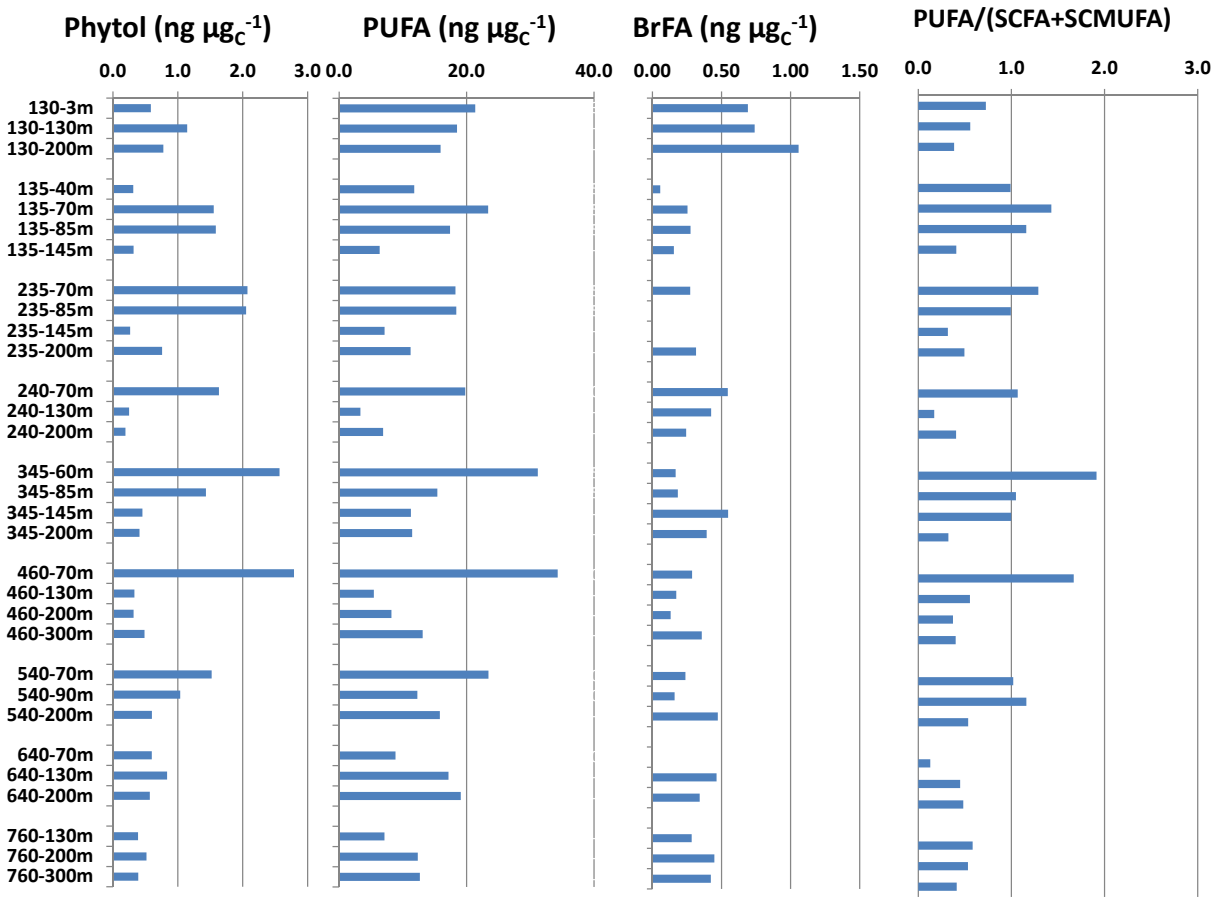

Fig. 10. Concentrations normalized to TOC of selected lipid biomarkers and diagnostic ratios in the SPM of offshore open waters (> 200 m depth) from the Mackenzie slope.

obtained from the ratio of an allochthonous biomarker (normalized to TOC) between marine sediments and the river mouth water (Bouloubassi et al., 1997; Saliot et al., 2002). This approach assumes that the allochthonous biomarkers are conservative and that the only factor affecting the ratio between allochthonous biomarkers and terrestrial organic carbon in sediments is dilution with the marine organic carbon. Table 13 shows the range in estimated % C-terr that resulted from our samples using this approach. Using the wax *n*-alkanes, 30 to 37 % of the organic carbon is of terrestrial origin in the inner shelf sediments (sites 690 and 390), and 20 to 27 % in the sediments from the outer shelf, Amundsen Gulf and slope. These values are much lower than those estimated in 1987 using the same approach where inner shelf and slope sediments contained 99 % and 62 % of terrestrial carbon, respectively (Belicka et al., 2004). Even when using other C_3 terrestrial biomarkers (Table 13), mean values in the inner shelf were 30–35 % (sitosterol excluded at 390) and between 15 and 25 % at the other sites. The variability between the different biomarkers is likely due to the different extent of the degradation process of terrigenous biomarkers, *n*-alkanes being more stable than their oxygenated precursors (*n*-alkanols and *n*-alkanoic acids) and *n*-alkanoic acids more stable than *n*-alcohols (Cranwell, 1981). Sitosterol exhibited similar percentages as the other terrestrial biomarkers except for site 390, where phytoplankton were the major source of this compound. Although fossil hydrocarbons might be generated also within the sediments, the percentage of fossil carbon preserved in the sediments was similar to that resulting from the C_3 plant biomarkers. Regardless of the compound series, the percentage of organic carbon preserved in the sediments decreased from the nearshore to offshore sites.

Our estimates of the allochthonous carbon content are low compared to other studies conducted 5–20 yr earlier and using the same (Belicka et al., 2004) or different approaches. The latter ones reported values mostly > 50 % (Magen et al., 2010; Macdonald et al., 1998; Goñi et al., 2000), some of them distinguishing between the fossil (40–70 %) and the vascular C3 plant (< 30 %) contribution (Drenzek et al., 2007; Goñi et al., 2005). Compared to the study of Belicka et al. (2004), the carbon content of our sediments could have been overestimated by the relatively higher contribution of labile components due to the sampling of only the topmost layer (few mm). However, when taking into account

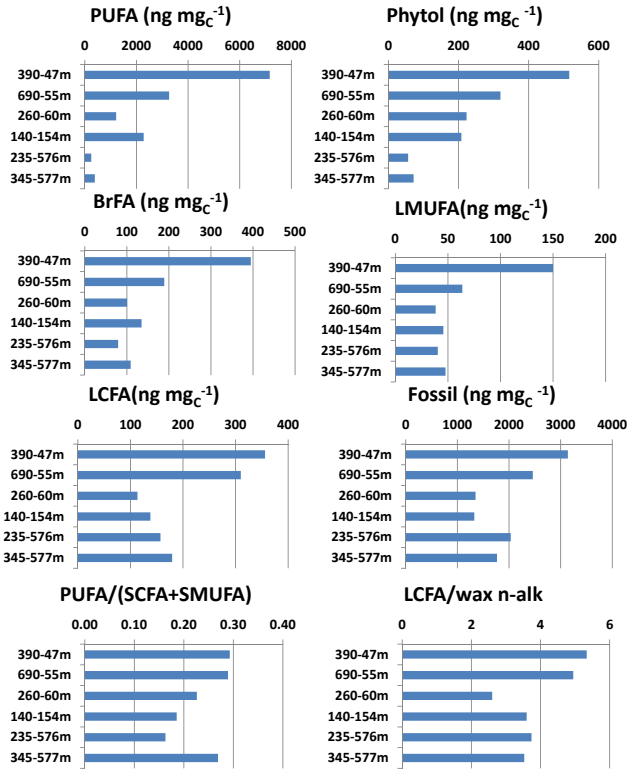

Fig. 11. TOC-normalized concentration of selected biomarkers and selected diagnostic ratios in surface sediments from the shelf, Amundsen Gulf and slope.

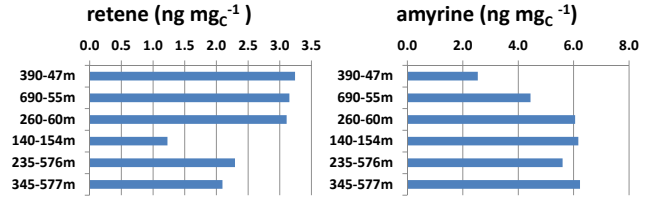

Fig. 12. TOC-normalized concentration of retene and α-amyrin in surface sediments from the shelf, Amundsen Gulf and slope.

a maximum overestimation of 20 % in the TOC from our upper sediments, this would result in an increase of the terrestrial contribution of only 4 to 12 %. Therefore more plausible reasons for the decrease of the terrestrial contribution in recent sediments are that the annual discharge of the Mackenzie River has actually decreased in the last years/decades (Durantou et al., 2012) and that primary production over the Canadian Beaufort Shelf has increased during the last decade. Recent works suggest that the Arctic Ocean carbon sink has tripled from 1972 to 2002 mainly because of the ice cover removal that maintained surface waters undersaturated with respect to CO_2 (Bates et al., 2006), and that annual primary production has increased by 25 % from 1998 to 2007 (Arrigo et al., 2008; Pabi et al., 2008) and quadrupled from 2004 to 2008 in the inner Mackenzie Shelf (Tremblay et al., 2011). This increase in annual production has been attributed to the longer phytoplankton growing season due to the increase in the number of ice-free days and to the strength and persistence of winds favouring upwelling. More data will be needed to monitor these trends and evaluate the associated changes.

Table 13. Percentage of terrigenous organic carbon with respect to the total organic content of the sediment sample, obtained from the ratio of different terrestrial biomarker concentrations (normalized to total organic carbon) at a given site versus the biomarker concentrations representative of the river.

	390 47 m	690 55 m	260 60 m	140 154 m	235 576 m	345 577 m
Wax *n*-alkanes	31	37	23	20	22	27
LCOH	20	21	13	13	15	19
LCFA	47	41	15	18	21	24
Sitosterol	93	27	16	18	14	27
Fossil*	39	30	17	16	25	22

*Fossil compounds include the unresolved complex mixture (UCM), petrol *n*-alkanes (wax *n*-alkanes were subtracted from total *n*-alkanes), pristane and phytane.

5 Summary and conclusions

The measurement of lipid biomarkers and their compound-specific isotope analysis allowed us to characterize the spatial variation of OM over the Mackenzie Shelf and the slope to better constrain the sources of terrestrial and marine organic matter. Our data highlight that fresh and labile organic matter from diatom blooms sinks to the bottom of the continental shelf and slope, whereas terrestrial material is likely transported to the slope by advective processes. Although sitosterol is generally considered to be of terrestrial origin, the carbon isotope ratios we obtained for this compound at site 390 indicated a high autochthonous production. Since $\delta^{13}C$ values obtained for marine phytoplanktonic biomarkers synthesized at this high latitude area with relatively high concentrations of CO_2 might be similarly depleted as the $\delta^{13}C$ values of C_3 terrestrial biomarkers, it is problematic to discern the sources of sitosterol in the marine SPM by using their $\delta^{13}C$.

Although the Mackenzie River is the primary source of C_3 terrigenous debris and fossil material to the Mackenzie Shelf sediments, refractory algae-derived material was the major lipidic component in the nearshore sediments. However, their relative contributions decreased with water column depth, which lead to an increase in the contributions of fossil and C_3 plant-derived material.

Our evaluations on the terrigenous POC fraction preserved in the surface sediments of the Beaufort Sea compared to studies prior to the recent decline in Arctic summertime ice indicate a decrease during the last decade implying a recent shift between autochthonous and allochthonous source input

over the sediments. Interestingly, these results are supported by the enhancement of the primary production in the Arctic Ocean in recent years. Our data provide an important baseline for future studies.

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