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The sequestration of terrestrial organic carbon in Arctic Ocean sediments: A comparison of methods and implications for regional carbon budgets

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Abstract

A variety of approaches have previously been developed to estimate the fraction of terrestrial or marine organic carbon present in aquatic sediments. The task of quantifying each component is especially important for the Arctic due to the regions' sensitivity to global climate change and the potential for enhanced terrestrial organic carbon inputs with continued Arctic warming to alter carbon sequestration. Yet it is unclear how each approach compares in defining organic carbon sources in sediments as well as their impact on regional or pan-Arctic carbon budgets. Here, we investigated multiple methods: (1) two end-member mixing models utilizing bulk stable carbon isotopes; (2) the relationship between long-chain *n*-alkanes and organic carbon (ALKOC); (3) principal components analysis (PCA) combined with scaling of a large suite of lipid biomarkers; and (4) ratios of branched and isoprenoid glycerol dialkyl glycerol tetraether lipids (the BIT index) to calculate the fraction of terrestrial organic matter components preserved in Arctic marine sediments.

Estimated terrestrial organic carbon content among approaches showed considerable variation for identical sediment samples. For a majority of the samples, the BIT index resulted in the lowest estimates for terrestrial organic carbon, corroborating recent suggestions that this proxy may represent a distinct fraction of terrestrial organic matter; i.e., peat or soil organic matter, as opposed to markers such as *n*-alkanes or long-chain fatty acids which measure higher plant wax inputs. Because of the patchy inputs of *n*-alkanes to this region from coastal erosion in the western Arctic, the ALKOC approach was not as effective as when applied to river-dominated margins found in the eastern Arctic. The difficulties in constraining a marine $\delta^{13}\text{C}$ end-member limit the applicability of stable isotope mixing models in polar regions. Estimates of terrestrial organic carbon using the lipid-based PCA method and the bulk $\delta^{13}\text{C}$ mixing model approach varied drastically at each site, suggesting that organic matter fractions such as amino acids or carbohydrates may affect bulk organic matter composition in a manner that is not captured in the lipid-based analysis. Overall, terrestrial organic matter inputs to the Chukchi and western Beaufort Seas using the average of the methods at each site ranged from 11% to 44%, indicating that land-derived organic matter plays a substantial role in carbon dynamics in the western Arctic Ocean.

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1. INTRODUCTION

Carbon budgets provide a means to quantify the sequestration and recycling of organic matter in the world's

oceans as well as an understanding of the linkages between carbon reservoirs. For a sensitive environment like the Arctic Ocean, they can also provide a conceptual understanding of how future climate change may affect biogeochemical cycling. In a typical open ocean setting, primary productivity and the uptake and recycling of generated organic matter are the overriding processes. In the Arctic, however, the terrestrial organic carbon reservoir is a significant contributor (Goni et al., 2000; Belicka et al., 2004;

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Yamamoto et al., 2008). Large quantities of both particulate and dissolved terrestrial organic carbon are delivered to Arctic waters, mainly from the Yenesei, Lena, and Ob Rivers in the Laptev and Kara Sea watersheds, and the Mackenzie River in Canada, which together deliver a freshwater flow of $1879 \text{ km}^3 \text{ yr}^{-1}$ and a combined total suspended particulate matter flux of $164.9 \times 10^6 \text{ t yr}^{-1}$ (Gordeev et al., 1996; Holmes et al., 2002). Although highly seasonal, this tallies to a combined dissolved and particulate organic carbon (TOC) flux of about $30 \times 10^6 \text{ t yr}^{-1}$ for the entire Arctic Ocean, with nearly 85% of this flux entering Eurasian waters (Rachold et al., 2004). In the Yenesei, Lena, and Ob rivers, dissolved organic carbon is the bulk of the TOC flux, accounting for approximately $12 \times 10^6 \text{ t yr}^{-1}$ compared to a particulate flux of about $1.7 \times 10^6 \text{ t yr}^{-1}$ (Rachold et al., 2004 and references therein). In the Mackenzie River, however, the high concentrations of suspended material lead to a particulate organic matter flux of $2.1 \times 10^6 \text{ t yr}^{-1}$, approximately twice as high as the estimated dissolved flux of $1.3 \times 10^6 \text{ t yr}^{-1}$ (Macdonald et al., 1998; Rachold et al., 2004). Coastal erosion also provides a significant quantity of terrestrial carbon to the Arctic, estimated in some locations to be greater than the delivery from rivers (Rachold et al., 2004).

Local and regional carbon budgets are being developed for the Arctic (Macdonald et al., 1998; Stein and Macdonald, 2004a); yet estimates of organic carbon reservoirs in the water column and sediments are lacking in many Arctic locations. The marine organic carbon component is better constrained, as primary productivity and microbial respiration have been measured over the wide continental shelves of the Arctic (Booth and Horner, 1997; Gosselin et al., 1997; Arnosti et al., 2005; Bates et al., 2005a; Hill and Cota, 2005). Nevertheless, the high temporal and spatial variability combined with the difficulty of estimating production and recycling in the waters and ice of the central Arctic basin make it challenging to extrapolate measurements to basin-wide estimates. The terrestrial organic carbon component and its retention in the system are poorly defined. Riverine delivery of terrestrial organic matter can be measured in large rivers; yet the redistribution of this material by entrainment in sea-ice as well as its remineralization rates are poorly understood.

Molecular organic markers and stable carbon isotopes are well established proxies for tracing both the sources and processing of organic matter (Meyers, 1997). The utility of these proxies, however, is limited to their source specificity. For a robust analysis, researchers have often utilized a suite of organic markers as opposed to a single class of lipids (Canuel and Zimmerman, 1999; Goñi et al., 2000; Belicka et al., 2002); and in several cases have coupled biomarker analysis with stable carbon isotopic measurements (Tolosa et al., 2003; Drenzek et al., 2007). These geochemical proxies are often combined to estimate terrestrial and marine organic matter fractions sequestered in water column particles and sediments. For example, two end-member mixing models of stable carbon isotopes exploit the differences in $\delta^{13}\text{C}$ between land plants and marine algae, providing an estimate of the fractions of marine and terrestrial organic matter in sediments (Hedges et al., 1988; Prahl

et al., 1994; Meyers, 1997). Lipid biomarkers have also been applied in varying degrees of complexity. Techniques can involve a single class of compounds, such as odd-carbon number long-chain *n*-alkanes, (Prahl and Carpenter, 1984; Bouloubassi et al., 1997; Fernandes and Sicre, 2000) to estimate terrestrial organic matter content of ocean margin sediments. More complex statistical approaches which combine regression of multiple lipid structures with principal components analysis (PCA) have also been used (Yunker et al., 1995, 2005; Goñi et al., 2000). This approach incorporates a linear regression on the biomarker loadings from the PCA, and source end-members are assigned to each end of the regression line. The regression line acts as a mixing line between molecular biomarkers that are solely derived from marine organic matter versus those derived from terrestrial organic matter. For markers that are less specific and fall between the two end-members, a relative contribution of each organic matter compartment is calculated by projecting the biomarker in PCA space onto the mixing line using the geometric distance formula. The concentration of individual biomarkers is then scaled to reflect the contribution of that biomarker to marine or terrestrial carbon and summed to estimate terrestrial carbon preservation.

Novel proxies have been suggested—including the BIT index (Branched and Isoprenoid Tetraether index), which diverges from the more standard approaches in that it utilizes compounds produced by organisms believed resident of terrestrial environments, rather than rely on the biomarkers specific to the vegetative component of terrestrial organic matter itself (Hopmans et al., 2004). The biological origin of these compounds, the glycerol dialkyl glycerol tetraethers (GDGTs), is not yet known; however, the abundance of several of the branched compounds in peat samples supports their terrestrial origin (Hopmans et al., 2004) and suggests the BIT index may track peat or soil inputs. In fact although originally developed as a terrestrial organic matter proxy (Hopmans et al., 2004), it has recently been proposed that the BIT index may more specifically approximate the soil component of terrestrial organic matter inputs (Huguet et al., 2007; Walsh et al., 2008; Weijers et al., 2009).

Each of these proxies may result in a disparate estimate of the marine or terrestrial organic carbon component (Stein and Macdonald, 2004b). If these proxies arrive at substantially different estimates of terrestrial or marine contents, it limits the ability to compare carbon budgets and models of carbon cycling among regions of the Arctic. Here, we investigate multiple methods for quantifying terrestrial organic matter in sediments: (1) A two end-member stable isotope mixing model; (2) the *n*-alkane ratio (ALKOC) method; (3) lipid biomarkers with PCA and regression scaling; and (4) the BIT index to compare differences in the estimated terrestrial organic carbon content among each method. For valid comparison, measurements were made using each approach on 19 surface sediment samples ranging from shelf to basin environments in the Chukchi/Alaskan Beaufort Sea. In addition, terrestrial samples collected from the North Slope of Alaska were analyzed to determine the range of terrigenous carbon from fluvial and coastal erosion inputs. The strong influence of terrestrial organic matter from rivers and erosion and the

potential global impacts of a changing carbon cycle make the Arctic a relevant location to investigate the comparability of terrestrial organic matter proxies. Results of these analyses over spatial scales also provide much needed data on the distribution of organic matter and its shelf to basin exchange in a region where climate change has already been observed.

2. MATERIALS AND METHODS

2.1. Study area and sampling

Surface samples were taken from 19 undisturbed sediment cores collected during the Shelf–Basin Interactions Program (SBI) process cruises in 2002 and 2004 aboard the USCGC *Healy*. Sample sites were chosen in shelf to basin transects in an area encompassing the Chukchi and Alaskan Beaufort Seas (Fig. 1). The Chukchi Sea is characterized by a broad, flat, shallow shelf (average depth of 50 m) which experiences extensive, but seasonal, ice cover (Grebmeier, 1993; Baskaran and Naidu, 1995). The high productivity characteristic of the Chukchi Sea is sustained largely by nutrient-rich waters from the Bering Sea (Walsh et al., 1989; Grebmeier et al., 1995). Eastward, the Alaskan shelf of the Beaufort Sea is narrower and drained by several small rivers, including the Colville, Kuparuk, and Sagavanirktok, which discharge relatively small amounts of freshwater and particulate matter mainly during a three-week time period in spring (Macdonald et al., 2004). Lowland tundra dominates northern Alaska, with moist to wet sedge tundra common near Barrow (Rhew et al., 2008) and tree-

less tussock tundra dominating towards the east near the Mackenzie River (Goñi et al., 2000).

Cores were taken with a Pouliot box corer with a 0.06 m² area, and sectioned in 1 cm intervals in the upper 10 cm of sediment, and 2 cm intervals below. Surface samples described here are the 0–1 cm sample of each core. Sediment sections were stored in pre-cleaned plastic or glass I-Chem jars and immediately frozen until chemical analysis. Prior to chemical analysis, each sediment section was thawed and thoroughly homogenized.

2.2. Chemical analyses

2.2.1. Bulk sedimentary composition

Sediment organic carbon and nitrogen content (after removal of all carbonates by acidification with 40% HCl) was determined with an elemental analyzer. Stable isotopic composition was measured with an Optima stable isotope ratio mass spectrometer. Internal laboratory reference gases for carbon and nitrogen were calibrated against the respective international standards NBS-19 and atmospheric N₂. Isotopic results were reported in delta notation (δ) as per mil deviations (‰) from the corresponding international standards of Pee Dee Belemnite (PDB) and atmospheric N₂ (air). Analytical precision for carbon and nitrogen was within $\pm 0.2\%$.

2.2.2. Lipid biomarker analysis

To quantify non-tetraether lipid biomarkers, 5–10 g of wet sediments were extracted three times with a mixture of methylene chloride:methanol (2:1) in solvent-rinsed glass

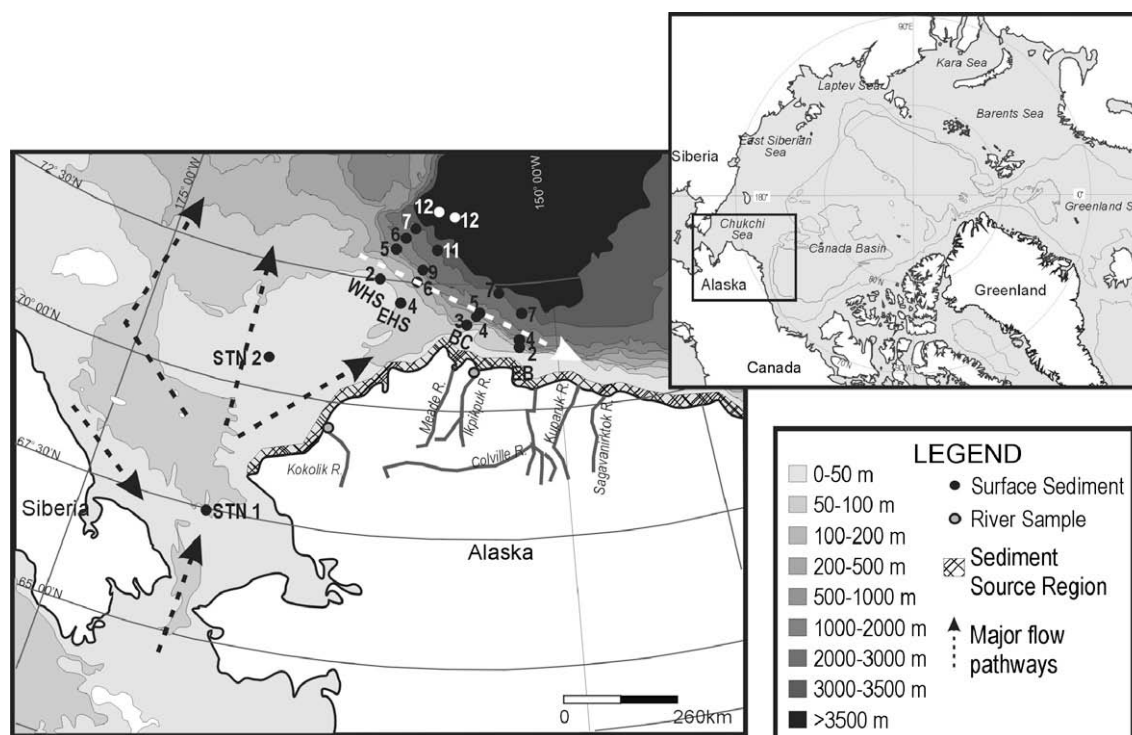


Fig. 1. Map of the western Arctic Ocean, showing the sampling stations along four shelf to basin transects, selected Alaskan rivers with river sampling stations, major coastal sediment source regions, and major water flow pathways. WHS, West Hanna Shoal; EHS, East Hanna Shoal; BC, Barrow Canyon; EB, East of Barrow Canyon. Inset shows location of sample sites relative to entire Arctic region.

test tubes with sonication for 2 min as described in Belicka et al. (2002). Partitioning of lipids was achieved by addition of Nanopure water and centrifugation at 1200 rpm for 5 min. The extraction was repeated twice, the three extracts were combined, and excess solvent was removed by rotary evaporation. Saponification was performed by reaction at 70 °C for 30 min after addition of a solution of 0.5 N KOH in methanol to dried extracts. Neutral lipids were partitioned three times with a 9:1 mixture of hexane:diethyl ether followed by fatty acid partitioning after acidification with HCl to pH <2. Neutral lipids were dried and derivatized at 50 °C for 15 min with bis-(trimethylsilyl)trifluoroacetamide amended with 25% pyridine. Fatty acids were dried and methylated at 70 °C for 30 min with boron trifluoride in methanol. Nonadecanoic acid and 5 α -cholestane added prior to saponification served as internal standards for the polar and non-polar phases, respectively. Polar and neutral lipids were quantified by capillary gas chromatography (GC) with flame ionization detection. Gas chromatography–mass spectrometry was performed with an Agilent 6890 GC and 5973 N MS for lipid identification with electron ionization mode. The instrument methods and column parameters were identical to those described in Belicka et al. (2002).

Glycerol dialkyl glycerol tetraether lipids (GDGTs) were analyzed using the method of (Hopmans et al., 2004) with minor modifications. Briefly, approximately 20 g wet sediments were extracted three times with a mixture of methylene chloride:methanol (9:1, v/v). The total lipid extract was then partitioned into apolar and polar fractions using alumina oxide column chromatography with hexane:methylene chloride (9:1, v/v) and methylene chloride:methanol (1:1, v/v), respectively, as eluents. The polar fraction was dried either by rotary evaporation or under N₂, redissolved ultrasonically in a mixture of hexane:propanol (99:1, v/v), and filtered through a 0.2 μ m pore size, 13 mm diameter Teflon filter in a Swinny stainless steel filter holder using a luer-lock syringe. GDGTs were analyzed using an Agilent 1100 Series High Performance Liquid Chromatography system coupled to an Agilent 1100 Series SL Ion Trap Mass Spectrometer equipped with an atmospheric pressure chemical ionization source. Separation was achieved on a Rainin Microsorb-MV NH₂ column (4.6 \times 250 mm; 5 μ m particle size) and a 3.0 \times 4.0 mm (i.d. \times L) Phenomenex Security Guard NH₂ column. The sample run time was 50 min with a constant flow rate of 1.0 mL/min, beginning with an isocratic hold at 99% hexane 1% propanol for 5 min, followed by a linear gradient to 1.8% propanol over 45 min. A post-run cleaning was achieved by a reverse gradient back to 1% propanol, followed by a 10 min flush of 99:1 hexane:propanol. Positive ion spectra were produced by scanning an *m/z* range from 950 to 1450 under the conditions of Hopmans et al. (2004). Concentrations of 5 major GDGTs were quantified by comparison of the [M + H]⁺ peaks to an external standard curve constructed with 1,2-di-*O*-phytanyl-*sn*-glycerol (Avanti Polar Lipids), with identical APCI-MS conditions except with scanning from *m/z* 650 to 1450. Because the ionization efficiency of the 1,2-di-*O*-phytanyl-*sn*-glycerol standard compound may differ from that of the tetraether compounds, the calculated concentrations of the

tetraether lipids may not reflect absolute concentrations. However, this potential discrepancy does not affect the BIT index values, as the BIT index is calculated from relative abundances based on the area of the [M + H]⁺ peaks instead of absolute concentrations.

2.3. Calculations of terrestrial organic carbon content

Multiple methods of estimating the terrestrial organic carbon fraction (% Terr OC) in sediment samples were compared. The first method, a two-end-member isotopic mixing model based on $\delta^{13}\text{C}$ (Eq. (1)), utilized a $\delta^{13}\text{C}_{\text{terrestrial}}$ end-member of -27.8‰ , the average of three terrestrial organic matter substrates collected on land near the study site (see Section 3 for description of samples and isotopic composition).

$$\text{Terr OC}(\%) = [(\delta^{13}\text{C}_{\text{sample}} - \delta^{13}\text{C}_{\text{marine}}) / (\delta^{13}\text{C}_{\text{terrestrial}} - \delta^{13}\text{C}_{\text{marine}})] * 100 \quad (1)$$

For the $\delta^{13}\text{C}_{\text{marine}}$ end-member, an assumed value of -17.5‰ was used, as this value is intermediary between the heavy isotopic values found characteristic of ice algal species during bloom conditions (-14.2‰ , -13‰ , Tremblay et al., 2006; Gradinger, 2009) and Arctic marine particulate organic matter (-27 to -18 , Goericke and Fry, 1994 and references therein).

The second method employed the relationship between long-chain *n*-alkanes and organic carbon content (Eq. (2)).

$$\text{Terr OC}(\%) = [((\text{C}_{25-31}(\mu\text{g/g sed}) / \text{OC}(\text{g/g sed}))_{\text{sample}}) / \text{ALKOC}] * 100 \quad (2)$$

ALKOC is the slope of a linear correlation between *n*-alkanes and organic carbon content, as proposed by Prahl and Carpenter (1984) and subsequently used by Fernandes and Sicre (2000) in the Kara Sea. A similar calculation utilizing the relationship between even carbon long-chain *n*-alcohol concentration (C₂₂–C₂₈) and organic carbon content was also examined.

In the third technique, we used detailed molecular-level analysis of lipid biomarkers together with principal components analysis (PCA) on an integrated dataset encompassing the samples presented in this study plus a set of six sediment cores from the western Arctic region previously analyzed for molecular organic markers (Belicka et al., 2004; Yunker et al., 2005). The data preparation and normalization and principal components analysis followed the methods presented in Yunker et al. (2005), where gaps in the dataset were filled with a random number between zero and one-half the minimum value detected for that variable in the entire dataset. Variables that were undetected in more than 20% of the samples were removed from the analysis. The final dataset contained a total of 93 observations (samples) and 92 variables (biomarkers). Biomarkers (in $\mu\text{g/g OC}$) were first normalized to concentration total, followed by a centered log-ratio and autoscaling normalization. PCA was performed with SAS 9.1 and following examination of the results, a varimax rotation was applied to the first three principal components to maximize or

minimize the loading of each variable on each principal component (see Yunker et al., 1995).

Based on the trends in variable loadings with respect to the principal components, each lipid biomarker can be assigned a value corresponding to its source or lability. For example, Yunker et al. (2005) found that for sediments from six cores collected in the western Arctic Ocean study region, both source (i.e., marine versus terrestrial) and reactivity (i.e., labile versus stable) drove the trends in biomarker loadings. Based on these trends, a geometric mean linear regression of the biomarker loadings provided a relative scale from 100% labile/marine material (or, correspondingly, 0% terrestrial/stable material) to 100% stable/terrestrial material. The relative contributions of labile/marine and stable/terrestrial sources for each biomarker were calculated using the linear distance along the regression line. Position along the regression line was determined using the intersection point between the regression line and a perpendicular between the line and biomarker position; the relative position on the line determined the per cent labile/marine content for each biomarker (see Yunker et al., 2005). Similarly, Goñi et al. (2000) utilized linear regression of the biomarker loadings together with the x -axis intercept to define the biomarkers position on the regression line and hence, its terrigenous contribution.

For the integrated dataset PCA presented here, principal component 1 corresponded to a trend from the most labile marine biomarkers (negative loadings for PC1) to the most recalcitrant and terrestrial markers (positive loadings for PC1). The relative contributions (%) to labile/marine and stable/terrestrial were calculated based on the position of each biomarker along PC1. The concentration of each biomarker in a given sediment sample was then multiplied by the per cent stable/terrestrial value for that biomarker to determine the concentration from stable/terrestrial organic matter. These concentrations were summed and divided by total biomarker concentration to determine the fraction of organic carbon from terrestrial/stable sources (see example provided in Section 3 below).

Fourthly, the BIT Index was calculated based on determination of the relative abundances of three branched GDGTs (I, II, and III) compared with the isoprenoid GDGT crenarchaeol (IV; Eq. (3)), as determined by the area of the $[M + H]^+$ peak for each compound (Hopmans et al., 2004). Roman numerals refer to the GDGT structures shown in Fig. 2.

$$\text{BIT} = \frac{[\text{I} + \text{II} + \text{III}]}{[\text{I} + \text{II} + \text{III} + \text{IV}]} \quad (3)$$

3. RESULTS

3.1. Bulk sedimentary characterization

Total organic carbon (OC) ranged from 0.75% to 1.9% in surface sediments (Fig. 3a) and showed no consistent pattern with water depth (Fig. 3a). The atomic C:N ratios in most sediments ranged from 7.2 to 10.4 (Fig. 3b) and were similar to those found in other Arctic Ocean sediments (Goñi et al., 2000; Naidu et al., 2000; Belicka et al., 2002). No shelf-to-basin gradients were observed, similar to trends

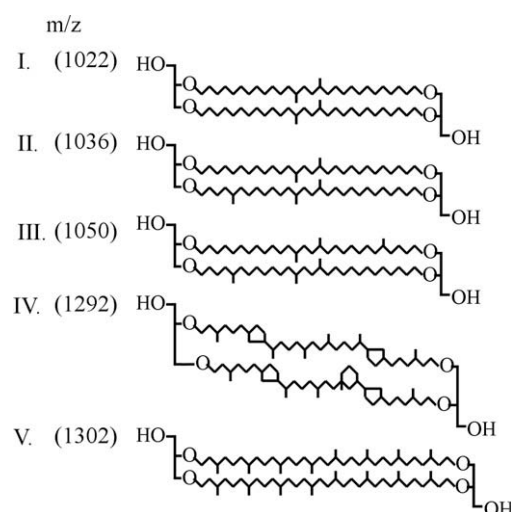


Fig. 2. Structures of glycerol dialkyl glycerol tetraether lipids quantified in this study. Structures I–IV are utilized for construction of the BIT index, as described in detail in the text.

in total organic carbon concentration. Bulk sedimentary $\delta^{13}\text{C}$ was higher overall compared to sediments to both the south and east in the Chukchi and Canadian Beaufort Seas (Naidu et al., 1993; Goñi et al., 2000), but lowest in the BC and EB transects (Fig. 3c). The spatial distribution of $\delta^{15}\text{N}$ was highly variable, but overall surface sediment $\delta^{15}\text{N}$ ranged from 2.0‰ to 7.8‰ (Table 1). To constrain the terrestrial organic carbon $\delta^{13}\text{C}$ end-member for this region of the Arctic, three samples from rivers on the Alaskan mainland were collected and analyzed: (1) Ikpikpuk River suspended particulate organic matter ($\delta^{13}\text{C} = -27.3\text{‰}$); (2) Ikpikpuk River Delta sediment consisting of peat and woody debris in a light sandy matrix ($\delta^{13}\text{C} = -28.3\text{‰}$); and (3) Kokolik River suspended particulate organic matter ($\delta^{13}\text{C} = -27.7\text{‰}$). Based on these analyses, an average $\delta^{13}\text{C}_{\text{terrestrial}}$ value of -27.8‰ was used. As explained in Section 2 above, the $\delta^{13}\text{C}_{\text{marine}}$ value was defined as -17.5‰ , yielding a wide range of estimates of % Terr OC from 6.8% to 44.5% in our two end-member mixing model, excepting station BC-7, where the high $\delta^{13}\text{C}$ value of -16.7‰ resulted in an estimate of wholly marine organic matter at this site.

3.2. Lipid biomarker distribution

A variety of lipid compounds were present in Chukchi and Beaufort Sea surface sediments. Because the focus of this study is on comparing methods for calculating terrestrial and marine organic matter components, a detailed spatial analysis of the more than 90 individual lipids quantified is beyond the scope of this paper. Instead, we focus on diagnostic groups of markers most useful for assigning organic sources and the interpretation of the principal components analysis. Concentrations of individual markers used in the PCA calculation are presented in the Electronic annex (Tables EA-1-1 to EA-1-5); a discussion of the detailed lipid composition observed and the implications for organic matter processing will be presented elsewhere.

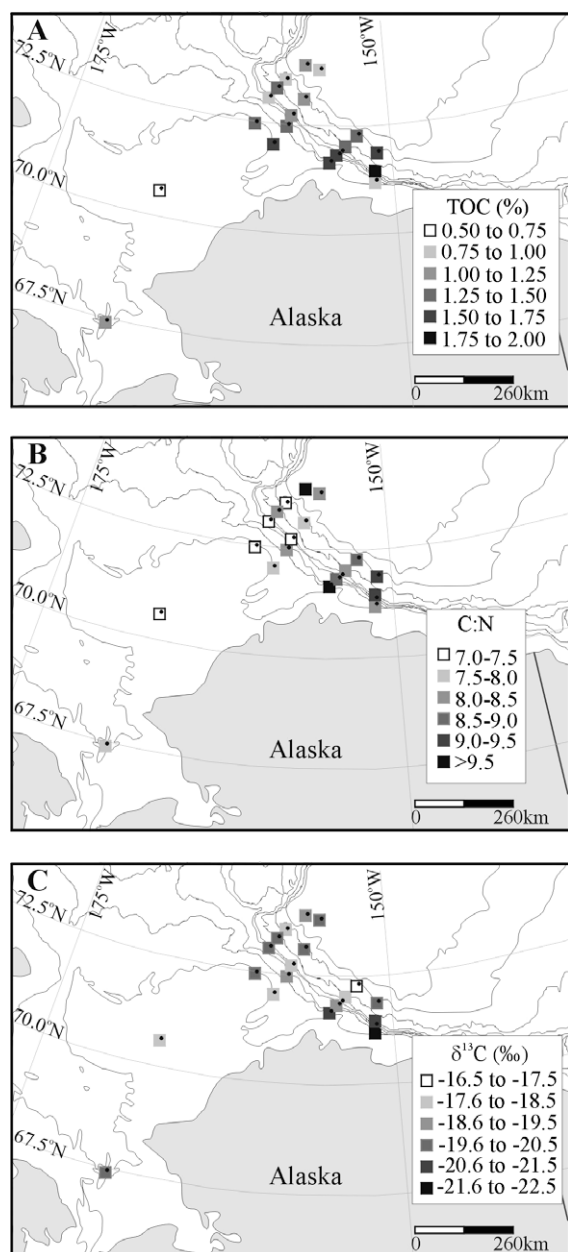


Fig. 3. Total organic carbon (TOC, %), atomic C:N ratio, and $\delta^{13}\text{C}$ (‰) among surface sediments of the 19 sites examined in the western Arctic Ocean.

Sediments contained a mix of both marine and terrestrial lipids; in general, lipid concentrations were highest in shallow sediments from shelf locations. Concentrations of *n*-alkanes (Table EA-1-1) were spatially variable, but in most stations exhibited the strong odd over even predominance indicative of fresh terrestrial material (Eglinton and Hamilton, 1969). Two notable exceptions were stations WHS-6 and WHS-7, where concentrations of odd and even carbon *n*-alkanes were similar (Table EA-1-1). This was reflected in the CPI index (Eq. (4)), an indication of the odd-over-even predominance of high molecular weight *n*-alkanes, which was calculated for the range C_{21} – C_{29} using the following formula (Vonk et al., 2008):

$$\text{CPI} = 1/2 \left[\frac{\sum (X_i + X_{i+2} + \dots + X_n)}{\sum (X_{i-1} + X_{i+1} + \dots + X_{n-1})} \right] + 1/2 \left[\frac{\sum (X_i + X_{i+2} + \dots + X_n)}{\sum (X_{i+1} + X_{i+3} + \dots + X_{n+1})} \right] \quad (4)$$

where *X* is the *n*-alkane abundance in the carbon number range from *i* to *n*. Low concentrations and chromatographic interferences precluded absolute quantification of the C_{32} and C_{33} *n*-alkanes; thus, the CPI was calculated for the range C_{21} – C_{29} . CPI values ranged from a minimum of 1.1 and 1.2 at WHS-6 and WHS-7, respectively, to a maximum of 3.3 at both Station 1 in the southern Chukchi Sea and EB-4 along the easternmost sampling transect (Table EA-1-1).

The sum of C_{25} – C_{31} odd-carbon *n*-alkanes (ΣALK_{25-31}) was only weakly correlated to sedimentary organic carbon content ($r = 0.65$, $p = 0.0004$; Fig. 4a). Water depth (shelf versus basin samples) did not show significant trends with either long-chain *n*-alkane concentration (Fig. 4a) or $\delta^{13}\text{C}$ (Fig. 4b). Using the ALKOC ratio (Eq. (2)), the % Terr OC estimates ranged from 9.0% to 94.5% for the 19 locations. The concentrations of C_{22} – C_{28} even carbon *n*-alcohols (ΣALC_{22-28}) per dry weight of sediment was also weakly correlated to sedimentary organic carbon content ($r = 0.60$, $p = 0.0068$). Performing an identical calculation as the ALKOC ratio using the relationship between long-chain *n*-alcohols and organic carbon content resulted in an equally diverse range of estimates of terrestrial organic carbon content, from a minimum of 4.4% at WHS-7 to an estimate of wholly terrestrial organic carbon at WHS-2 (Fig. 5).

Lipids representative of both marine and terrestrial organic matter were abundant in the surface sediments, especially in the EB and BC transects (Tables EA-1-1 to EA-1-4). Despite the high $\delta^{13}\text{C}$ values of the EHS and WHS transect sediments and their pelagic location, lipids indicative of terrestrial organic matter (including long-chain *n*-alkanes and *n*-alcohols and α -amyrin) were common in surface sediments. These compounds were, on average, lower than concentrations found in the EB and BC sediments; yet, concentrations of most marine markers were also lower near Hanna Shoal. As a result, the Hanna Shoal transects (EHS and WHS) contained proportionally more lipids derived from terrestrial material than the EB and BC transects.

The principal components analysis on the integrated data set encompassing lipid biomarkers in the 19 surface sediment samples presented here (Tables EA-1-1 to EA-1-4), plus six sediment cores and several surface sediment samples from basin stations in the western Arctic (Belicka et al., 2004; Yunker et al., 2005) revealed striking trends in biomarker composition and spatial differences among samples (Fig. 6). From the loadings plot, a clear shift from the most marine-derived biomarkers (mono- and polyunsaturated fatty acids together with short-chain saturated fatty acids, 24-norcholesta-5,22-dien-3 β -ol (nor $\text{C}_{26}\Delta^{5,22}$), 24-propylcholesta-5,24(28)-dien-3 β -ol ($\text{C}_{30}\Delta^{5,24(28)}$), and dinosterol ($\text{C}_{30}\Delta^{22}$)) towards terrigenous markers (including *n*-alkanes, α -amyrin, and long-chain fatty acids) was observed. Because of the chemical reactivity differences

Table 1

Locations of surface sediment (0–1 cm) stations and bulk geochemical parameters observed for the Arctic sediments analyzed.

Station name	Station Nos.	Longitude (W)	Latitude (N)	Depth (m)	Org. C (%)	TN (%)	C:N	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
STN 1	HLY02-01-001	168° 52.9'	67° 27.2'	52	1.13	0.17	7.8	−20.0	6.6
STN 2	HLY02-01-002	167° 28.0'	70° 38.0'	50	0.75	0.12	7.3	−18.4	5.9
WHS-2	HLY02-01-006	160° 34.0'	72° 50.5'	58	1.33	0.21	7.4	−20.2	7.3
WHS-5	HLY02-01-009	160° 06.7'	73° 16.8'	1198	0.99	0.16	7.2	−20.1	4.1
WHS-6	HLY02-01-010	159° 49.8'	73° 26.7'	1855	1.35	0.19	8.3	−19.9	2.6
WHS-7	HLY02-01-011	159° 33.2'	73° 36.7'	2443	0.92	0.15	7.2	−18.2	5.3
WHS-12	HLY04-03-052	157° 51.2'	73° 54.1'	3748	1.06	0.12	10.3	−19.2	7.6
EHS-4	HLY02-01-019	158° 44.2'	72° 36.3'	86	1.60	0.24	7.8	−18.3	7.8
EHS-6	HLY02-01-017	158° 28.5'	72° 51.1'	426	1.39	0.20	8.1	−19.3	7.0
EHS-9	HLY02-01-014	158° 08.8'	73° 06.1'	2158	1.05	0.17	7.2	−18.2	4.7
EHS-11	HLY02-01-012	157° 31.9'	73° 26.2'	2861	1.14	0.17	7.8	−20.3	5.0
EHS-12	HLY04-03-051	156° 45.9'	73° 47.9'	3778	0.92	0.13	8.3	−20.0	6.0
BC-3	HLY02-01-037	155° 45.3'	71° 39.0'	183	1.57	0.19	9.6	−20.6	2.0
BC-4	HLY02-01-031	154° 49.2'	71° 55.7'	401	1.53	0.20	8.9	−18.6	6.9
BC-5	HLY02-01-032	154° 27.8'	72° 04.2'	1317	1.43	0.20	8.3	−18.3	6.4
BC-7	HLY02-01-034	154° 29.9'	72° 32.0'	2934	1.41	0.19	8.7	−16.7	5.1
EB-2	HLY02-03-023	152° 33.2'	71° 27.4'	89	0.92	0.13	8.4	−22.1	5.0
EB-4	HLY02-03-021	152° 24.7'	71° 39.0'	498	1.87	0.21	10.4	−20.9	4.3
EB-7	HLY02-03-018	151° 59.1'	72° 19.3'	3264	1.59	0.18	10.1	−19.8	5.1

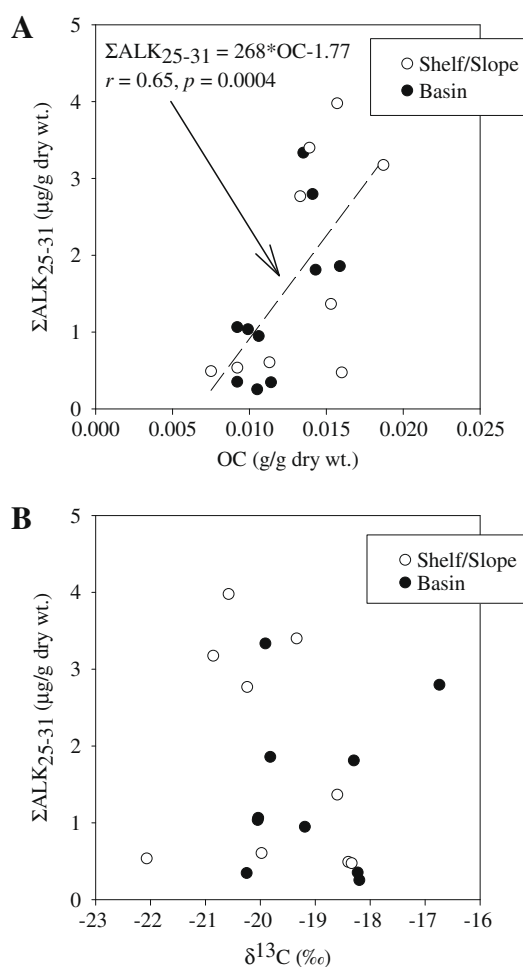


Fig. 4. Sum of C₂₅₋₃₁ odd-carbon number n-alkanes versus total organic carbon content (a) and $\delta^{13}\text{C}$ composition (b) in shelf and slope (<500 m) and basin (>500 m) environments.

between marine and terrestrial organic matter, inherent in this trend is also the shifting lability of organic matter, from fresh material represented by the most negative loadings on PC1 to highly recalcitrant material with the most positive loadings on PC1 (Fig. 6a). This lability shift was also noted through examination of the scores plot (Fig. 6b) which revealed a downcore shift for the six core samples along PC1 and indicates the diagenetic loss of the more labile marine components following burial. Similarly, some of the surface samples from the deepest basin stations (WHS-6, WHS-7, and EHS-12) also had strongly positive loadings in PC1, highlighting the possibility for both differential source delivery and diagenetic timescales represented by the surface sediment samples.

Principal component 2 corresponded to a transition from largely cyclic compounds, including α -amyrin and the sterols 24-methylcholesta-5,22E-dien-3 β -ol (C₂₈ $\Delta^{5,22}$), 24-methylcholesta-5,24(28)-dien-3 β -ol (C₂₈ $\Delta^{5,24(28)}$), cholesterol (C₂₇ Δ^5), as well as phytol and the C₁₄ and C₁₅ n-alcohols to largely acyclic long-chain mono- and dicarboxylic acids (Fig. 6a). The score plot (Fig. 6b) demonstrated a shift from samples collected closer to land (strong negative loadings) to basin stations (strong positive loadings on PC2).

As described, PC1 was defined as the shift from labile marine to recalcitrant terrestrial material. Therefore, along PC1, the biomarker with the most negative loading (the 16:1 ω 5 fatty acid) was assigned a relative stable/terrestrial value of 0% while the biomarker with the most positive loading (the C₁₉ n-alkane) was assigned a stable/terrestrial value of 100% (Fig. 6a). Each additional biomarker was assigned a relative stable/terrestrial value based on its position along the x-axis between these two end-members (Table 2). Each biomarker concentration was then multiplied by this stable/terrestrial value, resulting in a concentration attributed from stable/terrestrial sources. These concentrations were summed, then divided by total biomarker concentration to provide an estimate of stable/

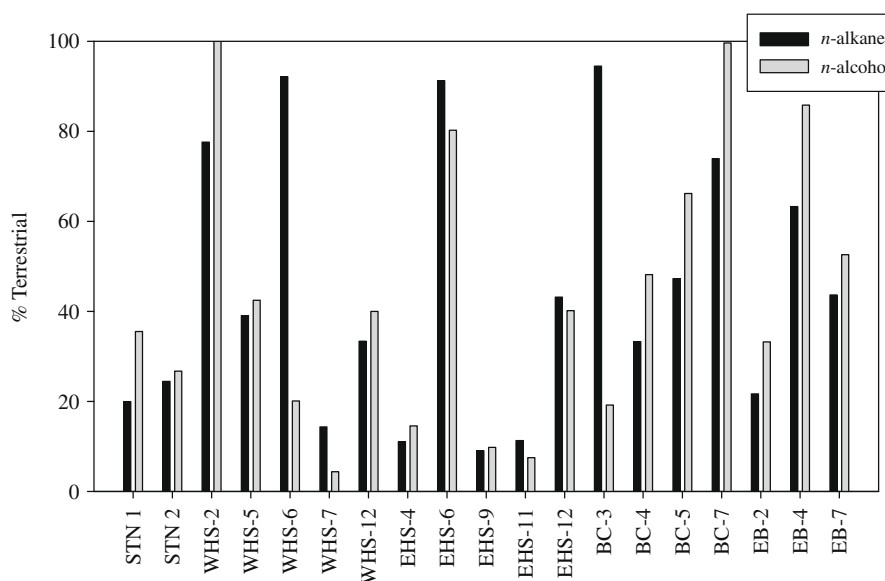


Fig. 5. A comparison between % terrestrial organic matter calculated based on the ALKOC ratio, the slope of relationship between long-chain *n*-alkane concentrations and organic carbon content, versus a similar calculation using the relationship between long-chain *n*-alcohols and organic carbon. See text for complete explanation of ALKOC derivation.

terrestrial organic matter for each site. For example, consider the $C_{29}\Delta^5$ sterol. Based on its position along PC1, its modeled stable/terrestrial input is 78%, which conceptually translated indicates that approximately 78% of the concentration of this compound derives from terrestrial/stable organic matter, while 22% derives from marine/labile material. The concentration of the $C_{29}\Delta^5$ sterol is then multiplied by 0.78, and together with the scaled concentrations from all the other biomarkers, is summed and divided by total (non-scaled) lipid biomarker concentration. Using this method, estimates for terrestrial/stable organic matter components in the 19 surface sediment samples ranged from 11.2% to 53.8%.

3.3. Tetraether lipids and the BIT Index

Five glycerol dialkyl glycerol tetraether (GDGT) lipids were quantified in all surface sediments excepting Station 2 where adequate sedimentary material for analysis was unavailable and are presented in the [Electronic annex \(Table EA-1-5\)](#). For this discussion we focus on general trends and the BIT index method of quantification for terrestrial organic matter components. Crenarchaeol (IV), the group 1.1 Crenarchaeota specific compound (Sinninghe Damsté et al., 2002), and the ubiquitous, non-specific compound (V) were the most abundant GDGTs found in sediments (Table EA-1-5, Fig. 7). Unlike most other lipid biomarkers, crenarchaeol concentrations were high in the Hanna Shoal and Barrow Canyon transects (Fig. 7), and were lower on average in the EB sediments. The branched GDGT compounds (I, II, and III, Fig. 2), thought to derive from bacteria living in terrestrial environments (Weijers et al., 2006b, 2007), were generally more abundant in the shallower regions of the BC and EB sediments (Fig. 7). Calculated BIT indices were overall quite low, ranging from 0.03 to 0.46 (Table EA-1-5, Fig. 8).

4. DISCUSSION

4.1. Spatial trends in bulk organic carbon and lipid biomarker preservation

In general, bulk sedimentary organic carbon increased towards the BC and EB transects (Fig. 3a), suggesting that burial efficiency of organic matter is greater in the eastern region of the study area, either from higher levels of primary productivity or lower organic carbon remineralization in the water column and sediments (Meyers, 1997). In concurrent studies of water column processes in the western Arctic (Grebmeier and Harvey, 2005), the area around Barrow Canyon was characterized by exceptionally high rates of primary productivity, estimated to reach a maximum of $430 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Hill and Cota, 2005), as well as the highest rates of export productivity for this study region (Moran et al., 2005). The Barrow Canyon feature appears to act as a focusing zone to funnel organic matter to the central canyon sediments, resulting in the elevated OC concentrations. The sedimentary distribution of total organic matter presented here closely reflects trends of water column particulate organic carbon (POC) presented by Bates et al. (2005b), with the highest concentrations of POC found in summertime over the BC and EB transects and the lowest OC from the EHS and WHS transects, and suggests a tight coupling between the pelagic and benthic realms. High concentrations of suspended organic matter were observed in tongues extending off the shelf into the basin in the SBI region (Bates et al., 2005b), which may also contribute to elevated sedimentary organic matter at the continental slope stations as compared to shallow shelf or deep basin environments. As a result, the sedimentary environment of the Barrow Canyon region may play an important role in the shelf to basin exchange of organic matter. Recent studies indicate that the flow of nutrient-rich waters

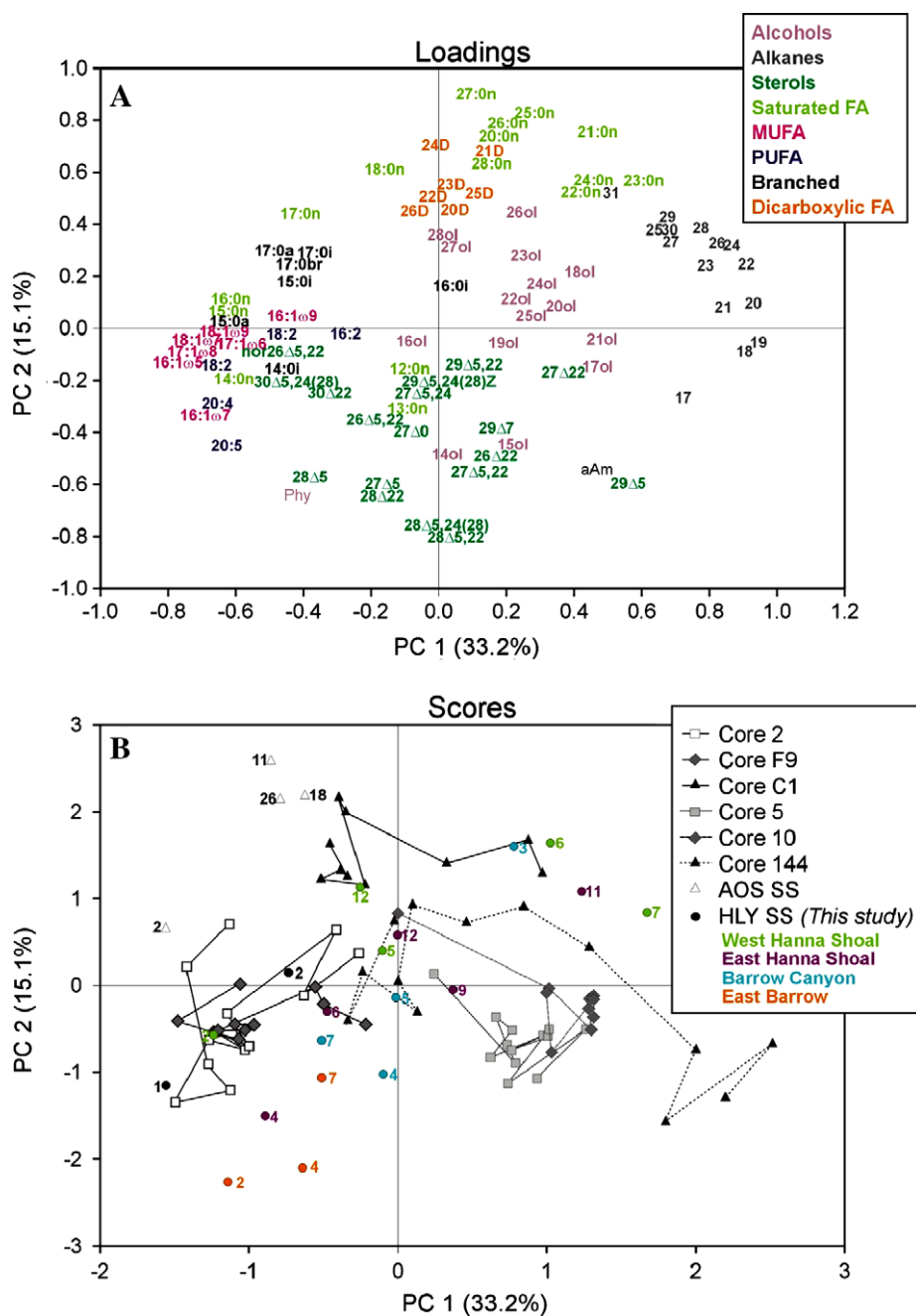


Fig. 6. Varimax rotated projections of the first two principal components displaying (a) biomarker loadings and (b) sediment sample scores for the integrated dataset principal components analysis. A total of 92 variables (lipid biomarkers) present in 93 observations (sediment samples) including the 19 surface sediment samples presented here were utilized for the statistical analysis. The remaining sediment core and AOS surface sediment sample data were taken from Belicka et al. (2004) and Yunker et al. (2005).

through Barrow Canyon is an important mechanism to deliver nutrients to the basin (Weingartner et al., 2005)—part of this off shelf flow may include nutrients regenerated from recently deposited sediments.

Atomic C:N ratios were also generally higher at the EB and BC transects (Fig. 3b) although only a narrow range in C:N ratios was observed overall. These sites are closer to the Alaskan shoreline, and the slightly elevated C:N ratio in these sediments is likely reflecting terrestrial inputs from

several small rivers and coastal erosion. This input of land-derived organic matter to the Barrow Canyon region is also suggested by the sedimentary $\delta^{13}\text{C}$ values, which were lowest in the BC and EB transects (Fig. 3c). The higher (more positive) $\delta^{13}\text{C}$ values in the transects to the east and west of Hanna Shoal are indicative of widespread marine material, and the lack of proximity of Hanna Shoal to either the Alaskan or Russian coastline limits direct inputs of terrestrial organic materials.

Table 2

Individual lipids used in PCA and the modeled fractional contribution of terrestrial organic matter.

Compound	Fraction terrestrial	Compound	Fraction terrestrial	Compound	Fraction terrestrial
<i>n</i> -alkanes		Other neutrals		Fatty acids (cont.)	
C ₁₇	0.87	Phytol	0.19	C21:0n	0.72
C ₁₈	0.98	α -Amyrin	0.72	C22:0n	0.69
C ₁₉	1.00			C23:0n	0.81
C ₂₀	0.99			C24:0n	0.72
C ₂₁	0.94	Sterols		C25:0n	0.61
C ₂₂	0.98	24-norcholesta-5,22-dien-3 β -ol (nor C ₂₆ $\Delta^{5,22}$)	0.33	C26:0n	0.56
C ₂₃	0.91	24-nor-5 α -cholest-22-en-3 β -ol (nor C ₂₆ Δ^{22})	0.55	C27:0n	0.51
C ₂₄	0.95	27-nor-24-cholesta-5,22-dien-3 β -ol	0.16	C28:0n	0.54
C ₂₅	0.83	Cholesta-5,22-dien-3 β -ol (C ₂₇ $\Delta^{5,22}$)	0.52	16:1 ω 9	0.18
C ₂₆	0.93	Cholest-22-en-3 β -ol (C ₂₇ Δ^{22})	0.67	16:1 ω 7	0.03
C ₂₇	0.85	Cholest-5-en-3 β -ol (C ₂₇ Δ^5)	0.34	16:1 ω 5	0.00
C ₂₈	0.90	Cholestan-3 β -ol (C ₂₇ Δ^0)	0.39	17:1 ω 8	0.01
C ₂₉	0.84	Cholesta-5,24-dien-3 β -ol (C ₂₇ $\Delta^{5,24}$)	0.42	17:1 ω 6	0.09
C ₃₀	0.84	24-methylcholesta-5,22-dien-3 β -ol (C ₂₈ $\Delta^{5,22}$)	0.47	18:1 ω 9	0.06
C ₃₁	0.74	24-methylcholest-22-dien-3 β -ol (C ₂₈ Δ^{22})	0.34	18:1 ω 7	0.02
		24-methylcholesta-5,24(28)-dien-3 β -ol (C ₂₈ $\Delta^{5,24(28)}$)	0.46	16:2	0.28
		24-methylcholest-5-en-3 β -ol (C ₂₈ Δ^5)	0.21	18:2	0.17
		24-ethylcholesta-5,22-en-3 β -ol (C ₂₉ $\Delta^{5,22}$)	0.51	18:2	0.05
<i>n</i> -alkanols		24-ethylcholest-5-en-3 β -ol (C ₂₉ Δ^5)	0.78	20:4	0.06
C ₁₄	0.46	24-ethylcholesta-5,24(28)Z-dien-3 β -ol (C ₂₉ $\Delta^{5,24(28)Z}$)	0.46	20:5	0.07
C ₁₅	0.57	24-ethylcholest-7-en-3 β -ol (C ₂₉ Δ^7)	0.55	14:0i	0.16
C ₁₆	0.39	4 α ,23,24-trimethylcholest-22-en-3 β -ol (C ₃₀ Δ^{22})	0.25	15:0i	0.19
C ₁₇	0.71	24-propylcholesta-5,24(28)-dien-3 β -ol (C ₃₀ $\Delta^{5,24(28)}$)	0.19	15:0a	0.07
C ₁₈	0.69			16:0i	0.46
C ₁₉	0.56			17:0br	0.19
C ₂₀	0.65	Fatty Acids		17:0i	0.22
C ₂₁	0.73	C12:0n	0.39	17:0a	0.15
C ₂₂	0.58	C13:0n	0.39	C20 DCA	0.47
C ₂₃	0.60	C14:0n	0.10	C21 DCA	0.54
C ₂₄	0.62	C15:0n	0.07	C22 DCA	0.44
C ₂₅	0.63	C16:0n	0.07	C23 DCA	0.45
C ₂₆	0.59	C17:0n	0.20	C24 DCA	0.45
C ₂₇	0.47	C18:0n	0.34	C25 DCA	0.52
C ₂₈	0.45	C20:0n	0.55	C26 DCA	0.41

Lipid biomarker concentrations generally paralleled organic matter distribution, with high concentrations of marine (diatom) markers (14:0n, 16:0n, 16:1 ω 7, 20:5) in the EB and BC sediments, consistent with the high levels of primary productivity noted in this location. However, the terrestrial markers including long-chain fatty acids and the triterpenoid α -amyrin were also very high in the BC and EB sediments, suggesting that the sediments east of Barrow Canyon appear to be a deposition center for both sources of organic matter in the western Arctic Ocean. Unlike most other lipids quantified, long-chain *n*-alkane concentrations were not enhanced in the EB sediments, possibly indicating a different source of these markers compared to α -amyrin.

Crenarchaeol (IV) and the non-specific tetraether (V) were the most abundant GDGTs in sediments (Table EA-1-5, Fig. 7). In contrast to most other lipid biomarkers noted above, crenarchaeol concentrations were high in the Hanna Shoal transects (Fig. 7). Group 1.1 Crenarchaeota

are believed to be the source of crenarchaeol in marine and lacustrine environments (Sinninghe Damsté et al., 2002). In the western Arctic Ocean, abundances of crenarchaeota in surface waters did not substantially decrease from shelf to basin; however, in terms of relative abundance, crenarchaeota increased from about 10% of total prokaryotes in surface waters to as high as 40% between 100 and 200 m (Kirchman et al., 2007). In addition, crenarchaeota relative abundance was weakly correlated to ammonium concentrations in the Chukchi and Alaskan Beaufort Sea regions (Kirchman et al., 2007). Although WHS-2, with high surface sediment crenarchaeol concentrations also contained the highest concentrations of ammonium ($\sim 2 \mu\text{M}$) in the near bottom waters (Codispoti et al., 2005), ammonium concentration alone cannot explain the distribution of crenarchaeol concentrations, as water column ammonium concentrations were higher in BC-3, which contained approximately 1/3 of crenarchaeol

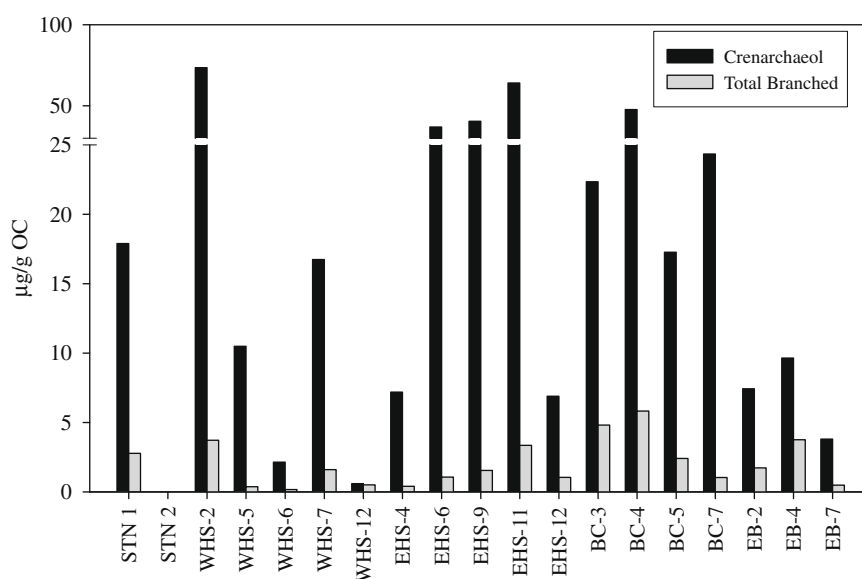


Fig. 7. Concentrations of crenarchaeol (structure IV) and total branched GDGTs (structures I, II, and III) in surface sediments along shelf to basin transects in the western Arctic Ocean.

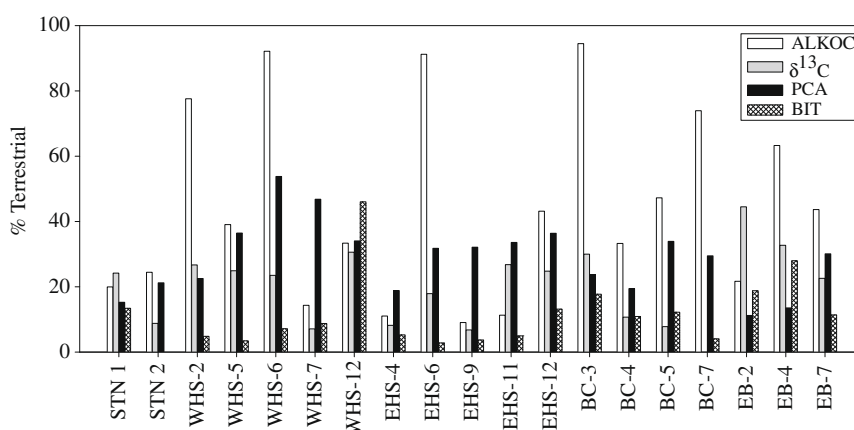


Fig. 8. Comparison of the four methods for calculation of preserved terrestrial organic matter in surface sediments of the western Arctic Ocean. Note the BIT index is multiplied by 100.

as WHS-2, and ammonium concentrations were extremely low at BC-4, which contained higher crenarchaeol than BC-3. Spatial patterns of water column crenarchaeol concentrations should be examined to further understand the correlations between Crenarchaeota and nutrients, as well as to elucidate controls on sedimentary crenarchaeol concentrations.

Branched GDGTs (I, II, and III) are assumed to be produced by bacteria as opposed to archaea, largely because of their branched alkyl chains and their 1,2-di-*O*-alkyl-*sn*-glycerol stereochemical configuration at C-2 in the glycerol backbone (Weijers et al., 2006a). It has been suggested that the organisms that produce branched GDGTs thrive in peat bogs (Sinninghe Damsté et al., 2000; Weijers et al., 2006a). The BC and EB sediments, where these markers were most abundant, are in close proximity to the Alaskan coastline which undergoes tremendous amounts of erosion.

This coastline is characterized by peat-rich deposits, and elevated concentrations of branched GDGTs in the BC and EB sediments may reflect mobilization of peat deposits into the Arctic Ocean.

4.2. Terrestrial organic carbon fractions among the methods

In general, the two end-member mixing model and the PCA/regression analysis typically resulted in intermediate estimates for the fraction of terrestrial organic carbon components, with very high estimates seen for the ALKOC ratio method and low terrestrial carbon values seen for the BIT index.

The $\delta^{13}\text{C}$ two end-member mixing model is the only technique among the four analyzed that incorporates bulk organic carbon, and it is also very sensitive to the assigned isotopic end-member values. The chosen terrestrial $\delta^{13}\text{C}$

value for our mixing model of -27.8‰ closely matches standard isotopic values of land plants that utilize the C_3 photosynthetic pathway (-26 to -28‰)—this pathway is most common in northern latitudes where C_4 or CAM plants do not thrive (Naidu et al., 2000). The range of reported $\delta^{13}C$ values for land-derived organic matter entering the Arctic Ocean is thus rather narrow. Sinking organic particles at the mouth of the Yenesei River had average $\delta^{13}C$ values of around -26.9‰ (Gaye et al., 2007), while those at the mouth of the Mackenzie River ranged from -25.4‰ to -26.0‰ (Goni et al., 2000; Drenzek et al., 2007). In a recent analysis of POC from three Alaskan Rivers, Guo et al. (2007) found $\delta^{13}C$ to range from -26.8‰ to -28.9‰ . Samples of peat and suspended organic matter collected at the Ikpikpuk and Kokolik river mouths were nearly identical to these additional Alaskan river particulate samples and ranged from -27.3‰ to -28.3‰ . These isotopic values also closely compare to sediments from estuaries of the Russian Arctic rivers (Ob, Yenesei, Lena, Indigirka, and Kolyma), which ranged from -25.0‰ to -27.4‰ (van Dongen et al., 2008).

Several authors have noted the difficulty in assigning a marine $\delta^{13}C$ end-member for polar waters, in part because of the increasing solubility of CO_2 with decreasing temperatures, differences in cell sizes and growth rates, and potential inputs of sea-ice algae, which may have limited access to dissolved inorganic carbon substrates (Laws et al., 1995; Gradinger, 2009). The $\delta^{13}C$ composition of Arctic sea-ice algae recently sampled from this study region ranged from -25‰ to -14.2‰ (Gradinger, 2009), with samples from the Canadian Arctic very similar, ranging from -24.9‰ to -13.2‰ (Tremblay et al., 2006). Both studies found increasing $\delta^{13}C$ values with increases in sea-ice biomass, an observation that supports DIC limitation leading to reduced isotopic fractionation. A wide range in isotopic composition of water column marine phytoplankton has also been reported for the Arctic (-16.7‰ to -30.4‰ , (Goericke and Fry, 1994)); however, for this study region, Gradinger (2009) found water column phytoplankton $\delta^{13}C$ to vary between -26.1‰ and -22.4‰ .

If we assume that the water column and ice phytoplankton $\delta^{13}C$ measured by Gradinger (2009) are representative of marine organic matter in this area, the heavy isotopic composition of most sediment samples in this study (-16.7‰ to -22.1‰) suggest substantial retention of carbon in sediments from ice algae. Additionally, we can also infer that the bulk preserved organic matter appears largely marine in origin, reflected by the relatively low estimates of terrestrial organic matter calculated using the mixing model (0–45%; Fig. 8). This assumption also relies on little to no input from plants using the C_4 photosynthetic pathway, which encompasses plants common in arid and tropical regions assumed to be negligible in the Arctic (Naidu et al., 2000 and references therein).

While $\delta^{13}C$ can be used to make these general claims about organic matter sources in Arctic sediments, the large variability in reported $\delta^{13}C$ values for both water column and ice phytoplankton and the difficulty in determining potential inputs from sea-ice algae in Arctic sediments are problematic and inhibit quantitative ability of $\delta^{13}C$ mixing

models. Additional constraints on the isotopic variability of ice and water column Arctic phytoplankton are necessary to improve the usefulness of this approach.

The three other approaches (*n*-alkane or *n*-alcohol to organic carbon ratios, PCA scaling, and BIT index) rely on preserved organic markers, in particular lipids such as *n*-alkanes, *n*-alcohols, fatty acids, sterols, and/or GDGTs. Lipid biomarkers, specific to their molecular precursors, impart modern or historical organic matter source information. For example, long-chain *n*-alkanes, based on their abundance in vascular plant waxes, are often used as terrestrial organic markers (Eglinton and Hamilton, 1969).

In river-dominated margins like the Columbia River, or the Laptev or Kara Seas in the eastern Arctic, there exists a relatively constant ratio of long-chain *n*-alkanes to organic carbon, often termed the ALKOC ratio (Prahl et al., 1994; Fernandes and Sicre, 2000). For the Laptev and Kara Seas, this ratio is 750 and 451, respectively (Fernandes and Sicre, 2000; Stein and Fahl, 2004). In contrast, the ALKOC for the western Arctic was 268 (Fig. 4), reflecting lower concentrations of *n*-alkanes per organic carbon content in the western Arctic than in the eastern Arctic. By dividing the organic carbon normalized long-chain *n*-alkane concentration by the ALKOC ratio, one can obtain an estimate of the fraction of terrestrial material preserved in sediments. We have expanded this approach and performed a similar calculation utilizing the relationship between *n*-alcohols and organic carbon content (Fig. 5). For this study region, the ALKOC routinely appears to overestimate preserved terrestrial organic components compared to the $\delta^{13}C$, PCA, and BIT index approaches for most sampling stations (Fig. 8); however, when compared to the similar calculation using *n*-alcohol concentrations, the ALKOC only resulted in substantially higher estimates for four stations (Fig. 5). The ALKOC method makes two assumptions—first, that *n*-alkanes are delivered at the mouth of the river to the coast in a fixed ratio and second, that a change in the ALKOC ratio in shelf sediments is caused by simple dilution with marine organic matter that does not contain long-chain *n*-alkanes (Prahl and Carpenter, 1984; Prahl et al., 1994; Fernandes and Sicre, 2000). The relatively poor correlation between long-chain *n*-alkanes and organic matter concentration (Fig. 4a) and the lack of relationship between *n*-alkane concentration and $\delta^{13}C$ with respect to shelf or basin location (Fig. 4b) in this study region suggest that these assumptions do not hold true for this area of the Arctic Ocean. Unlike the Laptev and Kara Seas, which are strongly influenced by a major river system, the eastern Chukchi and Alaskan Beaufort Seas contain numerous small rivers distributed along the coastline. The Colville River, for example, delivers an estimated $170,000 \text{ t yr}^{-1}$ of particulate organic carbon to this region (Macdonald et al., 2004). Estimates of coastal erosion along the Beaufort Sea coast range from 0.5 to 6 m yr^{-1} (Are et al., 2008; Lantuit and Pollard, 2008) and may even reach a maximum of 18 m yr^{-1} (Harper, 1990), demonstrating that this delivery pathway also plays a major role in carbon dynamics in this region. Although the ALKOC ratio was found to be quite useful for regions such as the Kara Sea where the simple dilution of river-derived terrestrial organic

matter occurs (Fernandes and Sicre, 2000), the patchy distribution of terrestrial organic matter inputs in the western Arctic precludes its quantitative use.

Although long-chain ($>C_{25}$) odd-carbon *n*-alkanes generally indicate terrestrial organic matter inputs, they may also derive from petrogenic organic matter from bedrock erosion (Yunker et al., 1993; Goñi et al., 2005). At first glance, the overestimation of terrestrial carbon inputs from the ALKOC ratio compared to the other approaches (Fig. 8) could suggest substantial inputs from petrogenic sources. Indeed, petrogenic inputs are clearly important in the Mackenzie River and shelf region of the Beaufort Sea to the east of this study region (Goñi et al., 2005; Drenzek et al., 2007); however, smaller Canadian Arctic rivers lacked other organic markers of petrogenic inputs (Yunker et al., 2002) and may indicate that large rivers are primarily responsible for the delivery of petrogenic organic matter to Arctic sediments. In order to examine the importance of petrogenic inputs to the western Arctic, we evaluated the carbon preference index (CPI) and a comparison between the ALKOC estimates with a similar calculation based on *n*-alcohols, which presumably do not derive from petrogenic inputs. Only four stations showed substantially enhanced terrestrial organic matter calculated using *n*-alkanes compared to *n*-alcohols, including WHS-6, WHS-7, EHS-6, and BC-3 (Fig. 5). Interestingly, three of these stations (WHS-6, WHS-7, and EHS-6) also had the lowest CPI values (Table EA-1-1), suggesting possible inputs of petrogenic carbon at these select sites. However, this was not true for BC-3 which had a higher CPI index. Also, CPI indices were low at EHS-9 and EHS-11 despite similar terrestrial estimates between *n*-alkanes and *n*-alcohols. Overall, however, the comparison between *n*-alkane and *n*-alcohol based estimates implies that unlike the Mackenzie Delta region of the western Arctic, petrogenic inputs to the Chukchi and Alaskan Beaufort Sea regions are not widespread or dominant.

For most transects, the PCA approach resulted in somewhat higher estimates of preserved terrestrial organic matter at deeper water stations compared to the shelf transect station. While at first glance the trend of increased terrestrial organic matter offshore may seem counterintuitive, especially for the WHS and EHS locations that are far removed from any direct source of terrestrial organic matter, several lines of evidence support this observation. First, terrestrial organic matter delivered to the pelagic WHS and EHS sediments likely arrives via melting sea-ice. A study by Eicken et al. (2005) in the region concluded that major ice transport trajectories, both observed and simulated, followed an east to west path, resulting in transport of particulate matter by sediment laden sea-ice towards the western-most transects. Furthermore, sediments were entrained into the ice by resuspension at water depths <20 m (Eicken et al., 2005), suggesting considerable incorporation of terrestrial organic matter at shallow depths near the coastline where erosion rates are high. Cooper et al. (2005) have found rapid (~ 3 month timescales) deposition of sea-ice rafted particulate matter to surface sediments in the study area, particularly on the shelf but also extending into deeper waters which highlights the ability for sea-ice to provide an effective mechanism for particle export (Cooper et al., 2005). In the

deep waters of the WHS and EHS regions, net daily production was still quite low in summertime compared to the BC and EB regions, despite high productivity on the shelf (Hill and Cota, 2005). In the absence of high levels of primary production, much of this marine organic matter is likely recycled in the water column prior to deposition, effectively leading to enhanced terrestrial organic matter preservation in deeper waters. Although the BC and EB transects were characterized by high levels of marine primary productivity as discussed above, the PCA-based estimation still showed increased levels of terrestrial organic matter at the basin stations, especially in the EB transect. This is likely reflecting decreased levels of primary productivity from longer sea-ice coverage, as well as inputs of coastal erosion that extend to the basin. The narrow Alaskan Beaufort shelf likely exerts more influence on the basin than the broad shelf near Hanna Shoal. It is possible that the terrestrial organic matter delivered to the BC and EB sediments arrives mainly via sediment slumping or water column transport, as opposed to the sea-ice rafting characteristic of the Hanna Shoal region.

The PCA approach is statistically robust in that it utilizes a large number of individual lipids (92 compounds in this case) derived from marine and terrestrial organic matter sources, and does not have the difficulties associated with choosing end-members or the constraints of spatial variability as described for the $\delta^{13}C$ mixing model and ALKOC methods. Because it relies on only preserved lipids, however, it may introduce bias into terrestrial organic matter estimates if the lipid distribution is not fully representative of the bulk organic matter inputs; also, as discussed, the reactivity as well as the source of organic matter is expressed in the PC model. Therefore the PCA-based estimate largely reflects the long-term preservation of terrestrial organic matter rather than its delivery.

The BIT index resulted in lower estimates of terrestrial organic matter than the other proxies for most stations and were representative of typical open ocean marine environments (Hopmans et al., 2004; Herfort et al., 2006). Out of the four proxies, the BIT index also showed the greatest differences between the western (EHS and WHS) and eastern (EB and BC) transects. In the western transects the BIT index increased offshore, indicating increased preserved terrestrial organic matter offshore in the basin similar to the results of the PCA-based approach as discussed above. In contrast, in the BC and EB transects the opposite trend as the PCA approach was found, with decreasing or stable estimates of preserved terrestrial material with water depth.

Using the BIT index in this regard as a two end-member mixing model relies on the assumption that crenarchaeol present in the sediments only derives from marine, not riverine or lacustrine, sources. While this may not be entirely appropriate because Crenarchaeota and crenarchaeol have been found in rivers and lakes (Crump and Baross, 2000; Powers et al., 2004; Herfort et al., 2006), our investigation of one pure terrestrial end-member revealed no detectable crenarchaeol in peat-like material from the Ikpikpuk River delta (Table EA-1-5). However, further investigations into the abundance of riverine or lacustrine inputs of crenarchaeol in Arctic systems may help the quantitative ability of the BIT index (Herfort et al., 2006).

Because the GDGT compounds are thought to occur from bacteria living in the terrestrial environment, as opposed to the terrestrial material itself, and from several observations that have noted the abundance of branched GDGT compounds in peat bogs (Hopmans et al., 2004; Herfort et al., 2006; Weijers et al., 2006b), the BIT index is now typically utilized to track inputs of soil organic carbon (Huguet et al., 2007; Walsh et al., 2008). As found by Walsh et al. (2008), the BIT index significantly underestimated terrestrial organic matter inputs in the soil-poor margin of the Washington and Vancouver Pacific Ocean coastlines, suggesting that the BIT index largely tracks soil OC and according to Weijers et al. (2009), although the branched GDGT compounds used in the BIT index are present in lower concentrations in soils than in peat bogs, soils are widespread and a substantial part of the terrestrial realm and likely to be the dominant source of the branched GDGTs in marine and lacustrine environments.

It is therefore not surprising that the BIT index values were lower than the other proxies for most stations evaluated here if in the western Arctic the BIT index most likely represents soil (with abundant peat) inputs, as opposed to proxies like $\delta^{13}\text{C}$ or the PCA approach that could encompass vascular plant debris combined with soil/peat inputs. Recently, however, concerns about intercomparability of the BIT index have been raised (Escala et al., 2009; Schouten et al., 2009). Discrepancies between calculated BIT index values among multiple laboratories may arise due to the large difference in molecular weight between the branched GDGTs versus crenarchaeol, resulting in variable responses, and therefore, highly variable BIT indices, depending on analytical instrumentation (Escala et al., 2009; Schouten et al., 2009). Alternatively, non-linear mixing between branched and isoprenoid GDGTs could account for the low estimates of terrestrial organic matter calculated by the BIT index. As described by Walsh et al. (2008) and Herfort et al. (2006), despite relatively high concentrations of branched GDGTs, large amounts of marine crenarchaeol at high productivity sites can result in artificially low terrestrial organic matter inputs. Several locations in this study demonstrated enhanced crenarchaeol concentrations (Table EA-1-5) and without further analysis we cannot confirm or deny that non-linear mixing of branched and isoprenoid GDGTs is affecting the BIT index. Based on the concerns of non-linear mixing and intercomparability, the BIT index values derived from this study should be utilized with caution until further calibration is achieved.

4.3. Implications for Arctic organic carbon budgets

The large differences between terrestrial organic matter approximations (Fig. 8) presented here highlight that we are still faced with the challenge of determining the “best” method to address the established geochemical question of the fate of terrestrial organic matter in the ocean (Hedges et al., 1997). Recent shifts towards three end-member mixing models, such as models developed by Gordon and Goni (2003) exploiting $\delta^{13}\text{C}_{\text{org}}$, lignin content, and the C:N ratio and Weijers et al. (2009) utilizing the BIT index, C:N ratio,

and $\delta^{13}\text{C}_{\text{org}}$, have made progress towards further refining the terrestrial component into vascular plant versus soil inputs for specific environments such as the Atchafalaya River and the Congo deep-sea fan, respectively. However, this approach remains challenging for the western Arctic system studied here. As discussed above, the constraining of a $\delta^{13}\text{C}_{\text{marine}}$ end-member remains a severe limitation, even if a four end-member mixing model is developed where the marine component is divided into sea-ice algae and water column phytoplankton inputs. The strong heterogeneity of the potential land-derived components and the necessity to choose an “average” C:N ratio for soil versus vascular plant material also strongly affects the outcome of 2 or 3 end-member mixing models, considering that between the terrestrial organic substrates presented here a range in C:N from 9 to 33 was observed. In addition, the newly raised concerns on difficulties in comparing BIT indices among laboratories suggest that until further calibration of the index is performed, any use in mixing models should proceed with caution. These conclusions have broad implications for the development of pan-Arctic carbon budgets as well as for attempts to follow the relative fate of marine and terrestrial organic matter components in other aquatic settings. Each quantification technique clearly has benefits and drawbacks, but caution must be taken when attempting to compare organic matter dynamics in various regions of the Arctic using these distinctly different proxies.

This point can be illustrated with a simple carbon budget calculation. Consider, for example, station EB-4, located in the eastern sampling section and likely receiving terrestrial organic matter inputs from both rivers (including the Colville) and coastal erosion. Holocene sedimentation rates for this region are not well constrained (Macdonald et al., 2004); however, on the inner shelf near the Colville Delta, an average sediment accumulation rate of $1 \text{ g cm}^{-2} \text{ yr}^{-1}$ was observed (Naidu et al., 1999). While it is likely that the delta region receives much higher sedimentary fluxes than the continental slope (EB-4), considerable amounts of POC were found to escape deltaic sedimentation through entrainment in sea-ice during the spring thaw and subsequently undergoing burial farther offshore (Macdonald et al., 2004 and references therein). If we conservatively assume that 10% of this material reaches water depths of 500 m near EB-4, we obtain an estimated sediment accumulation rate of $100 \text{ mg cm}^{-2} \text{ yr}^{-1}$ in the EB-4 region, which is similar to the average mass accumulation rate ($133 \text{ mg cm}^{-2} \text{ yr}^{-1}$) measured by Baskaran and Naidu (1995) for the adjacent Chukchi Sea. Utilizing the ALKOC method of preserved terrestrial organic matter (63.3%) and the organic carbon concentration (1.871%), we would estimate that surface sediments at EB-4 receive approximately $1.18 \text{ mg cm}^{-2} \text{ yr}^{-1}$ of terrestrial organic carbon. In contrast, if we were to use the result from the PCA-based model and assume that only 13.5% of the organic matter preserved in sediments was terrestrial in origin, we would conclude that about five times less ($0.25 \text{ mg cm}^{-2} \text{ yr}^{-1}$) terrestrial organic carbon is deposited in sediments. This discrepancy is also a concern when attempting to determine sedimentary reserves of marine organic matter by difference, as well as when extrapolating in a carbon budget to

determine the fraction of terrestrial organic matter that has been respired or exported.

The two end-member stable carbon isotopic mixing model and the ALKOC approach were not found to be suitable for the western Arctic based on the difficulties in assigning marine organic matter end-members and varied inputs from both small rivers and coastal erosion as discussed above. The BIT index approach may be promising for tracking soil or peat inputs; however, more information on the provenance and distribution of the branched and isoprenoid GDGT compounds in Arctic environments is needed as well as further recalibration based on recent concerns of the comparability of measurements among laboratories (Escala et al., 2009; Schouten et al., 2009). Because it is a multi-marker approach, the PCA-based method may provide the most appropriate current method of estimating terrestrial organic matter in the Chukchi and Alaskan Beaufort Sea region of the Arctic Ocean where standard mixing models are challenging, with the qualification that estimates reflect long-term preservation of organic matter as opposed to initial delivery of terrestrial or marine inputs since the reactivity of organic matter is an important component of the principal component analysis. Based on the PCA approach, estimates of the fraction of terrestrial organic matter ranged from 11% to 54%. Although estimates are not as high as the strongly river-dominated Canadian Beaufort shelf and Kara Sea shelf where land-derived inputs comprised 50–80% and 60–90% of total organic carbon, respectively (Fernandes and Sicre, 2000; Goñi et al., 2000), terrestrial organic matter plays a surprisingly important role in the organic carbon cycle in this non-river dominated, highly productive system. Implicit in these estimates is the assertion that unlike the traditional model of open ocean carbon dynamics where inputs are largely marine-derived and rapidly recycled, the abundant terrestrial organic carbon delivered to Arctic sediments is sequestered over much longer timescales. Few estimates of the differences in remineralization rates between marine versus terrestrial organic substrates exist for Arctic regions, but generalized pan-Arctic carbon cycle box models suggest marine organic matter on Arctic shelves is oxidized up to 70 times faster than shelf terrestrial organic matter (Stein and Macdonald, 2004a). The difference in recycling between marine and terrestrial sources and its implications for the rate of carbon turnover in sediments necessitate improved quantitative evaluations of preserved vascular plant, soil, water column phytoplankton, and sea-ice algae components in modern and historical Arctic sediments for modeling of the Arctic carbon cycle.

5. SUMMARY AND CONCLUSIONS

Current binary mixing models used to estimate fractions of terrestrial organic matter in marine sediments show considerable variation for identical sediment samples. This lack of consistency limits our ability to incorporate these types of estimates into pan-Arctic carbon budgets. The $\delta^{13}\text{C}$ and ALKOC methods were not appropriate for estimating terrestrial organic components in western Arctic sediments due to the difficulty in constraining marine isotopic end-

members and the lack of linear mixing from fluvial inputs of *n*-alkanes, respectively. The BIT index resulted in the lowest estimates for terrestrial organic matter of all techniques for a majority (58%) of stations, corroborating recent suggestions that this proxy represents a distinct fraction of terrestrial organic matter, namely soil, as opposed to markers such as *n*-alkanes or long-chain fatty acids which originate from vascular plant waxes. The lipid-based PCA approach resulted in consistently different estimates of terrestrial organic matter than bulk organic carbon proxies, suggesting that organic matter fractions such as amino acids and carbohydrates may be contributing to the bulk composition, but is likely the most appropriate current proxy for terrestrial organic matter in the western Arctic where more traditional mixing models are challenging to constrain. Overall, average terrestrial organic matter inputs to the Chukchi and western Beaufort Seas using the multi-marker PCA approach ranged from 11% to 54%, highlighting the importance of terrestrial organic matter in Arctic Ocean sediments, even on non-river dominated continental margins. The potential for increasing inputs of both fresh and ancient terrestrial organic matter with continued Arctic warming argues that Arctic sediments may play an increasingly important role in the sequestration of carbon in the future. Models which incorporate elemental cycling will require refinement to account for the multiple pools of organic matter and the potential for large differences in recycling rates.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.07.020.

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