The supply and preservation of ancient and modern components of organic carbon in the Canadian Beaufort Shelf of the Arctic Ocean

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Received 10 July 2003; received in revised form 30 July 2004; accepted 2 August 2004

Abstract

The provenance of organic matter in sediments from the Mackenzie River and Beaufort Shelf was investigated using the stable carbon and radiocarbon isotopic compositions of bulk organic matter and the stable carbon isotopic compositions of individual organic compounds, including lignin-derived phenols and lipid-derived fatty acids. Most river suspended sediments and shelf surface sediments contained organic carbon characterized by highly depleted $^{14}$C values that were consistent with average radiocarbon ages exceeding 7000 years. The stable carbon isotopic signatures of lignin phenols were uniformly depleted ($\delta^{13}C \approx -32\%$), indicating the predominant contributions of $C_3$ vascular plant sources. The isotopic compositions of $C_{14}$ and $C_{16}$ fatty acids exhibited important contrasts between the river ($-36\%$ to $-40\%$) and shelf ($-25\%$ to $-29\%$) sediments that were consistent with contributions from freshwater algae and/or vascular plants in the former and marine phytoplankton in the latter. Using $^{14}$C isotopic mass balance, the abundances of modern and ancient organic matter were quantitatively constrained. Ancient organic carbon, which may include old pre-aged soil material as well as fossil bitumen or kerogen, accounted for the majority (~70%) of the particulate organic matter exported by the Mackenzie River and deposited in surface sediments of the Beaufort Shelf. Modern organic carbon accounted for ~30% in both river and shelf sediments, with significant contributions from vascular plant-derived materials in both river and shelf samples and from marine algae in the shelf sediments. Respiration (and/or leaching) of particle-bound marine organic matter dominates the carbon metabolism in the Mackenzie Delta/Beaufort Shelf region. However, land-derived pools, including modern carbon derived from vascular plants as well as ancient carbon also appeared to undergo a degree of post-depositional degradation prior to burial in the shelf. These novel source apportionments are reflected in an updated carbon budget for the study area.

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Keywords: Organic carbon; Carbon 13; Carbon 14; Lignin phenols; Fatty acids; Arctic sediments; Beaufort shelf; Mackenzie River

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0304-4203/$ -$ see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.marchem.2004.08.001
1. Introduction

River-dominated shelves are some of the most important sites of organic carbon (OC) burial in marine environments (Berner, 1982; Hedges and Keil, 1995; Liu et al., 2000). High sedimentation rates, enhanced inputs of mineral surfaces, elevated fluxes of terrigenous nutrients and inputs of recalcitrant land-derived OC all point to the importance of these regions in terms of carbon sequestration. The Arctic Ocean, which is almost land locked, receives the discharge of some of the world’s largest rivers. Because of their relatively pristine state, high seasonality of discharge and efficient transport of terrigenous materials by ice-related processes, river-dominated shelves in the Arctic Ocean may contribute significantly to the global burial of carbon (Macdonald et al., 1998; Stein and Macdonald, 2004; Stein et al., 1994). Even more important is the role likely to be played by Arctic shelves in global change. The Arctic possesses some of the world’s largest shelves, which are poised to experience significant losses in sea-ice cover that will alter marine productivity and a range of physical processes (Stein and Macdonald, 2004). Moreover, the expected destabilization of permafrost and its consequences on hydrology and plant cover will change the input of terrigenous carbon to coastal seas (Benner et al., 2004; Guo et al., 2004; Dittmar and Kattner, 2003). How these very different responses to temperature rise will impact the delivery and preservation of organic carbon over the Arctic’s shelves remains unknown, but it is clear that we need baseline data before we can predict change or measure it in the decades to come.

Understanding the factors that control carbon burial in Arctic sediments requires an in-depth knowledge of the sources and chemical composition of organic matter. Recent studies have highlighted the heterogeneous nature of the organic matter in several river-dominated margins (Bianchi et al., 2002; Blair et al., 2003; Goñi et al., 2000, 2003; Gordon and Goñi, 2003; Guo et al., 2004; Leithold and Blair, 2001; Masiello and Druffel, 2001, 2003). Allochthonous organic carbon inputs include riverine and estuarine algae, vascular plant debris, soil organic matter, and ancient kerogen from sedimentary rocks. In the Arctic, coastal erosion also provides an additional and often dominant source of sediment and carbon (Stein and Macdonald, 2004). Although coastal erosion is as active in the Canadian Beaufort as anywhere else in the Arctic, the Mackenzie River is so large a source of particulate and organic material that it dominates the region and coastal erosion provides only a relatively small (~7%) proportion of material to the Mackenzie Shelf (Macdonald et al., 1998). Autochthonous sources of OC derived from marine productivity over continental margins include marine phytoplankton detritus, materials cycled and packaged through the guts of zooplankton, as well as marine bacteria (Sakshaug, 2004). Production from ice algae also represents an additional autochthonous OC contribution in the Arctic (Gradinger, 1996; Horner and Schrader, 1982; Sakshaug, 2004).

Our previous work in the Beaufort Shelf off the Mackenzie River shows that land-derived OC accounts for the majority (>60%) of the organic matter present in shelf sediments (Goñi et al., 2000; Macdonald et al., 1998; Yunker et al., 1995). Biomarker and stable carbon isotopic studies corroborate the importance of terrigenous OC and provide insight into its composition, which includes highly degraded materials derived from vascular plants (Goñi et al., 2000; Yunker and Macdonald, 1995; Yunker et al., 1991b). Our findings on the predominance of land-derived OC are similar to those of studies from other river-dominated Arctic margins such as the Lena River/Laptev Sea (Peulve et al., 1996; Zegouagh et al., 1998) and the Ob’ and Yenisei Rivers/Kara Sea (Fernandes and Sicre, 2000). Autochthonous production over the Beaufort Shelf contributes to the OC present in surface sediments of the Mackenzie shelf, although the levels of marine OC in this region are significantly lower than in other Arctic shelves that receive large imports of nutrients from, for example, the Pacific (Bering and Chukchi Seas) or the Atlantic (Barents Sea) (Grebeimeir et al., 1988; Naidu et al., 1993, 2000; Chen et al., 2002).

The focus of this paper is to investigate in detail the origin and distribution of organic matter in sediments from the Mackenzie River and Beaufort Shelf using the stable ($\delta^{13}C$) and radioactive ($^{14}C$) isotopic compositions of bulk organic carbon and the $\delta^{13}C$ compositions of individual CuO reaction products. Additionally, in order to gain a more quantitative understanding of the fate of the various sources of organic matter in the Beaufort Shelf, we use the
specific mineral surface area of sediments to examine the changes in the loadings of different OC pools. Based on these new analyses, we reassess the provenance of the organic matter present in Beaufort Shelf sediments with special emphasis on the role that ancient OC exported from the continent plays on the regional carbon cycle.

2. Materials and methods

2.1. Study site and samples

All samples were collected from the Mackenzie River Delta and the Beaufort Sea Shelf (Fig. 1), a region that has been the focus of previous investigations (Goñi et al., 2000; Yunker et al., 1991a, b, 1993, 1995, 2002). Briefly, the Mackenzie River exports materials mainly from its western drainage basin, which includes parts of the Canadian Cordillera. The vegetation in the drainage basin ranges from tussock tundra in its high latitude and altitude regions to boreal forests in the lower latitudes (Brunskill, 1986; Zoltai and Pettapiece, 1973). The timing of sediment export by the Mackenzie River is tightly coupled to its freshet and the breakup of land fast ice (Carson et al., 1998; Dean et al., 1994; Macdonald et al., 1998). In fact, most (90%) of the total sediment discharge to the shelf (124 ± 42 10^6 tons year\(^{-1}\) for the 1974–1994 period) occurs between June and August (Carson et al., 1998). On average, the Mackenzie River exports 2.1 \times 10^9 kg of particulate OC and 1.3 \times 10^9 kg of dissolved OC per year (Macdonald et al., 1998). Coastal primary productivity over the Mackenzie Delta/Beaufort Shelf (3.3 \times 10^9 kg OC year\(^{-1}\)) is mainly in the form of phytoplankton blooms in the open water regions of the shelf during late spring and summer and is restricted throughout the rest of the year by low light conditions and ice coverage (Macdonald et al., 1998). Production by ice algae accounts for a relatively minor (5–10%) fraction of the marine production in this area (Horner and Schrader, 1982).

The samples analyzed in this study were collected as part of a large sampling program of the Mackenzie Delta/Beaufort Shelf in 1987. Detailed descriptions of the sample locations and sampling protocols have been provided previously (Goñi et al., 2000; Yunker...
et al., 1991b, 1993, 1995, 1996). Briefly, bulk suspended sediment samples were collected from the East, Middle and Reindeer channels of the outer Mackenzie River delta by centrifugation during June and July of 1987 (Fig. 1). Surface sediments from the seabed were collected at different water depths along a shore-perpendicular transect in the Beaufort Shelf off the Mackenzie River mouth during August and September of 1987 (Fig. 1). The sample of coastal peat immediately below a thin layer of surface soil was also collected at this time. All of the analyses presented here are from unfractionated whole samples.

2.2. Analytical methods

Bulk elemental and stable carbon isotopic analyses were conducted using dried ground samples according to established procedures. Total carbon (%TC) and total nitrogen (%TN) contents were determined by high temperature combustion (Goñi et al., 2000). Total inorganic carbon (%TIC) was determined using an automated carbonate system (Ostermann et al., 1990). Organic carbon (%OC) content for each sample was determined by difference (%TC–TIC). The stable isotopic compositions of OC ($\delta^{13}C_{OC}$) were measured on pre-acidified sediments using a CHN analyzer coupled to a Finnigan Delta-S mass spectrometer (Fry et al., 1992). The $\delta^{13}C/^{12}C$ composition of the organic carbon ($\delta^{13}C_{OC}$) is reported relative to the PDB standard (VPDB) in the $\delta$ (‰) notation.

Radiocarbon analyses were performed at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution following established procedures (McNichol et al., 1992; Vogel et al., 1987). OC was combusted to CO$_2$, which was then converted to graphite via Fe/H$_2$ catalytic reduction. The graphite was pressed into targets and analyzed on the accelerator mass spectrometer. Radiocarbon values of OC were reported as $\Delta^{14}C_{OC}$ (‰). The $\Delta^{14}C_{OC}$ values were used to calculate conventional radiocarbon ages present in each sample (Stuiver, 1980; Stuiver et al., 1986; Stuiver and Polach, 1977).

The mineral surface area of each unground sediment sample was determined with a Coulter SA3100 Surface Area Analyzer using the BET technique (Keil et al., 1994; Mayer, 1994). Prior to analyses, all samples were thoroughly rinsed with distilled water to remove salts. We carried out two measurements of the specific surface area of these samples. First, we measured surface areas on rinsed samples without any other treatment. Additionally, we used combustion at 300 °C for 12 h (Keil and Cowie, 1999) to remove organic matter from splits of the rinsed sediments and then measured the surface area of these OC-free samples. Comparison between the two analyses revealed virtually identical values for these two treatments (e.g., Mayer, 1994). The procedure used to measure surface area involved outgassing approximately 1 g of unground sediment at 250 °C for 1 h under vacuum prior to analysis. The specific surface area was determined by a 5-point BET multilayer adsorption analysis. The correlation coefficient between each of these five equilibrium points was never less than 0.99996. Analytical precision, determined from replicate analyses of the same sample, averaged 0.1 m$^2$ g$^{-1}$. Analytical accuracy throughout the study was determined by analyzing alumina standards purchased from Coulter and was within 5% of accepted value.

The CuO analyses were conducted using the established technique of alkaline CuO oxidation (Goñi and Hedges, 1992). Briefly, dried ground samples were oxidized in stainless pressurized vessels containing 8% NaOH, CuO and Fe(NH$_4$)$_2$SO$_4$ at 155 °C for 3 h. Known amounts of recovery standards, ethylvanillin and $t$-cinnamic acid were added to the vessels after the reaction was completed. Following acidification to pH 1, aqueous solutions were extracted with diethyl ether. The ether extracts were dried and stored in the freezer. Prior to chromatographic analysis, extracts were redissolved in pyridine and reacted with BSTFA to form trimethylsilyl derivatives. Over 50 individual CuO products were quantified by gas chromatography. Here, we focus on specific CuO oxidation products, including lignin-derived phenols, lipid-derived fatty acids and aliphatic carbon-derived dicarboxylic acids. The yields of lignin phenols were determined based on the response factors of authentic standards, while the yields of the non-lignin products were quantified using the detector response of $t$-cinnamic acid. The identities of all products were corroborated by gas chromatography-
mass spectrometry (GC-MS) and comparison with published spectra.

Stable carbon isotopic analyses of selected CuO reaction products were conducted by isotope ratio monitoring-gas chromatography-mass spectrometry (irm-GC-MS) according to the technique of Gofii and Eglinton (1996). Briefly, splits of the CuO extracts were prepared in the same fashion as for GC and conventional GC-MS analyses. Prior to injection in the irm-GC-MS instrument (Varian 3000 GC-Finningan Delta-S isotope ratio mass spectrometer), ~0.5 μl of deuterated n-alkane standard (C20, C24 and C36 perdeuterated n-alkanes) solution was taken up on the sample syringe and co-injected along with ~0.5 μl of sample. Once the sample was run, we used the known isotopic composition of the perdeuterated n-alkane standards to calculate the isotopic compositions of the lignin phenols in their silylated forms (TMS ethers and esters). Since the isotopic compositions of ethylvanillin and t-cinnamic acid were known, we applied isotopic mass balance to estimate the isotopic composition of the TMS carbons added. The δ13C compositions of the derivative carbons determined for each sample run were used via isotopic mass balance to derive the δ13C signatures of the CuO reaction products, including lignin phenols, fatty acids and dicarboxylic acids. In this sample set, we routinely used t-cinnamic acid to estimate the δδ13C composition of the derivative carbon added since it was baseline-resolved in all irm-GC-MS traces. We estimated the reproducibility of the procedure by performing triplicate analyses of selected samples. In general, the precision of the measurement of a single compound was within 1.0‰, although higher variabilities were obtained in cases where compounds were either not completely resolved or less than 5 nmol/μl in concentration.

3. Results

The compositions of bulk sediments from the Mackenzie River and Beaufort Shelf are presented in Table 1. Although coastal peats are estimated to contribute less than 7% to the carbon budget in the area (Macdonald et al., 1998), we have included data for one coastal peat sample because it represents an important contrast to the compositions of the organic matter exported by the river and present in the surface sediments from the shelf.

3.1. Organic matter loadings

Sediment samples from both the river and shelf yielded SA values of 19–29 m² g⁻¹, %OC values of 1.1–2.0 wt.% and %TN values of 0.1–0.2 wt.% (Table 1). There was considerable variability in the SA, %OC and %TN compositions of the river suspended sedi-

<table>
<thead>
<tr>
<th>Sample description and water depth</th>
<th>Sample code</th>
<th>SA (m²/g)</th>
<th>%OC (wt.%</th>
<th>%TN (wt.%)</th>
<th>[C/N] (mol)</th>
<th>δ13COC (‰)</th>
<th>δ14COC (‰)</th>
<th>Age (ybp)</th>
<th>NOSAMS#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coastal Peat (T4)</td>
<td>PT</td>
<td>2.5±0.1</td>
<td>17.05±0.5</td>
<td>0.98±0.020</td>
<td>20.4±0.7</td>
<td>-26.0±0.05</td>
<td>-125.6</td>
<td>1030±45</td>
<td>OS-15640</td>
</tr>
<tr>
<td>Mackenzie River suspended sediments</td>
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<tr>
<td>East Channel (June-87); 1 m</td>
<td>EJe</td>
<td>20.9±0.6</td>
<td>1.46±0.04</td>
<td>0.14±0.003</td>
<td>12.2±0.4</td>
<td>-26.4±0.05</td>
<td>-594.2</td>
<td>7200±50</td>
<td>OS-15641</td>
</tr>
<tr>
<td>Middle Channel (June-87); 1 m</td>
<td>MeJe</td>
<td>18.8±0.6</td>
<td>1.57±0.05</td>
<td>0.13±0.003</td>
<td>14.6±0.5</td>
<td>-26.2±0.05</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>East Channel (July-87); 1 m</td>
<td>E-Jy</td>
<td>22.6±0.7</td>
<td>1.84±0.06</td>
<td>0.18±0.004</td>
<td>12.2±0.4</td>
<td>-26.9±0.05</td>
<td>-680.3</td>
<td>9110±55</td>
<td>OS-15643</td>
</tr>
<tr>
<td>Reindeer Channel (July-87); 1 m</td>
<td>R-Jy</td>
<td>22.2±0.7</td>
<td>1.67±0.05</td>
<td>0.13±0.003</td>
<td>15.4±0.6</td>
<td>-26.4±0.05</td>
<td>-714.4</td>
<td>10000±75</td>
<td>OS-15642</td>
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<tr>
<td>Beaufort shelf surface sediments</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Station 1/G1 (0–2 cm); 5 m</td>
<td>G1</td>
<td>19.2±0.6</td>
<td>1.13±0.03</td>
<td>0.14±0.003</td>
<td>9.4±0.3</td>
<td>-25.9±0.05</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>Station 5/G7 (0–2 cm); 25 m</td>
<td>G7</td>
<td>23.1±0.7</td>
<td>1.97±0.06</td>
<td>0.17±0.003</td>
<td>13.9±0.5</td>
<td>-25.5±0.05</td>
<td>691.3</td>
<td>9390±55</td>
<td>OS-15644</td>
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<tr>
<td>Station GRM1 (0–10 cm); 30 m</td>
<td>GRM1</td>
<td>26.6±0.8</td>
<td>1.44±0.04</td>
<td>0.14±0.003</td>
<td>11.6±0.4</td>
<td>-25.7±0.05</td>
<td>720.8</td>
<td>10200±55</td>
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</tr>
<tr>
<td>Station 9/G12 (0–2 cm); 61 m</td>
<td>G12</td>
<td>27.3±0.8</td>
<td>1.54±0.05</td>
<td>0.20±0.004</td>
<td>8.9±0.3</td>
<td>-24.4±0.05</td>
<td>590.9</td>
<td>7130±75</td>
<td>OS-21909</td>
</tr>
<tr>
<td>Station 10/G9 (0–2 cm); 210 m</td>
<td>G9</td>
<td>28.6±0.9</td>
<td>1.23±0.04</td>
<td>0.12±0.002</td>
<td>12.0±0.4</td>
<td>-25.1±0.05</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>Station 10/G10 (0–2 cm); 210 m*</td>
<td>G10</td>
<td>29.0±0.9</td>
<td>1.20±0.04</td>
<td>0.10±0.002</td>
<td>13.5±0.5</td>
<td>-25.5±0.05</td>
<td>-876.8</td>
<td>16750±100</td>
<td>OS-15645</td>
</tr>
</tbody>
</table>

Abbreviations: SA, mineral surface area; %OC, weight percent organic carbon; %TN, weight percent total nitrogen; [C/N] (mol), molar OC/TN ratio; δ13COC, stable carbon isotope composition of organic carbon; δ14COC, radiocarbon isotope composition of organic matter; ybp, years before present; NOSAMS#, AMS analysis number.
ments. All four samples yielded OC loadings of 0.7 to 0.8 mg C m\(^{-2}\) (Fig. 2a) that are consistent with those observed in many river and marine sediments (OC:SA=0.5 to 1.0) (Hedges and Keil, 1995; Keil et al., 1997; Mayer, 1999). The TN loadings of the four river samples ranged from 0.06 to 0.08 mg N m\(^{-2}\) (Fig. 2b) and are within the TN:SA ratios observed in river suspended sediments and depocenter bed sedi-

![Fig. 2. Plots of (a) specific surface area (SA) versus organic carbon (OC) content and of (b) specific surface area (SA) versus total nitrogen (TN) content for sediments from the Mackenzie River and the Beaufort Sea shelf. All sample codes are according to Fig. 1. The composition ranges measured in many river and marine sediments (e.g., Hedges and Keil, 1995; Keil et al., 1997; Mayer, 1999; Mayer et al., 1998) are highlighted in the graph.]
ments (Mayer et al., 1998). In contrast, the peat sample yielded predictably low mineral surface area (SA) values and elevated weight percent organic carbon (%OC) and total nitrogen (%TN) contents (Table 1).

SA and %OC values varied significantly among the surface shelf sediments (Table 1). The 5 m sample yielded the lowest SA and %OC values (19 m² g⁻¹ and 1.1 wt.%, respectively) while the 210 m and 210 m* samples exhibited the highest SA (29 m² g⁻¹) and the 25 m sample showed the highest %OC (2 wt.%).

With the exception of the 25 m sample (OC/SA=0.9 mg C m⁻²), all shelf sediments displayed lower OC loadings (0.4–0.6 mg C m⁻²) than the river-suspended sediments. However, with the exception of the 210 m and 210 m* samples, the OC loadings exhibited by the Beaufort Sea shelf sediments were still within typical range for most shelf sediments (Fig. 2a). In contrast to OC, the TN loadings of several Beaufort Shelf sediments (0.06–0.07 mg N m⁻²) were comparable to those measured in the river samples, and only the 210 m and 210 m* samples exhibited relatively low TN/SA values of less than 0.05 mg N m⁻² (Fig. 2b).

3.2. Bulk organic matter compositions

The molar organic carbon/total nitrogen ratios ([C/N]) of river suspended sediments and shelf sediments were comparable, ranging from 12 to 15 and 9 to 14, respectively (Table 1). In contrast, the PT sample had a significantly higher [C/N] ratio (20). The relationship between TN and OC contents in the sediments showed a weak correlation ($r^2=0.3$) and a positive OC intercept at TN=0. The latter observation is consistent with the presence of N-devoid organic matter in the sample mixtures and the absence of measurable amounts of inorganic nitrogen sorbed to mineral grains (Goñi et al., 1998). All the samples analyzed displayed a relatively narrow range in the stable isotopic composition of OC ($\delta^{13}$COC), with values of −26‰ to −27‰ for the peat and river suspended sediment samples and values of −24‰ to −26‰ for surface shelf sediments (Table 1). Notably, there were broad contrasts among the radiocarbon isotopic compositions ($\Delta^{14}$COC) of the samples analyzed, with values that ranged from −125‰ for the PT sample to −876‰ for the 210 m* sample.

These compositions translate to conventional $^{14}$C ages for the OC in these samples of ~1000 years before present (ybp) in the case of PT and of 7000 to 10,000 ybp for river-suspended sediments. The ages for the surface shelf sediments ranged from ~7000 ybp for the 61 m sample to over 16,500 ybp for the 210 m* sample (Table 1).

3.3. CuO reaction product yields and loadings

The yields of lignin-derived phenols, fatty acids and dicarboxylic acids obtained from the alkaline CuO oxidation of Mackenzie River/Beaufort Shelf samples are presented in Table 2. Goñi et al. (2000) discussed in detail the trends in the compositions of these (and many other) CuO oxidation products. In this paper, we provide new insights into the fate of different types of organic matter by examining the loading levels of these compound classes relative to the specific mineral surface area. As evident from Table 2, the peat sample differed from all the other sediments analyzed because of its extremely elevated yields of total lignin phenols ($\Sigma$Lig), total fatty acids ($\Sigma$FA) and total dicarboxylic acids ($\Sigma$DA), which were more than an order of magnitude higher than the rest of the samples. Furthermore, most of the PT sample was made up of organic particles (Yunker et al., 1991b) with a low SA value, unlike the rest of the samples in which OM was primarily associated with mineral particles (Goñi et al., 2003; Keil et al., 1994). For that reason, we have not included the PT compositions in the presentation of the compound/SA ratio results below.

In order to examine the loadings of different organic compound classes in the sediments from the study area, we normalized the yields of the CuO oxidation products (Table 2) to the mineral surface area of each sample (Fig. 3). The river suspended sediments were characterized by elevated $\Sigma$Lig loadings (>5 µg m⁻² sediment) whereas shelf sediments in general showed lower $\Sigma$Lig loadings (<3 µg m⁻²) that tended to decrease with distance from the mouth. The major exceptions were the E-Jy river sample, which was characterized by relatively low $\Sigma$Lig loadings (4 µg m⁻²), and the 5 m sample, which gave high $\Sigma$Lig loadings (6 µg m⁻²) similar to those obtained in three of the four river suspended sediments (Fig. 3). The distribution of $\Sigma$FA loadings among river suspended sediments ranged from 1 to
3 µg m\(^{-2}\), with the E-Jy sample giving the highest values. Most shelf sediments showed similar ΣFA loadings (2–3 µg m\(^{-2}\)). Notably, the 25 m sample yielded a markedly higher ΣFA loading (8 µg m\(^{-2}\)), whereas the 210 m\(^*\) sample had a low ΣFA loading (1 µg m\(^{-2}\)). Finally, unlike any other CuO product category, the ΣDA loadings (1–2 µg m\(^{-2}\)) were comparable throughout all the sediments analyzed, showing none of the contrasts displayed by ΣLig and ΣFA.

### 3.4. Stable carbon isotopic compositions of CuO reaction products

The δ\(^{13}\)C signatures of selected CuO reaction products estimated according to the procedure of
Goñi and Eglinton (1996) are presented in Table 3. Only a fraction of the compounds presented in Table 2 were sufficiently resolved or in high enough concentration to permit accurate isotopic determination. It is evident from these data that the lignin phenols from all samples (peat, river suspended

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**Figure 3.** Surface area-normalized loadings of CuO oxidation products from the Mackenzie River and the Beaufort Shelf samples. The loadings are calculated as the ratios between the yields of different CuO products (Table 2) and the specific surface area (SA) of each sample (Table 1). Included in this graph are the SA loadings of lignin phenols (ΣLig), fatty acids (ΣFA) and dicarboxylic acids (ΣDA). The error bars represent the variability of these ratios as determined from the standard deviations of the CuO yields and SA values using propagation of error (Taylor, 1997). The sample codes are according to Fig. 1.

<table>
<thead>
<tr>
<th>CuO oxidation products</th>
<th>PT</th>
<th>E-Je</th>
<th>E-Jy</th>
<th>5 m</th>
<th>25 m</th>
<th>30 m</th>
<th>61 m</th>
<th>210 m*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillin</td>
<td>−29.4</td>
<td>−27.9</td>
<td>−27.6</td>
<td>−28.2</td>
<td>−30.4±1.0</td>
<td>−28.3</td>
<td>−32.0±0.5</td>
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</tr>
<tr>
<td>Vanillic acid</td>
<td>n.m.</td>
<td>−31.8</td>
<td>−30.5</td>
<td>−30.7</td>
<td>−30.2±0.2</td>
<td>−29.9</td>
<td>−31.6</td>
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</tr>
<tr>
<td>Syringaldehyde</td>
<td>−29.7</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>Syringic acid</td>
<td>−30.1</td>
<td>−31.8</td>
<td>−27.9</td>
<td>−26.5</td>
<td>−31.0±0.1</td>
<td>−31.6</td>
<td>−28.0</td>
<td>−27.8±1.7</td>
</tr>
<tr>
<td>p-Coumaric acid</td>
<td>−31.3</td>
<td>−29.1</td>
<td>−27.6</td>
<td>−30.0</td>
<td>−28.5</td>
<td>−27.4</td>
<td>−25.4</td>
<td></td>
</tr>
<tr>
<td>Average lignin phenols</td>
<td>−30.1±0.9</td>
<td>−30.1±2.0</td>
<td>−28.4±1.4</td>
<td>−28.5±2.1</td>
<td>−30.4±0.4</td>
<td>−29.6±1.6</td>
<td>−27.7±0.4</td>
<td>−29.2±3.2</td>
</tr>
<tr>
<td>Tetradecanoic acid</td>
<td>n.m.</td>
<td>−39.5</td>
<td>−36.5</td>
<td>−25.4</td>
<td>−28.0±1.1</td>
<td>−28.8</td>
<td>−28.4</td>
<td>−23.6±0.3</td>
</tr>
<tr>
<td>Hexadecenoic acid</td>
<td>n.m.</td>
<td>−39.4</td>
<td>−35.8</td>
<td>−25.9</td>
<td>−27.0±1.5</td>
<td>−28.0</td>
<td>−26.0</td>
<td>−26.9±2.0</td>
</tr>
<tr>
<td>Hexadecanoic acid</td>
<td>n.m.</td>
<td>n.m.</td>
<td>−35.7</td>
<td>−24.7</td>
<td>−26.9±0.1</td>
<td>n.m.</td>
<td>−27.4</td>
<td>n.m.</td>
</tr>
<tr>
<td>Average fatty acids</td>
<td>−39.5±0.1</td>
<td>−36.0±0.4</td>
<td>−25.3±0.6</td>
<td>−27.3±1.9</td>
<td>−28.4±0.6</td>
<td>−27.3±1.2</td>
<td>−25.2±2.3</td>
<td></td>
</tr>
<tr>
<td>Octane-1,8-dioic acid</td>
<td>−28.2</td>
<td>−28.3</td>
<td>−28.7</td>
<td>−26.5</td>
<td>−26.6</td>
<td>−24.8</td>
<td>−27.8</td>
<td>−28.0±0.7</td>
</tr>
<tr>
<td>Nonane-1,9-dioic acid</td>
<td>−29.2</td>
<td>−27.2</td>
<td>−28.8</td>
<td>−27.1</td>
<td>−27.4±1.0</td>
<td>−27.7</td>
<td>−28.9</td>
<td>−28.3±2.0</td>
</tr>
<tr>
<td>Average dicarboxylic acids</td>
<td>−28.7±0.7</td>
<td>−27.8±0.8</td>
<td>−28.7±0.1</td>
<td>−26.8±0.4</td>
<td>−27.0±0.6</td>
<td>−26.3±2.0</td>
<td>−28.4±0.8</td>
<td>−28.1±2.1</td>
</tr>
</tbody>
</table>

Sample codes are according to Table 1. The standard deviations of the δ¹³C from individual compounds are representative of replicate analyses of same sample.

The average compositions for different classes of CuO reaction products are given. In cases where n.m. (not measured) is written, we were unable to accurately measure the isotopic composition of a given compound due to poor separation and/or small signal.
sediments and shelf surface sediments) were characterized by uniformly depleted isotopic signatures that ranged from $-25\%$ to $-32\%$. In contrast, the $\delta^{13}C$ compositions of the C$_{14}$ and C$_{16}$ fatty acids changed significantly between the river samples ($-36\%$ to $-40\%$) and the shelf sediments ($-25\%$ to $-29\%$). The dicarboxylic acids, on the other hand, showed relatively invariable $\delta^{13}C$ values among all samples, most of them falling within the $-27\%$ to $-29\%$ range (Table 3).

4. Discussion

The radiocarbon and stable carbon isotopic compositions presented above indicate that different carbon sources contribute to the organic matter in the river and shelf samples. Additionally, the SA-normalized loadings of OC, TN and CuO reaction products suggest that a significant fraction of the organic matter exported by the Mackenzie River is lost during its introduction into the shelf environment and replaced by autochthonous marine-derived organic matter. However, based on the SA-normalized OC loadings, the extent of diagenetic losses of organic matter in the Mackenzie shelf appear to be smaller than those measured in other river-dominated margins (Gordon and Goñi, 2003; Hedges and Keil, 1995; Keil et al., 1997; Mayer, 1999). In the following sections, we investigate the sources and sinks of the various OC pools exported by the Mackenzie River and deposited in Beaufort Shelf sediments. With that goal in mind, we use the $\Delta^{14}C_{OC}$, $\delta^{13}C_{OC}$ and compound-based $\delta^{13}C$ compositions to elucidate the provenance of the OC in the analyzed samples. Furthermore, we use the SA-normalized loadings to provide additional insights into the fate of organic matter in the study area. These new findings are contrasted to previously published results and used to reassess the importance of ancient organic matter in sediments from this region of the Arctic Ocean.

4.1. Importance of ancient and modern organic carbon

One of the most striking features of this data set is the highly depleted $\Delta^{14}C_{OC}$ values measured in both the river suspended sediments and shelf surface sediments. Even after accounting for a reservoir age of 500 years for marine carbon (Dumond and Griffin, 2002; Macdonald and Carmack, 1993), these measurements clearly indicate that the majority of the carbon in the river and shelf is much older than would be expected if it had been derived from recently synthesized sources (e.g., phytoplankton, vascular plants). Mixing of relict carbon by bioturbation and/or lateral inputs can result in older than expected ages for the bulk carbon in surface shelf sediments. However, the elevated deposition rates and high delivery of terrigenous materials in our study site (Macdonald et al., 1998) argues against this possibility and, most importantly, fails to explain the depleted $\Delta^{14}C_{OC}$ of river sediments. Instead, with the exception of the peat sample, the old ages of the organic matter (>7000 years) suggest significant contributions of ancient (14C depleted or dead) OC in both river and shelf sediments. Elevated contributions of ancient carbon sources to river suspended sediments and surface shelf sediments have been observed in other river-dominated margins (Kao and Lui, 1996; Blair et al., 2003; Gordon and Goñi, 2003; Masiello and Druffel, 2001; Guo et al., 2004).

In this study, the old ages could indicate the presence of fossil organic matter, such as bitumens or kerogens found in sedimentary rocks that have been thermally matured, or the entrainment of terrigenous organic matter pre-aged as a result of long residence times within the drainage basin. The observed delivery of large quantities of compositionally uniform, natural petrogenic hydrocarbons to the shelf each spring and summer (Yunker et al., 1991a,b, 1993, 2002) is consistent with significant fossil OC contributions from the Mackenzie River. An example of pre-aged matter would be contributions from the most recalcitrant fractions of soil organic matter and/or paleosols that exhibit turnover times of thousands of years (Torn et al., 1997; Trumbore, 1993). Additionally, the slow cycling of organic carbon and particle release from permafrost in the drainage basin is likely to result in longer residence times (e.g., Benner et al., 2004; Guo et al., 2004). In contrast to kerogen, these types of materials contain chemically recognizable biochemicals, such as for example lignin, albeit in a more extensively degraded and altered state. Quantitatively discriminating between the incorporation of fossil OC and the entrainment of
terrigenous organic matter from old soils or paleosols is difficult and beyond the scope of this work. For the purpose of the following discussion, we assume that all of the ancient OC is fossil in origin (i.e., $^{14}$C dead) although later on we examine compositional trends to assess the potential sources of ancient OC and highlight the need for further work to determine $^{14}$C-compositions of source specific compounds (Eglinton et al., 1997; Pearson et al., 2001; Drenzek et al., in preparation).

One way to illustrate the importance of ancient OC and constrain its composition is by plotting the bulk $\delta^{13}$COC vs. $\Delta^{14}$COC values for the samples analyzed (Fig. 4). In this graph, we have included compositional ranges of various potential sources of “modern” organic matter ($\Delta^{14}$C$_{MOD}$=0±50‰) derived from the literature, including fresh water and estuarine phytoplankton, C$_3$ terrestrial vascular plants, C$_4$ terrestrial vascular plants, heterotrophic bacteria and marine algae (e.g., Fry and Sherr, 1984; Fogel et al., 1992; Goñi and Hedges, 1995; Goñi and Thomas, 2000, Hedges et al., 1986, 1988a). Also included is the compositional range of ancient organic matter ($\Delta^{14}$C$_{ANC}$=−1000‰) as illustrated by the signatures of kerogens from different sedimentary rocks analyzed in other studies (Blair et al., 2003; Lewan, 1986).

Most samples in Fig. 4 plot away from the modern OC end members, highlighting the predominance of ancient carbon in all samples except the peat. Using isotopic mass balance, it is possible to quantitatively constrain ancient and modern carbon contributions in these samples (e.g., Blair et al., 2003). Assuming simple two end member mixing, the fraction of modern OC ($f_{MOD}$) and ancient OC in each sample ($f_{ANC}$=1−$f_{MOD}$) can be estimated from the $\Delta^{14}$C$_{OC}$ values presented in Table 1 using the following equations:

$$\Delta^{14}C_{OC} = [f_{MOD} \times \Delta^{14}C_{MOD}] + [f_{ANC} \times \Delta^{14}C_{ANC}]$$

(1)

$$1 = f_{MOD} + f_{ANC}$$

(2)

where $\Delta^{14}$C$_{MOD}$ and $\Delta^{14}$C$_{ANC}$ represent the $^{14}$C signature of the modern and ancient end members, respectively. As discussed above and illustrated by previous studies (e.g., Eglinton et al., 1997; Pearson et al., 2001; Blair et al., 2003), the values of modern and ancient end members can vary depending on the presence of pre- and post-bomb carbon and the contributions from fossil and pre-aged sources of organic matter. In the absence of direct measurements of $\Delta^{14}$C biomarker compositions, which can be used to constrain end member values, we assumed $\Delta^{14}$C$_{MOD}$= 0±50‰ and $\Delta^{14}$C$_{ANC}$=−1000‰ for the purpose of isotopic mass balance calculations.

The results of these isotopic mass balance calculations quantitatively demonstrate the importance of ancient organic matter, which contributes to the majority of the OC in all samples (Table 4). The major exception is the peat sample, which is characterized by predominant contributions from modern sources of organic matter (~90% of the total OC). Both the river suspended sediment samples and most all surface sediment samples contain comparable amounts of OC$_{ANC}$ (~60% to ~70% of OC). The major exception to this trend is the most offshore of the shelf sediments, the 210 m* sample, in which OC$_{ANC}$ accounts for almost 90% of the total OC (Table 4). It is important to note that these isotopic mass balance calculations are sensitive to the chosen isotopic end member values. For example, in the case of the peat, small changes in the $\Delta^{14}$C$_{MOD}$ that may reflect variable amounts of pre- and post-bomb carbon could have an impact on the estimates of $f_{MOD}$ for this sample. Nevertheless, although there is inherent variability in these estimates, the ancient and modern source apportionments presented here are robust and contribute to new insights into composition of the organic matter in the Mackenzie River Shelf (e.g., Goñi et al., 2000).

4.2. Constraints on the provenance of modern and ancient organic matter

We can use the chemical and stable carbon isotopic compositions of individual biomarkers (i.e., specific CuO products) to further elucidate the sources of the modern and ancient OC pools in the sedimentary samples from the Mackenzie River/Shelf region. For example, lignin phenols are good tracers of terrigenous vascular plant-derived organic matter since these compounds are uniquely synthesized by higher plants (e.g., Hedges and Mann, 1979; Sarkanen, 1971; Sarkanen and Ludwig, 1971).
The isotopic compositions of the lignin phenols ($\delta^{13}C$ of $-27\%$ to $-32\%$) from all the samples (Table 3) fall within the ranges typical of $C_3$ vascular plants (Goñi and Eglinton, 1996). These $\delta^{13}C$ compositions, along with the distribution of lignin phenols in the samples analyzed (Fig. 3), are consistent with important contributions from $C_3$ terrestrial plant sources to the organic matter in the Mackenzie Delta/Shelf region. If we assume that most lignin is associated with relatively modern sources (i.e., $\Delta^{14}C > -50\%$), it appears that a very significant fraction of OC_MOD exported by the Mackenzie River and a smaller but still substantial portion of the OC_MOD in the Beaufort Shelf sediments is derived from terrestrial $C_3$ plant sources. The significance of $C_3$ vascular plant carbon in this region of the Arctic is consistent with the vegetation of the tundra and conifer forests of the Mackenzie drainage basin (Brunskill, 1986; Zoltai and Petta-piece, 1973). Our results show no evidence for input of $C_4$ plants, which are absent from the high latitude grasslands (Teeri and Stowe, 1976).

$C_{14}$ to $C_{18}$ fatty acids are fairly ubiquitous and present in many sources of organic matter, including vascular plants, algae, and bacteria (Goñi and Hedges, 1995; Kattner et al., 1983; Zegouagh et al., 1996).
Typically, fatty acids are depleted in $^{13}$C by 5–10 $\%$. The variabilities in the estimates reflect errors in the fraction of modern organic carbon; n.a., not applicable; n.m., not enriched values ($\delta^{13}$C) in the shelf sediments, which display much more depleted values. The large changes that occur in the profiles for the algal sterols between the river delta and shelf sediments also are consistent with a substantial shift in algal source ($Yunker$ et al., 1995). Overall, these compositions suggest that the fatty acids (and by inference the associated organic matter) from freshwater algae/vascular plants are efficiently removed prior to deposition in surface shelf sediments and are replaced by contributions derived from marine algae.

A fundamental assumption in our quantitative interpretation of the isotopic data (Table 4) is that $\delta^{14}$C values reflect the dilution of modern organic matter sources with fossil ($^{14}$C-dead) organic matter. There are several lines of evidence to indicate the importance of kerogen as a major source of OC$_{ANC}$ in the Mackenzie River/Shelf region. For example, the compositional trends illustrated in Fig. 4 suggest that the $\delta^{13}$C signature of the OC$_{ANC}$ end member ranges from $-25\%$ to $-27\%$, which overlaps with the $\delta^{13}$C compositions of kerogens from different source rocks ($-24\%$ to $-30\%$; Lewan, 1986; Blair et al., 2003). Furthermore, the Mackenzie River differs from other Canadian Arctic rivers in having a well-defined signature of petrogenic hydrocarbons (alkyl PAHs, petroleum-derived alkanes, hopanes and steranes). The higher chain-length alkanes and petroleum PAHs are significantly correlated with suspended particle load, indicating that the Mackenzie River is homogeneous in alkane and PAH content during periods of high flow in spring and summer ($Yunker$ et al., 2002). $Yunker$ et al. (2002) have shown that immature bitumens, shales or coals from the Devonian Canol formation that outcrop into the lower Mackenzie River valley are the likely source of freshwater algal organic matter is entrainment from the myriad of shallow lakes and wetlands present in the Mackenzie River delta ($Burn$, 1995). The observation that the algal-related $n$-C$_{17}$ alkane becomes a prominent peak in many Mackenzie River suspended sediment samples in July ($Yunker$ et al., 2002) provides further evidence for the importance of freshwater algae. In contrast, the relatively $^{13}$C-enriched values of the fatty acids from shelf sediment samples suggest significant contributions from marine phytoplankton and/or bacteria (e.g. Fig. 4). In fact, the $\delta^{13}$C signatures of the fatty acids are consistent with the stable isotopic compositions of marine algal carbon ($\delta^{13}$C of $-19\%$ to $-24\%$) as determined from previous studies ($Goñi$ et al., 2000).

Table 4

<table>
<thead>
<tr>
<th>Sample description and water depth</th>
<th>Code</th>
<th>$f_{ANC}$</th>
<th>$f_{MOD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coastal Peat (T4)</td>
<td>PT</td>
<td>0.12±0.04</td>
<td>0.88±0.04</td>
</tr>
<tr>
<td>Mackenzie River suspended sediments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>East Channel (June-87; 1 m)</td>
<td>E-Je</td>
<td>0.59±0.02</td>
<td>0.41±0.02</td>
</tr>
<tr>
<td>Middle Channel (June-87; 1 m)</td>
<td>M-Je</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>East Channel (July-87; 1 m)</td>
<td>E-Jy</td>
<td>0.68±0.02</td>
<td>0.32±0.02</td>
</tr>
<tr>
<td>Reindeer Channel (July-87; 1 m)</td>
<td>R-Jy</td>
<td>0.71±0.01</td>
<td>0.29±0.01</td>
</tr>
<tr>
<td>Beaufort Shelf surface sediments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Station G1 (0–2 cm; 5 m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Station G7 (0–2 cm; 25 m)</td>
<td>25 m</td>
<td>0.69±0.02</td>
<td>0.31±0.02</td>
</tr>
<tr>
<td>Station GRM1 (0–10 cm; 30 m)</td>
<td>30 m</td>
<td>0.72±0.01</td>
<td>0.28±0.01</td>
</tr>
<tr>
<td>Station G12 (0–2 cm; 61 m)</td>
<td>61 m</td>
<td>0.59±0.02</td>
<td>0.41±0.02</td>
</tr>
<tr>
<td>Station G9 (0–2 cm; 210 m)</td>
<td>210 m</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>Station G10 (0–2 cm; 210 m)</td>
<td>210 m*</td>
<td>0.88±0.01</td>
<td>0.12±0.01</td>
</tr>
</tbody>
</table>

**Abbreviations:** $f_{ANC}$, fraction of ancient organic carbon; $f_{MOD}$, fraction of modern organic carbon; n.a., not applicable; n.m., not measured. The variabilities in the estimates reflect errors in the $\Delta^{14}$C measurements and variability in the modern end-member composition ($0±50\%$). Details on the calculations are explained in the text.
source of the refractory, petrogenic material found in the delta and in shelf sediments.

However, previous work has shown that sedimentary organic matter is composed of organic matter pools of heterogeneous ages that do not conform necessarily to simple “modern” and “ancient” provenance (e.g., Torn et al., 1997; Trumbore, 1993; Eglinton et al., 1997; Pearson et al., 2001). In the case of OC\textsubscript{ANC}, the relationship between the acid/aldehyde ratio of lignin-derived vanillyl CuO products ([Ad/Al]\textsubscript{V}) and \(\Delta^{14}\text{C}_{OC}\) (Fig. 5) raises the possibility that other sources besides kerogen may contribute to the \(14\text{C}\) depleted compositions. In general, the [Ad/Al] ratios of lignin phenols are robust indicators of the degree of oxidative degradation of the lignin macromolecule by aerobic degraders such as white-rot and soft-rot fungi (Goñi et al., 1993; Hedges et al., 1988b; Nelson et al., 1995). Hence, while [Ad/Al] ratios of less than 0.3 are characteristic of relatively undegraded lignin and are typically found in relatively fresh vascular plant detritus, [Ad/Al] ratios exceeding 0.5 tend to indicate elevated degrees of lignin biodegradation and are typically found in highly altered soils and/or humic/fulvic substances. The fact that the highest [Ad/Al]\textsubscript{V} values are obtained from samples with the most depleted \(\Delta^{14}\text{C}_{OC}\) signatures (Fig. 5) suggests that the old ages observed in these samples may be in part due to the presence of old soil organic matter that contains highly altered lignin remains. Such compositions are likely to be encountered in deep soils and/or paleosols that have undergone a large degree of weathering and degradation. Radiocarbon analyses of lignin phenols and other compounds derived from vascular plant and fossil sources (Eglinton et al., 1997; Pearson et al., 2001; Drenzek et al., in preparation) should provide additional quantitative constraints to differentiate the contributions of fossil bitumen/kerogen and old, nonthermally altered organic matter to the old carbon in the samples from the Mackenzie River/Beaufort Shelf.

4.3. Cycling and fate of organic matter

We investigated the behavior of the modern and ancient OC pools defined based on isotopic mass balance by normalizing their concentrations to the specific surface area of each sediment sample (Fig. 6). This normalization allows us to examine changes in the loadings of different types of organic matter independent of the behavior of the other OC pools (e.g., Blair et al., 2003). In the case of river-suspended sediments, these data illustrate the large variability in the loadings of OC\textsubscript{ANC} and OC\textsubscript{MOD} among these samples and also demonstrate the temporal variability in the composition of organic matter exported by the Mackenzie River. For example, the samples collected in the same site during June (E-Je) and July (E-Jy) exhibit comparable OC\textsubscript{MOD}/SA ratios (~0.3 mg/m\textsuperscript{2}) but statistically distinct OC\textsubscript{ANC}/SA ratios (0.4 and 0.55 mg/m\textsuperscript{2}). Notably, the two samples collected from different delta channels in July (E-Jy and R-Jy) display similar OC\textsubscript{MOD} and OC\textsubscript{ANC} loadings (Fig. 6).

In the Mackenzie River, the peak sediment load occurs in June, coinciding with peak flows in the Liard River (the southernmost of the main tributaries; Carson et al., 1998). The Mackenzie River load remains high from May through August, however, while the majority of the sediment input from the Arctic Red and Peel Rivers (which flow into the Mackenzie River just before the delta) is confined to

![Fig. 5. Plot of the $\Delta^{14}\text{C}_{OC}$ versus the acid/aldehyde ratios of lignin-derived vanillyl phenols ([Ad/Al]\textsubscript{V}) in sediments from the Mackenzie River and Beaufort Shelf. The error bars represent the variability of these ratios as determined from the standard deviations of the CuO yields using propagation of error (Taylor, 1997). The sample codes are according to Fig. 1.](image-url)
May and June. Accordingly, the shift in the proportions of OCMOD and OCANC between June and July is likely related to the decline in sediment input from tributaries such as the Arctic Red and Peel Rivers after the end of June.

Amongst the shelf sediments, high OCANC/SA ratios (0.6 mg/m²) characterize the 25 m sample, whereas lower values (~0.4 mg/m²) are measured in the rest of the samples (Fig. 6). These lower OCANC loadings may be interpreted as a loss of ancient carbon during offshore transport, although the variable values exhibited by the river suspended sediments indicate that heterogeneities in the river sediment load (Yunker et al., 2002) and its cross-shelf dispersal (Yunker et al., 1995) also contribute to the observed trends. In the case of OCMOD/SA ratios, two of the samples (25 and 61 m) display values that are comparable to those of the river samples (~0.3 mg/m²), while the 30 m and especially the 210 m* samples are characterized by significantly lower modern organic matter loadings (OCMOD/SA ratios of 0.15 and 0.05 mg/m², respectively). Combined with the patterns in $\Sigma$Lig/SA and $\Sigma$FA/SA ratios (Fig. 3) and the biomarker $\delta^{13}$C compositions (Table 3), these data are consistent with a significant loss of the modern fraction of terrigenous OM exported by the Mackenzie River and the partial replacement of that material by marine OM. The high losses of both OCMOD and OCANC inferred from the OC/SA ratios at the 210 m* site (Fig. 6) may be due in part to the longer residence time of OC in the surface layers of sediments from this part of the upper slope, which are characterized by relatively low accumulation rates (0.1 cm year$^{-1}$) (Gobeil et al., 1991).

Because of the temporal and spatial heterogeneity, it is difficult to use this small sample set to comprehensively assess the sources and sinks of the different types of organic matter in the Mackenzie River/Beaufort Shelf region. Nevertheless, the average abundances of modern and ancient organic matter (Table 4) and its plausible sources can be combined with the POC budget of Macdonald et al. (1998) to provide a first-order breakdown of the inputs and fates of different OC sources in the Mackenzie River Delta/Beaufort Shelf (Fig. 7). For example, using the average abundance of ancient carbon in river suspended sediment samples ($f_{ANC}$ ~0.66, Table 4) and the annual OC input by the Mackenzie River (2.2×10$^9$ kg year$^{-1}$; Macdonald et al., 1998), we estimate the annual OCANC input into the Beaufort Shelf to be ~1.4×10$^9$ kg year$^{-1}$. In contrast, marine productivity throughout the study area averages 3.1×10$^9$ kg year$^{-1}$ of OCMA (Macdonald et al., 1998).
Therefore, ancient carbon inputs via the Mackenzie River represent approximately 26% of the total OC inputs into this area of the Beaufort Shelf (Fig. 7), a substantial contribution that up to now has only been measured in small mountainous rivers such as the Eel River in California (Blair et al., 2003).

Based on the average abundance of OC\textsubscript{ANC} in surface sediments ($f_{\text{ANC}} = 0.72$, Table 4) and the OC burial rates ($0.71 \times 10^9$ kg year\textsuperscript{-1}; Macdonald et al., 1998), we estimate the total burial of OC\textsubscript{ANC} in the Beaufort Shelf sediments to be $0.51 \times 10^9$ kg year\textsuperscript{-1}. The difference between input and burial equals $0.89 \times 10^9$ kg year\textsuperscript{-1} and represents the net sink of OC\textsubscript{ANC} in this region, which includes burial within the delta and net respiration/leaching losses (Fig. 7). Since we did not characterize the OC abundances for any sediment sample from the delta, it is impossible to distinguish between respiration/leaching losses and delta burial. Nevertheless, the dominance of sand in bed material from the lower Mackenzie River (Carson et al., 1998) suggests that OC burial in the delta is likely to be only a minor process. Because the OC\textsubscript{ANC}/SA ratios from samples deeper than 30 m are $<0.4$ mg/m\textsuperscript{2} (Fig. 6), it is feasible that as much as 25% of the OC\textsubscript{ANC} ($0.35 \times 10^9$ kg year\textsuperscript{-1}) may be lost annually from the sediment particles prior to deposition in the outer shelf. Because of the large magnitude of OC\textsubscript{ANC} export by the Mackenzie River, this degree of remineralization has the potential to affect the $^{14}$C composition of aquatic food webs in the area (Schell, 1983; Parsons et al., 1989). Information on the composition of deltaic sediments should provide a better accounting of this potentially unrealized carbon sink (e.g., Dittmar and Kattner, 2003).

In terms of the sources and fate of modern organic matter, the average $f_{\text{MOD}}$ value of suspended...
river sediments (0.3; Table 4) indicates that ~0.7 × 10⁹ kg year⁻¹ of OC_MOD is exported to the Beaufort Shelf by the Mackenzie River, representing about 15% of the combined marine and terrigenous OC input to the region (Fig. 7). The average f_MOD value of shelf sediments (0.3; Table 4) indicates that 0.20 × 10⁹ kg year⁻¹ of modern organic carbon is buried in this region of the Arctic shelf, an estimate that represents ~4% of the total OC inputs (both terrigenous and marine) to the Beaufort shelf. Such large losses of modern organic matter prior to burial in the shelf is most likely fueled by the efficient mineralization of the organic matter derived from marine productivity and the mineralization and/or leaching of vascular plant-derived materials introduced by the Mackenzie River. Both of these organic matter sources contribute significantly to the OC_MOD preserved in shelf sediments, which accounts for approximately 30% of the total carbon burial in this region of the Arctic (Fig. 7).

5. Summary and implications

Our investigations clearly show that the particle-bound organic matter exported to the Arctic Ocean by the Mackenzie River is composed mainly of old and highly altered organic carbon. These results are consistent with the findings from the Siberian Arctic, where old ages for sedimentary OC have been measured in the eastern region of the Siberian continental shelf off the Khatanga, Lena and Indigirka rivers (Guo et al., 2004). However, they are in stark contrast to the finding of relatively young dissolved organic carbon (DOC) in several Eurasian and North American Rivers (Benner et al., 2004). The source of the ancient terrigenous particulate organic carbon is likely to be a combination of fossil carbon (i.e., bitumen and/or kerogen) eroded from sedimentary rocks in the drainage basin and highly degraded soil carbon with long residence times bound in permafrost. This finding is important because the composition of this material, with the lack of abundant and readily recognizable biochemicals, hinders its quantification in sedimentary mixtures. Furthermore, the recalcitrance of this OC pool likely minimizes post-depositional mineralization and facilitates its ubiquitous distribution. Hence, Arctic Ocean shelves that border the Canadian Basin in western North America and eastern Siberia may be significant repositories of highly degraded ancient carbon weathered from the surrounding continents.

Although the ancient OC appears to undergo some post-depositional decay once it is introduced to the Mackenzie Shelf, the predominance of this recalcitrant OC pool renders the overall sedimentary organic matter in this region unreactive to further metabolic losses. These characteristics may help explain the high OC loadings measured in the Beaufort Sea sediments relative to samples from other deltaic/shelf environments (Keil et al., 1997). In contrast to ancient OC, the organic matter contributions from modern sources (both terrigenous and marine) undergo extensive losses upon their entrainment into the Mackenzie Shelf. The efficient removal of these younger OC pools contributes significantly to the overall heterotrophic metabolism of this region of the Beaufort Sea, especially in the inner portions of the shelf where land-fast ice and turbidity minimize algal production (Macdonald et al., 1998). Although the vast majority of the carbon regeneration is sustained by marine organic carbon, the river-delivered carbon pools (both ancient and modern) together account for ~20% of the total carbon respired in the Mackenzie Delta/Shelf.

Climate change leading to a more productive shelf environment (Carmack and Chapman, 2003) has little leverage to alter the burial flux of carbon by itself because such a large percent of the marine primary production is recycled. However, the enhanced release of carbon from terrestrial soils due to permafrost degradation has a great potential to alter the input of ancient organic carbon and inorganic particulate matter (e.g., mineral surfaces). Furthermore, change from tundra toward leaf-bearing plants (e.g., willows) can occur rapidly under warming (Hinzman et al., 2004) and this would potentially enhance the delivery of modern vascular plant organic carbon to arctic rivers. It is these components of the allochthonous input that are most likely to alter the burial flux of organic carbon on arctic shelves as we move toward a warmer, ice-depleted Arctic. The challenge in front of us will be to determine with sufficient precision the modern supply, metabolism
and burial of organic carbon on each shelf and thereby put ourselves in the position to detect change as it occurs.

**Acknowledgements**

This paper benefited from comments by two anonymous reviewers. R. Potter and R. Gisewhite provided assistance with the surface area analyses. This research was funded by NSF Grants OCE-93008900 and OCE-9708478 to TIE and by NSF Grants OCE-9711822 and OCE-0223119 to MAG. Samples were originally collected under the NOGAP B.6 project with the support of the Canadian Departments of Fisheries and Oceans and Indian and Northern Affairs, and the assistance of the officers and crew of the CSS John P. Tully.

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