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Prominent bacterial heterotrophy and sources of ^{13}C-depleted fatty acids to the interior Canada Basin

S. R. Shah[1], D. R. Griffith[2], V. Galy[3], A. P. McNichol[1], and T. I. Eglinton[4]

[1]Geology and Geophysics Department, Woods Hole Oceanographic Institution,
266 Woods Hole Road, Woods Hole MA 02543, USA
[2]MIT/WHOI Joint Program in Oceanography, 266 Woods Hole Rd., Woods Hole, MA 02543,
USA
[3]Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic Institution,
266 Woods Hole Road, Woods Hole MA 02543, USA
[4]Swiss Federal Institute of Technology, Zurich, Switzerland

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Correspondence to: S. R. Shah (sshah@whoi.edu)

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Abstract

In recent decades, the Canada Basin of the Arctic Ocean has experienced rapidly decreasing summer sea ice coverage and freshening of surface waters. It is unclear how these changes translate to depth, particularly as our baseline understanding of organic carbon cycling in the deep basin is limited. In this study, we describe full-depth profiles of the abundance, distribution and carbon isotopic composition of fatty acids from suspended particulate matter at a seasonally ice-free station and a semi-permanently ice-covered station. Fatty acids, along with suspended particulate organic carbon (POC), are more concentrated under ice cover than in ice-free waters. But this influence, apparent at 50 m depth, does not propagate downward below 150 m depth, likely due to the weak biological pump in the central Canada Basin. Branched fatty acids have $\delta^{13}C$ values that are similar to suspended POC at all depths and are ^{13}C-enriched compared to even-numbered saturated fatty acids at depths above 3000 m. These are likely to be produced in situ by heterotrophic bacteria incorporating organic carbon that is isotopically similar to total suspended POC. A source of saturated even-numbered fatty acids is also suggested below surface waters which could represent contributions from laterally advected organic carbon or from chemoautotrophic bacteria. At 3000 m depth and below, a greater relative abundance of long-chain (C_{20-24}), branched and unsaturated fatty acids is consistent with a stronger influence of re-suspended sedimentary organic carbon on benthic particulate matter. At these deep depths, two individual fatty acids (C_{12} and iso-C_{17}) are significantly depleted in ^{13}C, allowing for the possibility that methane oxidizing bacteria contribute fatty acids, either directly to suspended particulate matter or to shallow sediments that are subsequently mobilized and incorporated into suspended particulate matter within the deep basin.

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1 Introduction

In the past two decades, the Arctic Ocean's Canada Basin has seen both rapidly decreasing summer sea ice coverage (Maslanik et al., 2011; McLaughlin et al., 2011; Stroeve et al., 2007) and freshening of surface waters (Macdonald et al., 2002; McPhee et al., 2009; Yamamoto-Kawai et al., 2009). These changes have been accompanied by a deepening of the chlorophyll maximum depth (Jackson et al., 2010; McLaughlin and Carmack, 2010), and a trend towards smaller phytoplankton cell sizes and increased bacterial abundance in surface waters (Li et al., 2009). Combined with the observed decrease in primary productivity in the increasingly ice-free Canada Basin (Cai et al., 2010; Grebmeier et al., 2010; Lee et al., 2012), these trends will likely result in decreasing export of organic carbon to the deep basin and sediments.

Across ocean basins, sinking particulate organic carbon (POC) flux has been shown to correlate with bacterial abundance and productivity at deeper depths (Nagata et al., 2010; Yokokawa et al., 2013). Prior to the recent decline in summer sea ice, ice-tethered sediment traps in the Canada Basin documented a much smaller POC flux through the upper 200 m than is observed in other oligotrophic regions (Honjo et al., 2010). Despite a vanishingly small, and likely decreasing supply of autochthonous organic carbon exported from the sea surface, prokaryotic abundance at mesopelagic and bathypelagic depths in the Canada Basin (> 100 m) were found to be comparable to subtropical and equatorial regions (He et al., 2012; Uchimiya et al., 2013). Heterotrophic production and prokaryotic turnover time was also similar to other ocean regions between 100 and 1000 m, although not at bathypelagic depths (Uchimiya et al., 2013). Heterotrophic bacterial productivity at mesopelagic depths could be supported by labile organic carbon produced by phytoplankton in the productive Chukchi Sea and laterally supplied as dissolved organic carbon (DOC) at mesopelagic depths (Davis and Benner, 2007; Mathis et al., 2007; Shen et al., 2012; Walsh et al., 1989). Long-distance transport of re-suspended sedimentary particles has also been observed below 100 m depth (Honjo et al., 2010; Hwang et al., 2008; Jackson et al., 2010; O'Brien et al., 2013), delivering associated organic carbon to the interior Canada Basin. In addition to bacterial heterotrophy, significant chemoautotrophy at bathypelagic depths of the deep basin is suggested by the radiocarbon and stable isotopic composition of dissolved inorganic carbon (DIC), sinking POC, and suspended POC (Griffith et al., 2012). The dynamics between prokaryotic production and organic carbon cycling appears to be distinct from other oligotrophic ocean basins and the questions of what carbon and energy sources support bacterial production in the dark Canada Basin and how they are changing with time will be highly relevant to predicting the future of organic carbon sequestration and cycling in this deep Arctic Basin.

Isotopic studies of bulk organic carbon pools have addressed the supply and fate of vertically- and laterally-delivered organic carbon to the interior Canada Basin (Griffith et al., 2012; Honjo et al., 2010; Hwang et al., 2008). But our understanding of the provenance and cycling of organic matter is much more detailed in the Mackenzie River and Beaufort shelf and slope because DOC and POC analysis has been complemented by isotopic studies of fatty acids and other biomarkers (Drenzek et al., 2007; Goñi et al., 2005; Tolosa et al., 2013). To advance our understanding of organic carbon cycling in Canada Basin, we investigated the distribution and isotopic composition of fatty acids from suspended POC collected at two deep-basin stations in 2008, a summer with record-low sea ice coverage (Maslanik et al., 2011). Here we present the results and discuss the multiple organic carbon sources and bacterial metabolic strategies that could contribute to the observed profiles.

2 Material and methods

2.1 Sampling

Suspended particulate matter was collected during the Joint Ocean Ice Study (JOIS) in 2008 from two stations in the Canada Basin of the Arctic Ocean: CB4 (seasonally ice-free; 74°59.9980′ N; 150°0.0020′ W; 3825 m bottom depth) and CB9 (semi-permanently ice-covered; 77°59.8590′ N; 150°4.8870′ W; 3821 m bottom depth). At both stations, McLane WTS-LV pumps filtered particulate material onto pre-combusted 142 mm glass fiber filters (Whatman GF/F; 0.7 µm) in situ after being lowered to specific depths. A more detailed description of sample collection is provided by Griffith et al. (2012). Filters were packaged into envelopes of pre-combusted aluminium foil, frozen at −20 °C, and were subsequently partitioned for radiocarbon analysis (Griffith et al., 2012) and for lipid analysis. Filter fractions destined for lipid extraction were maintained at −20 °C for 3 yr until processing.

2.2 Lipid extraction, identification and quantification

Total lipids were extracted from frozen filters in 50 mL of methylene chloride/methanol (9 : 1), assisted by the Microwave Accelerated Reaction System (MARS Xpress, CEM Corp) at 100 °C for 20 min. The filter extraction procedure was repeated with fresh solvents and both extracts were combined, passed through a 0.45 µm PTFE filter and evaporated to dryness under a stream of ultra-high purity N_2. Combined extracts were saponified in 1 mL of 0.2 M KOH in methanol/water (4 : 1) at 80 °C for 2 h. Neutral lipids were recovered by three extractions with hexane after addition of 10 % NaCl. The pH of the remaining aqueous layer was lowered to ∼ 1 by dropwise addition of 6N HCl, and the acid fraction was recovered by three additional extractions with hexane/methylene chloride (4 : 1). The distribution of total lipids in 10 % subsamples of neutral and acid fractions were determined by GC-TOF as trimethylsilyl ether derivatives. The remaining 90 % of acid fractions were trans-esterified to convert fatty acids into their methyl esters by refluxing in 5 % HCl in MeOH (with known δ^{13}C value) at 70 °C for 12 h. After adding MilliQ water to cooled vials, fatty acid methyl esters (FAMEs) were recovered by extracting three times with hexane/methylene chloride (9 : 1). Extracts were dried with sodium sulfate and concentrated under a stream of ultra-high purity N_2. FAMEs from trans-esterified acid fractions were identified by comparison of retention times with a 37-component FAME mixture (Supelco part number 47885-U) and bacterial FAMEs mixture (Matreya part number 1114), and for a few representative samples, by GC-MS.

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Quantification of FAMEs was performed by GC-FID with an external calibration curve and assigned a conservative 5 % uncertainty. The contribution of fatty acids from the sorption of organic carbon to the GF/F filter was subsequently corrected for by subtraction of surface-area-normalized abundances recovered from a 142 mm GF/F filter lowered to 3805 m water depth but not pumped through (Table 1).

2.3 Isotopic analysis of FAMEs

Compound-specific δ^{13}C analysis of FAMEs was performed at the Organic Mass Spectrometry Facility at the Woods Hole Oceanographic Institution (WHOI). GC-IRMS measurements were made in triplicate and uncertainty is reported as the larger of the standard deviation of three measurements or analytical uncertainty (0.3 ‰). Measured δ^{13}C values of FAMEs are expressed relative to the PDB standard and corrected for addition of the methyl carbon during trans-esterification using a mass balance calculation (Supplement Table 1). Values reported in Table 2 are also corrected by isotopic mass balance for fatty acids contributed by organic carbon adsorption. The adsorption blank was defined by the abundance and isotopic composition of fatty acids from the blank filter (Tables 1 and 2).

3 Results

3.1 Bulk analysis of suspended POC

The concentration and isotopic composition of suspended POC was described by Griffith et al. (2012) and exhibits similar profiles at both stations. At near-surface depths, the semi-permanently ice-covered station (CB9) has a higher concentration of suspended POC than the seasonally ice-free station (CB4). Despite similar radiocarbon ages, CB9 is also more ^{13}C-enriched at 9 and 50 m depth. But at deeper depths, suspended POC concentrations converge on similar, very low values (≤ 0.04 µM) with δ^{13}C values of −25 to −23 ‰ (Griffith et al., 2012).

The sorption of dissolved organic carbon onto glass fiber filters during their time immersed in seawater was also investigated. A 142 mm GF/F filter lowered to 3805 m water depth, but not pumped through, yielded 3.1 µmol of organic carbon from half of the filter area with a δ^{13}C value of −25.1 ‰ (Griffith et al., 2012). The distribution of fatty acids recovered from the other half of the blank filter and their δ^{13}C values are described in Tables 1 and 2 and discussed below.

3.2 Concentration of fatty acids

Analysis of fatty acids was performed on separate fractions of the same filters used for suspended POC measurements. At 50 and 150 m, the seawater-normalized concentration of total fatty acids is greater at ice-covered station CB9 than at seasonally ice-free station CB4 (Table 1, Fig. 1b). The difference between the two Canada Basin stations is small, however, compared to the difference between the cryopelagic Canada Basin (Honjo et al., 2010) and the much higher concentrations of fatty acids observed in low-latitude epipelagic regions, (e.g. Hamanaka et al., 2002; Tolosa et al., 2004; Wakeham, 1995; Wakeham et al., 2010). As with POC, fatty acid concentrations decrease with depth, and below 1500 m, the sill depth of the Canada Basin, fatty acid abundances at CB4 are $< 10\,\mathrm{ng\,L^{-1}}$. Despite these low abundances, the concentration of fatty acids recovered from the blank filter was less than fatty acids from filtered seawater at all depths.

Although both POC and fatty acid concentrations are higher (per liter seawater) in near-surface waters of station CB9 compared to station CB4, fatty acids account for a greater fraction of suspended particulate organic carbon at station CB4 (Figs. 2b and 3b). POC-normalized fatty acids also reveal a subsurface enrichment of saturated, even-numbered fatty acids in suspended POC at 2500 m depth (Fig. 2b). This peak results from disproportionately low suspended POC concentrations combined with fatty acid concentrations on par with the sample from 2000 m (Table 1). Near these depths, the possibility of significant DIC incorporation was suggested by an isotopic mixing model of radiocarbon and δ^{13}C values of bulk carbon pools (Griffith et al., 2012). At mesopelagic depths, between 150 and 1000 m, a more modest enrichment in POC-normalized bacterial branched fatty acids was revealed at station CB4 (Fig. 2b) where Honjo et al. (2010) have proposed intense bacterial heterotrophy contributes to a weak biological pump. These subsurface enrichments are superimposed on a general decreasing trend of POC-normalized fatty acids with depth. This trend, also seen in the oligotrophic central Pacific and Sargasso Sea (Loh et al., 2008; Wakeham, 1995), suggests fatty acids in the Canada Basin behave similarly to low-latitude oligotrophic oceans where they are thought to be among the more labile components of POC. Similar POC-normalized values were observed in the shallow profile from CB9 (Fig. 3b). In the abyssal Canada Basin, however, very low POC-normalized concentrations were found which did not decrease with depth, suggesting a different composition or source of suspended POC in the deepest 1000 m.

3.3 Distribution of fatty acids

At 50 m depth, the most abundant lipids at both stations were saturated C_{14} and C_{16} fatty acids (Fig. 1a). These are also the most abundant fatty acids in epipelagic waters of coastal and open-ocean ocean regions (Gutiérrez et al., 2012; Hamanaka et al., 2002; Loh et al., 2008; Schultz and Quinn, 1972; Tolosa et al., 2004, 2013; Wakeham, 1995; Wakeham et al., 2010; Xu and Jaffé, 2007). However, the next most typically abundant fatty acids in surface waters, monounsaturated (MUFAs) and polyunsaturated fatty acids (PUFAs), are only significant at station CB9 at 50 m depth. Appreciable concentrations of PUFAs were not recovered from either station. This absence of unsaturated fatty acids could result from their degradation during storage or extraction and may not reflect the true distribution of fatty acids in the Canada Basin. We therefore interpret the absence of unsaturated fatty acids with caution, particularly as PUFAs were detected in suspended POC collected from the coastal and more-productive Beaufort Sea (Connelly et al., 2012; Tolosa et al., 2013). Below 50 m, C_{16} and C_{18} fatty acids make up the majority of total fatty acids, as they do in other oligotrophic water columns (Loh et al., 2008; Wakeham, 1995), followed by iso- and anteiso-C_{15} at both stations.

There is a general pattern of decreasing relative C_{14} abundance and increasing C_{18} abundance with depth, and a proportionally important contribution from C_{15} fatty acids in the shallowest 1000 m (Fig. 1a). A similar pattern of relative abundances is observed at station CB9, although with two important exceptions: the C_{18}-dominated sample at 150 m where C_{18} also drives the larger concentration of total fatty acids found at CB9 compared to the same depth at CB4, and more abundant unsaturated fatty acids at 50 m. At station CB4, Fig. 1 illustrates a distinction between the distribution of fatty acids found above 3000 m, and those found at and below this depth. In the deepest 1000 m, saturated C_{16} and C_{18} continue to be the most abundant fatty acids although C_{14} is relatively more abundant than above. We also observe greater proportions of MUFAs and BFAs, as well as long-chain $C_{20–24}$ fatty acids.

3.4 Isotopic composition of fatty acids

At both stations in the Canada Basin, all individual fatty acids from 50 m depth are depleted in ^{13}C compared to the same lipids recovered from deeper depths (Fig. 3c). Saturated C_{14}, C_{15} and C_{16} fatty acids display the largest δ^{13}C deviations (e.g. 6–13 ‰ for C_{16} fatty acid), while others are more modestly depleted. A similar pattern can be observed in suspended POC from near-surface depths compared to below (δ^{13}C deviation of 3–6 ‰; Griffith et al., 2012).

In all samples, odd-numbered and branched fatty acids (orange shades in Figs. 2c and 3c) are generally enriched in ^{13}C compared to even-numbered fatty acids (blue shades in Figs. 2c and 3c). The abundance-weighted average δ^{13}C values of BFAs are within 1 ‰ of POC above 3000 m depth at station CB4 while the SFAs are depleted in ^{13}C by 4.3–5.8 ‰ (Table 2). This pattern is also reflected in an average 5 ‰ enrichment of BFAs compared to SFAs between 50 and 2500 m. δ^{13}C values from station CB9 hint at a similar pattern although sampling limitations resulted in fewer possible comparisons (Table 2).

At 3000 m and below, there is a shift towards ^{13}C-enriched SFAs such that the δ^{13}C values of SFA values more closely match suspended POC than the δ^{13}C values of

BFAs do (Table 2). The exceptions to this patterns are the C_{12} and iso-C_{17} fatty acids. The C_{12} fatty acid is depleted by 7–19 ‰ compared to average SFA values despite being within 1 ‰ higher in the water column. $\delta^{13}C$ values of C_{12} fatty acid that are not corrected for the organic carbon sorption blank are very similar, within analytical uncertainty between 3000 and 3750 m (Supplement Table 1), but isotopic variability emerged from mass-balance corrections (Fig. 2c). While it is possible that this variability is an artifact of our blank determination method, the C_{12} fatty acid is unambiguously ^{13}C-depleted compared to the rest of the water column in the abyssal Canada Basin. Branched iso-C_{17} fatty acid is also very depleted in ^{13}C at the same depths, with $\delta^{13}C$ values are more negative at 3000 and 3500 m than any fatty acid observed higher in the water column (Fig. 2c).

4 Discussion

The concentration and isotopic composition of fatty acids in suspended POC from the Canada Basin reflect vertically stratified organic carbon sources at surface depths, in the interior basin, and in the deepest 1000 m. In the following sections, we discuss the possible origin of fatty acids found on the blank filter as well as the phytoplanktonic, microbial, and advected sources of fatty acids to the Canada Basin.

4.1 Source of the DOC sorption blank

The sorption of DOC onto glass fiber filters is a widely-recognized contributor of non-particulate organic carbon to suspended POC samples collected by in situ pumps (Gardner et al., 2003; Moran et al., 1999; Schultz and Quinn, 1973). A likely depth at which the filters accumulate this organic carbon is near the surface as pumps are lowered into the water, where the highest concentrations of DOC, suspended POC and bacterial abundance are found, although the sampling depth at which the filter has the longest soaking time is also a possible contributor to the sorption blank. At station CB4, the radiocarbon content of adsorbed organic carbon measured on a filter that traveled the length of the water column and was held at 3805 m depth while POC from other depths were sampled (−247 ± 9 ‰) is very similar to DOC at 20 m water depth (−234 ± 5 ‰; Griffith et al., 2012) while the δ^{13}C value of adsorbed organic carbon (−25.1 ± 0.1 ‰, Table 2) is intermediate between the δ^{13}C values of DOC (−22.1 ± 0.1 ‰; Griffith et al., 2012) and suspended POC (−29.5 ± 0.1 ‰, Table 2) at the surface. Interestingly, the Δ^{14}C and δ^{13}C values from the blank filter are also similar to suspended POC at 3000 m and below (Δ^{14}C = −227 ± 40 ‰, δ^{13}C = −24.6 ± 0.1 ‰ at 3750 m; Griffith et al., 2012). Following the dual isotope mass balance approach outlined by Griffith et al. (2012), 27 % of the sorbed organic carbon blank could represent surface DOC (Δ^{14}C = −234 ± 5 ‰, δ^{13}C = −22.1 ± 0.1 ‰ at 20 m), 35 % surface POC (Δ^{14}C = +8 ± 9 ‰, δ^{13}C = −29.5 ± 0.1 ‰ at 50 m), and 38 % deep DOC (Δ^{14}C = −494 ± 2 ‰, δ^{13}C = −23.1 ± 0.1 ‰ at 3807 m), assigning the majority of organic matter sorption to surface waters.

The distribution and isotopic composition of fatty acids found in the adsorption blank do not resemble suspended POC in shallow waters, however. C_{16} and C_{18} fatty acids dominate, as they do in suspended POC from 150 m and below (Fig. 1a). Although fatty acids point toward a deeper source region for adsorbed organic carbon than bulk isotopic considerations do, it is possible that this discrepancy can be explained if adsorbed organic carbon incorporates attached bacterial biomass derived either from surface waters or from 3805 m depth with a fatty acid distribution that echoes that found at bacteria-dominated meso- and bathypelagic depths. The weighted average δ^{13}C value of fatty acids from the adsorption blank is similar to the δ^{13}C value of suspended POC (Table 2), following the pattern observed in bacterial BFAs from suspended POC between 150 and 2500 m, consistent with a heterotrophic bacterial source. The δ^{13}C value of the adsorption blank limits the contribution of surface-ocean bacteria incorporating phytoplankton-derived organic carbon with the Δ^{14}C value of DIC (+31 ± 4 ‰ at 20 m; Griffith et al., 2012), but not bacteria incorporating "aged" DOC which would have the same isotopic composition as the DOC sorption component of the blank. Bacterial cells that attach to the blank filter at bathypelagic depths would also contribute an "aged" Δ^{14}C value to the adsorption blank. Although the depth at which bacteria attach to glass fiber filters is ambiguous, we can assume that their fatty acids are represented in samples collected at all depths and correct for their contributions.

4.2 Semi-permanently ice-covered vs. seasonally ice-free surface waters

Previous work indicates that ice cover affects POC flux, bacterial abundance and bacterial productivity in the western Arctic Ocean, but these studies often investigate the combined influences of ice cover and seasonality (Honjo et al., 2010; Sherr and Sherr, 2003; Sherr et al., 2003) or compare the shallower, nutrient-rich and more ice-free Chukchi Sea with the western Canada Basin (He et al., 2012; Honjo et al., 2010; Moran et al., 2005; Rich et al., 1998). We find supporting evidence that ice cover affects the concentration and composition of epipelagic organic carbon within Canada Basin by comparing stations CB4 and CB9. At the time of our sampling, station CB9, which was ice-covered, hosted a greater concentration of suspended POC at 9 and 50 m depth which was more ^{13}C-enriched compared to ice-free station CB4 (3–6 ‰ ; Griffith et al., 2012). A larger survey of suspended POC from 9 m depth confirms ^{13}C-enrichment under ice cover in the western Canada Basin (Brown et al., 2013). In contrast, the δ^{13}C values of DOC were within 0.5 ‰ between stations at 20–25 m depth (Griffith et al., 2012).

Contrasting conditions between open water and ice cover also manifest themselves in the concentration and distribution of fatty acids. As with suspended POC, the absolute abundance of total fatty acids is greater and individual fatty acids are more ^{13}C-enriched at station CB9 compared to station CB4. However, normalizing fatty acid concentrations to suspended POC reveals the opposite pattern, indicating that the composition of suspended POC is different at the two stations. In addition, MUFAs and PUFAs are only significant contributors to total fatty acids at station CB9 (Figs. 2b and 3b), although this comparison may be affected by post-collection degradation in our samples. And while SFAs have more negative δ^{13}C values than bacterial BFAs at both stations, the isotopic contrast at station CB9 (8.4 ‰) is much greater than at station CB4 (5.3 ‰; Table 2) suggesting different dynamics between bacterial and other components of POC at the two stations.

Strong isotopic similarity is expected between fatty acids produced by bacterial heterotrophs and their organic carbon source (Blair et al., 1985; Hayes, 2001; Monson and Hayes, 1982). At station CB9, the average δ^{13}C value of BFAs falls between suspended POC (−27.0 ‰) and DOC (−21.7 ‰; Griffith et al., 2012) supporting greater bacterial incorporation of DOC under ice cover compared to station CB4 where the average BFA δ^{13}C value is more negative and very similar to suspended POC (Table 2).

Before the recent decline in summer sea ice in the Canada Basin, it was reported that ice algae contribute up to 57 % of total primary productivity, releasing a large fraction (31–65 %) of the resulting organic matter as DOC (Gosselin et al., 1998). This labile organic carbon is likely to be enriched in ^{13}C compared to organic carbon produced by phytoplankton in the water column (Belt et al., 2008; Forest et al., 2007; Budge et al., 2008). The relative ^{13}C-enrichment of BFAs at station CB9 compared to station CB4 (Figs. 2c and 3c) could therefore reflect organic carbon derived from sea-ice algae. It does not appear that SFAs at 50 m have a ^{13}C-enriched, ice-algal source. Instead they are isotopically similar to SFAs in open water and likely are derived from phytoplankton in the water column.

An expedition later in 2008 found that maximum bacterial abundances occurred within 10 m of the sea surface at an ice-covered station near CB9, while in open water near station CB4 bacterial abundances were lower overall (He et al., 2012). Near both stations, comparable bacterial abundances were observed at the chlorophyll maximum (our 50 m sampling depth). However, in open water near station CB4, this depth represents a maximum in both bacterial and phytoplankton abundance (He et al., 2012). The larger isotopic contrast between SFAs and BFAs at station CB9 could thus be a result of a spatial decoupling between primary production and heterotrophic production. The focusing of organic carbon production near the sea surface under greater sea ice coverage (Gosselin et al., 1998) suggests that DOC released from ice algae could fuel bacterial secondary production throughout the upper 50 m under ice cover while phytoplankton production at the chlorophyll maximum depth directly supports bacterial production in open water. It is also possible that the ∼2 ‰ enrichment in both suspended POC and SFAs at station CB9 is a reflection of larger overall contributions from heterotrophic bacteria compared to station CB4.

4.3 Sequestration of ^{13}C-depleted fatty acids in surface waters

A weak coupling between the organic matter in surface waters and below is caused by the ineffective biological pump that operates in the Canada Basin. The flux of organic carbon through the shallowest 200 m is orders of magnitude smaller than that found in other ocean basins, and this small flux is accompanied by similarly miniscule fluxes of diatom frustules and coccoliths (Honjo et al., 2010). The disconnect between surface waters and the basin interior allows for the strong contrasts observed in the δ^{13}C values of suspended POC and fatty acids between 50 m and below (Figs. 2c and 3c). Conditions and productivity at the sea surface do not appear to have a controlling influence on suspended POC and fatty acids at depth in the Canada Basin and the effects of sea ice coverage discussed above are confined to surface waters. Not only are the concentration and isotopic composition of suspended POC very similar below 150 m at stations CB4 and CB9 (Griffith et al., 2012), but a more extensive survey of suspended POC concentrations below 100 m has revealed a general absence of gradients in the interior Canada Basin (Jackson et al., 2010). Bacterial abundances are also similar below 50 m near stations CB4 and CB9 (He et al., 2012; Uchimiya et al., 2013). No significant differences can be observed in fatty acids recovered from both stations at 1000 m, either. Major differences do exist in the abundance and distribution of fatty acids at 150 m depth, but it is more likely that this sample represents an external influence such as POC delivered by a mesoscale eddy because fatty acids are both unlike station CB4 at 150 m (Fig. 1a) and unlike fatty acids above and below at station CB9 (e.g. small relative concentrations of C_{14}, iso-C_{15} and anteiso-C_{15} fatty acids compared to 50 and 1000 m). Such eddies have been documented at approximately 150 m depth at locations more proximal to the Northwind Ridge, and are known to transport nutrient- and organic carbon-rich Pacific-origin seawater to the western Canada Basin (Mathis et al., 2007; Pickart, 2004).

The near-surface ^{13}C depletion in suspended POC and individual fatty acids cannot be explained by phytoplankton incorporating ^{13}C-depleted DIC because DIC is more enriched in ^{13}C at 50 m than it is at 150 m (Griffith et al., 2012). An allochthonous source of ^{13}C-depleted particulate carbon, such as terrestrial material exported by the Mackenzie River, is possible, although neither station is proximal to a source of terrestrial organic carbon and a δ^{13}C transition from "light" terrestrial values to a more ^{13}C-enriched marine primary source has been documented in sedimentary organic carbon much closer to shore at the base of the Beaufort slope (Naidu et al., 2000). However, in some recent years, isotopic and elemental evidence indicates a substantial fraction of riverine fresh water gets stored in the surface layer of the central basin (Guay et al., 2009; Macdonald et al., 2002; Yamamoto-Kawai et al., 2009), and it has been shown that surface-water bacterioplankton can access and re-mineralize the presumably refractory terrestrial DOC delivered with it (Hansell et al., 2004). The summer halocline particle trap (Jackson et al., 2010) may isolate this influence from our 50 m samples, however, as these samples were collected below the halocline in the Pacific Summer Water (PSW) layer (Griffith et al., 2012). Isotopic evidence for proportionally greater terrestrial contributions to DOC in the surface layer in 2008 is also lacking at both stations because the δ^{13}C values of DOC are similar throughout the upper 350 m (Griffith et al., 2012).

An alternative explanation for "light" suspended POC and fatty acids at 50 m depth is a larger effective fractionation factor between DIC and phytoplankton biomass. This depth coincides with the chlorophyll maximum at both stations, which a previous study found to be dominated by diatoms (Gosselin et al., 1998). At this light-limited depth, the most ^{13}C-depleted fatty acids (C_{14}, C_{15} and C_{16}) could be produced by slowly growing marine diatoms expressing their maximum expected fractionation between ^{12}C and ^{13}C (Popp et al., 1998), with an additional isotopic effect on the large end of that observed between algal biomass and fatty acids (Schouten et al., 1998). The "heavier" fatty acids (e.g. iso-C_{15}, anteiso-C_{15} and C_{18}) are likely to have greater contributions from heterotrophic bacteria. Two of these, iso-C_{15}, anteiso-C_{15}, have a known bacterial source (Kaneda, 1991). The isotopic similarity between bacterial fatty acids and suspended POC (at station CB4) or between bacterial fatty acids and a combination of DOC and POC (station CB9) is consistent with bacterial heterotrophs incorporating organic carbon from POC and DOC (Blair et al., 1985; Hayes, 2001; Monson and Hayes, 1982).

4.4 Bacterial heterotrophy in the interior Canada Basin (150–2500 m)

Multiple features in the concentrations and δ^{13}C values of fatty acids indicate that heterotrophic bacteria suspended in the water column are important contributors compared to other sources of fatty acids in the interior Canada Basin. A broad subsurface peak in the POC-normalized abundance of BFAs in the shallowest 1000 m at station CB4 (Fig. 2b) may be produced by a relatively large proportion of productive bacterial heterotrophs synthesizing branched fatty acids at mesopelagic depths (Fig. 1). Arguably, the most consistent pattern in fatty acids above 3000 m depth is the isotopic divergence between BFAs and even-numbered SFAs (∼ 5 ‰, Table 2). Such divergent δ^{13}C values between BFAs and other fatty acids are not reported in suspended POC from surface waters of the Mediterranean (Tolosa et al., 2004) or near-surface, oxic depths of the Black Sea (Wakeham et al., 2007) or Cariaco Basin (Wakeham et al., 2010). Instead, δ^{13}C values of fatty acids and suspended POC in the interior Canada Basin evoke the isotopic relationship observed in sinking particulate matter (Tolosa et al., 2004) and net-heterotrophic riverine (Zou et al., 2006) and estuarine (Boschker et al., 2005) settings where external input of terrestrial organic carbon supports bacterial secondary production. Unlike turbid estuaries and rivers, the Canada Basin is particle-poor (Griffith et al., 2012), but a significant external source of laterally-transported organic carbon from the productive Chukchi Sea (Davis and Benner, 2007; Mathis et al., 2007; Shen et al., 2012; Walsh et al., 1989) or from re-suspended Beaufort Slope sediments (Honjo et al., 2010; Hwang et al., 2008; Jackson et al., 2010; O'Brien et al., 2013) has been shown. Previous studies have demonstrated that bioavailable DOC is delivered to the western Canada Basin at mesopelagic depths from the Chukchi Sea (Davis and Benner, 2007; Mathis et al., 2007; Shen et al., 2012) and may be an important organic carbon source in the interior Canada Basin.

The close isotopic relationship between BFAs and suspended POC (< 1 ‰ except 50 m at CB9, Table 2) at each individual depth above 3000 m is striking (Figs. 2c and 3c) and indicates BFAs are produced in situ by heterotrophic bacteria suspended in the meso- and bathypelagic Canada Basin. Between 500 and 2500 m at station CB4, however, the δ^{13}C values of suspended POC and DOC are very similar and ^{13}C cannot be used to determine whether the dominant organic carbon source fueling bacterial heterotrophy is organic carbon hydrolyzed directly from suspended POC or incorporation of DOC (Fig. 2c; Griffith et al., 2012). It is possible that heterotrophy at these depths is supported by DOC originating in the productive Chukchi Sea. A closer isotopic relationship between bacterial BFAs and suspended POC is apparent in the shallowest 150 m, however, as it is between suspended POC and the heterotrophic synthesizers of iso- and anteiso-C_{15} at 3000 and 3500 m (Figs. 2c and 3c). Odd-numbered SFAs are also isotopically more similar to average BFAs than average SFAs below 150 m, suggesting a significant fraction of straight-chain C_{15} and C_{17} fatty acids are produced by heterotrophic bacteria.

4.5 Sources of ^{13}C-depleted fatty acids in the interior Canada Basin (150–2500 m)

Multiple water masses stratify the water column in the Canada Basin, and the influence of the Pacific-origin, Atlantic-origin and isolated deep basin waters can been seen in the isotopic composition of DIC, DOC and suspended POC (Griffith et al., 2012). The vertical distribution and δ^{13}C values of fatty acids, however, do not appear to be strongly influenced by water mass except for the possibility of Pacific-origin Summer Water (PSW), from which the 50 m samples were obtained (Griffith et al., 2012). Instead, fatty acid distributions and isotopic compositions suggest three distinct zones in the water column: 50 m, 150–2500 m, and 3000–3775 m.

Here we discuss the largest region, 150–2500 m, where a ^{13}C-depleted source of SFAs is suggested by the subsurface peak in the POC-normalized abundance of SFAs at 2500 m depth (Fig. 2b), 95 % of which is made up of C_{16} and C_{18} fatty acids (Fig. 1a). The C_{16} fatty acid shows a progressive ^{13}C-depletion between 500 and 2500 m depth, opposite to the trend expected from decreasing contributions from surface-derived organic matter and increasing relative contributions from bacterial heterotrophs. The δ^{13}C value of saturated C_{18} fatty acid also remains similar to its value at 50 m rather than trending towards a more positive value with depth as would be consistent with an increasingly important bacterial heterotrophic source. We identify four sources of organic matter that may contribute to the total fatty acids that we recovered between 150 and 2500 m: (1) phytoplankton-derived organic carbon produced in surface waters; (2) laterally-delivered organic carbon originating either from primary productivity in the Chukchi Sea or from re-suspended shelf sediments; (3) suspended heterotrophic or chemoautotrophic bacterial cells; and (4) non-particulate organic carbon adsorbed onto the glass fiber filters during sample collection. We have explicitly corrected for adsorbed organic carbon (Tables 1 and 2) and only consider the first three fatty acid sources in the following model and discussion.

In order to explore the potential importance of the three fatty acid sources to the interior Canada Basin, we construct an isotopic mass balance model according to:

$$1 = f_{\text{surface}} + f_{\text{advected}} + f_{\text{bacteria}} \tag{1}$$

$$\delta_{\text{measured}} = f_{\text{surface}} \cdot \delta_{\text{surface}} + f_{\text{advected}} \cdot \delta_{\text{advected}} + f_{\text{bacteria}} \cdot \delta_{\text{bacteria}} \tag{2}$$

where δ represents δ^{13}C value. We focus on 1000–2500 m where the isotopic divergence between SFAs and BFAs is most pronounced at station CB4 (Fig. 2c). We also consider only C_{16} and C_{18} fatty acids which represent 84–95 % of total fatty acids at these depths (Table 1).

δ_{surface}: although the sinking flux of organic carbon is known to be very small (Honjo et al., 2010), and the ^{13}C-depleted isotopic signature of fatty acids in surface waters do not form the major component of fatty acids in suspended POC below 50 m depth (Figs. 2c and 3c), surface-derived organic matter delivered with sinking particles will still contribute some fraction of fatty acids to the interior Canada Basin. We assign δ_{surface} as the average δ^{13}C value of C_{14} and C_{16} at 50 m at station CB4. Because the δ^{13}C value of C_{18} is more similar to BFAs than SFAs, it likely represents significant contributions from heterotrophic bacteria and is therefore not included in our endmember value for phytoplankton-derived organic matter. Although 50 m may appear deep for a surface source, we believe our 50 m samples, taken at the chlorophyll maximum, to be a reasonable proxy for the isotopic composition of sinking fatty acids. The mechanisms of organic matter aggregation and the depths from which it is dominantly exported are not well-understood in the central Canada Basin, but the sequestration of nutrients below the summer halocline means that a large proportion of total water column primary productivity occurs at the subsurface chlorophyll maximum depth (Lee et al., 2012; Martin et al., 2012). A recent analysis of suspended particulate matter from the coastal Beaufort Sea also identifies a POC maximum and biomarker indications of “fresh” organic carbon at the chlorophyll maximum depth (Tolosa et al., 2013). This is unlike lower-latitude ocean basins where the subsurface chlorophyll maximum does not correspond to a biomass or productivity maximum.

δ_{advected}: the δ^{13}C values and distribution of fatty acids from allochthonous organic carbon in the interior Canada Basin are much more difficult to assign because of multiple and poorly-defined possible sources. Organic carbon from primary productivity over the Chukchi (Davis and Benner, 2005, 2007; Shen et al., 2012) or Beaufort shelves (Ortega-Retuerta et al., 2012) could be incorporated into suspended POC following deposition to sediments, re-suspension and lateral transport (Mathis et al., 2007). Saturated C_{14}, C_{16} and C_{18} fatty acids in sediments at the base of the Beaufort slope, presumably with a Beaufort Sea primary origin, have more enriched δ^{13}C values relative to those between 150 and 2500 m (Drenzek et al., 2007; Goñi et al., 2005). Sea-ice

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algae will also contribute organic carbon that is ^{13}C-enriched (Belt et al., 2008; Budge et al., 2008). Bioavailable DOC with undefined δ^{13}C value may also be incorporated directly into suspended POC by aggregation processes (Burd and Jackson, 2009; Engel et al., 2004). We use δ^{13}C values from ice algal, phytoplankton and copepod fatty acids measured on samples collected near Barrow, Alaska (Budge et al., 2008) to represent δ_{advected} values for fresh and re-worked sources of organic carbon from nearby productive waters (Table 3).

Beaufort shelf sediments also host organic matter delivered by the Mackenzie River (Drenzek et al., 2007; Goñi et al., 2005; Yunker et al., 2005), and their mobilization could deliver marine, terrestrial and riverine organic carbon to the interior Canada Basin. Although the distribution of fatty acids has been described in sediments of the Chukchi and Beaufort slopes (Belicka et al., 2002, 2004; Drenzek et al., 2007; Tolosa et al., 2013), δ^{13}C values are only reported for the Mackenzie River and Beaufort Slope (Drenzek et al., 2007; Goñi et al., 2005; Tolosa et al., 2013). We also use the δ^{13}C value of fatty acids from Mackenzie River suspended POC (Goñi et al., 2005; Tolosa et al., 2013) and Beaufort slope sediments (Drenzek et al., 2007; Goñi et al., 2005; Tolosa et al., 2013) to represent δ_{advected} values for sedimentary fatty acids (Table 3).

f_{bacteria}: because the δ^{13}C value of bacterial fatty acids will depend on the unknown fraction of bacterial heterotrophs vs. chemoautotrophs and on chemoautotrophic pathways, we allow δ_{bacteria} to be an unknown variable and instead estimate f_{bacteria} from prokaryotic abundances and a biomass-to-phospholipid fatty acid conversion factor assuming phospholipid fatty acids are the major source of fatty acids in marine bacteria (Oliver and Colwell, 1973; Oliver and Stringer, 1984). Using prokaryotic abundances reported by Uchimiya et al. (2013), the carbon content of bacterial cells in oligotrophic waters (4–7 fg C cell^{-1}; Christian and Karl, 1994; Gundersen et al., 2002), and considering that 49 % of microbial cells pass through GF/F filters (Lee et al., 1995), we calculate that 11–14 % of suspended POC captured in our samples could be attributed to prokaryotic biomass carbon between 1000 and 2500 m depth (Fig. 4a). Although δ^{13}C values of BFAs indicate that at least some of this prokaryotic biomass is heterotrophic bacteria (Sect. 4.4), this range falls within the 10–22 % of suspended POC that Griffith et al. (2012) attribute to chemoautotrophic biomass based on the radiocarbon similarity between DIC and suspended POC and the modest ^{13}C enrichment in POC between 1000 and 2500 m. Total prokaryotic biomass reported by Uchimiya et al. (2013) includes both bacterial and archaeal cells while only bacterial cells will be represented in fatty acid abundances. Still, there still appears to be a relatively constant offset between the fraction of POC from prokaryotic biomass and from fatty acid carbon (Fig. 4a) which supports suspended prokaryotes as a dominant source of fatty acids at these depths. In their intact phospholipid form, fatty acids are thought to be a constant fraction of bacterial biomass (Balkwill et al., 1988; Findlay et al., 1989; White et al., 1979). The ratio of fatty acid carbon to biomass carbon is poorly constrained for slowly-growing deep ocean bacterioplankton, but for a sedimentary enrichment culture with large bacterial cells (56 fg C cell^{-1}), 21 % of biomass carbon could be attributed to fatty acid carbon from phospholipids (Findlay et al., 1989). It has also been observed that approximately half of total phospholipid is lost upon transitioning a marine bacterium from nutrient-replete culture conditions to suspension in seawater (Oliver and Stringer, 1984), so we assume fatty acid carbon is approximately 10 % of biomass carbon. An additional assumption about the proportional balance between bacterial and archaeal cells must be made to calculate f_{bacteria}. A dominance of bacteria was reported below 500 m at the base of the Chukchi Slope (Kirchman et al., 2007), however this dominance would yield more bacterial fatty acid than we recovered from all depths between 500 and 2500 m. The maximum proportion of bacteria that fatty acid abundances allow is 54 %, closer to the fraction of bacteria found at meso- and bathypelagic depths of the oligotrophic North Pacific and Atlantic Oceans (Herndl et al., 2005; Karner et al., 2001). Conservatively, we assume that 50 % of prokaryotic cells are bacterial and that 10 % of their biomass carbon can be attributed to fatty acid carbon. Using an abundance-weighted fatty acid composition to calculate fatty acid carbon from observed fatty acid abundance, these assumptions yield an f_{bacteria} value that averages 80 % between 1000 and 2500 m.

Defining δ_{measured} as the average δ^{13}C value for C_{16} and C_{18} fatty acids between 1000 and 2500 m depth (−27.5 ‰), three unknown variables remain: f_{surface}, f_{advected} and δ_{bacteria}. Combining Eqs. (1) and (2) to eliminate f_{surface} leaves:

$$\delta_{\text{bacteria}} = \frac{\delta_{\text{surface}} - \delta_{\text{advected}}}{1 + f_{\text{bacteria}}} \cdot f_{\text{advected}} + \frac{\delta_{\text{measured}} + f_{\text{bacteria}} \cdot \delta_{\text{surface}}}{1 + f_{\text{bacteria}}} \qquad (3)$$

relating f_{advected} to δ_{bacteria} by a linear equation in the form $y = mx + b$. Fig. 4b illustrates the relationship between f_{advected} and δ_{bacteria} for the full range of possible f_{advected} values (0–20 %). Considering that $f_{\text{advected}} + f_{\text{surface}} = 20\,\%$, this corresponds to f_{surface} values of 20 % to 0 % (Fig. 4b, secondary horizontal axis). Each line in Fig. 4b represents a solution to the mass balance equation for a different advected component (summarized in Table 3).

Bacterial heterotrophs will likely synthesize fatty acids with δ^{13}C values similar to BFAs and POC at each depth (Sect 4.4): −21 to −23 ‰ between 1000 and 2500 m. Model results, however, are uniformly more negative than these values implying production of ^{13}C-depleted fatty acids by suspended bacteria at depth. Chemoautotrophic bacteria utilizing the RubisCO enzyme and Calvin Cycle to reduce inorganic carbon could contribute ^{13}C-depleted fatty acids to the interior Canada Basin while their biomass would be isotopically similar to heterotrophic bacteria (Hayes, 2001; Sakata et al., 2008). The genetic potential for this metabolic pathway has been identified at mesopelagic depths of other oligotrophic regions (Swan et al., 2011), and the expected δ^{13}C value of chemoautotroph-derived fatty acids of ∼ −28 ‰ is similar to observed δ^{13}C values for C_{16} and C_{18} between 1000 and 2500 m depth. This value is calculated from a likely isotopic fractionation between DIC and fatty acids of ∼ 29 ‰ (Sakata et al., 2008) and the δ^{13}C value of DIC between 500 and 2500 m which is +1 ‰ (Griffith et al., 2012). With defined end-member δ^{13}C values for bacterial heterotrophs and chemoautotrophs, it is also possible to calculate their proportions through two-component isotopic mixing based on model output δ_{bacteria} values (Fig. 4b, secondary vertical axis). Chemoautotrophic production of fatty acids appears to be a significant contributor to the total fatty acid pool regardless of the advected source of fatty acids. In the most extreme case of purely terrestrial advected fatty acids ($\delta_{\text{advected}} = -37.0$ ‰ representing Mackenzie River POC), mass balance requires 60 % chemoautotrophic bacteria.

4.6 Allochthonous fatty acids between 3000 and 3775 m

In the deepest 1000 m, the abundance of total fatty acids no longer decreases with depth (Fig. 2b), exhibiting a similar trend to prokaryotic abundance (Uchimiya et al., 2013). The distribution of fatty acids is also distinct from depths above with a greater representation of long-chain fatty acids (C_{20-24}), BFAs and MUFAs (Fig. 1a). This compositional difference is likely a reflection of an allochthonous source of particulate matter to the deep basin. Re-suspension and lateral transport of sediments from surrounding margins dominates sinking POC at these depths (Hwang et al., 2008; Honjo et al., 2010), and this has also been identified as an important component of suspended POC (Griffith et al., 2012). The source of this allochthonous organic carbon could be the terrestrially-influenced Mackenzie and Beaufort slopes to the south or the marine-dominated Chukchi slope and base of the Northwind Ridge to the west. At the base of the Beaufort Slope, shallow sediments host abundant short-chain SFAs and MUFAs, as well as proportionally important long-chain fatty acids (C_{23-32}) and BFAs (Belicka et al., 2004). Further investigations of long-chain fatty acids at the base of the Beaufort slope revealed a normal distribution of even-numbered SFAs centered around C_{24} which derive primarily from plant waxes (Drenzek et al., 2007). Combined, these resemble the distribution of fatty acids in suspended POC (Fig. 1) with the exception of the shorter maximum chain length. Although C_{24} is the most abundant long-chain fatty acid in suspended POC, we do not detect C_{26-32} fatty acids and suspect these may have been lost to degradation during their suspension in oxic bottom waters (cf. Rontani et al., 2012). Organic carbon in the sediments of the Chukchi slope reflects primarily a marine source from the productive Chukchi Sea (Belicka et al., 2002, 2004). The distribution of fatty acids is subtly different than the base of the Beaufort slope (Belicka et al., 2004) with only trace C_{14} saturated fatty acids, and a distribution of long-chain fatty acids centered around C_{26} rather than C_{24} (Belicka et al., 2002). These differences, combined with the greatest particle load observed in the southern Canada Basin (Jackson et al., 2010), make the Beaufort slope a more likely source region for suspended POC in the abyssal Canada Basin than the base of the Northwind Ridge.

There are also isotopic differences between the deepest 1000 m and above. The δ^{13}C value of DOC and suspended POC are different by ~ 1.5 ‰, unlike the majority of the water column above (Fig. 2c; Griffith et al., 2012). But, in general, there is a general trend towards ^{13}C-enrichment of SFAs resulting in more isotopic similarity between suspended POC and SFAs, as well as between SFAs and BFAs at these depths (Table 2; Fig. 2c). It is possible that intense bacterial heterotrophy supported by re-suspended sedimentary organic carbon contributes a larger proportion of SFAs at deep depths. Another possibility is that a larger proportion of total fatty acids is delivered to the suspended POC reservoir from a sedimentary source. The isotopic variability in fatty acids from the deepest depth, 3775 m, may reflect this greater allocthonous source.

The exceptions to this pattern are C_{12} and iso-C_{17} fatty acids, both which have δ^{13}C values more negative than any value higher in the water column (Fig. 2c). δ^{13}C values of iso-C_{17} and C_{12} at 3000 m are also more negative than fatty acids in the Mackenzie River (Goñi et al., 2005). Although some of these values at 3000 m and below can therefore be explained by a terrestrial source, a more ^{13}C-depleted origin is required for iso-C_{17}. Bacterial oxidizers of ^{13}C-depleted methane may be their origin since methane and gas hydrates have been observed in the coastal Beaufort Sea (Dallimore and Collett, 1995; Paull et al., 2007). Synthesis of iso-C_{17} could occur in sediments hosting methane hydrates that are subsequently mobilized, or iso-C_{17} could be produced in situ if there is a source of methane to the deep basin.

5 Conclusions

In the interior Canada Basin, suspended fatty acids show evidence of both advected and in situ sources. Surface waters host fatty acids that are more depleted in ^{13}C than in the dark basin below and also reflect contrasting ecological conditions under ice cover compared to open water. The ^{13}C depletion, not observed in DIC or DOC, could result from slowly-growing diatoms, but possibly also from the delivery of terrestrial organic carbon to the central Canada Basin. Deeper depths appear to be isolated from the effects of ice cover, but at all depths, a strong isotopic similarity between POC and branched fatty acids is apparent supporting the hypothesis that intense bacterial heterotrophy contributes to a weak biological pump in the Canada Basin (Honjo et al., 2010). An additional, ^{13}C-depleted source of saturated, even-numbered fatty acids between 1000 and 2500 m is also indicated, at least partially of chemoautotrophic origin. Lateral advection of DOC from the Chukchi Sea, and POC re-suspended from sediments are also potential sources. We believe that the excess abundance of prokaryotes in the deep Canada Basin compared to sinking POC flux (Nagata et al., 2010; Uchimiya et al., 2013; Yokokawa et al., 2013) could therefore be explained by a combination of bacterial heterotrophs supported by a lateral supply of organic carbon and chemoautrotrophic bacteria utilizing the Calvin Cycle to fix inorganic carbon with a yet unknown energy metabolism. Fatty acids in the deepest 1000 m reflect the contributions of re-suspended sediments (Hwang et al., 2008) with greater relative abundances of long-chain fatty acids (C_{20-24}), and isotopic dissimilarity compared to shallower depths. Two individual fatty acids recovered from 3000 m and below, C_{12} and iso-C_{17} are too depleted in ^{13}C to derive from the water column or shallow sediments and more likely are produced by methane oxidizing bacteria hinting at a poorly-defined methane cycle in the abyssal Canada Basin.

Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/10/6695/2013/ bgd-10-6695-2013-supplement.pdf.

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Table 1. Concentration of POC and FAMEs in the Canada Basin.

	DOC blank	seasonally ice-free station CB4								ice-covered station CB9			
		50 m	150 m	1000 m	2000 m	2500 m	3000 m	3500 m	3750 m	50 m	150 m	500 m	1000 m
	(ng/filter)	($\mathrm{ng\,L^{-1}}$ seawater)								($\mathrm{ng\,L^{-1}}$ seawater)			
POC	**74954**	**10081**	**2390**	**828**	**558**	**338**	**485**	**498**	**478**	**15853**	n.d.	**1528**	**993**
Total FA	**2116**	**406.88**	**60.27**	**20.01**	**8.34**	**7.80**	**2.17**	**2.93**	**1.93**	**559.01**	**180.15**	**16.15**	**15.20**
12 : 0	51	0.00	1.50	0.38	0.00	0.00	0.02	0.08	0.02	1.47	0.08	0.01	0.00
13 : 0	0	0.00	0.26	0.05	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.04	0.00
14 : 0	100	125.09	9.72	1.62	0.11	0.18	0.32	0.35	0.19	128.85	5.04	2.35	0.43
15 : 0	26	4.68	1.69	0.51	0.10	0.07	0.09	0.10	0.07	6.57	1.02	0.44	0.20
16 : 0	906	206.35	25.19	7.34	3.07	3.30	0.68	1.05	0.83	271.53	59.56	7.53	5.66
17 : 0	17	0.73	0.55	0.19	0.07	0.04	0.01	0.03	0.02	1.87	0.61	0.20	0.14
18 : 0	891	46.91	16.38	7.67	4.36	3.74	0.47	0.70	0.31	67.60	108.51	3.43	7.61
20 : 0	24	0.00	0.00	0.00	0.05	0.03	0.02	0.03	0.01	1.68	1.18	0.00	0.00
22 : 0	0	2.24	0.10	0.00	0.03	0.03	0.01	0.02	0.00	0.00	0.21	0.10	0.04
24 : 0	0	0.96	0.18	0.18	0.00	0.03	0.07	0.07	0.08	3.53	0.00	0.00	0.00
SFA	**2015**	**386.98**	**55.57**	**17.93**	**7.79**	**7.42**	**1.71**	**2.44**	**1.53**	**483.10**	**176.22**	**14.09**	**14.10**
i-15 : 0	0	6.40	1.72	0.70	0.10	0.08	0.09	0.09	0.10	9.73	0.75	0.62	0.25
ai-15 : 0	0	4.66	1.30	0.75	0.13	0.08	0.10	0.09	0.08	4.54	0.60	0.51	0.28
i-16 : 0	0	0.52	0.35	0.22	0.03	0.02	0.02	0.03	0.03	0.00	0.26	0.18	0.11
i-17 : 0	0	0.52	0.32	0.18	0.06	0.04	0.04	0.03	0.04	1.10	0.29	0.16	0.12
ai-17 : 0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BFA	**0**	**12.10**	**3.69**	**1.85**	**0.32**	**0.22**	**0.25**	**0.23**	**0.25**	**15.37**	**1.89**	**1.46**	**0.75**
Σ16 : 1	0	0.94	0.14	0.02	0.01	0.01	0.07	0.05	0.04	31.94	0.35	0.05	0.04
Σ18 : 1	47	1.98	0.28	0.06	0.00	0.01	0.05	0.04	0.01	14.04	0.13	0.14	0.05
MUFA	**47**	**2.92**	**0.42**	**0.08**	**0.01**	**0.02**	**0.12**	**0.09**	**0.05**	**45.98**	**0.48**	**0.19**	**0.09**
18 : 2n6	0	1.49	0.41	0.00	0.05	0.00	0.00	0.02	0.00	5.22	0.38	0.13	0.10
18 : 3n6	0	3.39	0.19	0.15	0.07	0.14	0.08	0.11	0.08	9.34	0.49	0.28	0.16
20 : 2	54	0.00	0.00	0.00	0.11	0.01	0.00	0.03	0.02	0.00	0.70	0.00	0.00
PUFA	**54**	**4.88**	**0.60**	**0.15**	**0.23**	**0.15**	**0.08**	**0.16**	**0.09**	**14.56**	**1.57**	**0.41**	**0.26**

n.d. not determined

Table 2. Blank-corrected δ^{13}C values of POC and FAMEs in the Canada Basin.

	DOC blank		**seasonally ice-free station CB4**															
			50 m		150 m		1000 m		2000 m		2500 m		3000 m		3500 m		3750 m	
	(‰)	±	(‰)	±	(‰)	±	(‰)	±	(‰)	±	(‰)	±	(‰)	±	(‰)	±	(‰)	±
POC	**−25.1**	**0.1**	**−29.5**	**0.1**	**−24.8**	**0.1**	**−22.7**	**0.1**	**−23.0**	**0.1**	**−22.7**	**0.1**	**−24.5**	**0.1**	**−24.3**	**0.1**	**−24.6**	**0.1**
12 : 0	−27.9	1.0			−29.6	0.3	−27.4	0.4					−42.9	2.6	−32.0	0.9	−37.7	0.6
14 : 0	−30.0	0.3	−36.2	0.7	−30.1	0.5	−23.6	0.5	−20.4	0.6	−25.5	0.3	−25.1	0.3	−25.3	0.4	−25.0	0.3
15 : 0			−34.0	0.7	−25.7	0.3	−22.7	1.1	−22.4	1.1	−24.8	0.6	−26.2	0.6	−25.7	0.3	−28.3	0.5
16 : 0	−26.5	0.4	−36.0	0.3	−29.7	0.3	−26.0	0.5	−27.2	0.4	−28.1	0.4	−22.9	0.3	−24.5	0.3	−25.8	0.4
17 : 0					−28.5	0.5	−23.3	1.0	−23.7	1.0			−23.1	0.6	−23.0	0.8	−23.8	0.6
18 : 0	−25.9	0.3	−30.4	0.5	−28.8	0.3	−28.4	0.3	−27.8	0.3	−27.7	0.3	−22.2	0.6	−22.8	0.3	−29.8	0.3
SFA	**−26.4**	**2.3**	**−35.4**	**3.1**	**−29.7**	**2.6**	**−27.0**	**2.3**	**−27.6**	**2.4**	**−27.8**	**2.4**	**−23.8**	**1.9**	**−24.7**	**2.1**	**−27.2**	**2.3**
i-15 : 0			−31.2	0.5	−24.6	0.5	−21.8	0.5	−21.7	0.8	−23.1	0.7	−24.4	0.9	−25.1	0.5	−22.7	0.5
ai-15 : 0			−28.4	0.3	−24.1	0.3	−22.7	0.3	−22.7	0.5	−22.6	1.3	−23.8	0.6	−24.6	0.3	−22.7	0.6
i-17 : 0							−21.0	0.9					−41.8	2.8	−39.8	0.3	−22.1	0.9
BFA			**−30.0**	**2.6**	**−24.4**	**2.0**	**−22.1**	**1.8**	**−22.3**	**1.6**	**−22.8**	**1.3**	**−27.4**	**1.6**	**−27.3**	**2.3**	**−22.6**	**1.6**
16 : 1n9																		
18 : 1n9																		
MUFA																		
18 : 2n6																		
$\Delta_{\mathrm{POC-SFA}}$	**1.3**		**5.8**		**4.9**		**4.3**		**4.7**		**5.1**		**−0.7**		**0.3**		**2.6**	
$\Delta_{\mathrm{POC-BFA}}$			**0.5**		**−0.4**		**−0.6**		**−0.7**		**0.1**		**2.9**		**3.0**		**−2.0**	
$\Delta_{\mathrm{SFA-BFA}}$			**−5.3**		**−5.3**		**−4.9**		**−5.4**		**−5.0**		**3.6**		**2.6**		**−4.6**	

n.d. not determined

Table 2. Continued.

	ice-covered station CB9							
	50 m		150 m		500 m		1000 m	
	(‰)	±	(‰)	±	(‰)	±	(‰)	±
POC	**−27.0**	**0.1**	n.d.		**−24.1**	**0.1**	n.d.	
12 : 0	−34.5	0.4	−27.9	0.3	−26.9	0.4	−24.8	1.3
14 : 0	−30.8	0.4			−25.4	0.4	−22.3	0.9
15 : 0	−35.2	0.3	−29.1	0.6	−28.0	0.4	−27.3	0.4
16 : 0					−25.2	0.7		
17 : 0	−29.8	0.7	−29.1	0.3	−28.7	0.3	−28.6	0.3
18 : 0								
SFA	**−34.2**	**3.0**	**−29.1**	**2.5**	**−27.9**	**2.4**	**−27.9**	**2.4**
i-15 : 0	−26.3	0.4			−23.9	0.3	−22.6	1.5
ai-15 : 0	−24.7	0.3			−22.9	0.3	−22.0	0.3
i-17 : 0					−23.0	0.3		
BFA	**−25.8**	**2.2**			**−23.4**	**2.0**	**−22.3**	**1.4**
16 : 1n9	−28.6	0.3						
18 : 1n9	−32.7	0.4						
MUFA	**−29.9**	**2.7**						
18 : 2n6	−26.5	0.9						
$\Delta_{\mathrm{POC-SFA}}$	**7.2**				**3.7**			
$\Delta_{\mathrm{POC-BFA}}$	**−1.2**				**−0.7**			
$\Delta_{\mathrm{SFA-BFA}}$	**−8.4**				**−4.5**		**−5.6**	

n.d. not determined

Table 3. δ^{13}C values of organic matter sources that could be laterally supplied to Canada Basin.

Source	**representative** δ_{advected} (‰)	**reference**
Ice Algae	−24.0	avg. $C_{16:4}$ δ^{13}C values; Budge et al., 2008
Phytoplankton	−30.6	avg. $C_{16:0}$, $C_{16:1}$, $C_{16:4}$, $C_{18:0}$, $C_{18:1}$ δ^{13}C values; Budge et al., 2008, chlorophyll maximum from Tolosa et al., 2013
Copepod	−27.4	avg. $C_{16:4}$ δ^{13}C values; Budge et al., 2008
Beaufort Slope Sediments	−27.0	avg. $C_{16:0}$, $C_{16:1}$, $C_{18:0}$ δ^{13}C values; Goñi et al., 2005, Drenzek et al., 2007; slope sites from Tolosa et al., 2013
Mackenzie River POC	−37.0	avg. $C_{16:0}$, $C_{16:1}$ δ^{13}C values; Goñi et al., 2005

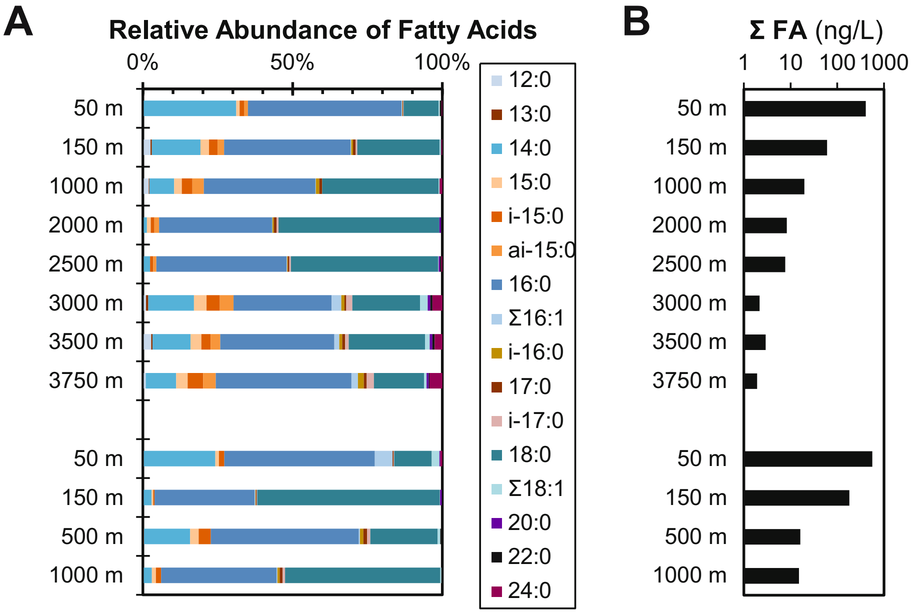

Fig. 1. (A) Relative abundances of individual fatty acids with blue shades representing even-numbered fatty acids and orange shades representing odd-numbered and branched fatty acids. **(B)** Summed concentration of total fatty acids corrected for the sorption or organic carbon.

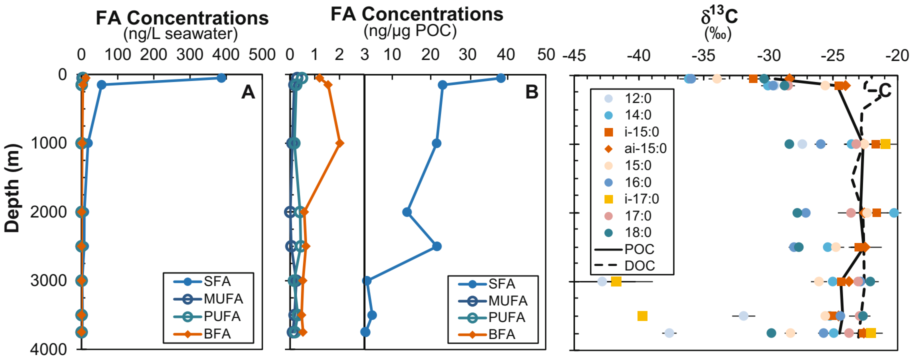

Fig. 2. Station CB4 – **(A)** Seawater-normalized concentrations of fatty acids and **(B)** POC-normalized concentrations of fatty acids grouped into saturated (SFA), branched (BFA), monounsaturated (MUFA) and polyunsaturated (PUFA) and plotted with depth. **(C)** δ^{13}C values of individual fatty acids with depth where SFAs are in blue shades, BFAs are in orange shades and open circles represent MUFAs and PUFAs.

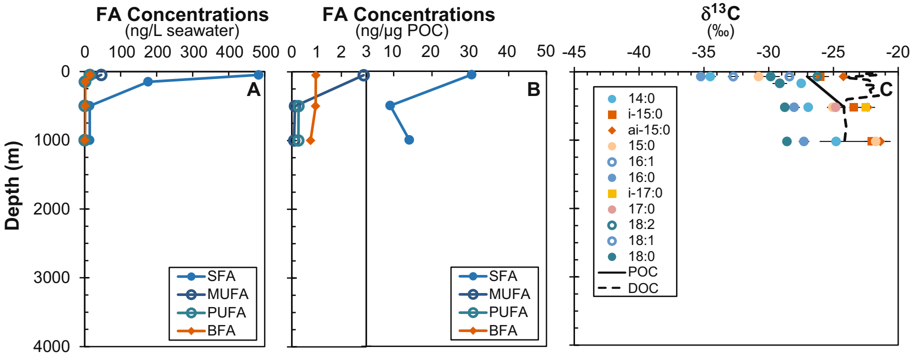

Fig. 3. Station CB9 – **(A)** Seawater-normalized concentrations of fatty acids and **(B)** POC-normalized concentrations of fatty acids grouped into saturated (SFA), branched (BFA), monounsaturated (MUFA) and polyunsaturated (PUFA) and plotted with depth. **(C)** δ^{13}C values of individual fatty acids with depth where SFAs are in blue shades, BFAs are in orange shades and open circles represent MUFAs and PUFAs.

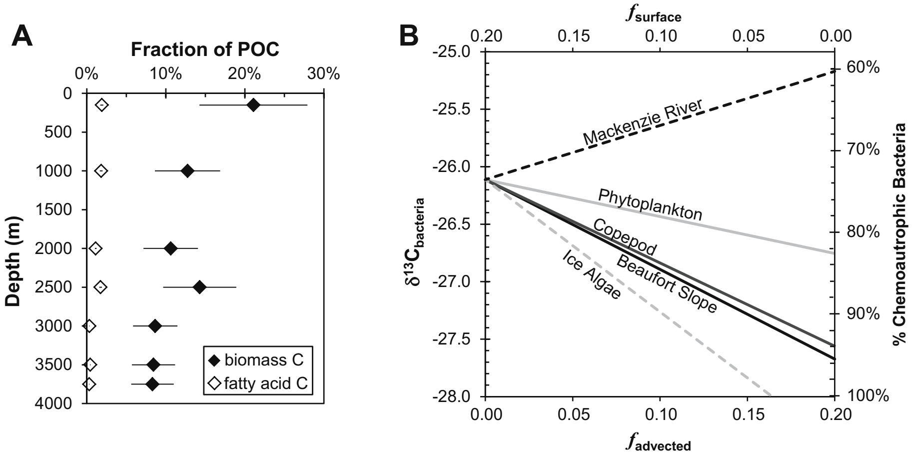

Fig. 4. (A) Proportions of total POC that can be attributed to organic carbon from prokaryotic biomass and organic carbon from fatty acids (FA). Prokaryotic organic carbon calculated from abundances reported by Uchimiya et al. (2013) with a conversion factor of 6.5 ± 2.5 fg carbon cell^{-1} (Christian and Karl, 1994; Gundersen et al., 2002) and assuming 51 % recovery on GF/F filters (Lee et al., 1995). Fatty acid abundances converted TO organic carbon equivalents using the weighted average %C for fatty acids at each depth. **(B)** Results of isotopic mass balance model for $\delta^{13}C_{bacteria}$ as a function of $f_{advected}$ for isotopically distinct sources of advected organic carbon with $f_{surface}$ plotted on the secondary horizontal axis and the fraction of chemoautotrophic vs. heterotrophic bacteria on the secondary vertical axis.