

Abstract

Microphytobenthos (MPB) tends to be omitted as a possible carbon source to higher trophic level consumers in high latitude marine food web models that use stable isotopes. Here, we used previously published relationships relating the concentration of aqueous carbon dioxide ($[CO_2]_{aq}$), the stable carbon isotopic composition of dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$), and algal growth rates (μ) to estimate the stable carbon isotope composition of MPB-derived total organic carbon (TOC) ($\delta^{13}C_p$) and fatty acid (FA) biomarkers ($\delta^{13}C_{FA}$). We measured $[CO_2]_{aq}$ and $\delta^{13}C_{DIC}$ values from bottom water at sampling locations in the Beaufort and Chukchi Seas ($n = 18$), which ranged from 17 to 72 $mmol\ kg^{-1}$ and -0.1 to 1.4‰ ($0.8 \pm 0.4\text{‰}$, mean ± 1 s.d.), respectively. We combined these field measurements with a set of stable carbon isotopic fractionation factors reflecting differences in algal taxonomy and physiology to determine $\delta^{13}C_p$ and $\delta^{13}C_{FA}$ values. The $\delta^{13}C_p$ and $\delta^{13}C_{FA}$ values for a mixed eukaryotic algal community were estimated to be $-23.6 \pm 0.4\text{‰}$ and $-30.6 \pm 0.4\text{‰}$, respectively. These values were similar to our estimates for *Phaeodactylum tricornutum* ($\delta^{13}C_p = -23.9 \pm 0.4\text{‰}$, $\delta^{13}C_{FA} = -30.9 \pm 0.4\text{‰}$), a pennate diatom likely to be a dominant MPB taxon. Taxon-specific differences were observed between a centric diatom (*Porosira glacialis*, $\delta^{13}C_p = -20.0 \pm 1.6\text{‰}$), a marine haptophyte (*Emiliana huxleyi*, $\delta^{13}C_p = -22.7 \pm 0.5\text{‰}$), and a cyanobacterium (*Synechococcus* sp., $\delta^{13}C_p = -16.2 \pm 0.4\text{‰}$) at $\mu = 0.1\text{ d}^{-1}$. $\delta^{13}C_p$ and $\delta^{13}C_{FA}$ values increased by $\approx 2.5\text{‰}$ for the mixed algal consortium and for *P. tricornutum* when growth rates were increased from 0.1 to 1.4 d^{-1} . We compared our estimates of $\delta^{13}C_p$ and $\delta^{13}C_{FA}$ values for MPB with previous measurements of $\delta^{13}C_{TOC}$ and $\delta^{13}C_{FA}$ values for other carbon sources in the Arctic, including ice-derived, terrestrial, and pelagic organic matter. We found that MPB values were significantly distinct from terrestrial and ice-derived carbon sources. However, MPB values overlapped with pelagic sources, which may result in MPB being overlooked as a significant source of carbon in the marine food web.

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1 Introduction

Projected impacts of climate change and industrial development on the marine environment necessitate an improved understanding of energy flow and food web structure in the Arctic (Carmack et al., 2006). Stable carbon isotope analyses of total organic carbon (TOC) and specific compounds (e.g., fatty acids – FAs) from organisms can provide an effective tool to determine contributions from different primary production sources to arctic food webs (Budge et al., 2008; Dunton et al., 2012; Hobson et al., 2002). Typically assessed primary producer sources in arctic food web studies are pelagic, sympagic and terrestrial primary production. These sources differ in their $\delta^{13}C$ values due to variation in the composition and availability of the carbon source used in photosynthesis. Pelagic phytoplankton source dissolved inorganic carbon (DIC) from surface ocean waters where the global mean stable carbon isotope composition ($\delta^{13}C_{DIC} = 1.5 \pm 0.8\text{‰}$) (Gruber et al., 1999) is higher than that of terrestrial sources such as atmospheric CO_2 ($\delta^{13}C_{atm.} = -7.9\text{‰}$) (Farquhar et al., 1989) or DIC from arctic lacustrine environments (e.g., $\delta^{13}C_{DIC} = -2\text{‰}$) (Hecky and Hesslein, 1995). Ice algae can have a unique stable carbon isotope composition relative to pelagic and terrestrial sources due to limited exchange of DIC in the brine channel matrix (e.g., Fischer, 1991; Kennedy et al., 2002; Wang et al., 2013). At high levels of photosynthesis in a closed or semi-closed system, restricted exchange results in decreased expression of isotopic fractionation (Hobson et al., 1995; McMahan et al., 2006; Soreide et al., 2013).

Microphytobenthos (MPB) is often not included as a potential source of primary production to arctic food webs despite its prevalence on shallow shelves in the Arctic (Glud et al., 2009; Horner and Schrader, 1982; Matheke and Horner, 1974). MPB is a distinct algal community dominated by pennate diatoms in the Arctic that develops exclusively on the sediment surface (Glud et al., 2009; Wulff et al., 2009 and references therein). We might expect MPB to be isotopically distinct from pelagic, sympagic, and terrestrial sources given distinct benthic conditions such as DIC limitation through the benthic boundary layer at the seafloor (Hecky and Hesslein, 1995). However, due to challenges

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acid (EMD Chemicals HPLC grade). Samples were allowed to equilibrate for 10 h before stable carbon isotope analysis. DIC samples were analyzed using a Finnigan Gas-Bench II interfaced with a Delta V Plus (Thermo Fisher Scientific, Bremen, Germany) continuous-flow isotope ratio mass spectrometer (CF-IRMS). Instrumental calibration was based on calcium carbonate (solid) international laboratory standards (NBS19 and NBS20). An internal laboratory standard (3 mM sodium bicarbonate in solution) that could be analyzed similar to the water samples was used for secondary calibration (Torres et al., 2005). Analytical precision was $\pm 0.04\text{‰}$, expressed as 1 standard deviation (s.d.) calculated from replicate ($n = 10$) analyses of aqueous 3 mM sodium bicarbonate (internal laboratory standard) performed throughout the sample run. Sample precision ($n = 3$, station 48, expressed as 1 s.d.) was $\pm 0.01\text{‰}$. Sample reproducibility, calculated from replicate ($n = 11$) sample analyses was $\pm 0.06\text{‰}$ (expressed as 1 s.d.). Stable carbon isotope compositions of DIC are expressed using conventional delta (δ) notation in parts per thousand (‰) based on the following equation:

$$\delta^{13}\text{C} = [R_{\text{sample}}/R_{\text{standard}} - 1] \cdot 1000 \quad (1)$$

where R_{sample} is the ratio of $^{13}\text{C}/^{12}\text{C}$ in seawater and R_{standard} is that of the standard reference material Vienna Pee Dee Belemnite (VPDB).

2.3 Calculations

CO_2 concentration ($[\text{CO}_2]_{\text{aq}}$, $\mu\text{mol kg}^{-1}$) was calculated using CO2SYS version 1.05. DIC, TA, temperature, salinity, phosphate, and silicate data were input using the thermodynamic model, dissociation constants, and solubility equations following Lewis and Wallace (1995).

Fractionation factors for C_3 photosynthesis (ε_p) were modeled using a suite of equations that describe the relationship between $[\text{CO}_2]_{\text{aq}}$, algal growth rate μ (d^{-1}), and ε_p (Laws et al., 1995; Popp et al., 1998). Laws et al. (1995) expressed ε_p in terms of μ

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and $[\text{CO}_2]_{\text{aq}}$, ($r^2 = 0.97$, $n = 5$) as follows:

$$\mu/[\text{CO}_2]_{\text{aq}} = -0.015 \cdot \varepsilon_p + 0.371 \quad (2)$$

In a subsequent study, Popp et al. (1998) examined the influence of cell geometry on ε_p for a diverse group of algal taxa, all of which occur in the sub-arctic and arctic marine environments (Flombaum et al., 2013; Krebs, 1983; Medlin et al., 1996; Smyth et al., 2004, von Quillfeldt et al., 2003): *Porosira glacialis* (centric diatom), *Phaeodactylum tricornutum* (pennate diatom), *Emiliana huxleyi* (haptophyte), and *Synechococcus* sp. (cyanobacterium). Regression relationships between ε_p and $\mu/[\text{CO}_2]_{\text{aq}}$ for those microeukaryotic species (all except *Synechococcus* sp.) converged at $\varepsilon_p \approx 25\text{‰}$ when $\mu \approx 0$ (ε_p^a). We used ε_p^a , the maximum ε_p resulting from Rubisco and β -carboxylase discrimination for marine eukaryotes, to estimate $\delta^{13}\text{C}_p^a$ for a mixed microphytobenthic algal community at $\mu \approx 0$.

At $\mu > 0$, differences in algal morphology influence carbon supply ($[\text{CO}_2]_{\text{aq}}$) and demand, resulting in species-specific ε_p (Popp et al., 1998). Empirically-derived regression relationships have been determined to describe the term ε_p for a centric diatom (*P. glacialis*, $\varepsilon_p^b = 25.5 - 1118.2 \mu/[\text{CO}_2]_{\text{aq}}$, $\mu = 0.3 \text{ d}^{-1}$, $r^2 = 0.75$, $n = 7$), a marine haptophyte (*E. huxleyi*, $\varepsilon_p^c = 24.6 - 137.9 \mu/[\text{CO}_2]_{\text{aq}}$, $\mu = 0.6 \text{ d}^{-1}$, $r^2 = 0.87$, $n = 9$), a pennate diatom (*P. tricornutum*, $\varepsilon_p^d = 25.5 - 52.6 \mu/[\text{CO}_2]_{\text{aq}}$, $\mu = 1.4 \text{ d}^{-1}$, $r^2 = 0.78$, $n = 8$), and a cyanobacterium (*Synechococcus* sp., mean $\varepsilon_p = 17.3$, $\mu = 0.3 \text{ d}^{-1}$, $n = 10$) (Popp et al., 1998). The cyanobacterium (*Synechococcus* sp.) showed no response to changes in availability or demand for $[\text{CO}_2]_{\text{aq}}$ (Popp et al., 1998), so a fixed fractionation factor ($\varepsilon_p = 17.3$) was used to model $\delta^{13}\text{C}_p$ values. We also calculated ε_p for the pennate diatom, *P. tricornutum* exposed to the range of $[\text{CO}_2]_{\text{aq}}$ and $\delta^{13}\text{C}_{\text{DIC}}$ observed at our field sites at three growth rates ($\mu = 0.1 \text{ d}^{-1}$, $\mu = 0.8 \text{ d}^{-1}$, $\mu = 1.4 \text{ d}^{-1}$) for the pennate diatom, *P. tricornutum*. We selected the pennate diatom as representative of MPB due to its relative dominance in polar MPB community assemblages. We investigated

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changes in ε_p over a range of typical growth rates given low levels of irradiance and cold temperatures in polar environments (Karsten et al., 2006; Longhi et al., 2003). Although growth rates for polar benthic diatoms are typically $\mu = 0.3\text{--}0.5\text{ d}^{-1}$, growth rates as high as $\mu = 1.24\text{ d}^{-1}$ have been observed (Karsten et al., 2006; Longhi et al., 2003). We selected $\mu = 1.4\text{ d}^{-1}$ as the upper limit for algal growth rate following Laws et al. (1995) because μ rarely exceeds two doublings per day in the natural environment (Laws et al., 1987).

Fractionation factors (ε_p) can then be used to determine the stable carbon isotope composition of bulk algal biomass ($\delta^{13}\text{C}_p$) following the theoretical relationship between the stable isotopic compositions of the carbon source ($\delta^{13}\text{C}_{\text{DIC}}$) and product ($\delta^{13}\text{C}_p$) for photosynthesis:

$$\varepsilon_p = 1000 \cdot \left(\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_p \right) / \left(1000 + \delta^{13}\text{C}_p \right) \quad (3)$$

We also estimated the $\delta^{13}\text{C}$ values of two algal FAs found in MPB: $16 : 4n - 1$ (a 16-carbon FA with four double bonds) and $20 : 5n - 3$ (eicosapentaenoic acid, a 20-carbon FA with five double bonds). $16 : 4n - 1$ is known to be synthesized predominantly by diatoms (Dunstan et al., 1994; Viso and Marty, 1993) and $20 : 5n - 3$ by a broader consortium of algal taxa including *Phaeocystis* sp., *Amphidinium* sp., and prasinophytes (Booth and Horner, 1997; Tang et al., 2001; Viso and Marty, 1993). We modeled $\delta^{13}\text{C}_{\text{FA}}$ from bulk $\delta^{13}\text{C}_p$ values by applying the isotopic offset (Δ) between reported values for bulk algal biomass ($\delta^{13}\text{C}_p$) and individual FAs ($\delta^{13}\text{C}_{\text{FA}}$) (McMahon et al., 2006) that range from 6.2–7.9‰ due to differences among distinct FAs ($16 : 4n - 1$ and $20 : 5n - 3$) and variation in the offset that may result from lipid-extracted (McMahon et al., 2006) and non-lipid extracted TOC (Wang et al., 2013). We selected a mean Δ of 7‰ as a best estimate to determine $\delta^{13}\text{C}_{\text{FA}}$ from $\delta^{13}\text{C}_p$. $\delta^{13}\text{C}_{\text{FA}}$ for $16 : 4n - 1$ and $20 : 5n - 3$ were calculated by subtracting Δ from our estimates of the $\delta^{13}\text{C}$ value of MPB TOC

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($\delta^{13}\text{C}_p$):

$$\delta^{13}\text{C}_{\text{FA}} = \delta^{13}\text{C}_p - \Delta \quad (4)$$

We subsequently modeled $\delta^{13}\text{C}_{\text{FA}}$ from a mixed microphytobenthic algal community at $\mu \approx 0$, from a centric diatom sp. at $\mu = 0.1\text{ d}^{-1}$, and from a pennate sp. at $\mu = 0.1, 0.8,$ and 1.4 d^{-1} . Significant differences between $\delta^{13}\text{C}_p$ values estimated for *P. tricornutum* at each growth rate were tested using a one-way analysis of variance (ANOVA) with growth rate as the factor.

3 Results

$[\text{CO}_2]_{\text{aq}}$ ranged from $17\text{--}72\ \mu\text{mol kg}^{-1}$ and $\delta^{13}\text{C}_{\text{DIC}}$ values varied from -0.1 to 1.4% (0.8 ± 0.4 , mean ± 1 s.d.) for samples of bottom water at our sampling locations in the Beaufort and Chukchi Seas. The lowest $[\text{CO}_2]_{\text{aq}}$ were observed near the mouth of the Mackenzie River and corresponded to the highest $\delta^{13}\text{C}_{\text{DIC}}$ values (Fig. 1). The highest $[\text{CO}_2]_{\text{aq}}$ was observed in Barrow Canyon and corresponded to the lowest $\delta^{13}\text{C}_{\text{DIC}}$ value. For sites at depths shallower than 200 m, there was an inverse correlation between $\delta^{13}\text{C}_{\text{DIC}}$ and depth ($r = -0.89$, $n = 14$). Samples from Barrow Canyon did not follow this depth gradient.

Modeled $\delta^{13}\text{C}_p$ values of eukaryotic MPB ranged from -24.5 to -23.1% ($\delta^{13}\text{C}_p^a = -23.6 \pm 0.4\%$) (Table 1, Fig. 2). Based on a low algal growth rate ($\mu = 0.1\text{ d}^{-1}$) and our field measurements of $[\text{CO}_2]_{\text{aq}}$ and $\delta^{13}\text{C}_{\text{DIC}}$, our modeled $\delta^{13}\text{C}_p$ values were highest for the centric diatom (*P. glacialis*, $\delta^{13}\text{C}_p^b = -20.0 \pm 1.6\%$), relative to those for the haptophyte (*E. huxleyi*, $\delta^{13}\text{C}_p^c = -22.7 \pm 0.5\%$, mean ± 1 s.d.), and the pennate diatom species (*P. tricornutum*, $\delta^{13}\text{C}_p^d = -23.9 \pm 0.4\%$, mean ± 1 s.d.) (Table 1). Cyanobacterium (*Synechococcus* sp.) $\delta^{13}\text{C}_p$ values were distinct from the eukaryotic

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algal taxa ($-16.2 \pm 0.4\text{‰}$). Modeled values for algal FAs ($\delta^{13}\text{C}_{\text{FA}}$) from centric and pennate diatoms at the lowest growth rate ($\mu = 0.1 \text{d}^{-1}$) were -27.0‰ and -30.9‰ , respectively. For the pennate diatom species, each successive increase in μ resulted in significantly higher $\delta^{13}\text{C}_p$ values (one-way ANOVA, $F = 37.32$, $p < 0.001$) and, by extension, $\delta^{13}\text{C}_{\text{FA}}$ values, with an increase of 2.5‰ over the growth range of $\mu = 0.1$ to 1.4d^{-1} . $\delta^{13}\text{C}_{\text{FA}}$ values increased slightly to -29.5‰ and to -28.4‰ at the intermediate and maximum μ (0.8d^{-1} and 1.4d^{-1} , respectively).

4 Discussion

MPB, a potential source of primary production to benthic food webs (Alderson et al., 2013; Glud et al., 2009; McTigue and Dunton, 2013; Oakes et al., 2010), has rarely been considered in stable isotopic food web studies in the Arctic because it has not been described isotopically. Here, we estimated the $\delta^{13}\text{C}$ values for TOC ($\delta^{13}\text{C}_p$ values) as well as two algal FAs ($\delta^{13}\text{C}_{\text{FA}}$ values of the FAs $16:4n-1$ and $20:5n-3$) derived from MPB for consideration in future arctic food web analyses. The $\delta^{13}\text{C}_p$ values of mixed community MPB at growth rates approaching zero had a narrow isotopic range ($\delta^{13}\text{C}_p^a = -24.5$ to -23.1‰) across our sampling locations in the Chukchi and Beaufort Seas (Fig. 2). The mean value ($\delta^{13}\text{C}_p^a = -23.6 \pm 0.4\text{‰}$) was higher relative to previously reported values of terrigenous TOC, including benthic-POM (b-POM) from river sediments and pelagic-POM (p-POM) from arctic rivers and lagoons feeding into the Beaufort Sea (Fig. 2, color symbols). The mean $\delta^{13}\text{C}_p$ value for mixed community MPB was lower relative to ice algae and from sea ice particulate organic matter (i-POM). Although MPB $\delta^{13}\text{C}_p$ was higher than marine p-POM from regions of low productivity such as the Canada Basin, it fell between reported ranges for most values for marine p-POM from the Beaufort and Chukchi Seas and from neighboring regions in the Arctic (Fig. 2).

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In addition to TOC $\delta^{13}\text{C}$ values, food web studies can also utilize fatty acid stable carbon isotope analysis to constrain source contributions with unique stable isotopic signatures to the sediment organic pool (Goni et al., 2005; Tolosa et al., 2013) and to higher trophic level organisms (Budge et al., 2008). The FAs $16:4n-1$ and $20:5n-3$ are useful algal biomarkers because they are produced predominantly by diatoms (Dunstan et al., 1994; Viso and Marty, 1993) and pennate diatoms are the dominant taxa comprising MPB in the Beaufort Sea (Glud et al., 2009; Horner and Schrader 1982; Matheke and Horner, 1974). The mean $\delta^{13}\text{C}_{\text{FA}}$ values for $20:5n-3$ from the pennate diatom we investigated ($\delta^{13}\text{C}_{\text{FA}}^d = -30.9 \pm 0.4\text{‰}$) and from the mixed eukaryotic algal consortium ($\delta^{13}\text{C}_{\text{FA}}^a = -30.6 \pm 0.4\text{‰}$) were higher relative to terrestrial p-POM sources and were relatively lower than those from ice algae and i-POM sources (for both FAs) from a broad region, including the Bering Sea (Wang et al., 2013), the Beaufort Sea (Budge et al., 2008), and the Greenland Sea (McMahon et al., 2006) (Fig. 2). Modeled values for $\delta^{13}\text{C}_{\text{FA}}$ for our algal FA biomarkers ($\delta^{13}\text{C}_{\text{FA}} = -25.9$ to -27.9‰ and -29.9 to -31.9‰ for centric and pennate diatom species, respectively) overlapped with reported values for $16:4n-1$ and $20:5n-3$ from p-POM in the Arctic and sub-Arctic (Budge et al., 2008).

Given the distinct $\delta^{13}\text{C}$ values for MPB TOC and FAs, future research could seek to discern the proportional contribution of these sources to sediments and benthic consumers following an approach outlined by Phillips and Gregg (2003) and Phillips (2012) by combining certain sources (e.g., marine pelagic and MPB-derived FAs). Bayesian mixing models (Moore and Semmens, 2008; Parnell et al., 2010; Solomon et al., 2011) could also be employed to determine the likely probabilities of the terrigenous, p-POM + MPB and i-POM sources to components of the arctic marine ecosystem. The overlapping range of $\delta^{13}\text{C}$ values for MPB and p-POM suggest that stable carbon isotope values from benthic organisms previously ascribed to p-POM could have originated from two different sources, notably p-POM and/or MPB. In this case, relationships between food web structure and productivity, typically only measured as p-POM, may be invalid.

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There are a number of factors that can influence the range of $\delta^{13}\text{C}$ values of primary production in the marine environment (Freeman and Hayes, 1992; Fry and Wainright, 1991; Laws et al., 1995; Rau et al., 1996). Estimates of $\delta^{13}\text{C}_p$ and $\delta^{13}\text{C}_{FA}$ values from MPB primarily rely on both the availability and isotopic composition of the carbon source ($[\text{CO}_2]_{aq}$ and $\delta^{13}\text{C}_{DIC}$ in bottom water) (Freeman and Hayes, 1992; Freeman et al., 1994). $\delta^{13}\text{C}_{DIC}$ values have been described for surface waters in the world ocean as part of the Geochemical Ocean Sections (GEOSECS) program (Gruber et al., 1999) and, more recently, at varying depths in the Ocean (Griffith et al., 2012). Global measurements of $\delta^{13}\text{C}_{DIC}$ values, which are highly consistent across regions ($\delta^{13}\text{C}_{DIC} = 1.5 \pm 0.8\%$), were higher than those observed in our study ($\delta^{13}\text{C}_{DIC} = 0.8 \pm 0.4\%$). Griffith et al. (2012) reported a range of $\delta^{13}\text{C}_{DIC}$ values (0.13–1.63%) from off-shelf sites in the Canada Basin that are consistent with those we observed. Our study contributes a unique dataset by describing $\delta^{13}\text{C}_{DIC}$ values from arctic bottom water under ice-free waters and complements published full-depth profiles of $\delta^{13}\text{C}_{DIC}$ values from the adjacent Canada Basin in the Arctic Ocean (Griffith et al., 2012). Although we report some variability in $\delta^{13}\text{C}_{DIC}$ values and $[\text{CO}_2]_{aq}$ across our study region, the ranges have little influence ($\sim 1.6\%$) on modeled $\delta^{13}\text{C}_p$ values of pennate diatoms, a likely dominant algal constituent of MPB (Horner and Schrader, 1982), or on the mixed algal eukaryotic consortium ($\sim 1.5\%$) (Table 1). Variation in $\delta^{13}\text{C}_{DIC}$ values can be explained by processes involving preferential uptake of the light stable isotope of carbon (^{12}C) (e.g., biological production) and those that release it into the DIC pool (e.g., carbon remineralization) (Gruber et al., 1999; Holmden et al., 1998) and by contributions from isotopically distinct sources such as terrigenous DIC (Macdonald et al., 2004). In the marine environment, biological production and carbon remineralization occur largely in surface waters and at the seafloor, respectively, creating a depth-dependent gradient in $\delta^{13}\text{C}_{DIC}$ values (Emerson and Hedges, 2008).

DIC measurements from this study revealed statistically significant depth-dependent gradients in $[\text{CO}_2]_{aq}$ and $\delta^{13}\text{C}_{DIC}$ values consistent with reported trends (Emerson and

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Hedges, 2008), wherein deeper sites contained higher $[\text{CO}_2]_{aq}$ and lower $\delta^{13}\text{C}_{DIC}$ values relative to shallower sites. An exception to this pattern was the Barrow Canyon transect, which is hydrographically and biologically distinct from the other Beaufort shelf sites. Barrow Canyon is a major channel for Pacific water inflow into the Arctic Ocean and, as such, is an active upwelling region (Pickart et al., 2009). This subsequently raises levels of secondary production and carbon remineralization (Hill and Cota, 2005). In regions of elevated carbon remineralization, we might expect MPB $\delta^{13}\text{C}$ values to be low due to the prevalence of isotopically light DIC.

$\delta^{13}\text{C}_{DIC}$ values can be a useful indicator of DIC source given observed differences in $\delta^{13}\text{C}_{DIC}$ values from terrigenous and marine sources (Patterson and Walter, 1994). To this end, one might have expected the Mackenzie River delta transect, where terrestrial organic material enters the Arctic Ocean (Macdonald et al., 2004) to have the lowest $\delta^{13}\text{C}_{DIC}$ values. Contrary to this expectation, $\delta^{13}\text{C}_{DIC}$ values at the Mackenzie River delta were most isotopically enriched in ^{13}C relative to other sampling locations. These relatively high $\delta^{13}\text{C}_{DIC}$ values corresponded with the lowest $[\text{CO}_2]_{aq}$, possibly indicating that elevated benthic primary production resulted in subsequent depletion of $[\text{CO}_2]_{aq}$ and drawdown of isotopically light DIC.

In addition to $\delta^{13}\text{C}$ values of MPB being influenced by characteristics associated with the carbon source (concentration and $\delta^{13}\text{C}_{DIC}$ values), $\delta^{13}\text{C}$ values of primary producers in the marine ecosystem can also be influenced by algal growth rate which is often mediated by environmental conditions, such as light and nutrient availability (Fry and Wainright, 1991; Korb et al., 1996; Pancost et al., 1997). We determined that within a selected growth range, $\delta^{13}\text{C}_p$ and $\delta^{13}\text{C}_{FA}$ values for the dominant algal constituent of MPB (pennate diatoms) increased on the order of approximately -2.5% . This indicates that isotopic values for MPB may vary seasonally but within a relatively small range (Fig. 2). Seasonal variability in $\delta^{13}\text{C}_p$ and $\delta^{13}\text{C}_{FA}$ values may be more pronounced if algal community succession occurs in the benthos as in the pelagic realm during the course of the growing season (Moran et al., 2012) because individual taxa had distinct modeled values (Table 1).

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Isotopic measurements from isolated MPB from the same study region or those with similarly described DIC pools could help verify our modeled values. These measurements could serve as a calibration to observe model behavior and adjust regression relationships used to model $\delta^{13}\text{C}_p$ values and, by extension, $\delta^{13}\text{C}_{\text{FA}}$ values. In summary, we provide estimates of the $\delta^{13}\text{C}$ values of TOC and algal FAs originating from MPB in the Arctic. We also report a narrow distribution of $\delta^{13}\text{C}$ values of DIC and provide measurements of $[\text{CO}_2]_{\text{aq}}$ from bottom water across the Beaufort and Chukchi Seas during the onset of winter. Based on published $\delta^{13}\text{C}$ values of TOC and FAs from other sources of primary production in the Arctic and sub-Arctic, we conclude that the $\delta^{13}\text{C}$ values of MPB may be distinct from those of terrigenous and sympagic origins, and from marine p-POM under conditions of low productivity. However, the stable carbon isotope composition of MPB was indistinguishable from that of marine p-POM, which may cause MPB to be overlooked as an important source of carbon to the benthic community.

Supplementary material related to this article is available online at <http://www.biogeosciences-discuss.net/10/18151/2013/bgd-10-18151-2013-supplement.pdf>.

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Table 1. Estimates of ϵ_p and $\delta^{13}C_p$ values for MPB based on measured $\delta^{13}C_{DIC}$ values and calculations of $[CO_2]_{aq}$ measured in bottom water in the Beaufort Sea.

Station	Water depth (m)	$\delta^{13}C_{DIC}$	$[CO_2]_{aq}$	$\delta^{13}C_p^a$	ϵ_p^b	$\delta^{13}C_p^b$	ϵ_p^c	$\delta^{13}C_p^c$	ϵ_p^d	$\delta^{13}C_p^d$
9	47	1.0	18	-23.4	19.2	-17.8	23.8	-22.2	25.2	-23.6
14	112	-0.1	72	-24.5	24.0	-23.5	24.4	-23.9	25.4	-24.9
17	66	0.2	43	-24.2	22.9	-22.2	24.3	-23.5	25.4	-24.5
23	33	1.1	19	-23.3	19.6	-18.1	23.9	-22.3	25.2	-23.5
26	55	1.2	17	-23.3	19.1	-17.6	23.8	-22.1	25.2	-23.4
28	165	0.5	33	-23.9	22.1	-21.2	24.2	-23.2	25.3	-24.3
48	134	0.5	23	-23.9	20.7	-19.8	24.0	-23.0	25.3	-24.2
49	346	0.8	23	-23.6	20.7	-19.5	24.0	-22.7	25.3	-23.9
50	284	0.9	27	-23.5	21.4	-20.1	24.1	-22.7	25.3	-23.8
52	172	0.6	36	-23.8	22.4	-21.3	24.2	-23.0	25.4	-24.1
53	132	0.6	42	-23.8	22.8	-21.7	24.3	-23.1	25.4	-24.1
55	75	0.9	28	-23.6	21.5	-20.2	24.1	-22.7	25.3	-23.8
57	60	0.8	30	-23.6	21.8	-20.6	24.1	-22.8	25.3	-23.9
59	54	0.9	30	-23.5	21.8	-20.4	24.1	-22.7	25.3	-23.8
68	50	1.0	27	-23.4	21.3	-19.9	24.1	-22.6	25.3	-23.7
69	42	1.3	20	-23.1	20.0	-18.3	23.9	-22.1	25.2	-23.4
70	35	1.3	20	-23.2	20.0	-18.3	23.9	-22.1	25.2	-23.4
71	28	1.4	21	-23.1	20.3	-18.5	24.0	-22.1	25.3	-23.3
mean		0.8	30	-23.6	21.2	-20.0	24.1	-22.7	25.3	-23.9
1 standard deviation		0.4	13	0.4	1.4	1.6	0.2	0.5	0.1	0.4

^a Mixed microeukaryotic community.

^b Centric diatom (*P. glacialis*).

^c Haptophyte (*E. huxleyi*).

^d Pennate diatom (*P. tricorutum*).

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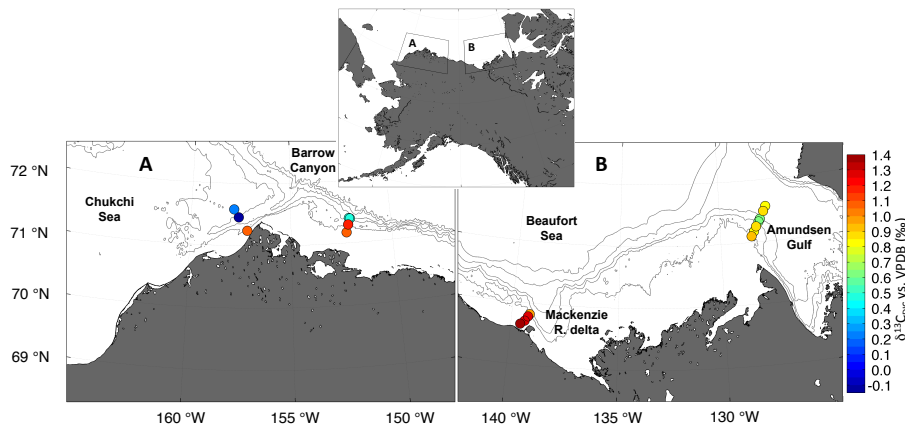


Fig. 1. $\delta^{13}\text{C}_{\text{DIC}}$ values (‰) measured from bottom water (~ 5 m from sediment-water interface) at sampling locations in the Beaufort and Chukchi Seas for seawater collection and CTD casts.

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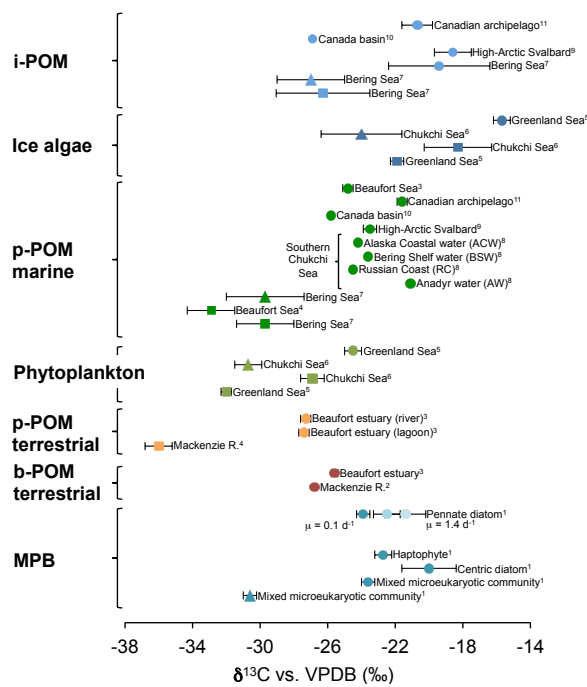


Fig. 2. $\delta^{13}\text{C}$ (‰) values for TOC (circles), 20 : 5n - 3 (squares), and 16 : 4n - 1 (triangles) from primary production sources in the arctic and sub-arctic marine environment (mean ± 1 s.d.). Particulate organic matter (POM) measured in ice (i-POM), water (p-POM), and sediment (b-POM) from the marine and terrestrial environment (¹ this study, ² Naidu et al. (2000), ³ Dunton et al. (2012), ⁴ Tolosa et al. (2013), ⁵ McMahon et al. (2006), ⁶ Budge et al. (2008), ⁷ Wang et al. (2013), ⁸ Iken et al. (2010), ⁹ Soreide et al. (2013), ¹⁰ Iken et al. (2005), ¹¹ Hobson and Welch, 1992).

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