Research papers

Molecular and isotopic insights into particulate organic carbon sources and dynamics in Jordan Basin, Gulf of Maine

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ABSTRACT

The carbon isotope and lipid biomarker composition of suspended particles and surface sediment was measured to examine the impact of sediment supply, redistribution and post-depositional alteration processes on organic matter cycling in the Gulf of Maine, a semi-enclosed shelf sea in the northwest Atlantic. A beam attenuation profile revealed a > 50 m-thick benthic nepheloid layer (BNL) in the Jordan Basin at the time of sampling (April 2006). The relatively low radiocarbon content of suspended particulate organic carbon (POC) in the BNL indicates that up to 82% of the POC in this layer was supplied from resuspension of sediment. The concentration of alkenones normalized to POC increased with increasing depth in the water column and was highest in the surface sediment. In contrast to these markers of surface ocean photoautotrophy, the vertical profiles for the concentration and composition of short-chain (C_{14}–C_{18}) n-alkanoic acids provided evidence for enhanced heterotrophic processes near the top of the BNL. Suspended POC samples from two depths within the BNL exhibited marked differences in radiocarbon content and fatty acid composition, suggesting that biological activity and associated processes within the BNL are vertically heterogeneous.

1. Introduction

The Gulf of Maine is a semi-enclosed continental shelf sea bordering the Northwest Atlantic Ocean (Fig. 1). It has two major basins deeper than 200 m: the Jordan Basin in the northeast and the Wilkinson Basin in the southwest of the Gulf. Slope water enters the gulf through the Northeast Channel and mixes with Scotian Shelf water (Mountain and Jessen, 1987). This mixture circulates counterclockwise, filling the Jordan Basin and Wilkinson Basin, and exits the gulf via the Great South Channel and the northern boundary of Georges Bank.

A pronounced benthic nepheloid layer (BNL) is known to persist in the Gulf of Maine (Spinrad, 1986; Townsend et al., 1992; Pilskaln et al., 1998, 2013a, 2013b). In the Jordan Basin, this BNL is influenced by tidal mixing and inflow of the slope water (Townsend et al., 1992). Locally, strong tidal currents (> 50 cm/s) measured near the northern edge of the Jordan Basin may transport mud to the basin (Moody et al., 1984; Pilskaln et al., 2013a, 2013b). Another study suggested

that the BNL in the Jordan Basin may be maintained by sediment influx from the Bay of Fundy based on mineralogical and textural data (Pilskaln et al., 1998). In addition to natural processes, bottom trawling results in anthropogenic sediment resuspension. This heavy trawling is particularly pronounced in the Wilkinson Basin, the western part of the gulf and Georges Bank (Pilskaln et al., 1998).

The BNL represents an interface through which POC produced in surface waters must pass before it is deposited and removed from the carbon cycling in the water column. It is particularly important to understand the role of BNLs in carbon cycling on the continental shelf where primary productivity is high, where POC can be supplied from terrestrial and marine sources, and where the proportion of materials exported from surface waters that reaches the seafloor is comparatively high because of short vertical travel distance (Pilskaln et al., 2013a, 2013b). Sediment resuspension processes have many implications for the biogeochemistry and fate of particulate matter in the BNL, such as organic matter degradation and subsequent release of nutrients to the water column and lateral dispersal (Pilskaln et al., 1998, 2013b). For example, resuspension of sediment facilitates degradation of organic matter by aerobic bacteria, and heterotrophic consumption by zooplankton and suspension feeders. Prior studies of the nature of organic matter in the BNL have shown that particulate

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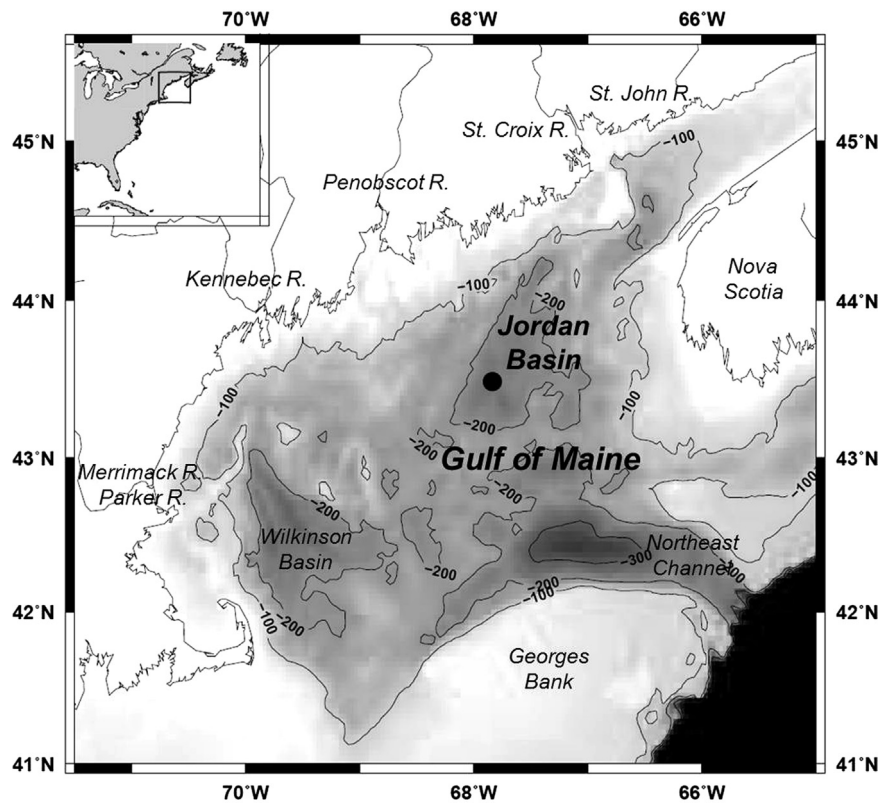E-mail address: jhwang@postech.ac.kr (J. Hwang).

Fig. 1. A map showing the study site and sampling location in the Gulf of Maine.

organic carbon (POC) was relatively labile, suggesting that the BNL represented a zone of enhanced biological activity (Townsend et al., 1992 and references therein). However, it is not well understood whether the relatively labile nature of POC is because it originates from the resuspension of recently deposited unconsolidated organic matter residing at the water–sediment interface (Lampitt, 1985) or because refractory, resuspended POC is rendered labile by heterotrophic activity.

Radiocarbon content, expressed as $\Delta^{14}C$, of organic matter can be influenced by aging processes and/or by incorporation of carbon of a different $\Delta^{14}C$ value ($\Delta^{14}C$ is an isotopic fractionation-corrected $^{14}C/^{12}C$ ratio of a sample relative to a standard; Broecker and Olson, 1959; Stuiver and Polach, 1977). In cases where the timescales of processes are short (< 40 years) relative to the half-life of ^{14}C (5730 years), $\Delta^{14}C$ variations as a consequence of aging can be ignored within the uncertainty of the $\Delta^{14}C$ measurement ($\pm 5\permil$). However, resuspension of POC from a significantly pre-aged sediment source can alter the $\Delta^{14}C$ value of the suspended POC pool in the overlying water column (Druffel et al., 1998). Heterotrophy and transfer of carbon through a food chain do not alter this $\Delta^{14}C$ value. Combined analysis of $\Delta^{14}C$ with compositional analysis of lipid biomarkers diagnostic of POC source and degradation can shed light on the sources of organic matter and its subsequent alteration within the BNL. For example, n-alkanoic acids may be derived from diverse sources and their distribution can provide clues regarding organic matter sources in suspended POC and sediment on the continental shelf. Long-chain n-alkanoic acids that originate from terrestrial organic matter (Eglinton and Hamilton, 1967) are prominent in shelf sediments because of the proximity to continental sources (Mollenhauer and Eglinton, 2007). Short-chain n-alkanoic acids that are considered more labile than the long-chain counterparts are produced not only by phytoplankton in the euphotic zone but also by zooplankton and bacteria at depth. Hence, their composition in suspended POC often reflects heterotrophic activity. In comparison,

alkenones are exclusively produced by haptophytes that grow in the euphotic zone and therefore they enter the suspended POC pool via supply from above or from sediment resuspension at depth. In addition, alkenone-derived temperatures provide constraints on the seasonal timing of production, the major source(s), and hence, turnover time of POC within the water column (Hwang et al., 2009, submitted). Taking advantage of these different ^{14}C and biomarker characteristics of suspended POC, we adopted a two-pronged approach to examine biogeochemical processes occurring within the BNL of the Jordan Basin. This study forms a part of a larger study to understand the role of BNLs in modulation of particulate organic matter delivery and composition on the continental margins.

2. Methods

Samples were collected during a cruise (OCE 422) aboard the R/V Oceanus from April 20 to April 24 in 2006 in the Jordan Basin (43.49 °N, 67.84 °W; water depth=285 m) in the Gulf of Maine. We deployed in situ filtration devices (LVPs, McLane Research Laboratories, Inc.) equipped with pre-combusted 142 mm diameter glass fiber filters (Whatman GF/F, nominal pore size=0.7 μm) at five depths, and collected four suspended particle samples (one unit failed) (Table 1). The volume of seawater filtered (between 460 and 720 l) was determined from the flow meter of each filtration unit. Suspended particles in surface water were also collected by filtration of water from the ship's uncontaminated seawater intake (2 m nominal depth) using 293 mm diameter filters (Gelman Science, type A/E glass fiber, nominal pore size=1.0 μm). The filters were stored frozen until further analysis. A multicore sediment sample (43.41°N, 67.41°W, 285 m water depth) collected during a cruise (OCE 400) in April 2004 aboard the R/V Oceanus was stored frozen and was used for isotope and biomarker analyses.

Table 1
Biogeochemical properties of the suspended particle and sediment samples collected from the Jordan Basin, Gulf of Maine.

Depth (m)	Volume filtered (L)	POC (µgC/L)	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	$U^{k'}_{37}$	Alkenone temp. (°C)	Alkenone conc. (ngC/L)	Alkenone conc. (µgC/gPOC)	FAME (ngC/L)	FAME mgC/gPOC	Long-chain FA (%)
2			30	−21.2	0.253	6.2					
40	605	9.3	21	−21.0	0.245	6.0	0.07	7	88	9.5	2
120	464	11.7	18	−19.8	0.300	7.6	0.13	11	56	4.8	5
235	537	10.9	−91	−20.7	0.399	10.6	0.17	15	207	22	2
260	724	0.9	−171	−22.1	0.388	10.3	0.02	25	5	5.7	14
Sediment 0–1 cm		1.90 wt%	−214	−22.1	0.358	9.4	1.1 µgC/g sediment	58	2.3 µgC/g sediment	0.12	79
Sediment 1–2 cm		1.99 wt%	−226	−22.0	0.378	9.9	1.2 µgC/g sediment	60	No data	No data	No data

Details on sample treatment and determination of $\Delta^{14}C$, alkenones, and n-alkanoic acids are described elsewhere (Hwang et al., 2009). Briefly, a quarter of each filter was freeze-dried and used for quantification of POC concentration and carbon isotope analyses. POC concentration was determined by manometric measurement of the volume of CO_2 gas produced by closed-tube combustion of filter samples pre-treated to remove inorganic carbon. Carbon isotopic measurements were made on the resulting CO_2 gas at the National Ocean Sciences Accelerator Mass Spectrometry facility at Woods Hole Oceanographic Institution using standard techniques (McNichol et al., 1994). The $\Delta^{14}C$ values were not blank-corrected. The amount of procedural blank carbon associated with sample combustion was 4.3 µgC (± 1.9, $n=7$) based on the processing of pre-combusted GF/F filters. In the worst case scenario (*i.e.*, if the blank carbon was ^{14}C-free), incorporation of ^{14}C-dead carbon blank would result in at most as 23‰ decrease in $\Delta^{14}C$ for the 260 m sample because of the small size of the processed sample (154 µgC), but less than 3‰ for the other samples (sample amounts were larger than 1350 µgC). For blank-correction, Griffith et al. (2012) used the amount of blank carbon and its $\Delta^{14}C$ value of a GF/F filter that was retrieved from an *in situ* pump that was deployed to 3805 m in the Arctic Canada Basin but failed to pump. If this type of blank-correction was applied under the assumption that the amount and the $\Delta^{14}C$ value of inclusive procedural blank were the same, the correction would be between −2 and −8‰ for our samples. The empirical precision for $\Delta^{14}C$ and $\delta^{13}C$ measurements for this type of samples in our laboratory based on multiple duplicate analyses is smaller than ± 10‰ and ± 0.1‰, respectively.

For lipid biomarker analyses, one half or three quarters of each filter was subjected to accelerated solvent extraction (DIONEX, ASE200) using a dichloromethane:methanol (93:7 v:v) mixture in February 2007. After saponification of each dried extract, the neutral fraction containing alkenones was extracted into hexane phase. A ketone fraction was separated by column chromatography and this fraction was injected into an HP-5890II gas chromatograph (GC) equipped with a capillary column (Varian, CP-SIL 5CB, 30 m × 0.25 mm ID × 0.25 µm film thickness) and a flame ionization detector (FID) for determination of alkenones. The acid fraction containing fatty acids was extracted into an apolar phase (hexane:dichloromethane, 4:1 v/v) after acidification to pH of 1–2 with HCl. The latter fraction was stored ($-10\ ^\circ$C) until fatty acid analysis in January 2008. Fatty acids were quantified as fatty acid methyl esters (FAMEs) by GC/FID. Individual n-alkanoic acids were identified using a Supelco FAME standard. The long-chain fatty acid index (%) was defined as the ratio of the sum of the long-chain even-numbered n-alkanoic acids (n-$C_{24:0}$–n-$C_{30:0}$) to the total even-numbered ones (n-$C_{14:0}$–n-$C_{30:0}$) (Bourbonniere and Meyers, 1996).

Beam attenuation and fluorescence data were obtained by a transmissometer (C-STAR, WET Labs, Inc.; 25 cm path length) and a fluorescence sensor (WET Labs, Inc., ECO-AFL/FL; 470/695 nm wavelengths were used for excitation/emission), respectively, attached to the CTD-Rosette system. These data were mainly used for qualitative comparison.

3. Results

The temperature profile at the time of sampling in the Jordan Basin showed that stratification with a distinct surface layer had begun to develop in response to warmer air temperatures (Fig. 2a). A remnant cold water layer was evident as the Intermediate Water centered at around 70 m. The Bottom Water, defined as the water whose salinity is higher than 34 (Townsend et al., 1992), occupied depths greater than 146 m.

The beam attenuation coefficient was low and almost constant down to about 200 m except for slightly higher values at around 80 m coinciding with the depth of the Intermediate Water (Fig. 2). The beam attenuation coefficient increased dramatically from immediately below 210 m to the sea floor, reflecting the presence of a thick BNL (for transects of beam attenuation coefficient in October 2004 in the Gulf of Maine, see Fig. 2 in Pilskaln et al., 2013b). Fluorescence intensity was the highest in the surface mixed layer and decreased down to about 120 m and remained constant, then increased from 260 m to the bottom. It is notable that the beam attenuation was low in the surface mixed layer whereas fluorescence was considerably higher (Fig. 2b). In comparison, at the bottom 20 m layer, both beam attenuation and fluorescence exhibited higher values than in the immediately overlying water column.

POC concentration (as determined by large volume filtration) at 40 m and 120 m was similar, with values of 9 and 12 µgC/L, respectively. The uniformly low values at these depths correspond well with the beam attenuation data. Time series of chlorophyll-*a* (chl-a) obtained from four GoMOOS buoys (Pettigrew et al., 2008 cited in Jönsson et al., 2011) showed concentrations were highest in late February and early March and remained low until the sampling time in 2006. Therefore, our suspended POC sampling occurred when surface chl-a concentrations were relatively low. Two of the suspended POC samples were collected within the BNL, one at near the top of the BNL (235 m) and one at 25 m above the bottom (260 m). The POC concentration at the top of the BNL was similar to that in the overlying water column whereas that at 25 m above the bottom was markedly lower (~ 1 µgC/L). Although several-fold higher than those observed in the adjacent New England slope (Hwang et al., 2009), the POC concentrations were 3–10 times (up to two orders of magnitude in the case of 260 m sample) lower than previously reported values for this region, albeit obtained from filtration of much smaller volumes of seawater (Townsend et al., 1992; Gardner et al., 2003). Another set of
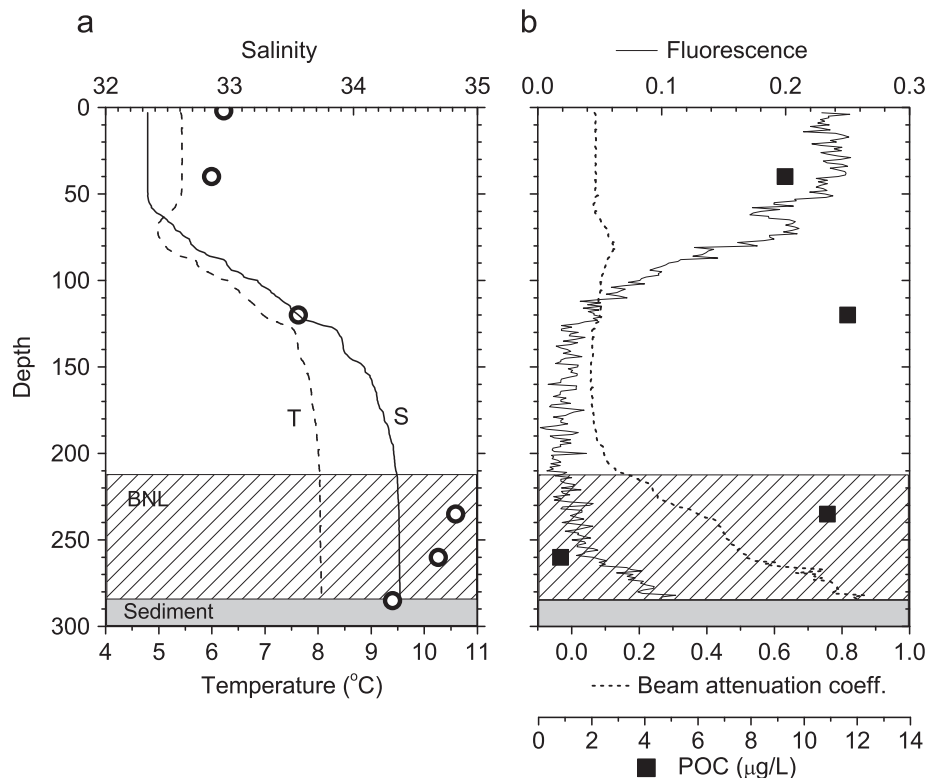
Fig. 2. Vertical profiles of (a) temperature (dashed line), salinity (solid line), and alkenone-derived temperature (open circles) and (b) beam attenuation coefficient (dashed line), fluorescence (solid line), and POC concentration (closed squares).

POC concentration data obtained by large volume filtration in Jordan Basin in March 1995 showed that POC concentrations ($> 0.7\ \mu m$) were higher than 12 μgC/L (Charette et al., 2001) in the upper 150 m of the water column.

The minimum value for POC concentration obtained from the 260 m sample, recovered from within 25 m of the sea floor, is puzzling. The color of the corresponding filter was visibly paler in comparison to those recovered from the other depths which were covered with thick brown material. There is no evidence that the *in situ* filtration unit did not function properly, so this low value at 260 m may be a true reflection of the POC concentration at this depth at the time of sampling. Townsend et al. (1992) also observed disagreement between beam attenuation and suspended particulate matter in the Gulf of Maine and suggested that factors such as particle size distribution and/or particle type may affect the correlation between the two in the BNL. In fact, Townsend et al. (1992) found the lowest suspended particulate matter loads at a station in the western Jordan Basin where the highest beam attenuation was observed among the BNLs sampled. However, we focus our discussion on properties relative to POC rather than absolute concentration in seawater in order to remove effects of fluctuation in particle concentration (Wakeham, 1995).

The radiocarbon content of suspended POC (expressed as $\Delta^{14}C$) at the surface and at 40 m was similar (30‰ and 21‰, respectively), indicating relatively uniform composition within the surface mixed layer (Fig. 3). The $\Delta^{14}C$ value of POC at the surface is consistent with the GLODAP data based on the late 1980s measurements of dissolved inorganic carbon (Key et al., 2004). While the $\Delta^{14}C$ value of POC at 120 m (18‰) was not significantly different from the values in the overlying water column (Fig. 3), $\Delta^{14}C$ values of POC within the BNL were considerably lower (−91‰ and −171‰ at 235 m and 260 m, respectively). It is notable that $\Delta^{14}C$ value at 260 m was lower than that at 235 m by 80‰ despite the fact that the sampling depths were only 25 m apart. The $\Delta^{14}C$ value at 260 m approached the value of the underlying
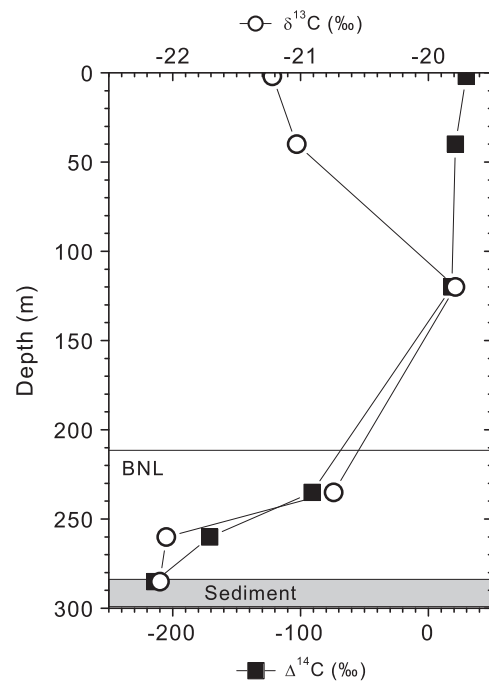
Fig. 3. Vertical distributions of $\Delta^{14}C$ and $\delta^{13}C$ values of bulk suspended POC and surface sediment.

core-top sediment (0–1 cm), −214‰. Notably, these $\Delta^{14}C$ values in the BNL are significantly lower than those of suspended POC collected at 20–40 m above the bottom on the New England slope at total water depths of 2500–3500 m (−23 to −77‰; Hwang et al., 2009).

The $\delta^{13}C$ values of all suspended POC samples varied within a relatively narrow range (−19.8‰ to −22.1‰; Fig. 3), and are similar

to those observed for both suspended POC and surface sediments on the New England slope (Hwang et al., 2009). The $\delta^{13}C$ values at 120 m and 235 m were slightly higher than other values while that at 260 m was the lowest in the water column and identical to that of the core-top sediment (−22.1‰). The $\delta^{13}C$ values of both suspended POC and core-top sediment indicate that the organic matter in the Gulf of Maine is dominantly marine in origin. POC supplied via rivers is expected to have considerably lower $\delta^{13}C$ values in this region because of the C_3-dominated vegetation in the adjacent drainage basin as well as because of aquatic production. Raymond and Hopkinson (2003) measured values near or lower than –30‰ in the Parker River, which drains into the western Gulf of Maine.
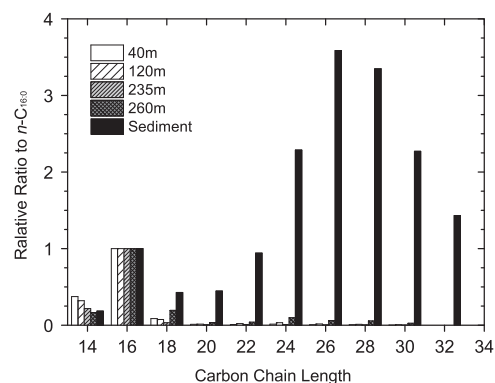
Even-numbered *n*-alkanoic acids were dominant over odd-numbered homologues for both suspended POC and core-top sediment in the Jordan Basin. The ratio of the sum of odd-numbered FAMEs (n-$C_{15:0}$–n-$C_{31:0}$) to the sum of even-numbered ones (n-$C_{14:0}$–n-$C_{30:0}$) was < 10% for suspended POC and ~20% for surface sediment. Concentrations of *n*-alkanoic acids, expressed as the sum of even-numbered FAMEs (n-$C_{14:0}$–n-$C_{30:0}$), ranged between 5 and 22 mgC/gPOC in the POC samples (Fig. 4). These values were 1–2 orders of magnitude higher than that of the core-top sediment, 0.12 mgC/gPOC. Concentration normalized to water volume (ngC/L) exhibited a similar vertical distribution to that of POC-normalized concentration (Fig. 4). With the exception of the sample from 235 m, the concentration of *n*-alkanoic acids appears to decrease with increasing depth. Interestingly, while *n*-alkanoic acid concentration at 235 m depth was several-fold higher than those at other depths, the POC concentration was similar to those in the overlying water column. In the majority of samples, n-$C_{16:0}$ was the most abundant saturated fatty acid homologue in suspended POC followed by n-$C_{14:0}$ then n-$C_{18:0}$ (Fig. 5). The 260 m sample is the exception, where n-$C_{18:0}$ was slightly higher than n-$C_{14:0}$. This observation is consistent with selective accumulation of n-$C_{18:0}$ than n-$C_{14:0}$ and n-$C_{16:0}$ as demonstrated in a feeding experiment (Harvey et al., 1987), and in observations of oceanic suspended POC (Hama, 1999 and references therein). Alternatively, it may indicate an enhanced contribution from zooplankton (Wakeham et al., 1984) and/or bacterial biomass (Volkman et al., 1980b). Long-chain *n*-alkanoic acids (n-$C_{24:0}$–n-$C_{30:0}$) accounted for only a small fraction (< 5%) of the total even-numbered *n*-alkanoic acids of suspended POC, with the exception of the 260 m sample where they accounted for 14% (Figs. 4 and 5). In contrast, the distribution of *n*-alkanoic acids of the core-top sediment was distinct from those of the suspended POC. Long-chain *n*-alkanoic acids were dominant in the core-top sediment, accounting for 79% of the total even-numbered *n*-alkanoic acids (Figs. 4 and 5). In the core-top sediment, concentrations of n-$C_{26:0}$ and n-$C_{28:0}$ were the highest followed by n-$C_{24:0}$ and n-$C_{30:0}$. The concentration of n-$C_{16:0}$ was less than a third of those of n-$C_{26:0}$ and n-$C_{28:0}$. Similar enrichment of long-chain *n*-alkanoic acids was also observed in core-top sediments on the New England slope, where they accounted for 57–74% of total even-numbered *n*-alkanoic acids (Hwang et al., 2009). This observation suggests preferential accumulation or preservation of terrestrial organic matter in Jordan Basin sediments. The Penobscot, Kennebec, St. John, and St. Croix Rivers drain into the Gulf of Maine at 560 m³/s (USGS river discharge data, http://waterdata. usgs.gov/nwis). A fraction of particulate organic matter supplied by these rivers should reach the Jordan Basin, overcoming trapping by estuaries and salt marshes. Alternatively, terrestrial organic matter can be supplied via dominant westerly winds (Flores-Cervantes et al., 2009). The slightly lower $\delta^{13}C$ values of the 260 m sample and core-top sample appear to be consistent with this interpretation. It is important to bear in mind, however, that long-chain *n*-alkanoic acids are only a small fraction of organic matter, and that $\delta^{13}C$ value of bulk POC suggests that marine organic matter was the major overall source of sedimentary organic matter in this region.

C_{37} alkenone concentrations in the water column, expressed as the sum of [$C_{37:2}$] and [$C_{37:3}$] in ngC/L, increased with increasing depth to 235 m, but the value at 260 m was much lower (Fig. 6). The lower alkenone concentration near the surface than at greater depths may reflect low haptophyte productivity during and immediately before the sampling. Alkenone flux in the nearby Wilkinson Basin was reported to be lowest in May and peaked in September in a sediment trap study performed in 1995 (Prahl et al., 2001). If we assume a similar seasonal variability in 2006, low production of alkenones is expected in April. Another sediment trap study on the New England slope (Station W, 39.47 °N, 68.37 °W), showed biannual peaks in alkenone flux, a larger one in August–November 2005 and a smaller one in late April–May 2006 (Hwang et al., submitted for publication). Considering that our study site is located farther north (by ~4 ° meridionally) where spring blooms presumably start later at our site than at
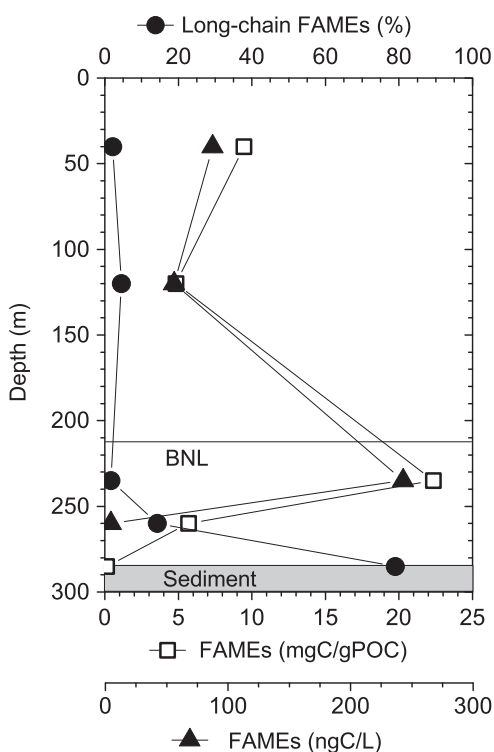
Fig. 4. Concentration of even-numbered *n*-alkanoic acids (n-$C_{14:0}$–n-$C_{34:0}$) in mgC/gPOC and in ngC/L, and % even-numbered long-chain *n*-alkanoic acids (n-$C_{24:0}$–n-$C_{30:0}$) to the total even-numbered *n*-alkanoic acids (n-$C_{14:0}$–n-$C_{30:0}$) in suspended POC and surface sediment.

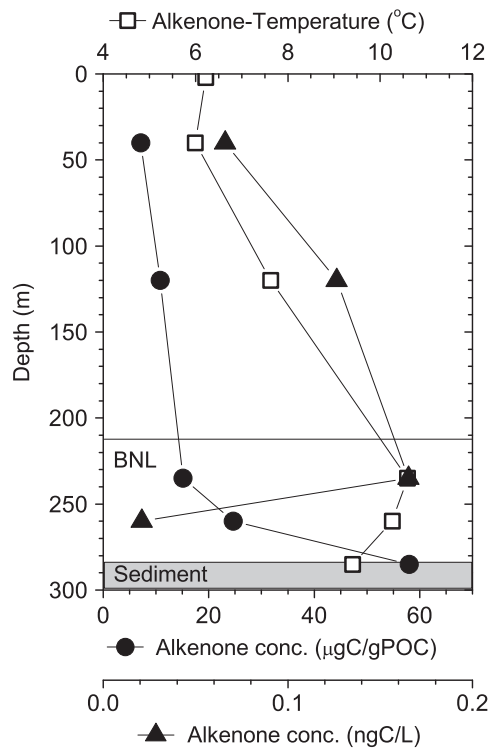**Fig. 5.** Ratios of even-numbered *n*-alkanoic acids, normalized to n-$C_{16:0}$.

Fig. 6. Concentration of $C_{37:2}$ and $C_{37:3}$ alkenones (in µgC/gPOC and in ngC/L), and alkenone-derived temperature based on calibration for core-top sediment by Conte et al. (2006).

Station W, it is likely that our samples were collected prior to a peak in coccolithophore production. The turnover time of alkenones in suspended particles in the upper water column appears to be short enough to reflect the seasonal production cycle. The higher concentrations at greater depth may imply that alkenones in deeper waters have a sufficiently long turnover time to include the periods of higher alkenone production. Organic carbon-normalized C_{37} alkenone concentrations increased with increasing depth, ranging from 7 to 25 µgC/gPOC in the water column, and to 60 µgC/gPOC in the core-top sediment (Fig. 6). The several-fold lower C_{37} alkenone concentrations in suspended POC relative to core-top sediment also suggests low alkenone production in the upper water column at the time of sampling. These values are consistent with the lowest values in sinking POC in the Wilkinson Basin reported from April to early June in 1995 (29–51 µgC/gPOC as the total of C_{37}, C_{38}, and C_{39} alkenones; Prahl et al., 2001) considering that C_{37} alkenones account for 45–60% of C_{37} to C_{39} alkenones (Prahl et al., 2006; Hwang et al., submitted for publication). The C_{37} concentration in the core-top sediment is about one-sixth of the previously measured C_{37} to C_{39} alkenone concentration in a Wilkinson Basin sediment, 351 µgC/gPOC (Prahl et al., 2001). The vertical distribution of alkenone concentrations relative to POC resembles that of long-chain fatty acid index (Fig. 4). Alkenones and long-chain n-alkanoic acids share common characteristics in that they are not produced in the water column below the euphotic depth and are selectively preserved relative to bulk POC (Volkman et al., 1980a; Wakeham et al., 1997).

Alkenone-derived temperatures, estimated using the calibration for core-top sediment by Conte et al. (2006), increased from 6 to 10 °C with increasing depth (shown both in Figs. 2a and 6). In the surface mixed layer, the alkenone-temperatures were within 1 °C of the measured water temperature at the corresponding depth, which is smaller than the uncertainty of the alkenone-temperature estimation (Conte et al., 2006). The highest alkenone-temperature in the water column was observed in the BNL and this value was slightly (by 0.9 °C) higher than that of core-top sediment (9.4 °C). The measured

alkenone-temperature of the core-top sediment was identical to the published values at other locations in the Gulf of Maine (Prahl et al., 2001). The satellite-measured sea surface temperature (SST, obtained from http://las.pfeg.noaa.gov/oceanWatch/oceanwatch.php) in the study site varied between 2.5 and 18 °C in the preceding year, and the annual average SST, 9.5 °C, agrees well with the alkenone-temperature of the core-top sediment. The flux-weighted alkenone-temperature from sinking POC collected at 25 m above the bottom in the Wilkinson Basin was reported to be 9.9 °C during the period of March 1995–January 1996 (Prahl et al., 2001). The higher alkenone-temperatures in the BNL imply that it represents a mixture of different age compounds that includes alkenone signals produced during the warmer season(s). The alkenones in the BNL also likely include material resuspended from underlying sediment, as the low $\Delta^{14}C$ values of bulk POC suggest.

4. Discussion

Although the existence of a pronounced BNL in the Gulf of Maine sustained by sediment resuspension has been widely known, the influence of these mobilization and distribution processes on the biogeochemical properties of particles during their reintroduction to a more oxygenated water column is far less well understood (Townsend et al., 1992; Pilskaln et al., 1998). One question is whether the organic matter that is subject to resuspension is composed of relatively fresh aggregates stemming from recent production or whether it is aged organic matter that is more closely associated with mineral particles. The $\Delta^{14}C$ values of suspended POC clearly show a distinction between the upper water column and the BNL (Fig. 3): the POC in the BNL was strongly influenced by resuspension of aged sediment. This was also evident from the observation that total particle flux to a sediment trap deployed at 260 m was two orders of magnitude higher than that at 150 m (Pilskaln et al., 2013a). The low $\Delta^{14}C$ values of suspended POC within the BNL suggest that the resuspended organic matter must be almost as old as the core-top sediment. We calculated the estimated contribution of resuspended sediment to the particles within the BNL based on isotope mass balance using the $\Delta^{14}C$ values of suspended POC at 2 m depth and core-top sediment as the end-members for freshly produced POC and resuspended sedimentary POC, respectively. The resuspended sediment was estimated to account for 50% and 82% of POC in the two suspended particle samples at 235 m and 260 m, respectively, in the BNL whereas it corresponded to less than 5% of POC in the upper water column. It should be noted that in addition to the sediment, fresh POC that settled as fluffy flocs or flocculated at the water–sediment boundary can be remobilized repeatedly before it is incorporated into solidified sediment (Thomsen and van Weering, 1998).

The large difference in $\Delta^{14}C$ may imply that the quality of suspended POC as a food source is heterogeneous in the BNL, and depends amongst other things on the height above the sea floor. Townsend et al. (1992) found that the sample near the top of the BNL in the Jordan Basin exhibited maxima in concentrations of bacteria and heterotrophic nanoplankton, respiratory electron transfer (as a measure of respiration rate), and extracellular proteolytic enzyme activity. They suggested that zooplankton may select for either "clean", better quality food containing less lithogenic material resuspended from sediment, over for the overall quantity of food (i.e., POC concentration). In the present study, certain biogeochemical properties of the two samples collected at different depths in the BNL exhibited clear differences while other properties did not. We compare the two samples as representing the top of the BNL and the middle/bottom of the BNL. POC concentration was much lower for the 260 m sample than

235 m sample. Although it is a surprising result, we refrain from placing emphasis on absolute concentrations as we are lacking supporting data. The $\Delta^{14}C$ values imply that the 235 m sample was composed of a mixture of both fresh POC and resuspended POC ($\sim$50% of each), whereas the 260 m sample was mostly (82%) resuspended sediment. POC-normalized alkenone concentrations may also be explained by mixing between the two end members (fresh POC and resuspended sediment) and additional degradation. However, fatty acid concentrations and chain-length distributions provide different information. The fatty acid concentration of the 235 m sample was about four times higher than those at the adjacent depths (Table 1 and Fig. 4). The contribution of long-chain n-alkanoic acids of this sample was similar to or even lower than the other samples in the overlying water column. Together, these results imply *in situ* production of mostly short-chain n-alkanoic acids at this depth. Both bacteria and zooplankton can synthesize n-$C_{14:0}$, n-$C_{16:0}$, and n-$C_{18:0}$ (Wakeham et al., 1997 and references therein). Zooplankton contain abundant wax esters as energy reserve lipids, and hydrolysis of samples, as in our analytical procedure, releases n-$C_{16:0}$–n-$C_{24:0}$ fatty acids and alcohols (Wakeham et al., 1997). Bacterial biomarker lipids such as odd-numbered (C_{15}, C_{17}) branched fatty acids were present but their contribution was very low compared to n-$C_{14:0}$, n-$C_{16:0}$, and n-$C_{18:0}$ (data not shown; The existence of C_{15}, C_{17} branched alkanoic acids was confirmed by a GC–MS analysis in summer 2012, however, as the lipid fraction containing fatty acids had dried out completely during storage, these findings remain tentative). The $\delta^{13}C$ value of suspended POC at 235 m was similar to that in surface waters but higher (by 1.4‰) than that in the lower portion of the BNL and in the core-top sediment. This ^{13}C-enrichment may reflect organic carbon transfer through a food chain (Fry and Sherr, 1984; Peterson and Fry, 1987) or preferential consumption of marine organic carbon. Abundant macrozooplankton were collected in sediment traps deployed in the BNL (Pilskaln, unpublished data). Other grazing-specific biomarkers such as pyrophaeophorbide-a in suspended particles may be useful in revealing the vertical distribution of heterotrophic activity (Bianchi et al., 1998).

Overall, the above observations suggest that the upper BNL represents a "hot spot" of heterotrophic activity. While the abundance of short-chain n-alkanoic acids implies the presence of active heterotrophic processes, it is not known whether the organisms selectively consume fresh organic matter or utilize both fresh and resuspended (aged) organic matter as the carbon substrate. Additional information of $\Delta^{14}C$ values of individual n-alkanoic acids and measurements of species-specific compounds, accompanied by micro- and molecular biological assays, will be necessary to answer this question (*e.g.*, Ingalls and Pearson, 2005). Compared to the 235 m sample, the 260 m sample appears to have been more strongly affected by resuspended sediment than by *in situ* alteration of organic matter, indicating that biological activity and consequent alteration of particulate organic matter is vertically heterogeneous in the BNL.

5. Summary and conclusions

Carbon isotopic characteristics and lipid biomarker compositions of suspended particles and surface sediment shed new light on the nature and impact of sediment resuspension and post-depositional processes on organic matter cycling in Jordan Basin in the Gulf of Maine:

- A > 50 m-thick BNL was present in the Jordan Basin at the time of sampling.
- Suspended POC in the BNL contained aged organic matter, with 50% and 82% of suspended POC stemming from sediment

resuspension at 235 m and 260 m, respectively, based on ^{14}C mass balance. This observation indicates that resuspension of aged sedimentary organic matter (compared to remobilized freshly settled particles) can account for a major fraction of suspended POC in the BNL.
- Suspended POC is influenced by heterotrophic activity in the upper BNL as indicated by fatty acid concentrations and compositions that were distinct from those in the overlying water column.
- While significant heterotrophic modification of organic matter occurs in the upper BNL (235 m), there is no clear evidence for similarly pronounced heterotrophic activity in the lower BNL (260 m). This observation supports the previously suggested hypothesis of zonation of biological activity within the BNL (Townsend et al., 1992).

Many questions still remain concerning the dynamics of the BNL in the Gulf of Maine, and more generally on the role of BNLs in biogeochemical processes on continental margins. The BNL is expected to vary seasonally in response to the relative strength of the primary production in surface water and the hydrodynamic features that influence sediment resuspension. Further studies on the underlying mechanisms that support BNLs, on the biological processes that they in turn support, and on their role in organic matter alteration and redistribution in shelf seas are needed. Improved constraints on the role of BNLs in lateral transport of POC (both fresh POC and resuspended sedimentary POC) from shelf seas to the interior ocean are also needed.

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