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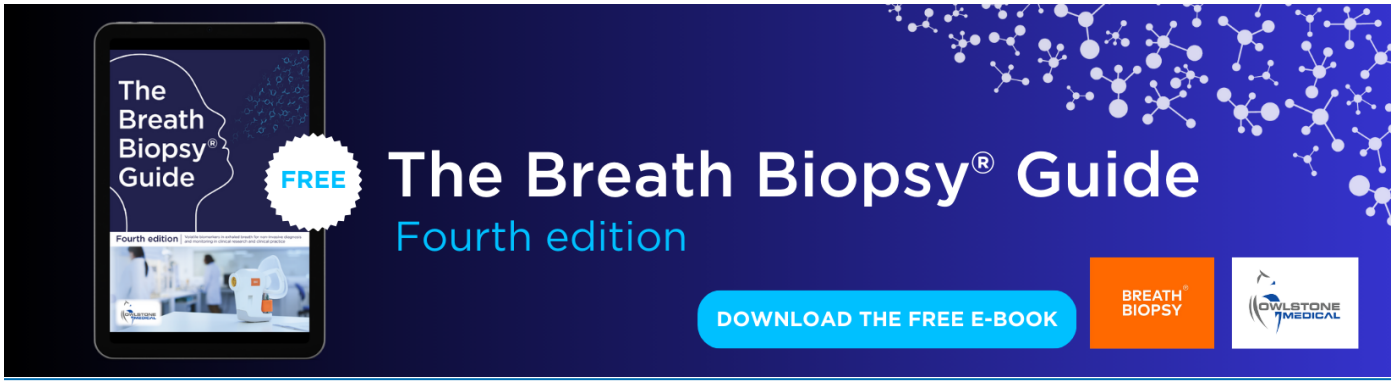

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Oil carbon entered the coastal planktonic food web during the Deepwater Horizon oil spill

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Abstract
The Deepwater Horizon oil spill was unprecedented in total loading of petroleum hydrocarbons accidentally released to a marine ecosystem. Controversial application of chemical dispersants presumably accelerated microbial consumption of oil components, especially in warm Gulf of Mexico surface waters. We employed $\delta^{13}C$ as a tracer of oil-derived carbon to resolve two periods of isotopic carbon depletion in two plankton size classes. Carbon depletion was coincident with the arrival of surface oil slicks in the far northern Gulf, and demonstrated that subsurface oil carbon was incorporated into the plankton food web.

Keywords: zooplankton, petroleum hydrocarbon, stable isotope, Gulf of Mexico

S Online supplementary data available from stacks.iop.org/ERL/5/045301/mmedia

1. Introduction

Following the sinking of Deepwater Horizon (DWH) on 22 April 2010, an estimated 780 000 m^3 of Sweet Louisiana Crude (SLC) and 205 000 mT of methane [1] were released into the northern Gulf of Mexico over an 85 d period. General agreement exists that ~25% was directly recovered or burned at sea, leaving ~75% to be degraded naturally or with the aid of chemical dispersants [2]. Recent publications document the scope of deep subsea oil and methane along the northern Gulf slope [1, 3, 4], but scant evidence exists for the presence of subsea oil in warm (>25 °C), shallow shelf waters.

A large pool of isotopically depleted carbon from dispersed oil and methane is presumably available for biological consumption via prokaryotic consumers [5]. Isotopic depletion extending into marine zooplankton grazers, a pathway mediated by the microbial food web [6], is a good proxy for food web modification by the spill. Here we present quantitative data collected as a rapid-response effort to track carbon isotopic signal in two size classes representing a pathway into the bulk zooplankton community of the northern Gulf of Mexico. The present study reflects only the initial steps of a larger and continuing laboratory experimental and field effort aimed at understanding how oil affects pelagic communities of the northern Gulf and vice versa effects of the biological community on the fate of the oil.

2. Methodology

We employed $\delta^{13}C$ as a tracer of oil-derived carbon incorporation into the lower marine food web across the middle and inner continental shelf. During June–August 2010, we followed two plankton size classes: the nominally 1 μm–0.2 mm 'small suspended particulate' and the >0.2–2 mm 'mesozooplankton' fractions, with the former considered likely food for the latter. The study region, >100 km north of the DWH well head, had three defined northward pulses of surface

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Table 1. The location and depth of surface and deep sampling stations in the Gulf of Mexico and reference sites within Mobile Bay, AL, including mean (±SD) salinity at each depth. n.d. = no data, dash = not deep enough to collect separate Deep sample. Symbols next to station names are for reference to figure 1.

			Surface		Deep	
Station, symbol	Latitude	Longitude	Depth (m)	Mean salinity (psu)	Depth (m)	Mean salinity
Gulf sites						
T35, ■	29.7989	−88.2083	1	27 ± 3	33	36 ± 0
T20, ♦	30.0902	−88.2116	1	25 ± 3	18	33 ± 4
T10, ●	30.1609	−88.1229	1	24 ± 3	8	32 ± 3
Buoy M (BM), ▼	30.1306	−88.1097	1	23 ± 4	15	n.d.
Mobile Bay reference sites						
Cedar Point Reef, +	30.3256	−88.1327	1	12 ± 6	—	—
Sand Reef, −	30.2772	−88.1052	1	18 ± 6	—	—

oil: two prior to the well's 15 July shut-in, and one in August (figures 1(A), (B), movie S1 available at stacks.iop.org/ERL/5/045301/mmedia). Samples were collected in surface and bottom waters of the Gulf of Mexico at four shelf and two inner Mobile Bay reference sites (figure 1(A), table 1).

2.1. Plankton and suspended particle collection

Suspended particulates (1 μm–0.2 mm) were collected using 1.7 l vertical Niskin bottles deployed at target depths of one meter above the bottom and one meter below the surface at stations T10, T20, and T35 at two-week intervals from 2 June to 15 August, 2010. At Buoy M, and the two bay reference sites, Cedar Point Reef and Sand Reef, only water from one meter below the surface was collected owing to shallowness of the water column; these were collected at 1–2 week intervals. At the Sand Reef reference station, samples were collected using a 1 l horizontal sampler. Air-filled balloons, released at depth from bottle ends, were used to avoid surface oil contamination during sampling. Water was vacuum filtered ($\leqslant$5 psi) onto pre-combusted GF/F filters, and dried to a constant weight at 60 °C.

Mesozooplankton were collected at the same stations and with the same timing as above with opening–closing plankton nets (3.5 m long, 0.25 m diameter), using 333 μm for surface and bottom and 202 μm for oblique samples at Gulf sites. A 202 μm mesh (1 m long, 0.5 m diameter) ring plankton net was used at BM and reference sites (mesozooplankton were not collected at Sand Reef). Samples were rinsed with ultrapure water, dried at 60 °C, and homogenized by mortar and pestle.

Additional historical pre-spill mesozooplankton samples from Buoy M and suspended particulate samples from T35, T20 and Buoy M were collected in May–August of both 2008 and 2009 (all data within each station were pooled as 'pre-spill'. Collections were similar to those described for 2010. These samples were historically analyzed only for carbon (C) and nitrogen (N) content; no pre-spill stable isotope data exist for continental shelf stations. All mesozooplankton samples are being processed for community assemblage changes with respect to the spill; however, assemblage analysis is beyond the scope of this study. That said, a cursory review of the samples for presence of contaminating oil droplets revealed the samples were clear of both oil and resuspended sediments. In addition, the zooplankton samples were dominated by organisms typical of spring–summer assemblages such as calanoid copepods.

2.2. Stable isotope analysis

Bulk carbon (C) stable isotope ratios (δ^{13}C, ‰) were measured by continuous flow isotope ratio mass spectrometry at the University of Utah Stable Isotope Facility (USA) and on a Picarro cavity ringdown spectrometer coupled to a Costech elemental analyzer at Dauphin Island Sea Lab (DISL). Bulk carbon isotopic composition in organisms reflects both short-term energy stores (i.e., lipids) and relatively longer turnover in tissues [7]. Since lipids are isotopically depleted and do not necessarily reflect time-integrated diet of organisms, variation in lipid content may introduce bias into stable isotope analyses. Established mathematical normalization techniques allow correction of δ^{13}C values in lipid-rich samples, but preserve sample integrity for other analyses [7]. Here, bulk δ^{13}C values in mesozooplankton were lipid-corrected according to [7], after comparison to C:N in mesozooplankton samples (figure 2(A). Comparison of δ^{13}C values to the C:N and relative C content (mg l^{-1}) in suspended particulates indicated no correction was needed for the smaller fraction (figures 2(A) and (B)). C and N content were obtained during stable isotope analysis.

2.3. Source crude oil samples

We analyzed δ^{13}C of oil in both weathered and fresh condition. Weathered surface oil was collected in the nearshore waters off Dauphin Island, Alabama, on 11 June 2010, and stored in the dark at 5 °C. Prior to carbon stable isotope analysis, the weathered oil was further dried at 60 °C for 48 h to remove residual water. This sample was analyzed for δ^{13}C at the University of Utah Stable Isotope Facility. Fresh Source Oil B (SOB) supplied by BP was collected on 22–23 May 2010, from the riser insertion tube on board the drill ship Enterprise. Accompanying documentation for two samples (SOB-20100716-067 and SOB-20100716-130) reported Nalco EC9323A defoamer was injected topsides, and subsea injections included methanol with 10 000 ppm VX9831 oxygen scavenger/catalysts solution. Fresh oil was stored at 5 °C until analysis by saturating a small piece of pre-combusted GF/F filter with oil and analyzed using a Picarro cavity ringdown spectrometer coupled to a Costech elemental analyzer at DISL.

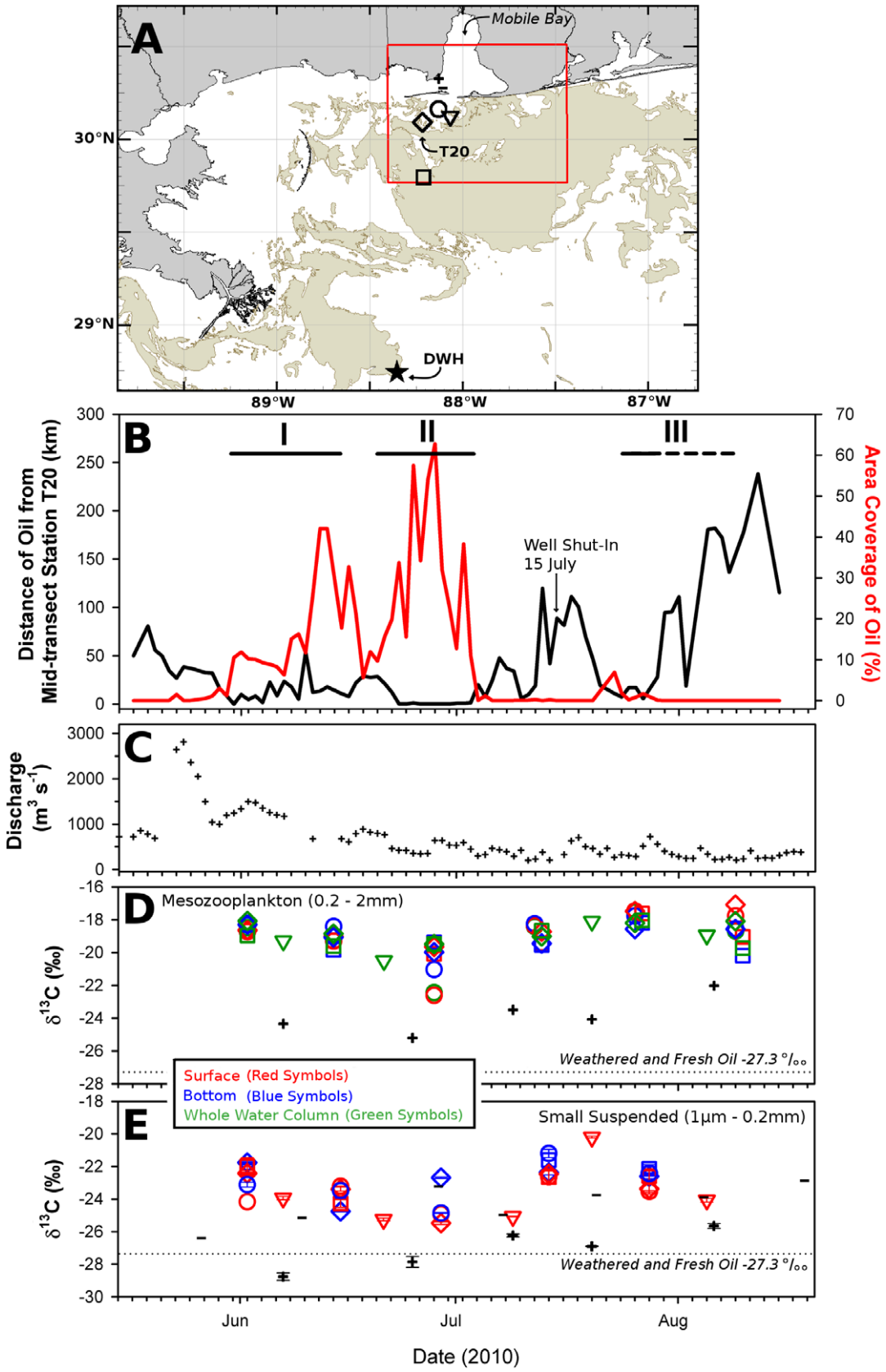

Figure 1. (A) Sample sites, symbols relating to (D) and (E); box defines area used to calculate oil % coverage in (B) with example of peak oil coverage 28 June 2010. A full animation of oil movement around these sites can be found in the supplementary data (movie S1 available at stacks.iop.org/ERL/5/045301/mmedia). (B) Timing of three shoreward pulses of oil, I–III (cf movie S1 available at stacks.iop.org/ERL/5/045301/mmedia). (C) Daily averaged river discharge into Mobile Bay. (D) δ^{13}C values for mesozooplankton fraction (0.2–2 mm). (E) δ^{13}C values for suspended particulate fraction (1 μm–0.2 mm). Both (D) and (E) referenced against δ^{13}C values from Mobile Bay and weathered and fresh SLC oil. Error bars show standard deviation.

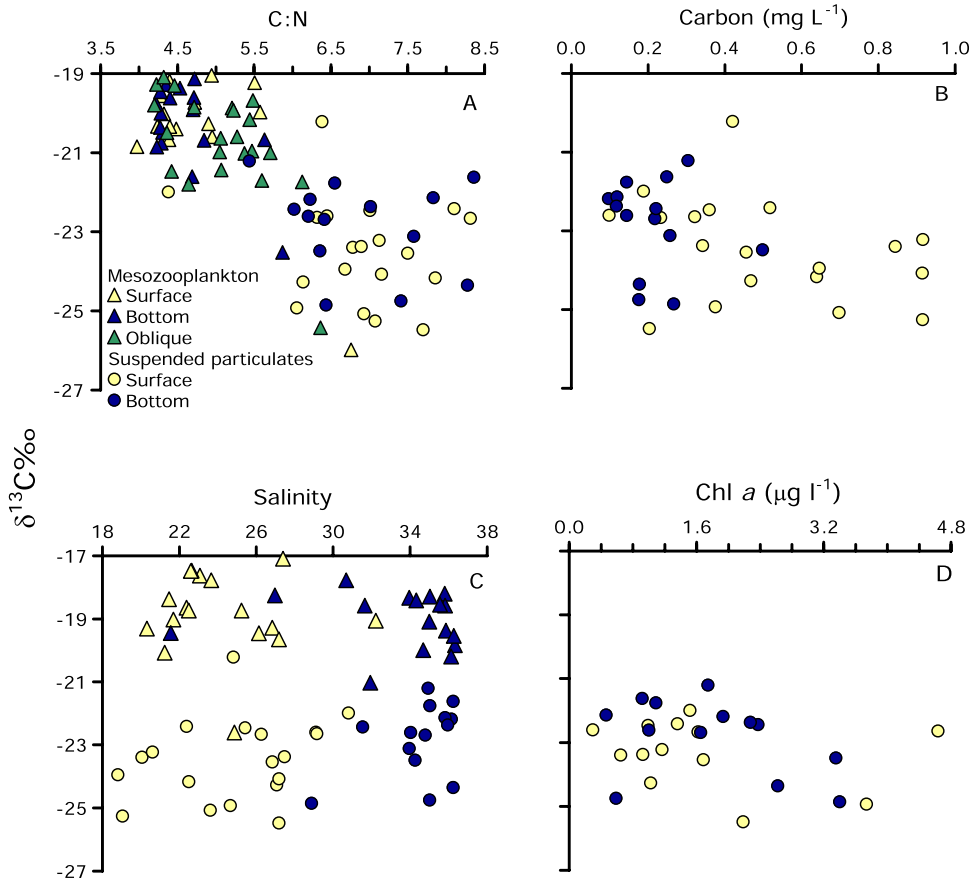

Figure 2. Analysis of C stable isotope ratios. (A) Bulk δ^{13}C in mesozooplankton (0.2–2 mm) and suspended particulates (1 μm–0.2 mm) compared to C:N in surface, deep, and oblique (mesozooplankton only) samples. (B) δ^{13}C compared to carbon content in suspended particulates. (C) Corrected δ^{13}C in mesozooplankton and δ^{13}C in smaller suspended particulates compared to salinity at surface and deep sampling locations. (D) Bulk δ^{13}C in suspended particulates compared to chlorophyll *a* (chl *a*) in water samples from stations T10, T20, and T35.

2.4. Chlorophyll a

Whole water samples collected at Stations T10, T20 and T35 (1 m below surface and 1 m above bottom) were stored on ice in the dark and filtered in the laboratory onto GF/F filters within 2 h of collection. Extracted chlorophyll a was fluorometrically determined with a Turner Designs fluorometer [8].

2.5. Oil proximity data

Surface layer slick distribution was defined from Geographical Information System (GIS) data (ftp://satepsanone.nesdis.noaa.gov/OMS/disasters/DeepwaterHorizon/). Per cent coverage of oil and distance from the nearest slick to station T20 were measured by mapping oil layers in ESRI ArcMap v9.3 GIS software.

2.6. Freshwater discharge

To determine potential effects of freshwater discharge on δ^{13}C, riverine discharge into Mobile Bay was estimated by adding daily discharge rates at two US Geological Survey gauging stations (http://waterdata.usgs.gov/usa/nwis/sw), the Coffeeville Dam on the Tombigbee River (#02469765) and the Claiborne Dam on the Alabama River (# 02429500). There is an estimated 5–10 d flow-dependent lag between readings at gauging stations and reference sites in Mobile Bay [9]. Daily mean discharge is reported in figure 1(C) (not including lags as it did not change the pattern). Salinity was measured at Gulf stations T10–T35 using a Sea Bird SBE 25 conductivity–temperature–depth (CTD) probe and at Buoy M and the two Mobile Bay reference sites using a handheld YSI 85 salinity probe.

2.7. Statistical analyses

Analysis of variance (ANOVA) was used for comparison of δ^{13}C values, C:N, and chl a among sample types. If ANOVAs were significant, post hoc pairwise comparison of means using Tukey's test of variability were performed. All linear correlations were tested using the Z-test. These analyses were performed in StatView 5.0.1. An additional three-way ANOVA with location, sample depth and condition (pre- or post-spill years) was performed on C:N values for suspended particulates and mesozooplankton using Minitab 15. All data were normally distributed and did not require transformation, and also conformed to the assumption of homogeneity of variance.

3. Results and discussion

δ^{13}C depletion occurred in each size fraction at middle and inner shelf stations coincident with two sequential northward pulses of surface oil slicks from DWH (figures 1(D), (E)). Relative to early June, an isotopic shift of −1 to −4‰ (toward weathered and fresh oil, −27.23 ± 0.03‰ and −27.34 ± 0.34‰, respectively) occurred during the peak of areal coverage of oil over the sites (figures 1(B), (D), (E)). Recovery from this depletion to the pre-spill baseline was 2–4 wks. A third pulse of residual oil occurred in late July, and depleted δ^{13}C was observed in mid-August at the furthest offshore stations. Depletion and recovery cycles on the order of a few weeks are consistent with published warm water petroleum hydrocarbon decay timescales [10].

The apparent oil-related δ^{13}C depletion occurred in both fractions and throughout the water column. The pattern was consistent despite the differences in both δ^{13}C and C:N between the two size fractions. δ^{13}C and C:N values differed between mesozooplankton and suspended particulates, with mesozooplankton having heavier δ^{13}C (−20.44 ± 1.37‰ compared to −23.19 ± 1.26‰) and lower C:N (4.8 ± 0.6 compared to 6.9 ± 0.9) than suspended particles (ANOVA: δ^{13}C:$F_{4,84}$ = 23.29, $P < 0.001$; C:N:$F_{4,84}$ = 43.04, $P < 0.001$; figure 2(A). Comparisons among surface, bottom, and oblique samples did not differ for either size fraction (Tukey's post hoc test: $P > 0.05$ for all comparisons).

Bulk δ^{13}C values were correlated with C:N in surface ($r = -0.64$), bottom ($r = -0.61$), and oblique ($r = -0.63$) mesozooplankton samples ($P < 0.01$) for all comparisons; figure 2(A), consistent with a mesozooplankton fraction (largely composed of animals) and requiring correction for lipid-related depletion of δ^{13}C [7]. In contrast, δ^{13}C in suspended particulates was not correlated with C:N (figure 2(A)), and was weakly correlated with the relative C content in the sample only when surface and bottom fractions were considered together ($r = -0.44$, $P < 0.01$; figure 2(B)). These findings suggest a small particle fraction of mixed composition, including algal and detrital matter that did not demand lipid correction despite a higher C:N ratio than mesozooplankton [7, 11]. The mean correction applied to bulk δ^{13}C in mesozooplankton samples was 1.49 ± 1.73‰. The relative shift in sample values can be seen by comparing panels A and C in figure 2.

3.1. Discounting masking effects or sample contamination

In comparison to reference sites inside Mobile Bay, offshore depletion of δ^{13}C was not related to timing of freshwater discharge from the Bay, phytoplankton blooms, or direct contamination of samples with external oil. Corrected δ^{13}C in mesozooplankton and bulk δ^{13}C values in suspended particulates were compared to salinity at each station to detect potential freshwater influence (figure 2(C)). The hydrology of Mobile Bay is dominated by freshwater inputs, which lead to salinity stratification [12] and may convey isotopically light suspended particles and biota from the upper reaches of the Bay to the Gulf [13]. δ^{13}C in reference oil samples was similar to δ^{13}C typically found in freshwater-derived vegetation, suspended particles, and some primary consumers in Mobile Bay and elsewhere [13, 14]. δ^{13}C values in mesozooplankton were not related to salinity (figure 2(C)), and δ^{13}C in suspended particulates showed a weak positive correlation only when surface and bottom samples were considered together ($r = 0.37$, $P = 0.03$). This finding is consistent with the relatively low discharge to Mobile Bay during most of the sampling period (figure 1(C)). The similar patterns of δ^{13}C depletion in both mesozooplankton and small suspended fractions, despite decreasing discharge to Mobile Bay and little or no relationship to salinity during the period of greatest oil proximity and coverage in the region, supports an oil-derived C source mediating this shift as opposed to a freshwater-derived source from Mobile Bay.

Since phytoplankton were a component of the mixed small suspended particulate fraction (1 μm–0.2 mm), isotopic depletion of C in this fraction and subsequently in the mesozooplankton could result from dominance by isotopically depleted phytoplankton. Given the range of δ^{13}C values typical in marine phytoplankton (−20 to −24‰; [15, 16]) and the lack of evidence for a significant freshwater influence during the period of depletion, phytoplankton alone are unlikely to account for the observed depletion (figures 1(D), (E)). The concentration of chlorophyll pigments extracted from water samples collected at stations T10 through T35 varied relatively little during the study period and did not indicate a bloom of shelf phytoplankton (1.50 ± 1.02 μg l^{-1}; figure 2(D)). Chl *a* concentration also was not related to δ^{13}C of the suspended particulate fraction ($F_{\text{reg}1,24}$ = 2.33, P = 0.14). Surface and bottom samples were not different and were combined for further analysis (two-way ANOVA with station and depth as variables: $F_{3,26}$ = 1.30, P = 0.29) (figure 2), indicting that a change in phytoplankton abundance made no measurable contribution to the isotopic depletion of C shown in figure 1.

To elucidate whether the observed δ^{13}C depletion was due to the contaminating presence of oil in the water column or to the assimilation and incorporation of oil-derived C by resident biota, we compared C:N for mesozooplankton and suspended particulate fractions during pre- (2008–2009) and post-oil spill (2010) years between May and August. The expectation was that presence of SLC oil on or inside the animals would yield anomalously high C:N values. For the suspended particulate fraction, there was no difference in C:N (by weight) between any of the sampling stations within and across pre- and post-spill years (three-way ANOVA with station, pre- and post-spill years, and sample depth as variables: $F_{9,89}$ = 1.46, P = 0.18) (figure 3). Similarly, there was no significant difference in mesozooplankton C:N at station BM in pre- and post-oil spill years (ANOVA: $F_{1,17}$ = 0.69, P = 0.42), and while we do not have pre-spill C:N data for stations T35, T20 and T10, post-spill C:N data from these sites were the same as those at station BM (ANOVA: $F_{1,68}$ = 2.30, P = 0.09) (figure 3). Combined, these results suggest that the depleted C isotope values were not driven by direct oil contamination in the samples (e.g., oil micro-droplets collected on the filter). That similar results were found for both mesozooplankton and suspended particulate fractions suggests oil-derived C was transferred through the food web.

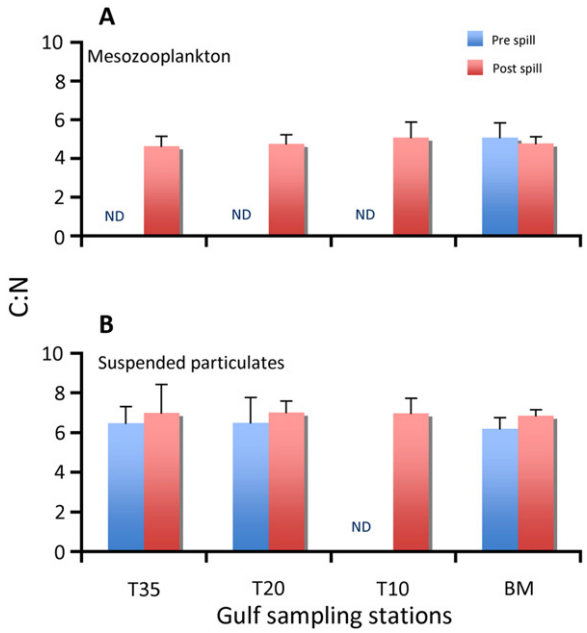

Figure 3. Particulate organic carbon to particulate nitrogen ratios (C:N) of (A) mesozooplankton (0.2–2 mm) and (B) smaller suspended particulates (1 μm–0.2 mm) collected at stations T35, T20, T10 and BM (cf figure 1 and table 1). There was no significant difference between surface and bottom C:N within each station, thus data were pooled for all pre- and post-spill analyses (ANOVA: $F_{1,97} = 0.04$, $P = 0.85$). ND indicates data were not available.

4. Conclusions

Carbon isotopic depletion in mesozooplankton and suspended particulate samples throughout the water column (figures 1(D) and (E)) indicates trophic transfer of oil carbon into the planktonic food web. A similar response found in benthic communities around natural seeps [5] suggests that carbon isotopic shifts in the plankton fractions are likely due to the duration and magnitude of depleted carbon released into the system. These data provide strong evidence that labile fractions of the oil extended throughout the shallow water column during northward slick transport and that this carbon was processed relatively quickly at least two trophic levels beyond prokaryotic hydrocarbon consumers given our understanding of microbial-zooplankton trophic linkages [6, 17]. Further, this study provides a launching point for follow up experimental laboratory and field exercises aimed at understanding the fate and transport of petroleum hydrocarbons in marine planktonic ecosystems under the influence of natural or human-mediated chemical dispersion.

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