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Tracing the intrusion of fossil carbon into coastal Louisiana macrofauna using natural ^{14}C and ^{13}C abundances

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ABSTRACT

The *Deepwater Horizon* oil spill released a large volume of ^{13}C and radiocarbon depleted organic matter to the northern Gulf of Mexico. Evidence of petroleum-derived carbon entering the offshore planktonic foodweb, as well as widespread oiling of coastal areas documented in previous studies suggests that hydrocarbons could have entered the near shore foodweb. To test this hypothesis, we measured radiocarbon ($\Delta^{14}C$‰) and stable carbon isotopes ($\delta^{13}C$) in an assortment of fish tissue, invertebrate tissue and shell samples collected within a year of the spill at seven sites from Louisiana to Florida USA across the northern Gulf of Mexico. We observed a west–east gradient with the most depleted radiocarbon values found in Terrebonne Bay, Louisana and increasingly enriched radiocarbon values in organisms collected at sites to the east. Depleted radiocarbon values as low as −10% in invertebrate soft tissue from Terrebonne suggest assimilation of fossil carbon (2.8 ± 1.2%), consistent with the hypothesis that organic matter from petrochemical reservoirs released during the *Deepwater Horizon* spill entered the coastal food web to a limited extent. Further there was a significant correlation between radiocarbon and $\delta^{13}C$ values in invertebrate tissue consistent with this hypothesis. Both oyster tissue and hard head catfish tissue collected in impacted areas of coastal Louisiana were significantly depleted in ^{14}C and ^{13}C relative to organisms collected in the unaffected Apalachicola Bay, Florida ($p < 0.014$). Alternative explanations for these results include the influence of chronic hydrocarbon pollution along the western gulf coast or that the organisms ingest carbon derived from ^{14}C depleted organic matter mobilized during the erosion of coastal marshes in southern Louisiana.

1. Introduction

The *Deepwater Horizon* oil spill released an estimated 750,000 m^3 of oil (Adcroft et al., 2010) and 500,000 mT of hydrocarbon gas (Joye et al., 2011; Kessler et al., 2011) into the northern Gulf of Mexico between 10 April 2010 and 4 July 2010. While approximately 25% was recovered or burned, 75% of the volume remained in the marine environment (Kerr, 2010; Lehr et al., 2010). Much of this organic, petroleum-derived carbon was rapidly consumed by microbial communities (Hazen et al., 2010; Redmond and Valentine, 2011) became incorporated into microbial biomass (Du and Kessler, 2012), and some of it consequently became available to higher trophic levels and particulate organic matter offshore (Graham et al., 2010; Chanton et al., 2012; Cherrier et al., 2014). However, oil also reached the shoreline and a 'substantial portion' was trapped in coastal ecosystems where it fueled the increase of bacterial hydrocarbon-degrader abundances (Kostka et al., 2011) which may have acted as a vector to similarly introduce oil-derived carbon into near shore foodwebs.

Sammarco et al. (2013) found elevated levels of polyaromatic hydrocarbons (PAHs) in fish and shellfish from coastal sites along the northeastern Gulf of Mexico which they attributed to the *Deepwater Horizon* spill. However, PAHs undergo significant trophic dilution (Wan et al. 2007) limiting their sensitivity as a tracer for determining the full extent that petroleum-derived carbon has infiltrated a marine food web. Graham et al. (2010) and Chanton et al. (2012) demonstrated how the simultaneous application of stable and radiocarbon isotopes can be used as a particularly sensitive tracer to infer inputs of petroleum-derived carbon to offshore planktonic foodwebs. Measurement of radiocarbon content can provide insights into the relative age of carbon sources in the marine environment. On the $\Delta^{14}C$ scale (Stuiver and Polach,

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1977), surface radiocarbon values for dissolved inorganic carbon (DIC) in the northern Gulf of Mexico are approximately +40‰ (Chanton et al., 2012), while petroleum-derived radiocarbon values have a value of −1000‰, reflecting the complete absence of ^{14}C (e.g. Wang et al., 2001). This large isotopic separation between the two endmembers makes ^{14}C a sensitive tracer for petroleum-derived carbon in the marine system. Surface ocean organic production (−20‰ to −22‰) (Chanton and Lewis, 2002; Chasar et al., 2005) and measured oil (−27‰) (Graham et al., 2010) are only separated by 5–7‰ in stable carbon isotope ($\delta^{13}C$) values. The isotopic signal, once incorporated into biomass, can be traced throughout the foodweb providing a proxy for assimilation of oil spill-derived carbon (Chanton et al., 2012; Cherrier et al., 2014).

The objective of this study was to use three different approaches to evaluate whether carbon from the *Deepwater Horizon* spill entered the coastal food web. Measurements of radiocarbon ($\Delta^{14}C$) in a selection of invertebrate and fish tissue at seven sites along the coast will allow us to make inferences about the extent of petroleum intrusion into coastal food webs along the northeastern Gulf of Mexico coast by comparing more affected, less affected, and unaffected sites. In addition, we will compare radiocarbon content in coastal organisms to values for recently fixed carbon to evaluate the uptake of radiocarbon depleted sources into the coastal foodweb. Thirdly, we will use comparisons of radiocarbon content in invertebrate soft tissues relative to their shells to provide insight into possible perturbations in water-column DIC values.

2. Materials and methods

Six coastal sites and one offshore Gulf of Mexico site were sampled for fish and invertebrate tissues along the northeastern Gulf of Mexico coast ranging from Terrebonne, LA near the oil spill to Apalachicola Bay, FL in the east (Fig. 1). Sites from Terrebonne, LA to Pensacola Bay, FL experienced oil but with effects decreasing from Louisiana to Florida (Hayworth et al., 2011; Kostka et al., 2011), while Apalachicola Bay represents an unaffected site where we did not expect to find evidence of petrocarbon in the foodweb. All samples were collected within a year of the oil spill from July, 2010 to May, 2011. We were unable to collect the same animals at every site.

Invertebrates and small fish were collected by oyster dredge, oyster tongs, hand, dip and cast nets and hook and line. Soft tissues were removed, washed in distilled water, oven dried at 60 °C and ground for isotopic analysis. Tissues for all animals were combusted at FSU (Peterson et al., 1994) and sent as CO_2 (following purification on a vacuum line) to the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) or to the Lawrence Livermore National Laboratories (LLNL). At these labs the CO_2 was converted to graphite targets and analyzed by accelerator mass spectrometry (Vogel et al., 1984). To report values, we use the Δ notation which normalizes the radiocarbon content of a sample to nominal $\delta^{13}C$ value (−25‰) and the time the sample was collected. This linear scale starts at −1000‰ when a sample has undetectable levels of ^{14}C. Recently fixed carbon currently has a value of about +35‰, and DIC from the Gulf of Mexico averages +40‰ (Chanton et al., 2012). These values reflect additional ^{14}C in the atmosphere due to nuclear weapons testing from the late 1940's to the early 1960's (Graven et al., 2012). A ^{14}C blank consisting of reagent tubes that were combusted and analyzed were less than 5 micrograms of C, producing a negligible effect on samples which were over 1200 micrograms of C. Analyses of 17 replicate samples yielded an average analytical reproducibility of ± 6.5‰ for ^{14}C measurements.

Shell tissues were dissolved in 10% phosphoric acid in serum vials and the CO_2 stripped in a helium stream and purified on a vacuum line and the resulting CO_2 treated as above. The $\delta^{13}C$ analysis of tissue samples was conducted at the National High Magnetic Field Laboratory in Tallahassee, Florida, on a CHN

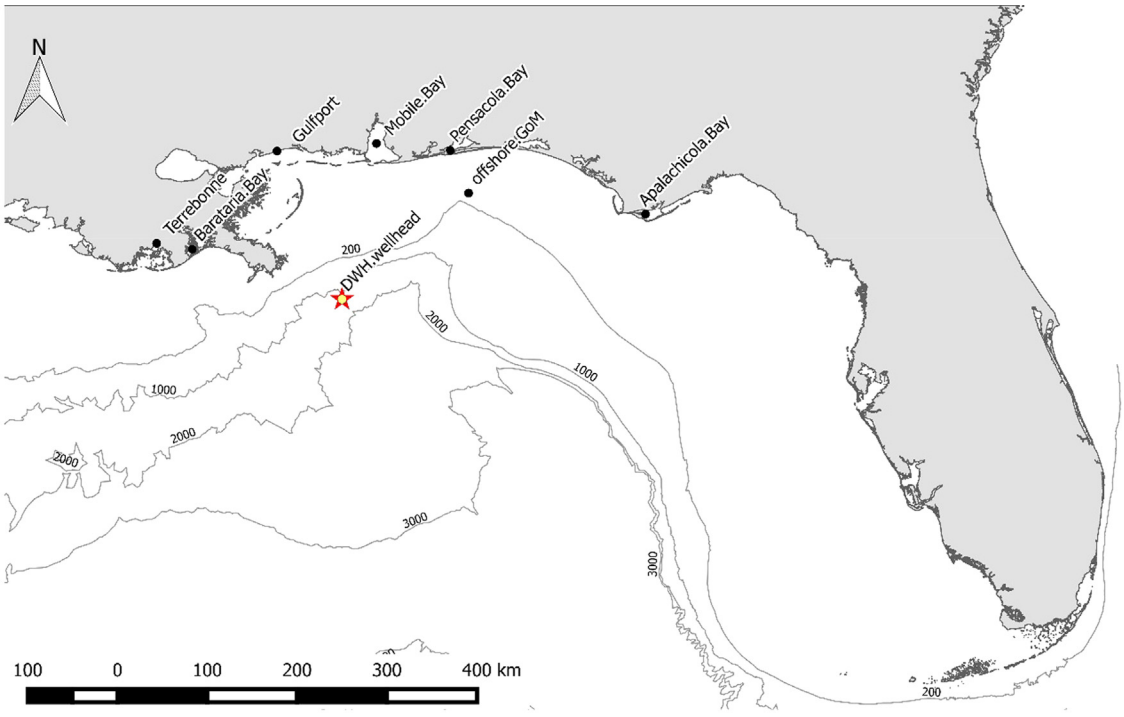

Fig. 1. Map of sampling locations. Points mark the center of sampling locations for fish and invertebrate species collected at each of the seven sites. The star marks the *Deepwater Horizon* well site. Lines indicate the depth-labeled (m) isobaths. Map created using USGS Gulf of Mexico region data (http://coastalmap.marine.usgs.gov/regional/contusa/gomex/gloria/data.html) in QGIS (QGIS Development Team, 2014).