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Employing extant stable carbon isotope data in Gulf of Mexico sedimentary organic matter for oil spill studies

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ABSTRACT

We have compiled and mapped available carbon isotope data from sedimentary organic material sampled from the Gulf of Mexico prior to 2010. These data provide a baseline to which any changes in the Gulf of Mexico after the 2010 Deepwater Horizon oil spill can be compared. The mean ($\pm 1\sigma$) $\delta^{13}C$ values, relative to PDB, are -21.4 ± 1.9‰ (entire Gulf of Mexico), -21.7 ± 1.2‰ (shelf sediments), -20.4 ± 1.6‰ (deepwater sediments), and -25.2 ± 4.1‰ (seep-affected sediments). We compare pre-spill mean $\delta^{13}C$ values to carbon isotope measurements of sedimentary organic material from coretop samples collected after the 2010 Deepwater Horizon oil spill. The differences between the mean compiled $\delta^{13}C$ values and the post-spill $\delta^{13}C$ values are corroborated by qualitative relationships with the concentration of polycyclic aromatic hydrocarbons (PAHs), a proxy for oil contamination, in the sediment. The relationships between $\delta^{13}C$ of the sedimentary organic material and PAH concentrations allow estimation of background levels of PAHs on the shelf and in the deep Gulf of Mexico. Higher background levels of PAH on the shelf likely relate to Mississippi River outflow and its deposition of petrogenic PAH in riverine sediments.

1. Introduction

On April 20, 2010, the Deepwater Horizon (DWH) drilling platform exploded in the Gulf of Mexico, killing 11 workers and beginning a prolonged spill event that admitted an estimated 4.9×10^6 barrels of oil into the Gulf of Mexico, only approximately 0.8×10^6 which was collected onto ships during the ensuing clean-up (McNutt et al., 2011). Accounting for this oil has been a complex task; it was released at depth (1500 m) and the hydrocarbons separated by phase and density. Some oil fractions dissolved, some were compressed to neutral density at depth, and some surfaced as a plume to be transported by wind and surface currents (Reddy et al., 2011; Ryerson et al., 2011; Valentine et al., 2010; Weber et al., 2012). Oil reached over 800 km of the northern coast of the Gulf of Mexico over the nearly 3-month period that the well was leaking (NOAA, 2013).

A large research effort ensued, aimed in part to budget all of the oil released from DWH (Camilli et al., 2010; McNutt et al., 2011). The question of the location and shape of both the subsurface and surface plume between emergence from the wellhead and deposition, evaporation, dispersion, biodegradation, and/or dissolution persists. Satellite imagery tracked the oil, however this technique can only detect the surface plume and is sensitive to consistency of the oil in the plume and the type of imaging used (NOAA-ERMA, 2013). Monitoring the location and extent of underwater plumes was logistically much more difficult, although several successful observations were made (Chanton et al., 2012; Diercks et al., 2010; Edwards et al., 2011; Mitra et al., 2012; Reddy et al., 2011; Valentine et al., 2010). Potential traces of oil biodegradation in the water column, which may have left an isotopic signature in dissolved inorganic carbon (DIC) at depth, were confounded (Joye et al., 2011; Kessler et al., 2011a, 2011b; Valentine et al., 2010) by the lack of pre-existing isotope measurements of DIC in the Gulf of Mexico.

Soon after the spill, oil was observed covering parts of the seafloor (Joye et al., 2011). The seafloor represents a potentially longer term sink for oil than the water column. Whereas only a

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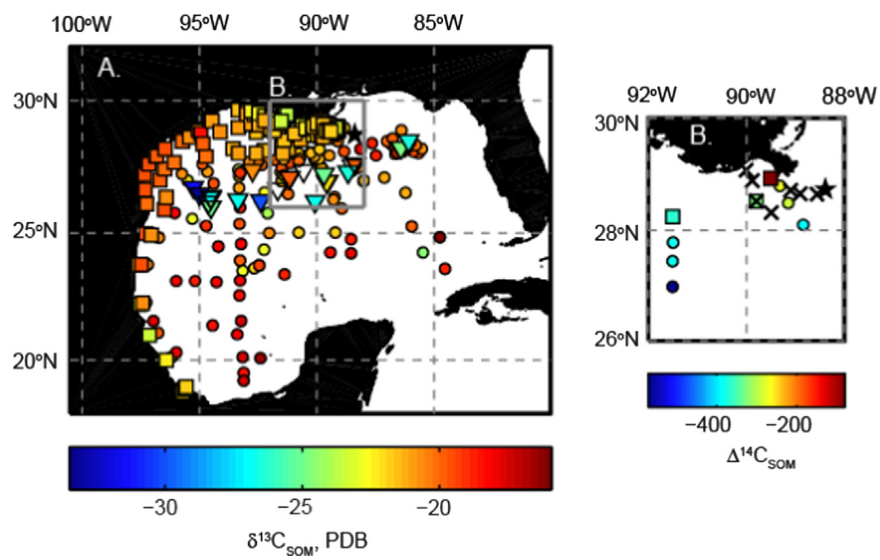

Fig. 1. (A) Map of extant $\delta^{13}C_{SOM}$ data and (B) extant $\Delta^{14}C_{SOM}$ data. In both maps, circles represent open Gulf of Mexico sediments, squares represent shelf samples, and triangles represent seeps. Location of seven CARTHE expedition sites are shown by x-symbols in (B). The DWH spill site is shown by the black star in all maps.

fraction of DWH oil was likely deposited on the seafloor, these deposits offer the potential to track that fraction of oil. Unlike the dearth of seawater chemistry data for the Gulf of Mexico prior to the DWH spill, there have been substantial measurements of the stable carbon isotope composition of organic material in seafloor sediment at the sediment–water interface of the Gulf of Mexico pre-dating the DWH oil spill (Fig. 1). Here we explore the use of these pre-DWH data, specifically $\delta^{13}C$ and $\Delta^{14}C$ measurements from sedimentary organic materials (SOM), to screen for the presence or absence of oil in Gulf of Mexico SOM. Compilation of these data allows for geospatial determination of mean isotope abundances where there are enough data, and comparison with post-spill values. Deviations between these values can be compared to polycyclic aromatic hydrocarbon (PAH) concentrations measured in seafloor sediment after the DWH spill. PAH analysis is effective as a proxy for oil contamination because some PAHs can persist in the environment for decades (Wang et al., 1999; Alimi et al., 2003; White et al., 2005; Short et al., 2007).

2. Methods

Data for carbon isotope compositions of Gulf of Mexico sedimentary organic material were taken from several sources dating between 1963 and 2011 (Bianchi et al., 2011; Demopoulos et al., 2010; Gallaway et al., 1988; Gearing et al., 1977; Goñi et al., 1997; Gordon and Goñi, 2003, 2004; Gordon et al., 2001; Mansour and Sassen, 2011; Mayer et al., 2007; Morse and Beazley, 2008; Newman et al., 1973; Roberts et al., 2010; Rosenbauer et al., 2009; Sackett and Thompson, 1963; Santschi et al., 2007; Swarzenski et al., 2008; Wakeham et al., 2009). We constructed a data base including both the stable carbon isotope and radiocarbon composition of sedimentary organic material, bulk sediment, and carbonate minerals, where available. Information including water depth of the core, depth of sample in core, thickness of the sample from core, stable carbon isotope measurement scale employed, whether the authors noted that the core was from a known hydrocarbon seep, and latitude and longitude of the coring location were noted. In some cases (Gearing et al., 1977; Newman et al., 1973; Sackett and Thompson, 1963) we used graphical analysis software to digitize figures containing the data due to the absence of data tables or archives in older publications. In one case, a significant proportion of the data graphed in the manuscript was not able to be digitized except for a few labeled points (Sackett and Thompson, 1963). Some data needed to be transposed from other isotope scales onto the internationally recognized PDB scale (Newman et al., 1973). In two manuscripts that did not mention which carbon isotope scale was used (Bianchi et al., 2011; Mayer et al., 2007), we assumed the PDB scale due to the recent publication dates. These compiled data are available on the GRIID-C data repository (Rosenheim, 2013). Data coverage within the Gulf of Mexico is shown in Fig. 1, and statistics and distributions are shown in Fig. 2.

Compilation of the SOM data provides a valuable tool for discerning spatial patterns in the Gulf of Mexico (Fig. 1). Removal of seep data strengthens comparison to current values for assessment of effects of the DWH spill. We use two criteria to remove seep data: 1. if the authors identified or assumed sediment to be affected by seep hydrocarbon and 2. if the value is less than −25‰ PDB, a value generally lower than most measurements of the nearshore sediments expected to contain the most terrigenous organic matter (Gearing et al., 1977; Sackett and Thompson, 1963).

For determination of canonical mean values of $\delta^{13}C_{SOM}$, we use depth to partition the remaining data into shelf and open Gulf of Mexico data. Where available, we used published water depths of cores. In other cases, we use Gulf of Mexico geo-referenced bathymetry, available from the National Oceanographic and Atmospheric Association's National Geophysical Data Center, coupled with GIS techniques, to separate shelf (<200 m) from open ocean (>200 m) samples. Comparison of GIS depth with published depth, where available, yields a strong relationship with a root mean square error of 4 m compared to a 1:1 line (Fig. 3), and the addition of GIS depth to the database allows for comparison of depth to $\delta^{13}C_{SOM}$ for the entire compilation (Fig. 3).

Stable carbon isotope data from the Gulf of Mexico were contoured using the Golden Software© Surfer11 mapping program. A total of 130 points were included to calculate the grid using a linear variogram with default values taken for all kriging options. The resulting grid was blanked and contoured with a contour interval of 2‰ (which is between the 1σ and 2σ levels of the open Gulf of Mexico, 1.6‰ and 2.3‰, respectively); contours were edited to remove unconfirmed features on the map which lacked at least two data points within a given contour. The kriged $\delta^{13}C_{SOM}$ data, excluding seep and shelf data, are shown in Fig. 4.

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