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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 ($\pm 1\sigma$) δ^{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 δ^{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 δ^{13}C values and the post-spill δ^{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 δ^{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.

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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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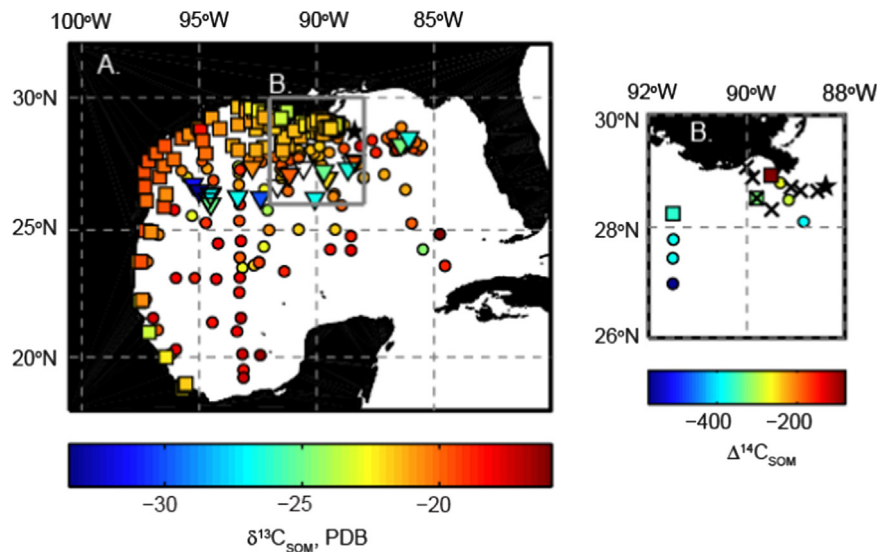**Fig. 1.** (A) Map of extant $\delta^{13}C_{SOM}$ data and (B) extant $\Delta^{14}C_{SOM}$ data. In both maps, circles represent open Gulf of Mexico sediments, squares represent shelf samples, and triangles represent seeps. Location of seven CARTHE expedition sites are shown by x-symbols in (B). The 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.
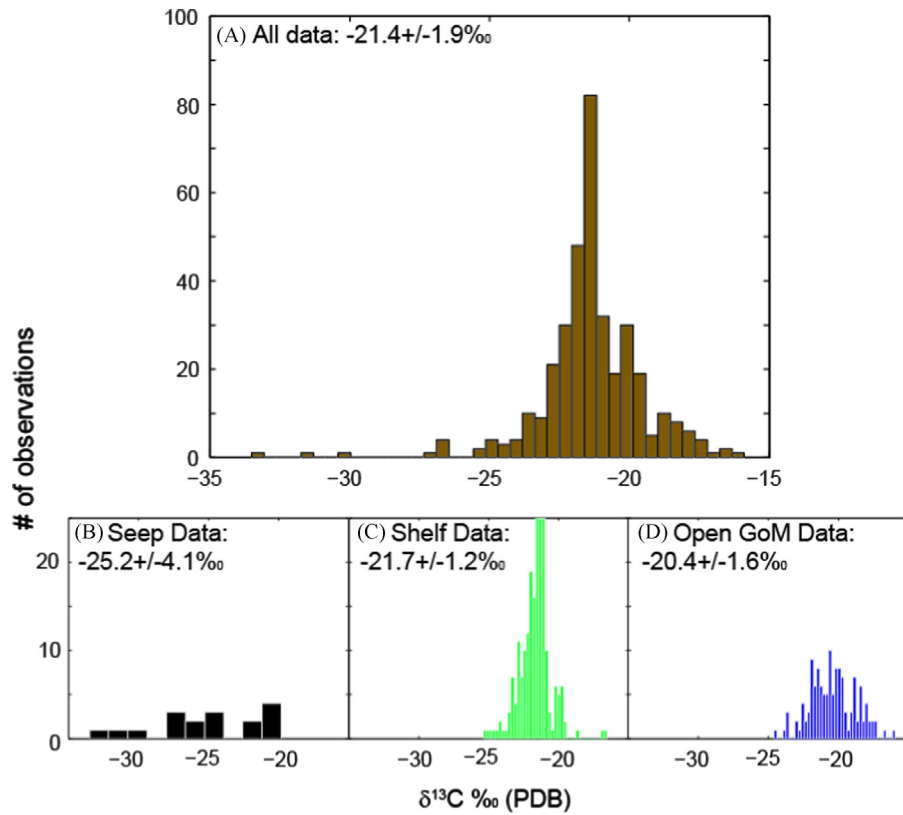
Fig. 2. (A) Distribution of all $\delta^{13}C_{SOM}$ reported in this manuscript. (B) Distribution of seep data ($n=27$). (C) Distribution of shelf data ($n=211$). (D) Distribution of open Gulf of Mexico data ($n=130$).
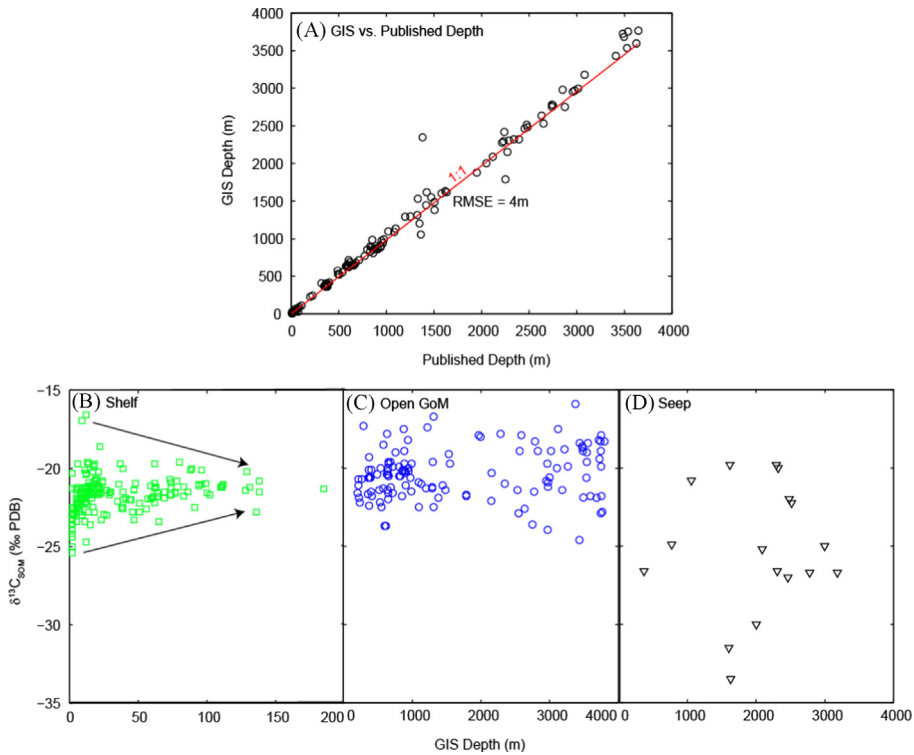

Fig. 3. (A) Depth relationship between GIS-determined data and published data (where available). Root mean square error (RMSE) is calculated from 1:1 line, not a linear regression. (B) Shelf $\delta^{13}C_{SOM}$ shows no relationship with depth, however variability decreases with depth (arrows hand-drawn to show convergence of values). (C) Open Gulf of Mexico samples do not show any relationship with depth, nor do they show as narrow a distribution as the deepest shelf values. (D) Seep values have the highest variability and no apparent relationship with depth.
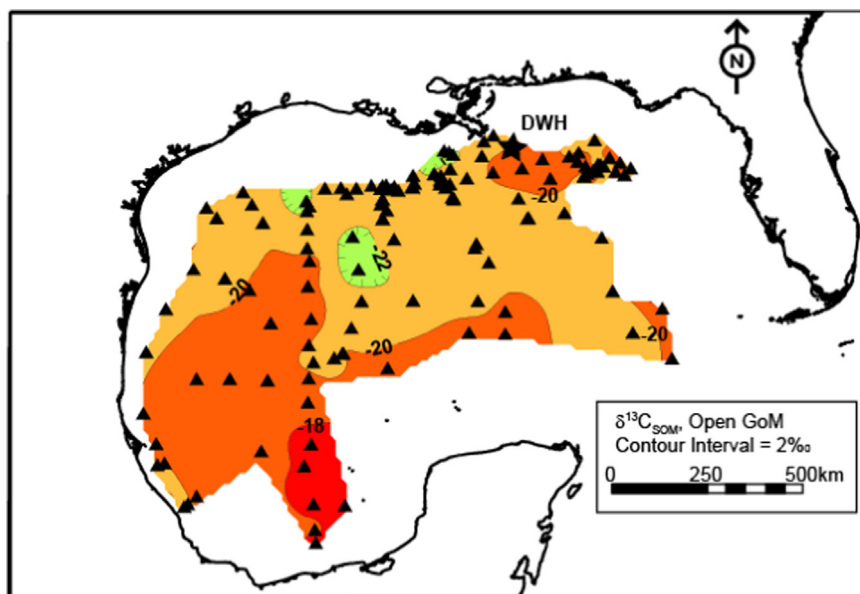
Fig. 4. Contour map of extant δ^{13}C values in the open Gulf of Mexico, measured prior to 2010 and excluding seep and shelf (< 200 m depth) data. In the open Gulf of Mexico, there is no readily-apparent relationship between δ^{13}C$_{SOM}$ and distance from the Mississippi River outflow.

For comparison to our analysis of pre-spill SOM data, sediment samples were collected by multicore from the R/V *Pelican* between June 30 and July 2, 2012. Cores were extruded on board the ship at increments of 0.5 cm (PAH analysis) or 1 cm (δ^{13}C analysis) and frozen in pre-combusted glass jars with plastic caps lined with pre-combusted aluminum foil. Once in the laboratory, samples for isotope analysis were weighed, dried at 60 °C, ground, re-weighed, treated with 10% HCl to remove mineral carbonates until evolution of CO_2 could no longer be observed, rinsed to neutral pH, dried and re-weighed. Isotope analyses were carried out on a CHN analyzer coupled to a Thermo IRMS Delta XP. Based on replicate analysis of sediment samples, reproducibility of measurements made on this instrument is 0.2‰.

Coretops from separate multicore tubes on the multicore apparatus were extruded for PAH analysis. These samples were shipped frozen to the Geochemical Environmental Research Group (GERG) at Texas A&M University for analysis following GERG's standard operating procedures. Briefly, samples were freeze-dried, ground, and approximately 1–2 g loaded into stainless steel cells before accelerated solvent extraction (ASE) using dichloromethane. Prior to ASE, the appropriate surrogate standards (d8-Naphthalene, d10-Acenaphthene, d10-Phenanthrene, d12-Chrysene, and d12-Perylene) were added to all sediment and QA/QC samples. Extracts were then concentrated to about 1–2 mL in hexane and purified by partially deactivated silica gel–alumina column chromatography by elution with a 1:1 mixture of dichloromethane and pentane. The eluted extracts were finally concentrated to 1 mL in hexane before instrumental analysis. PAHs were quantitatively analyzed by gas chromatography with mass spectrometric detection (HP-5890 and HP-5970-MSD) in the selected ion mode. The samples were injected in the splitless mode into a 30 m × 0.25 mm i.d. (0.25 μm film thickness) DB-5 fused silica capillary column (J&W Scientific) at an initial temperature of 60 °C and temperature programmed at 15 °C min^{-1} to 150 °C, then at 5 °C min^{-1} to 220 °C, and finally at 10 °C min^{-1} to 300 °C. The final temperature is held for 10 min. Total runtime was 38 min. The mass spectral data were acquired, and the molecular ions for each of the PAH analytes were used for quantification. The gas chromatograph/mass spectrometer was calibrated by the injection of standards at five different concentrations. Analyte identification was based on the retention time of the corresponding quantitation ion and a series of confirmation ions. Deuterated aromatic compounds [d10-Fluorene, d12-Benzo(a) pyrene] were used as internal standards.

3. Results

The mean carbon isotopic composition of all data ($n=368$) used in this compilation is $-21.4‰$ ($1\sigma=1.9‰$) and the median is $-21.4‰$ (all values reported relative to PDB, Fig. 2). Both the mean and median are indicative of organic material formed in the open ocean (published ranges are wide, but on average values are near $-20‰$ PDB (Sharp, 2007); here we use the narrower range of $-22‰ < \delta^{13}$C$_{OC, \ marine}, < -20‰$). However, the distribution (Fig. 2A) shows that there are several 10 s of measurements outside of normal marine OC bounds at both ends of the distribution. More positive values that occur in both the shelf and open Gulf of Mexico data are largely from river-influenced samples which contain fractions of C4 plant-derived OC (Bianchi et al., 2002, 2011; Duan et al., 2007; Gordon and Goñi, 2003, 2004; Gordon et al., 2001). Objective removal of samples taken from shallower than 200 m ($n=211$) increases the mean δ^{13}C$_{SOM}$ to $-20.9‰$ ($1\sigma=2.6‰$) and the median to $-20.6‰$. Shelf samples ($n=211$) have a mean value of $-21.7‰$ ($1\sigma=1.2‰$) and a median of $-21.6‰$. These values show a large amount of variability at shallow depths, between values observed in Mississippi River outlet particulate organic carbon (POC) ($-25.2‰$, Rosenheim et al., 2013) and values more typical of C4-sourced POC. At greater depths they converge toward a value similar to open marine δ^{13}C$_{SOM}$ (Fig. 3). Open Gulf of Mexico samples ($n=130$) have a mean value of $-20.4‰$ ($1\sigma=1.6$) and a median of $-20.5‰$. Seep samples ($n=27$) have a mean and median of $-25.2‰$ ($1\sigma=4.1‰$ on the mean).

Only 9 values of Δ^{14}C have been reported for Gulf of Mexico coretop sedimentary organic material (Fig. 1B). The mean of all these data is $-342‰$ ($1\sigma=130‰$, permil difference from radiocarbon content of 1950 wood) and the median is $-367‰$, lower than values observed in both the Mississippi and Atchafalaya River channels (Goñi et al., 1997; Rosenheim et al., 2013). These values correspond to ages of approximately 1000–5000 ^{14}C years, which is in excess of typical reservoir ages of organic material and

Table 1
Coretop data from CARTHE 2012 benthic observations cruise. Sites CARTHE 4–6 were treated as shelf sites, despite the depth of CARTHE-4 being 510 m. The reason it was included as a shelf site is because of focusing of shelf sediment that occurs at this site, the throat of the Mississippi Canyon. The four other sites were considered open Gulf of Mexico. The appropriate mean $\delta^{13}C_{SOM}$ values were subtracted from measured values to calculate $\Delta\delta^{13}C_{SOM}$, and relationships between this parameter and PAH values are shown in Fig. 6. These data are also plotted in Fig. 5, showing no spatial relationship between any of the proxies of oil contamination and distance from the spill site.

Site	Latitude	Longitude	Depth (m)	$\delta^{13}C$	$\Delta\delta^{13}C$	PAH (ng/g dw)	PAH (ng/g OC)
CARTHE-1	28.6527	−88.5607	1000	−21	0.6	400.65	21,204.73
CARTHE-3	28.3243	−89.4893	940	−21.5	1.125	488.05	27,947.48
CARTHE-4	28.5292	−89.8007	510	−21.9	0.2	429.9	24,617.48
CARTHE-5	28.8917	−89.8868	40	−22.1	0.35	476.05	30,951.58
CARTHE-6	29.0777	−90.0108	14	−23.0	1.29	281.5	46,967.74
CARTHE-A1	28.6607	−88.9058	990	-22.1	1.7	495.2	34,123.1
CARTHE-A2	28.7205	−89.0997	505	−22.3	1.9	634.9	33,537.22

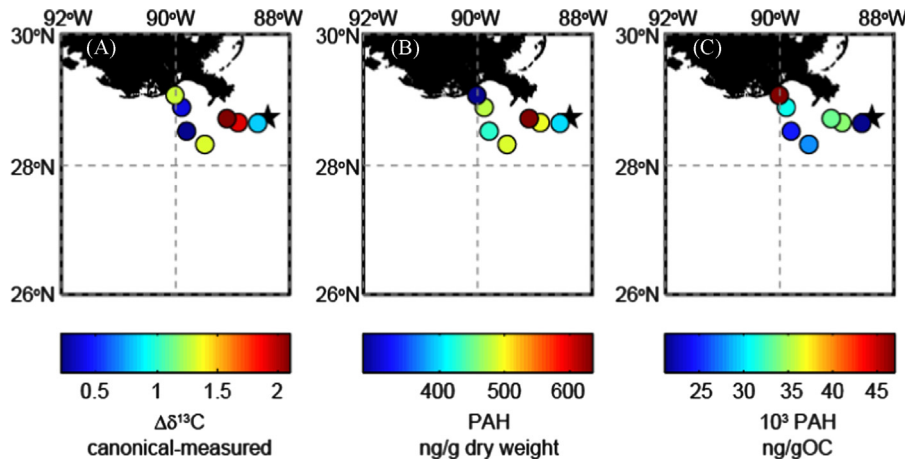**Fig. 5.** (A) Difference between canonical values of $\delta^{13}C$ determined in this compilation for the shelf and open Gulf of Mexico and the post-spill measured $\delta^{13}C_{SOM}$. (B) Difference between $\Delta\delta^{13}C_{SOM}$ and coretop values for PAH per dry weight of sediment. (C) Difference between $\Delta\delta^{13}C_{SOM}$ and PAH per mass of organic matter. In all of these measurements, there is no strong correlation between high values and proximity to the wellhead (black star). More similarity in spatial distributions is found between $\Delta\delta^{13}C_{SOM}$ and PAH normalized to organic content of the sediment.

calcium carbonate presently drawing from the marine DIC pool (Graham et al., 2010). The most negative $\Delta^{14}C$ value reported in the Gulf of Mexico is −572‰ (Goñi et al., 1997; Ruttenberg and Goñi, 1997), still far more enriched in ^{14}C than petroleum (−1000‰). However, such a value can be potentially indicative of admixture of ^{14}C-depleted carbon from older reservoirs below the sediment surface, from land via terrigenous sediment, or from natural seepage of petroleum.

Post-DWH spill measurements from 7 sites do not approach the quantity of data available before the spill, but they do offer a case study for how new data can be used with our compilation. Coretop samples from the top 1 cm of sediment measured for PAHs (without perylene, a biogenic and pyrogenic PAH) ranged between 282 and 635 ng/g dry weight (dw) of sediment, with an average of 447 ($1\sigma=104$) ng/g dw (Table 1). Normalizing for organic matter content (%OC) rather than dry weight of the sediment results in a mean of 30,120 ($1\sigma=8440$) ng/g OC. The locations of different values of PAHs within the sediments were not strongly correlated with the distance from the DWH wellhead (Fig. 5). Stable carbon isotope values measured in the sediments ranged between −23‰ and −21‰, with an average of −22.0‰ ($1\sigma=0.62‰$). Values from the shelf and Mississippi Canyon average −22.2‰ PDB ($1\sigma=0.5‰$) and values from the open Gulf of Mexico average −21.7‰ PDB ($1\sigma=0.6‰$). On average, samples were 1.14‰ ^{13}C-depleted with respect to shelf and open Gulf of Mexico isotope values measured before 2010. Correlation between PAHs (normalized to %OC) and departure from these canonical means of $\delta^{13}C$ are shown in Fig. 6. All measured values from coretops are shown in Table 1.

4. Discussion

Previous investigations of $\delta^{13}C_{SOM}$ showed evidence of the influence of coastal and estuarine outflows on isotope composition of the sedimentary organic material (Gearing et al., 1977; Goñi et al., 1997; Sackett and Thompson, 1963); however the Mississippi and Atchafalaya outflows do not display the most depleted carbon isotope ratios (Fig. 1B). Initial investigations into the distribution of $\delta^{13}C_{SOM}$ (Gearing et al., 1977; Sackett and Thompson, 1963) contained data from inland rivers and estuaries along the Gulf coast, but those points could not be included in this data compilation. Still, consulting these data sets as originally plotted is useful for understanding variability in the northern Gulf of Mexico. The inland, largely freshwater data show evidence of admixture of C3 terrigenous organic matter along the northern Gulf of Mexico coast, with more depleted carbon isotope ratios (−26‰ to −24‰ PDB) than the average values from shelf and offshore measurements prior to 2010 (Gearing et al., 1977; Sackett and Thompson, 1963). Values from sites adjacent to the coasts of southern Texas and Mexico west of the Yucatán Peninsula (Bay of Campêche) showed admixture of ^{13}C-enriched C4 vegetation (−18‰ to −12‰ PDB) to the north and more C3 vegetation (−23‰ to −22‰ PDB) to the south. Despite the potential for a land–sea gradient of carbon isotope ratios from these terrestrial vegetation endmembers, measurements display a tendency to approach open-ocean values of $\delta^{13}C_{SOM}$ in rather short distances over the shelf and the gradient in the data is not readily visible on a regional spatial scale (Fig. 4). Shelf data, however, do converge toward marine values further from the coast (Fig. 3).
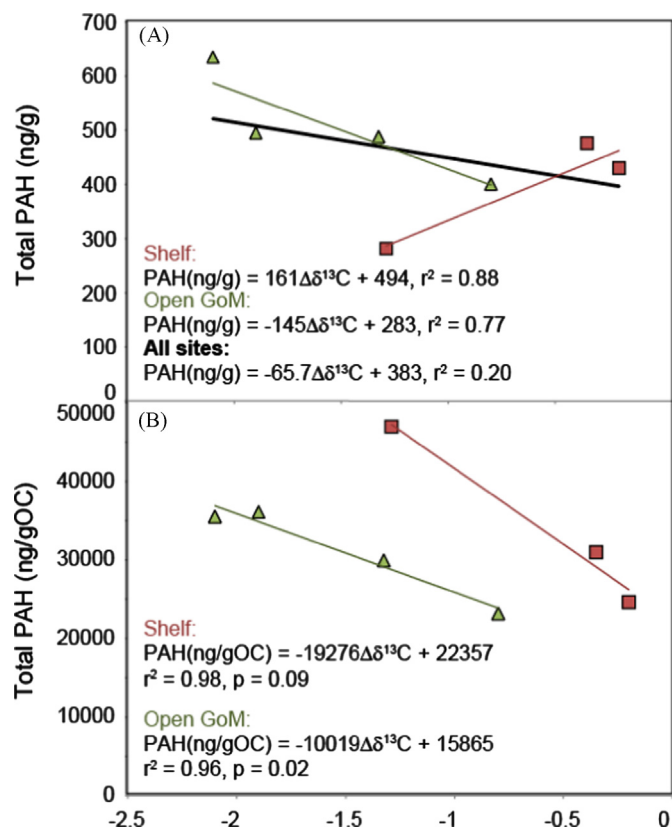
Fig. 6. Relationships between PAH content and $\Delta\delta^{13}C$ (the difference between values measured in 2012 and the canonical means from the shelf and open Gulf of Mexico): (A) normalizing PAH concentrations to dry sediment weight produces ambiguous results. (B) Normalizing PAH concentrations to the mass of organic matter in each sample elucidates relationships between the values. These values suggest a background value of PAH in both the shelf and open Gulf of Mexico sediment. Statistical significance of the models is limited by low number of samples.

Fig. 7. (A) Stable carbon isotopic composition of Macondo wellhead crude oil evaporated at 60 °C and sampled intermittently over a 2 week period. Controls were prepared at outset, stored in dark at < 0 °C, and analyzed at similar time intervals. (B) Stable carbon isotopic compositon of oil from a rock groin at Grand Isle, Louisiana. Oil here was subject to evaporation and photodegradation but limited microbial degradation due to a lack of moisture.

The most depleted stable carbon isotope ratios in this data set come from the open Gulf of Mexico, predominantly where seeps are present (Fig. 1). Seeps in the Gulf of Mexico are primarily aggregated at the intersection of the seafloor and fault-associated conduits. Such conduits may be relatively shallow and provide a migration path for biogenic methane hydrates or charged sediments. Deeper conduits provide migration paths for thermogenic gases and liquid hydrocarbons. The spatial configuration of seepage at the seafloor is highly variable and is assumed to change over time due to deposition of authigenic carbonate within the system of conduits (Roberts and Carney, 1997). Gas bubbles and liquid petroleum drops may seep from bottom sediments at points as small as a few square centimeters or extending to 100's of square meters, as observed in asphalt flows (Sassen et al., 1993; Weiland et al., 2008). A common configuration is for an area of a few 100's of square meters to contain scattered seeps over a range of sizes and flow rates. There are two routes by which seep hydrocarbons add to the total sediment carbon pool. The first is simply residual seepage components retained within the sedimentary matrix on a small spatial scale. The second is through incorporation into living biomass which eventually adds to an "old" organic carbon pool over larger spatial scales. The low likelihood of sampling a seep-influenced bottom sediment in the Gulf of Mexico can be seen from the examination of surface geochemical exploration data (Cole et al., 2001; Horvitz, 1985). Out of approximately 2100 piston cores specifically targeting likely petroleum reservoirs, only 100 were assessed to reflect seepage based on fluorescence intensity. Isotopic ratios, especially $\Delta^{14}C$, may be more sensitive to oil contributions to SOM due to their persistence
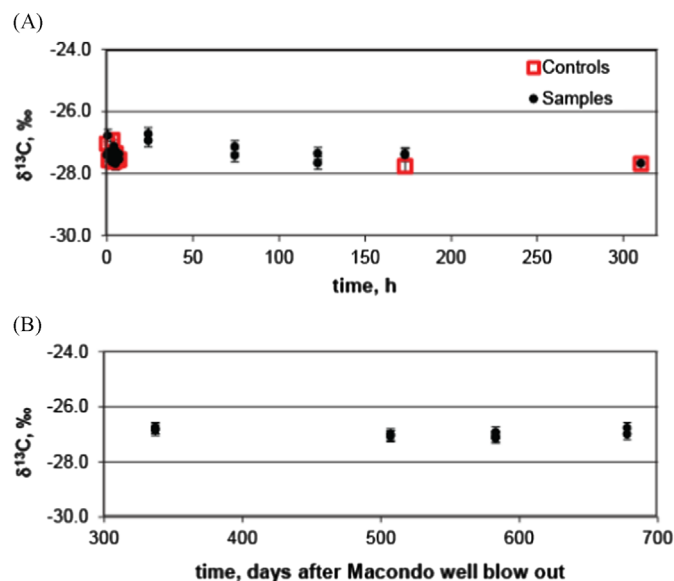
through chemical changes, including incorporation into biomolecules, which can affect chemical tests for the presence of oil such as fluorescence. In this compilation, there are only 9 reported measurements of $\Delta^{14}C$, not enough to be diagnostic of areas with prevalence of seep carbon affecting SOM. However, there is a higher proportion of seep samples (27 of 368, 7.3%) in this compilation versus the exploration data of Cole et al. (2001) and Horvitz (1985) (100 out of 2100, 4.8%).

Oil from the Gulf of Mexico has been shown to have a consistent stable carbon isotope signature ($-27.3‰$ PDB) (Graham et al., 2010; Macko et al., 1981), and the signature of the DWH-sourced oil seems to remain constant through the different processes of evaporation, photodegradation, and/or microbial degradation (Fig. 7). It is well-established that oil also is devoid of radiocarbon due to the time frame of processes that create it. In a typical open ocean setting, pre-existing organic material would also have nearly constant $\delta^{13}C_{SOM, pre}$ and $\Delta^{14}C_{SOM, pre}$, with the former being controlled simply by photosynthetic fractionation of $\delta^{13}C_{DIC}$ ($\approx 0‰$ PDB) resulting in $\delta^{13}C_{SOM, pre} \approx -20‰$ PDB. Relatively constant $\Delta^{14}C_{SOM, pre}$ values would likely be controlled by the amount of mixing between deep ocean and mixed layer DIC and the age of deepwater DIC. In this case, Figs. 1 and 2 would show nearly constant values of these parameters and the uncertainty of these values at points between actual measurements would approach analytical uncertainty as a minimum bound. Compilation of the data shows more complexity. First, petroleum seeps in the Gulf of Mexico (Cordes et al., 2009) hold the potential to incorporate isotopically depleted organic matter into the sediment in confined areas. Some of these areas are easily discernible from studies that have targeted or included seeps and their unique biogeochemistry (Fig. 1 (Gallaway et al., 1988; Mansour and Sassen, 2011; Morse and Beazley, 2008; Roberts et al., 2010; Sackett, 1964)). Even within sites that were not identified as seeps by primary authors, there are points that are abnormally ^{13}C-depleted for open marine organic material (i.e., more than 2σ lighter than the mean, values less than $-25.2‰$). Furthermore, sites in the open Gulf of Mexico also include heavy isotope values in the realm of mixtures of marine organic matter and C4 terrestrial vegetation. Such points lend variability to the open Gulf of Mexico canonical

mean, and prevent the open Gulf of Mexico distribution from being as narrow as shelf samples near or at the slope break ($1\sigma = 0.61‰$ between 100 and 200 m, as opposed to 1.2‰ in less than 100 m depth (Fig. 2)).

Even with variability beyond the expectation of open marine $\delta^{13}C_{SOM}$, the contrast between stable carbon isotope ratios of Gulf of Mexico oil and the rather constant non-seep $\delta^{13}C_{SOM}$ values compiled herein is useful. The difference ($\sim 7‰$) is easily recognizable by modern methods of measuring stable carbon isotopes (analytical precision typically at or better than 0.2‰ PDB), and the proliferation of laboratories making such measurements since the earliest measurements in this compilation renders the technique affordable and readily available. To use canonical means in evaluating oil contamination, we employ a binary mixing model to relate post-2010 spill observations of $\delta^{13}C_{SOM}$ and $\Delta^{14}C_{SOM}$ for the Gulf of Mexico to the values compiled as above:

$$\delta_{post} = f\delta_{oil} + (1-f)\delta_{pre} \tag{1}$$

$$\frac{\delta_{post} - \delta_{pre}}{\delta_{oil} - \delta_{pre}} = f \tag{2}$$

where δ is either the $\delta^{13}C$ or $\Delta^{14}C$ value for sedimentary organic material measured at some point after the spill (*post*), pre-existing sedimentary organic material (*pre*), or DWH oil (*oil*, $-27.3 \pm 0.34‰$ PDB for $\delta^{13}C$ (Graham et al., 2010) and $-1000‰$ for $\Delta^{14}C$), and f is the fraction of organic material made up by the oil. A similar approach has been used for petro-carbon analysis of plankton from the Gulf of Mexico (Chanton et al., 2012; Graham et al., 2010). In the case of both isotopes, the DWH oil is the most depleted endmember when seep data have been removed from the data set. Uncertainty propagates into f (Eq. (2)) from analytical precision of SOM measurements, DWH oil, and the pre-existing canonical mean through the expression:

$$\sigma_f^2 = \sigma_{\delta_{post}}^2 \frac{1}{(\delta_{oil} - \delta_{pre})^2} + \sigma_{\delta_{pre}}^2 \frac{(\delta_{post} - \delta_{oil})^2}{(\delta_{oil} - \delta_{pre})^4} + \sigma_{\delta_{oil}}^2 \frac{(\delta_{pre} - \delta_{post})^2}{(\delta_{pre} - \delta_{oil})^4} \tag{3}$$

where uncertainties are represented by σ and all other symbols and subscripts are the same as Eqs. (1) and (2). We use 0.12‰ for $\sigma_{\delta_{oil}}$ based on our suite of measurements of oil deposited on Grand Isle, LA, USA, on June 4, 2010. These expressions are used to generate information about the range of measurements that would imply oil contamination in the sea floor sediments.

Using Eqs. (2) and (3) along with the compiled means of $\delta^{13}C_{SOM}$ from the shelf and the open Gulf of Mexico ($-21.7 \pm 1.2‰$ and $-20.4 \pm 1.6‰$ PDB, respectively), it is possible to relate differences between measured $\delta^{13}C_{SOM}$ after the DWH oil spill and the canonical mean before the DWH spill ($\Delta\delta^{13}C$) to the fraction of SOM comprised of oil contamination (Fig. 8). This relationship can be used to determine, at least qualitatively, whether or not DWH oil contamination is likely present in the sediment. It is important to note that the relationship in Fig. 8 is determinant for f, the fraction of oil in sediment. This fraction is not solely controlled by oil contamination falling out of surface or subsurface plumes; high rates of infaunal mixing and natural sedimentation can diminish the amount of oil in a contaminated coretop sample through time and variability in sampling procedure are not incorporated into the uncertainty bounds of Fig. 8. This method is imprecise, as a result of its dependence on the sampling method of the sediment (i.e., to what depth below the interface sediment is taken versus how deep below the interface the contamination is admixed) and the sedimentation and infaunal mixing rates of the sediment. Therefore it is limited to an inexpensive screening method for oil contamination. Such a method would allow a high degree of spatial coverage, with a small possibility of false positives where seeps are sampled. Our coretop data show that $\Delta\delta^{13}C_{SOM}$ and measured values of PAH content do not show a spatial relationship to the DWH wellhead (Fig. 5). The uneven coverage implied by the lack of a relationship is potentially valuable information when evaluating coupled multiphase plume models and regional scale plume circulation models, as well as comparison to assessments of spatial biological impacts (Montagna et al., 2013).

Despite the patchiness of oil contamination evidence in coretop samples, we observe suggestive relationships between $\Delta\delta^{13}C_{SOM}$
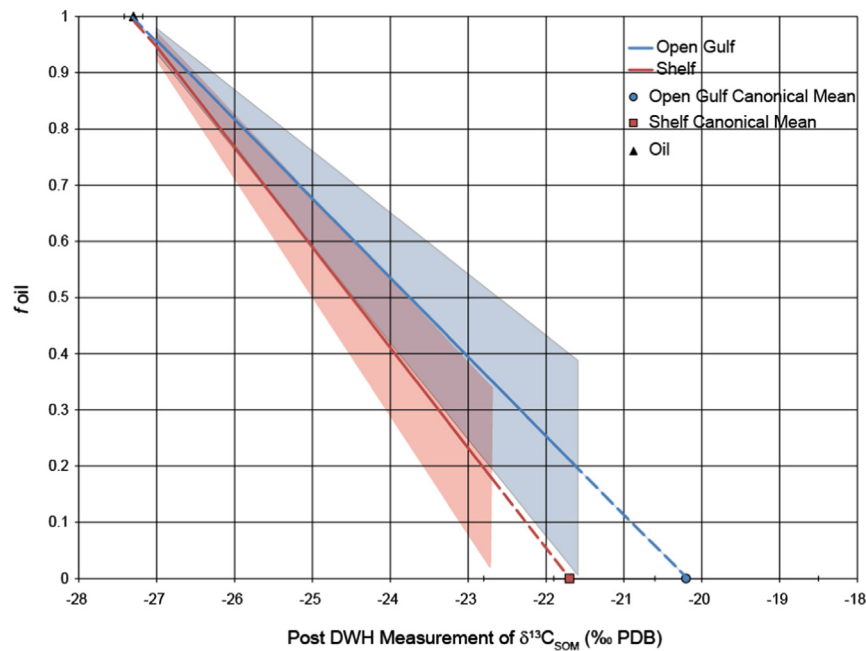

Fig. 8. Uncertainty analysis of binary mixing models of DWH oil (black triangle) and sedimentary organic matter from the shelf (red square) and the open Gulf of Mexico (blue circle). Shaded polygons surrounding the mixing models delineate uncertainty as per Eq. (3). Dashed portions of the mixing models indicate inclusion of numbers that are less than 0 and greater than 1 within the 95% confidence intervals of the solution to Eq. (2). Contribution to uncertainty in f is provided disproportionately by the variance of the canonical means from the shelf and open Gulf of Mexico SOM. As the models approach a higher fraction of oil contamination, uncertainty envelopes grow narrower due to the increased precision of DWH oil measurements.

and PAH content (Fig. 6A). Post-DWH measurements of δ^{13}C values are more precise than the spread about the canonical means from data compiled herein (natural variability). Thus, despite the high analytical precision of modern δ^{13}C measurements, this approach is limited by the natural variability in cases where only small fractions of oil are incorporated into the sediment (Fig. 8). However, it is interesting to consider the relatively good relationship between difference from the canonical mean $\delta^{13}C_{SOM}$ ($\Delta\delta^{13}C_{SOM}$) and PAH content (without perylene, Fig. 6). Polycyclic aromatic hydrocarbons are only a small fraction of oil content, but we use PAHs as a proxy for oil in the sediment because they have been shown to resist degradation better than other oil-associated compounds (Alimi et al., 2003; Wang et al., 1999). In other words, we do not expect the PAHs to directly affect $\delta^{13}C_{SOM}$, but they can indicate the presence of oil-related compounds and their degradation products in the sediment. Furthermore, PAHs are routinely analyzed in sediment due to known toxicity to organisms, so framing any relations to PAH as a proxy for oil is immediately useful to ecologists. Normalized to dry weight of sediment, this relationship shows a statistically insignificant negative slope (Fig. 6A, less PAH when $\Delta\delta^{13}C_{SOM}$ approaches 0). Shelf sediments seem to show the opposite slope from open Gulf of Mexico sediments, but none of these relationships are statistically significant. Sedimentary processes that resuspend and focus sediments of different grain size and density vary widely across our samples sites; thus normalization of PAHs to the dry weight of sediment may not be helpful in relating changes in carbon isotope composition of SOM to oil contamination.

Normalization of concentrations of PAHs to the amount of SOM rather than the dry mass of sediment removes sedimentary processes unrelated to oil plume location and deposition from the water column (Fig. 6B). Here, a negative correlation becomes rather clear for both shelf (including the Mississippi Canyon site located at 510 m depth due to the focusing of shelf sediment and the high rates of deposition (Allison et al., 2005; Sampere et al., 2011)) and open Gulf of Mexico data (open water: $p=0.02$, $n=4$; shelf: $p=0.09$, $n=3$; Fig. 6B). Intercepts of linear regressions through the data provide estimates of background values of petrogenic and anthropogenic PAHs, which can be produced by combustion of organic matter and transported to marine sediment by rivers and atmospheric processes. Background concentrations on the shelf are higher than in the open Gulf of Mexico (Fig. 6B), which would be expected due to the addition of petrogenic PAHs closer to land, especially near the outflow of the Mississippi River where our shelf sites were located. With a small sample size, these background levels derived from intercepts of linear models are not precise (Fig. 6B). However, they compare within reason to previously measured values in sediment (Kennicutt et al., 1996; Soliman and Wade, 2008; Wade et al., 2008). Compared to other values in the literature that are published with %TOC (Soliman and Wade, 2008), our background PAH estimations are lower (22,357 ± 450 ng/gOC herein versus 105,635 ± 41,529 ng/gOC, $n=3$). Direct measurements taken at different times are also quite variable (Soliman and Wade, 2008), which is likely a property of the dynamic sedimentary processes in the shelf are as sampled. Indeed, this relationship may be masked by different rates of infaunal mixing at different sites, effectively diluting the oil contamination signal at different rates, but this consideration serves to make the relationships more suggestive. Excess radiocarbon age observed in this compilation (Fig. 1B) is likely due to infaunal mixing of the sediments, which incorporates older sediment from below with sediment that is being deposited at the sediment–water interface. Effectively, increased rates of infaunal mixing, if not altered by the petroleum contamination directly or indirectly, would serve to dilute the isotope and chemical evidence of pollution. Constraint of infaunal mixing rates will aid in determining
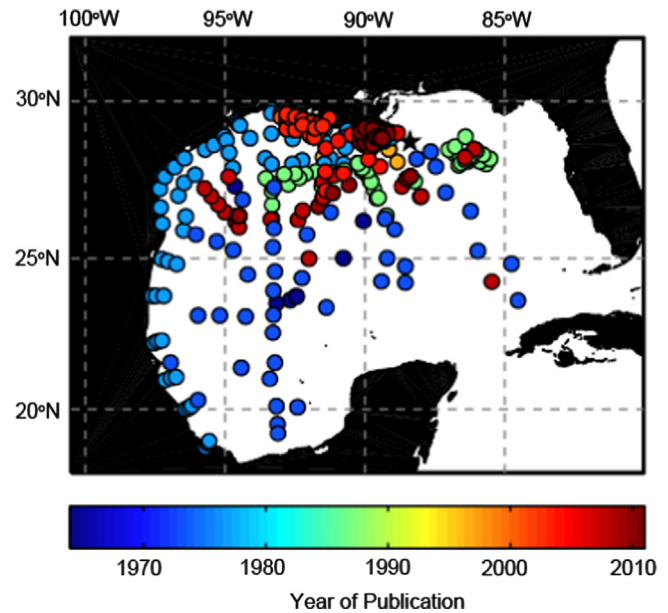

Fig. 9. Isotopic data used in this compilation plotted as year of publication. Since the 1960s and 1970s, the geographic scope of sampling has decreased, with most focus being devoted to the river outlets and seep communities. Coupled with the cost of more recent analytical techniques (radiocarbon, PAHs), background data for more unequivocal indicators of oil contamination are not available.

the utility, if any, of the observed relationship between PAHs and $\Delta\delta^{13}$C. Interestingly, the slopes of the two linear regressions in Fig. 6B seem different, but statistically they are indistinguishable (intercepts are statistically distinct).

Pre-existing radiocarbon (^{14}C) content of the SOM (Fig. 1) could potentially be used in the same way as the $\delta^{13}C_{SOM}$ data except that it has inadequate spatial coverage. Unlike the relationships of $\Delta\delta^{13}C_{SOM}$ (which are being measured near detection limits) and PAHs, measurement of $\Delta\Delta^{14}$C in SOM can be a powerful indicator of oil contamination due precise measurement capability and a large dynamic range between modern sediment and oil. Not enough baseline (pre-2010) data exist for the application of simple mixing models (Eqs. (1) and (2)) using the radiocarbon system, but the data compiled herein can serve as a reference for future studies. In fact, over the same time period (1969–2010) that the isotope data compiled herein were being gathered and more precise measurement techniques were being developed, the geographic scope of research in the Gulf of Mexico was contracting (Fig. 9). The reduced geographic scope of modern ocean-going expeditions and the increased cost of current analytical methods useful in identifying and quantifying oil contamination imply that comparably expansive background data will be difficult to find for scientific questions that involve the geographic expanse of oil contamination.

5. Conclusions

1. Mapping of $\delta^{13}C_{SOM}$ data from the past 5 decades elucidates spatial variability that is not significantly different from open ocean values despite the semi-enclosed nature of the Gulf of Mexico and the large source of terrigenous organic matter from the Mississippi River system. We calculate canonical means for the entire Gulf of Mexico, shelf sediments, deepwater sediments, and seep-affected sediments (-21.4 ± 1.9‰, -21.7 ± 1.2‰, -20.4 ± 1.6‰, -25.2 ± 4.1‰, respectively, $\pm 1\sigma$). Spatial coverage of radiocarbon data is not as wide and limited to recent investigations.

2. Variability in δ^{13}C is largely due to petroleum seeps and, to a smaller spatial extent, river outlets. Ratios approach open

ocean values over relatively short distances seaward from river outlets of all sizes. Removal of the seep data from the data set allows the establishment of canonical pre-2010 $\delta^{13}C_{SOM}$ values for the shelf and the open Gulf of Mexico.

3. Measured values of PAH content (without perylene) and the difference in current $\delta^{13}C_{SOM}$ and canonical values from the pre-2010 compilation of data show that oil incorporation into benthic and littoral sediments are not spatially coherently related to distance from the DWH wellhead site. This is either due to spatially incoherent coverage of this region by DWH spill plumes, different infaunal mixing and sediment focusing processes between sites, or a combination of both.

4. Despite measured values of $\Delta\delta^{13}C_{SOM}$ and PAH being low and close to detection limits in some cases, suggestive relationships between PAH content and $\Delta\delta^{13}C_{SOM}$ are established both for the shelf and open Gulf of Mexico. These relationships suggest background levels of PAH that are higher on the shelf where PAHs can be supplied from river outlets carrying sediment from terrigenous sources. These relationships will need to be tested with more data – this represents a challenge to the community of scientists currently involved in Gulf of Mexico research following the DWH spill.

Acknowledgments

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