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Sediment-preserved diatom assemblages can distinguish a petroleum activity signal separately from the nutrient signal of the Mississippi River in coastal Louisiana

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ABSTRACT

We analyzed the preserved diatom assemblages in dated sediment cores collected from five locations in the Louisiana Bight to test if there was a signature of petroleum extraction activities (hopanes and barium) distinct from the well-documented effects of nutrient loading. The results of a multi-dimensional scaling analysis indicate that the diatom assemblage changes documented throughout the 40 year record could be explained by three variables: barium and hopanes concentrations, and Mississippi River nitrogen loading. The results of a canonical correspondence analysis demonstrated that these signals could be distinguished through correlations with specific diatom species. The abundance of *Actinopterychus senarius*, for example, was negatively correlated with barium and the *Pseudo-nitzschia delicatissima* complex was positively correlated with nitrogen loading. These results provide a “proof-of-concept” demonstration that diatom assemblages preserved in the sediments can be used to study the effects of petroleum extraction activities, and that these ‘petroleum signals’ may be distinguished from other significant influences such as nutrient loading.

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1. Introduction

Oil extraction activities have played significant economic and ecologic roles in coastal Louisiana since the 1940s. Canals, for example, were dredged in coastal wetlands for navigation, pipeline installation, and to transport drilling equipment to inshore and offshore oil fields, resulting in wetland loss (Scaife et al., 1983). Oil production in Louisiana nearshore waters spiked in the early 1970s, and began migrating farther offshore in the 1980s and 1990s (Louisiana Department of Natural Resources; U.S. Department of the Interior, Bureau of Safety and Environmental Enforcement). Produced water discharges increased steadily over this time frame (Turner et al., 2004), whereas the percentage of extracted oil that was spilled has decreased since the 1970s – until the 2010 Macondo oil spill. The State of Louisiana mandated baseline monitoring of background petroleum levels in 1999, resulting in several monitoring efforts over the next decade (e.g., Gisclair and McMillan, 2001; Gisclair and Iqbal, 2005). Although Louisiana has had an extensive oil industry for decades, studies on the potential

impacts of oil spills on the coastal ecosystems were limited prior to 2010. The few ecological studies were primarily concerned with marsh plants (Pezeschki et al., 2000), zooplankton (e.g., Carman and Todaro, 1996), and benthic food webs (e.g., Carman et al., 2000). This dearth of studies meant there were many unknowns in assessing the impacts caused by large oil spills in the northern Gulf of Mexico. The 2010 Macondo oil spill brought these short comings to light.

The Macondo oil spill began on April 20, 2010 when the Deep-Water Horizon drilling rig failed catastrophically, resulting in the release of 4.9 million barrels of oil (Camilli et al., 2010). This oil spill was likely the largest in U.S. history and, coupled with the depth at which the spill occurred (>1500 m), created an unprecedented large and unique set of ecological impacts for the Gulf of Mexico, including coastal Louisiana. Approximately 75 linear km of Louisiana coastline was oiled, primarily on the seaward margins, with additional significant oil landings in northern Barataria Bay (Lin and Mendelssohn, 2012; Silliman et al., 2012). The initial impacts of the oil landfall included marsh grass mortalities and increased margin erosion (Silliman et al., 2012). In addition to the immediate impacts of the oil spill, there is concern as well for long-term (i.e., decadal) effects. For example, ecological impacts

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were still evident in Prince William Sound ten years after the Exxon Valdez accident (Peterson et al., 2003).

The planktonic foodweb component of the Louisiana coastal ecosystem provides a good example of a component where the impacts (especially long-term) of an oil spill are relatively unknown. Numerous studies have examined the toxic effects of oil, the associated water soluble fraction, and dispersants (Corexit®), on various phytoplankton species. Because the composition of crude oil varies according to the geographic region from which the oil was extracted, different crude oils have been tested for toxicological effects (e.g., Nigerian crude oil, Adekunle et al., 2010; Prudhoe Bay crude oil, Harrison et al., 1986). Of all the studies reviewed, the following commonalities were noted: (1) oil is more toxic to diatoms than other phytoplankton groups; (2) toxic effects are greater with increasing light and temperature; and (3) toxicity is associated with continued exposure to the weathering oil, not in response to the volatile aromatic hydrocarbons. Therefore, because diatoms are the dominant group of phytoplankton on the Louisiana shelf (Turner et al., 1998; Dortch et al., 2001), and serve as the base of the foodweb for higher trophic levels, we expect that the fresh and weathered crude oil will likely affect diatom biomass.

Other less affected groups will subsequently increase in abundance (e.g., flagellates), which may divert the trophic transfer of organic matter away from diatom-eating copepods towards ciliates and heterotrophic flagellates, resulting in a trophic cascade. In such cases, the resultant biomass will not be transferred into commercially important species (e.g., menhaden and shrimp), but jellyfishes and comb jellies instead (Greve and Parsons, 1977). It is imperative, therefore, that the impact of the oil on the phytoplankton population (particularly diatoms) is assessed to evaluate what measures can be taken to mitigate the impacts and repair the trophic structure and to weight alternatives to conserve ecosystem functions. The impacts cannot be confronted without an understanding of how the oil spill is impacting the coastal foodweb.

The patchy nature of phytoplankton populations (both temporally and spatially) can make the study of oil impacts difficult. Fortunately, however, the sediment record can be used as a proxy to examine the historical phytoplankton population dynamics in the overlying water column. Diatoms are excellent organisms to use for biological monitoring (Dixit et al., 1992; Smol and Stoermer, 2010). They have a cell wall (frustule) composed of silica that generally preserves well in sediments, the ornamentation of the frustule is species-specific, and many species are sensitive to various environmental parameters (e.g., pH, salinity, and nutrient loading).

Detecting the potential consequences of one stressor, such as oil, are complicated by the changes due to eutrophication. Nitrogen and phosphorus concentrations in the Mississippi River have doubled since the 1950s due to the increased use of fertilizer and subsequent run off in the watershed (Turner and Rabalais, 1991; McIsaac et al., 2001), that has led to severe hypoxia on the Louisiana shelf (Rabalais et al., 2002). Additionally, the concentration of silicate in the Mississippi River decreased by 50% since the 1950s, probably in response to upstream sequestering of silica by freshwater diatoms impounded behind reservoir dams (Turner and Rabalais, 1991). These changes in nutrient inputs to the Gulf Mexico are thought to have altered the nutrient stoichiometry in such a way to favor fast-growing, lightly and/or un-silicified phytoplankton including the toxigenic diatom, *Pseudo-nitzschia*, which appears to have increased in abundance since the 1950s according to sediment core analyses (Parsons et al., 2002). *Pseudo-nitzschia* now commonly blooms and produces the neurotoxin domoic acid, posing a novel harmful algal bloom threat that was likely absent in the past (Parsons et al., 2013).

Diatoms have been used in the northern Gulf of Mexico to identify hurricane layers in sediment cores (Parsons, 1998), to study historical salinity changes in estuaries (Parsons et al., 1999), and

to document the development of eutrophication in salt marshes and shelf waters (e.g., Turner and Rabalais, 1994; Parsons et al., 2002, 2006; Turner et al., 2004). The sediment record has also been used to look for preserved signals of oil extraction activities. For example, Turner et al. (2004) measured barium concentrations in sediment cores collected from the shelf waters of Louisiana as an indicator of barite (BaSO_4) use in the region. Barite is a weighting agent added to oil well-drilling mud which is pumped into the drill hole, counteracting the force of the oil and gas when it is released from the ground, which allows the rig operators to prevent explosive releases of the oil and gas during extraction. Over 75% of barite consumption in the United States is for this drilling application (<http://www.mii.org/Minerals/photovan.html>, Mineral Information Institute). Turner et al. (2004) showed that barium signatures preserved in the sediment cores coincided with historical barite production and consumption in the United States (see Figure 7 in Turner et al., 2004), demonstrating that such barium signatures can be useful as a proxy for oil extraction activities. Overton et al. (2004) analyzed sediment cores collected from Louisiana shelf waters for pyrogenic and petrogenic PAHs. They concluded that the majority of the pyrogenic PAHs (e.g., fluoranthene and pyrene) gradually increased over time, suggesting a chronic contaminant loading from the Mississippi River. Total hopanes proved to be the best-preserved petrogenic PAH group based on oil-fingering analyses and appeared to be related to oil extraction activities and/or natural seeps.

While the above studies demonstrate that the sediment record is capable of preserving signals of oil extraction activities, we know of no study that utilized the preserved diatom record as indicators of such activities. The purpose of this study was to determine if diatom remains could discern a hydrocarbon signal separately from the known nutrient signal present in the sediment record.

2. Methods

2.1. Core collection

Sediment cores were collected at five sites in the Louisiana Bight (D50, E30, E50, E60, and F35) in April 1997 (Fig. 1). Box cores were collected at all sites, with an additional gravity core collected at D50 in anticipation of higher sedimentation rates expected at this site based on previous studies (Turner, unpubl. data). Box core collections were deemed successful if they had an undisturbed sediment–water interface and vertical integrity (i.e., lack of sloughing). Three 3-inch diameter core tubes were inserted into each box core sample to create triplicate subsamples. Compaction measurements were made both after tube insertion and after removal, and

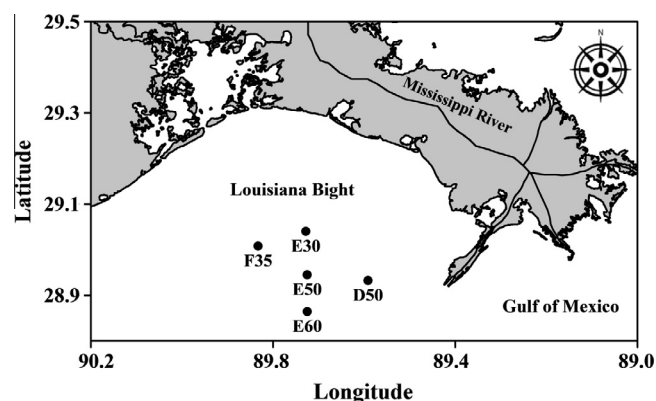


Fig. 1. A map of coastal Louisiana showing the locations of the five coring stations in the Louisiana Bight where sediment cores were collected for this study.

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