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# Fresh and weathered crude oil effects on potential denitrification rates of coastal marsh soil

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## HIGHLIGHTS

- First study to compare effects of fresh and weathered crude oil on denitrification.
- Crude oil decreased marsh soil denitrification rates by ½.
- Fresh crude oil further decrease denitrification after longer exposure.

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## ABSTRACT

On April 20, 2010, the Deepwater Horizon oil platform experienced an explosion which triggered the largest marine oil spill in US history, resulting in the release of ~795 million L of crude oil into the Gulf of Mexico. Once oil reached the surface, changes in overall chemical composition occurred due to volatilization of the smaller carbon chain compounds as the oil was transported onshore by winds and currents. In this study, the toxic effects of both fresh and weathered crude oil on denitrification rates of coastal marsh soil were determined using soil samples collected from an unimpacted coastal marsh site proximal to areas that were oiled in Barataria Bay, LA. The 1:10 ratio of crude oil:field moist soil fully coated the soil surface mimicking a heavy oiling scenario. Potential denitrification rates at the 1:10 ratio, for weathered crude oil, were 46 ± 18.4% of the control immediately after exposure and 62 ± 8.0% of the control following a two week incubation period, suggesting some adaptation of the denitrifying microbial consortium over time. Denitrification rates of soil exposed to fresh crude oil were 51.5 ± 5.3% of the control after immediate exposure and significantly lower at 10.9 ± 1.1% after a 2 week exposure period. Results suggest that fresh crude oil has the potential to more severely impact the important marsh soil process of denitrification following longer term exposure. Future studies should focus on longer-term denitrification as well as changes in the microbial consortia in response to oil exposure.


## 1. Introduction

Oil platforms and associated infrastructure are located within the coastal zone all around the globe. Oil spills can be the result of leakage from storage tanks, distressed vessel, onshore and offshore petroleum wells, or accidental releases during transportation. While infrequent oil spills are likely an unavoidable consequence of oil extraction, transportation, and refinement, it is critical to understand the extent of damage to ecosystem functions, once exposed. In the Gulf of Mexico, there are over 3800 fixed structures and 6500 producing wells connected to an integrated pipeline network more than 48,000 km in length (Kaiser, 2009). In Louisiana alone, there are approximately 1500 oil spill notifications to the National Response Center each year with an annual mean volume of 1.25 million L $yr^{-1}$ (Louisiana Oil Spill Coordinator's Office, 2013). Oil spills in Louisiana account for 20% of the total number of incidents and volume of oil spilled in the United States.

The location of an oil spill (on-shore vs off-shore) can determine the characteristics of the oil that impacts the coastal system. The amount of time the crude oil is in contact with the atmosphere can change both its physical and chemical composition through an initial fractionation (volatilization) process. Fractionation results in the greater loss of the lighter, more volatile, smaller carbon chain fractions (Wang and Fingas, 1995). The most recent and notable example of an offshore oil spill affecting the U.S. coast with

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primarily weathered crude oil is the Deepwater Horizon oil spill which occurred 66 km off the Louisiana coast. This spill released ~795 million L of crude oil over the 87 d event (McNutt et al., 2012; Paris et al., 2012). Once the oil was released from the wellhead, 1.5 km below the surface, the oil rose through the water column and began impacting shorelines in about a week's time (Paris et al., 2012). The south Louisiana light sweet crude oil came ashore in the states of Louisiana, Alabama, Mississippi and Florida driven by wind, waves and currents (Levy and Gopalakrishnan, 2010). However, due to differences in travel time, one can expect that the oil that reached the coastline exhibited variable levels of fractionation due to differences in length of time of exposure.

The characteristics of the crude oil and the extent of the weathering process are important in determining the extent of the impacts to coastal wetland ecosystems, including important biogeochemical processes. Highly weathered oil is dense, forming tar-ball masses and has a tendency to sink affecting benthic communities. Fresh crude oil has components of both heavy fractions that sink and lighter fractions which more effectively cover the plants and surface marsh soils due to high buoyancy related to hydrophobicity. The hydrocarbons in crude oil have variable size ranges of carbon chains. Lighter fraction compounds are with 16 carbon chains or less, and the heavy fraction comprised of >16 carbon chains. The significance of the number of carbons in the chain is that smaller chains are most susceptible to volatilization. In addition, the lighter fractions are not only the more volatile but tend to be more toxic and include decane, undecane, and napthalene (Van Hamme et al., 2003).

The effects of spilled oil on benthic communities, invertebrates, and marsh vegetation have been widely documented (Delaune et al., 1979; Elmgren et al., 1983; Gesteira and Dauvin, 2000; Hester and Mendelssohn, 2000). Various field and greenhouse studies have been conducted to evaluate crude oil effects on selected Gulf Coast salt marsh plants (Delaune et al., 1979; DeLaune et al., 2003). The extent of oiling tends to determine salt marsh vegetation responses which show different levels of sensitivity to oiling (DeLaune et al., 2003). Therefore, while there has been significant research on the effect of oil spills on various coastal ecosystem components, few studies have been conducted on oil impacts on the wetland microbial communities or microbial-driven ecosystem functions (Hamdan and Fulmer, 2011).

Microbes facilitate many biogeochemical processes in coastal wetlands and estuaries, including carbon sequestration (DeLaune and White, 2012), water quality improvements (Gardner and White, 2010) and serve as the essential component that regulates the base of the detrital food chain through enzymatic degradation of soil organic matter (Vidon et al., 2010). Some species of heterotrophic microbes also play an active role in the breakdown of hydrocarbons which can be released as a consequence of natural oil seeps as well anthropogenic hydrocarbon releases into the coastal and marine environments (Hamdan and Fulmer, 2011; Mahmoudi et al., 2013). Denitrifying bacteria, a facultative functional microbial group, reduces nitrate through their respiratory pathway by converting nitrate ($NO_3^-$) to nitrous oxide ($N_2O$) and nitrogen gas (Tiedje et al., 1982). Therefore, denitrification is an important ecosystem function of coastal wetlands as it is an important N removal process in coastal marshes (Gardner and White, 2010; VanZomeren et al., 2012). This ecosystem function is particularly important in coastal Louisiana as excess nitrate in coastal waters can promote significant springtime phytoplankton blooms followed by large expanses of coastal water hypoxia and anoxia (Rabalais et al., 2009).

There have been past studies conducted on the effect of crude oil on denitrification with some conflicting results (Haines et al., 1981; Griffiths et al., 1982; Bonin et al., 1990; Shi and Yu, 2014). However no published study, to our knowledge, has been conducted on the effects of fresh and weathered Louisiana light sweet crude oil on Louisiana coastal saltmarsh in Barataria Basin, the site that received the heaviest oiling during the Deepwater Horizon oil spill. Therefore, the goal of this study was to determine the impact of fresh and weathered crude oil on denitrification and observe the toxicological impacts of the oil on deltaic coastal marsh soil. The secondary goal of this study was to determine any effects of both immediate and longer term exposure of fresh and weathered crude oil on the microbial mediated process of potential denitrification, as microbial communities have shown the ability to rebound or adapt after contaminant exposure.

## 2. Materials and methods

### 2.1. Study site

Barataria bay complex is an interdistributary estuary bordered by the Mississippi River and by Bayou Lafourche containing large tracts of marshes along the coast dominated by *Spartina alterniflora* and interspersed with small bays. The estuary system is shallow and turbid with an average depth of about 2 m (Happ et al., 1977). Several marshes in the Barataria Basin received light to heavy oiling (impacted by oil contamination) during the Deepwater Horizon oil spill (Lin and Mendelssohn, 2012). Twelve marsh soil samples were collected on April 8, 2013 from a *Spartina alterniflora* marsh site within Wilkinson Bay in the Barataria Basin, LA (Fig. 1; N29°27, 976 W89°56, 072). The Emergency Response Management Agency (ERMA) Deepwater Gulf Response mapping efforts documented that sections of the Wilkinson Bay were deemed non-oiled from the Deepwater Horizon oil spill (Fig. 2).

### 2.2. Soil sampling

Surface marsh soil was collected from three, 3 × 3 m quadrants randomly positioned within the Wilkinson bay marsh deemed to be unoiled by the NOAA emergency response team. Each of the quadrants were five meters apart in a triangle formation. Four replicate 10 cm long (7 cm diameter) cores were taken from each 3 × 3 m quad area by push-core and extruded in the field. The samples were placed in 1 L polyethylene containers, stored on ice and upon return to the lab, were refrigerated at 4 °C until analysis. The top 10 cm of soil was the focus of this study since this top interval of soil contains the volume of soil most likely impacted by surface oiling and is the interval in which the majority of denitrification has been found in other Louisiana coastal wetlands (Gardner and White, 2010; VanZomeren et al., 2012).

### 2.3. Soil characteristics

The following soil characteristics were determined; moisture content, bulk density, weight% organic matter, particle size distribution, soil pore water salinity, total carbon (C), nitrogen (N), phosphorus (P), and microbial biomass (N). Moisture content was determined by placing homogenized field moist soil subsamples into a drying oven at 70 °C until constant weight. Bulk density was calculated for the collected soil intervals and expressed on a dry weight basis. Weight% organic matter content was determined as loss on ignition (LOI) using ash weight divided by pre-burned soil weight (White and Reddy, 1999). Particle size analysis was determined by Settling velocity (Patrick, 1958). Salinity of the pore water was measured by first determining the moisture content of samples from the three replicate sampling quads and then combining the field moist samples with DI water at a 1:1 ratio (by weight) in a beaker, mixing well (Putnam-Duhon et al., 2012). The solution