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Spatial Biodegradation Of MC252 Crude Oil On A Coastal Headland Beach

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SPATIAL BIODEGRADATION OF MC252 CRUDE OIL ON A COASTAL HEADLAND BEACH

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College In partial fulfillment of the Requirements for the degree of Master of Coastal and Ecological Engineering

in

The Department of Civil and Environmental Engineering

By
Zachary Joseph Romaine
B.S., Louisiana State University, 2014
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ABSTRACT

Following the Deepwater Horizon oil spill in April, 2010, hard structures were constructed to deter oil migration into sensitive marsh areas behind Fourchon Beach, LA. These hard structures created conditions for accumulation and burial of oil across an 8 foot deep beach vertical profile. Buried oil persists in these areas due to anaerobic conditions of beach groundwater. The objectives of this thesis are to compare the rate and extent of biodegradation of 3-ring PAHs in crude oil deposits from the surface and subsurface, and to investigate effects on beach groundwater after introduction of O₂. Field samples were removed from 2011-2016 from the area including oil samples from depth with a Geoprobe, oil-sand aggregates distributed over the surface of the beach, free oil floating on the groundwater surface and oil recovered during excavations used as part of response in 2013 and 2015. Weathering of PAHs was estimated based on ratios of alkylated phenanthrenes and dibenzothiophenes to poorly biodegradable chrysenes. The average weathering ratio was 0.731±0.22 for phenanthrenes and 0.48±0.22 for dibenzothiophene. Results indicate that oil weathers significantly differently based on location in the beach vertical profile. Oil above the groundwater table was significantly more than buried oil below the groundwater table. Oil above the groundwater table weathers up to 2 orders of magnitude faster than buried oil below the groundwater table. A field trial of in situ biostimulation demonstrated the ability to amend groundwater with oxygen. Weathering of oil buried below the groundwater surface was observed. Terminal electron acceptors and nutrients were evaluated based on repetitive (pre and post oxygen introduction) groundwater analysis of O₂, nitrate, nitrite, ferrous and ferric iron, sulfate, sulfide, ammonium, orthophosphate, pH and alkalinity. Results suggest that oxygenated groundwater is confined locally to emitter wells due to slow groundwater movement. Nutrient concentrations pH and temperature are sufficient for
microbial function; however the hypersaline nature of the groundwater may limit microbe population.
CHAPTER 1: INTRODUCTION AND OUTLINE

1.1. Background

1.1.1 British Petroleum 2010 Crude Oil Spill

The British Petroleum (BP) Deepwater Horizon (DWH) oil platform exploded and began burning on April 20, 2010 (McNutt 2011). Over the next 87 days, roughly 4.9 million barrels of crude oil were released into the Gulf of Mexico (Henaff 2012). Oil was washed ashore across as 1,773 km of the Gulf of Mexico shoreline (Michel 2013). Fourchon Beach, a dynamic 14.5 km (9 miles) stretch of coastal headland beach in Lafourche Parish, LA, was one such location (Figure 1).

In May 2010, an oil-water emulsion, combined with sand, began washing ashore Fourchon Beach (Urbano et. al 2013). Oil/sand mixtures began to adhere to the lower end of the intertidal beach zone as “oil mats” (Michel 2013). These mats became sources of material that washed further onshore (Michel 2013). Two primary forms of Mississippi Canyon Block 252 (MC252) oil residue deposited on shore were supratidal buried oil (SBO) and small surface residual balls (SRBs) (OSAT-2 2011). SBO is found on the supratidal portion of the beach (above the mean high tide water line) below the 6 inch surface cleaning depth and can also become exposed (OSAT-2 2011). SRBs are small oil/sand pieces that are typically found on the beach surface, although they can be covered in sand by physical processes such as wind, tide and storm events. SRBs are typically 5-12 percent oil by weight (OSAT-2 2011).

1.1.2 Crude Oil Weathering

Crude oil is a mixture of numerous compounds, including both hydrocarbons and non-hydrocarbons. Polycyclic aromatic hydrocarbons (PAHs) are hydrocarbons present in crude oil
that are made up of two or more fused benzene rings in linear, cluster or angular arrangements (Eisler 1987). PAHs are highly associated with sediments and tend to linger in the environment. Higher molecular weight PAHs, such as phenanthrene and chrysene, are more persistent (Haritash 2009). As molecular weight increases, water solubility and vapor pressure decrease
(Eisler 1987). These 3 and 4 benzene ring compounds are likely to be found in oil that made landfall. PAHs are the most toxic group of hydrocarbons, with naphthalenes, fluorenes and phenanthrenes being some of the most acutely toxic (OSAT-2 2011; Eisler 1987). While the relative concentration on PAHs in crude oil is small, the concern lay primarily with their carcinogenesis and mutagenic effects (Almeda 2013). PAHs tend to affect membrane fluidity in cells (Cerniglia 1992; Almeda 2013).

PAHs found in water face many possible fates (Liu 2012). It is estimated that roughly one-fourth of the oil from the DWH spill evaporated or dissolved; one-fourth was skimmed, burned or captured; 24 percent of the oil was dispersed; the last 24 percent believed to be still in the water by the beginning of August 2010 (Liu 2012).

Oil can dissolve, evaporate, be chemically or biologically oxidized, or be taken up by aquatic biota. Roughly one-third of PAHs in water are dissolved in the water fraction (Atlas 2011). These are mainly lower molecular weight compounds with higher water solubility (Liu 2012). A large amount of chemical dispersant, COREXIT 9500, was injected directly at the wellhead in an attempt to prevent large slicks from forming at the water surface above the well (Atlas 2011). Due to the extreme depth of water, the oil was successfully dispersed under high pressure (Atlas 2011). This introduced dispersant, along with natural dispersion due to wave turbulence effectively decreased oil droplet size in the Gulf of Mexico (Atlas 2011). This dispersion led to more favorable conditions for the dissolution of some oil compounds into the water column, although most lightweight PAHs dissolved upon reaching the water surface (Liu 2012).

The MC252 spilled during this event was a sweet, light crude. This meant a majority of the PAHs released were considered lightweight PAHs (Liu 2012). Hydrocarbons’ vapor pressure
decreases with molecular weight. Many lightweight PAHs evaporated upon reaching the water surface after exiting the wellhead (Ryerson 2011). Summer temperatures during the months following the spill also provided favorable conditions for evaporation.

Many lightweight PAHs were photo-oxidized following the DWH spill. Photo-oxidation of oil is a key weathering process, especially in a marine environment, in which the photolysis of PAHs occurs. Oil slicks are often found in water with high water content, subject to high amounts of surface solar radiation (Lee 2003). High temperatures such as those experienced during the summer months led to more favorable conditions for photo-oxidation (Eisler 1987). Photo-oxidation of oil leads to formation of oxygenated hydrocarbons and sulfur compounds. This process can occur to oil in several phases, including dissolved droplets and emulsified (water suspended in oil mixture) portions (Lee 2003).

PAH degradation by microbial communities is a major process in soil decontamination (Cerniglia, 1992). Bacteria can completely transform PAHs into organic matter, with CO$_2$ and H$_2$O as byproducts (Atlas 2011). Hydrocarbon degrading bacteria are abundant in marine environments (Kostka, 2011). Groundwater on Fourchon beach is naturally anaerobic. Rates of hydrocarbon microbial degradation are much higher in aerobic conditions compared to anaerobic conditions (Atlas 2011; Beazley, 2012; Xu, 2003). Oxygen is typically found only in the top few centimeters of coastal sediments (Militon, 2015). With the introduction of oil, and thus higher oxygen demand, the groundwater is pushed into a sulfidic state. Factors such as inorganic nutrients, including nitrogen and phosphorus, salinity and temperature are also crucial to successful hydrocarbon degradation (Beazley, 2012). These factors can change significantly throughout the year. Relatively little is known about degradation of PAHs, or pollutants of any
kind for that matter, in high salinity environments (Oren 1992), such as the supratidal portion of Fourchon beach.

1.1.3 Previous Research at Fourchon Beach

Fate and transport of crude oil has been researched on Fourchon Beach prior to this study. This work has shown that vast portions of Fourchon Beach remained oiled well after the spill and response efforts. Curtis mapped and analyzed samples from washover areas on Fourchon Beach (Curtis 2014). Results showed that the most heavily oiled areas are those where physical breaches formed (Curtis 2014), such as Breach 1. This is where large amounts of biodegradation of oil could potentially happen. Westrick showed via lab studies that there can be optimal conditions for oil degradation on a beach. Favorable groundwater conditions include DO > 5 mg/L, > 6 mg-N/L, and > 0.6 mg-P/L (Westrick 2014). Due to the slow rate of oxygen transport and thus low oxygen concentrations in these particular soils though, oil degradation is likely severely impeded, especially at depth.

Urbano showed that individual SRBs have different characteristics, such as nutrients, salinity and moisture content, at different locations of the beach profile (Urbano 2013). While moisture and nutrient limited conditions are commonly found in SRBs in the supratidal portion of the beach, it was demonstrated by Elango that the potential for SRBs in this region to still biodegrade (Elango 2014). In agreement with this, supratidal SRBs were found to have PAH concentrations an order of magnitude lower than those in oil mats near the ocean edge in Urbano 2013 (Urbano 2013). The hypothesis that oil degradation potential can vary due to location on a beach can be thus be made.

1.2. Research Objectives

The objectives of this study are
1) Determine how the weathering and the rate of weathering of crude oil is affected by location across a beach vertical profile.

2) Develop an understanding of groundwater movement and chemistry, such as electron acceptors, nutrients, salinity and pH at Fourchon Beach.

Objective 1 will be discussed in Chapter 2, and Objective 2 will be discussed in Chapter 3.

1.3. Environmental Relevance

The research presented in this paper seeks to determine the effects of crude oil on Fourchon Beach, LA. Specifically, it will address how oil is weathering, if at all, at varying portions of the beach vertical profile, for example surface vs subsurface. It will also address the effect of buried oil on groundwater below the beach surface. While much research about oil degradation has been conducted on Fourchon beach, this paper intends to present oil weathering data for all oil sample types across the entire vertical profile, rather than one beach section or oil sample type. This will assist oil response team leaders in the future in choosing the correct course of remedial action.

1.4. Organization of Thesis.

Chapter 2 reviews weathering rates for various oil sample types at different locations of a coastal headland beach. Chapter 3 presents results of a groundwater assessment of the supratidal portion of Fourchon Beach. This includes nutrient and electron acceptor analysis, as well as physical groundwater flow rate and direction. Chapter 4 summarizes these results and discusses future research avenues.
CHAPTER 2: RELATIVE WEATHERING RATES OF MC252 OIL ACROSS A COASTAL HEADLAND BEACH PROFILE

2.1 Introduction

Following the Deepwater Horizon oil spill on April 2, 2010, an estimated 4.9 billion barrels of crude oil spilled into the Gulf of Mexico over the next 87 days (Henaff 2012). Fourchon Beach, a dynamic 14.5 km stretch of coastal headland beach in Lafourche Parish, LA, was oiled in the following months (Michel, Owens et al. 2013). An oil-water emulsion, combined with sand, began washing ashore Fourchon Beach in May 2010 (Urbano, Elango et al. 2013). These oil/sand mixtures began to adhere to the lower end of the intertidal beach zone like slabs, or “oil mats” (Michel, Owens et al. 2013). These mats became parent sources of material that washed further onshore in the following months and years (Michel, Owens et al. 2013).

Following the spill, Fourchon Beach possessed poorly developed dune systems, with mudflats and sensitive mangrove and marshes to its rear (Curtis et al. 2016). Occasional tropical weather events and cold fronts produce high water events of more than 1-2 meters which produce beach erosion, overwash and barrier breaching (Georgiou et al. 2005). These processes led to oil mobilization and distribution throughout the beach vertical profile of the including transport to supratidal areas (Urbano 2013) and the mudflats, mangroves and marshes behind the beach (Curtis et al, 2016).

The two primary forms of Mississippi Canyon Block 252 (MC252) oil deposited on Fourchon Beach were supratidal buried oil (SBO) and small surface residual balls (SRBs) (OSAT-2 2-11). SBO is found below the 6 inch surface cleaning depth and can also become exposed (OSAT-2 2011). SRBs are small oil/sand pieces, generally 0.5-5cm in diameter, with an oily core coated in a layer of sand and shell (OSAT-II 2011, Urbano, Elango et al. 2013,
Dalyander, Long et al. 2014, Lemelle, Elango et al. 2014). SRBs are typically 5-12 percent crude oil by weight (OSAT-2 2011). They are typically found on the beach surface, although they can be buried by sand by physical processes such as wind, tide, overwash and storm events (Georgious et al. 2005; OSAT-2 2011). Many standard cleanup methods, primarily via manual and mechanical methods (i.e. excavators, backhoes, etc.), were disruptive to the natural beach system and its inhabitants (OSAT-2 2011). Beach sand was hand sieved to separate sand from SRBs (OSAT-2 2011). Periodically, however, SRBS are left on a beach during a response effort due to the assumption that they will degrade naturally over time (OSAT-2 2011).

Weathering processes for PAHs including volatilization, photodegradation, dissolution and biodegradation. For buried crude oil, these processes have the potential to slow significantly. PAH degradation by microbial communities is a major process in soil decontamination (Cerniglia 1992). Bacteria can completely transform crude oil, including PAHs, into organic matter, with CO₂ and H₂O as byproducts (Atlas 2011). In a previous study at Fourchon Beach, Urbano showed that individual SRBs have different characteristics, such as nutrients, salinity and moisture content, at different locations of the beach profile (Urbano, Elango et al. 2013). Factors such as inorganic nutrients, including nitrogen and phosphorus, salinity and temperature are crucial to successful hydrocarbon degradation (Beazley 2012). While moisture and nutrient limited conditions are commonly found in the SRBs in the supratidal portion of the beach, it was demonstrated by Elango that there is potential for SRBs in this region to biodegrade (Elango 2014). In agreement with this, supratidal SRBs were found to have PAH concentrations an order of magnitude lower than those in oil mats near the ocean edge in Urbano 2013 (Urbano, Elango et al. 2013). Oxygen is typically found only in the top few centimeters of coastal sediments (Militon 2015). Oil degradation of buried oil is typically very slow in oxygen-deprived areas.
(Atlas 2011), such as the supratidal, subsurface layer of fine grained Louisiana beaches (OSAT-2 2011). Rates of hydrocarbon microbial degradation are much higher in aerobic conditions compared to anaerobic conditions (Atlas 2011; Beazley 2012; Xu 2003). Westrick showed via lab studies that there can be optimal conditions for oil degradation on a beach (Westrick et al. 2014). Favorable groundwater conditions include DO > 5 mg/L, > 6 mg-N/L, and > 0.6 mg-P/L (Westrick et al. 2014). Due to the slow rate of oxygen transport and thus low oxygen concentrations in these particular soils (OSAT-2 2011), oil degradation is likely severely impeded, especially at depth. High water salinity, high temperatures and nutrient availability may also inhibit degradation (Atlas 2001; Oren 1992) of buried oil on the supratidal portion of Fourchon Beach.

In this paper, rates of weathering were assessed for oil samples collected from a segment of Fourchon Beach where a hard structure was used to close a breach (Bayou Ferblanc) in the beach surface centered at 29.166148 N, -90.092755 W. Following the oil spill, several hard structures including rock dams and bulkheads were built across open breaches on Fourchon Beach to deter oil migration to the sensitive marsh areas behind the beach. The area under study was designated “Breach 1” and was located on the easternmost mile of Fourchon Beach (Figure 2). Oil was distributed across the breach area on the surface and subsurface. In previous work, Curtis mapped and analyzed samples from washover areas on Fourchon Beach (Curtis et al. 2016). Results showed that the most heavily oiled areas are those where physical breaches formed (Curtis et al. 2016). While the goal of oil entrapment was accomplished by the dam at Breach 1, the former breach channel was filled with oil and sand. This created a beach surface contiguous with the adjoining beach (Figure 3).
Figure 2- Hard structure dam at Breach 1, July 2010

Figure 3- Hard structure dam at Breach 1, November 2012
The hypothesis that oil degradation potential can vary due to location on a beach can be thus be made. The intent of this paper is to understand oil weathering and determine weathering rates of oil at different locations on Fourchon Beach, in order to assist future response efforts in making remedial decisions.

2.2 Material and Methods

2.2.1 Study Location and Sampling Events

The study site for this field study was located on the easternmost mile segment of Fourchon Beach, a 14.5 km coastal headland beach in Port Fourchon, LA. The segment under study includes the area designated during the cleanup as “Breach 1”, the location of the now former Bayou Ferblanc where a hard structure was installed following the Macondo oil spill to deter oil migration into the marsh. Twenty four separate sampling events occurred at Breach 1 from 2012 to 2016. Five types of samples were taken from the supratidal portion of Breach 1 for oil extraction and analysis: surface and subsurface SRBs, excavation and drill spoils from response activities and monitoring well construction, respectively, loose oiled-sands, subsurface cores obtained using direct push (Geoprobe) and oil floating on groundwater in monitoring wells. The number of dates each type of sample was collected is as follows: SRB (16), excavation and drill spoils (6), loose oiled-sand (6), subsurface cores (2) and oil floating on groundwater (4).

Details on these samples are presented below.

Several sample types were taken from the supratidal zone of the beach, north of the beach crest. Three main general classifications were used: (1) surface oil, (2) subsurface oil above the water table and (3) buried oil beneath the water table. Surface oil consisted of SRBs, oil:sand aggregates, and loose oiled samples collected from the beach surface and placed in 125 mL jars.
Subsurface oil above the groundwater level consisted of SRBs sampled following storm events. Wind and beach overwash created shallow washover channels on the beach, exposing once buried SRBs. These samples are representative of subsurface SRBs previously residing in the top ~30 cm of beach sands above the typical groundwater depth on the beach. These SRBs were collected and stored in as described above. Finally, several types of buried oil below groundwater level were collected. During attempts to clean Breach 1 using manual and mechanical response methods, samples were collected of previously buried oil from the spoils immediately after excavation. Also, buried oil during rotary drilling for monitoring well installation, previously buried oil was sampled from the drill spoils. These samples represent homogenized sections from 0-1.5 and 1.5-3 m below ground surface. In addition, free oil samples were collected floating on the groundwater surface. Oil was collected in plastic sample tubing in monitoring wells. The portion of heavily oiled tube was cut with a knife and placed in a labeled 125 mL glass jar. Hexane:acetone (50:50 v:v) was then used to removed oil from the tubing. Finally, core samples were taken before and after oxygen addition using a skid steer-mounted Geoprobe direct push sampling device. Samples were taken adjacent to wells currently used for an aerobic bioremediation field study and a reference area approximately 100m west of the Breach 1 in a beach section with no buried oil. The sample sleeves were labeled and capped for transportation to the laboratory. Once in the lab, four inch sample segments were taken from each core at standardized vertical profile depths: 0.56, 0.84, 1.5 and 2.1 meters below ground surface. Samples were also taken in sections where oil was visually seen or smelled along the core segments. All oil samples were kept at -18 degrees Celsius until laboratory analysis.
2.2.2 Oil Extraction and Analysis

Samples were kept on ice until they were brought to the lab, where they were then stored in freezers at -18 degrees Celsius. Oil extractions were performed by thoroughly mixing the sample, weighing approximately 10 grams, and then mixing the sample with diatomaceous earth. Once the soil and diatomaceous earth were thoroughly mixed, they were transferred into individual stainless steel cells for accelerated solvent extraction. The cells were placed in a Dionex Accelerated Solvent Extractor (ASE) 350 (Thermo Scientific), and extracted with a 50:50 mixture of hexane and acetone under 1700 psi of pressure at a temperature of 100°C. Once completed, the solvent sample volume was reduced to 10 mL using a RapidVac N2 Evaporation System (Labconco, USA) at 35% speed and 70 degrees Celsius. Highly viscous samples were concentrated to 20 mL. One mL subsample of the concentrated eluate and 5 μL deuterated internal standard (naphthalene, acenaphthylene, phenanthrene, and chrysene) were combined in 1.5 mL Agilent screw-top vials. Analysis was performed using a Hewlett Packard 6890N gas chromatograph equipped with a 5973N mass selective detector. The GC conditions were: 1 μl of the sample; DB 5 capillary column (30 m x 0.25 mm x 0.25 μm film), carrier gas (helium) at a rate of 5.7 mL/min, temperature program: injector 300°C, detector 280°C, oven temperature: 45°C for 3 min then increased at 6°C/min to 315°C and held for 15 min. For each set of samples, the QA/QC included adding blanks (1 mL hexane/acetone at 50:50 with 5 μL internal standard), using internal standard within each sample and running a calibration check sample. The PAH method calculates the following compounds: naphthalene (C0N), C1-naphthalenes (C1N), C2-naphthalenes (C2N), C3-naphthalenes (C3N), C4-naphthalenes (C4N), acenaphthylene (ACL), acenaphthene (ACE), fluorene (F), C1-fluorenes (C1F), C2-fluorenes (C2F), C3-fluorenes (C3F) phenanthrene (C0P), C1-phenanthrenes (C1P), C2-phenanthrenes (C2P), C3-phenanthrenes
(C3P), C4-phenanthrenes (C4P), dibenzothiophene (C0D), C1- dibenzothiophenes (C1D), C2-dibenzothiophenes (C2D), C3- dibenzothiophenes (C3D), fluoranthene (FAN), pyrene (PY), C1-pyrene/fluoranthene (C1-PY/FA), chrysene (C0C), C1-chrysenes (C1C), C2- chrysenes (C2C), and C3-chrysenes (C3C). C30-Hopane was also quantified in order to ratio the oil concentration (Urbano et al., 2013).

2.2.3 Weathering Ratio

Weathering ratios were used in order to normalize concentrations of various PAHs to demonstrate the extent of weathering (Curtis et al. 2016; Diercks et al. 2010; Hong et al. 2016; Ruby et al. 2016; Westrick et al. 2014) In particular, 2 sets of ratios are presented in this paper that compare concentrations of 3 ring alkylated PAHs (phenanthrene and dibenzothiophenes) with recalcitrant 4-ring chrysenes. The phenanthrene (Eq. 1) and dibenzothiophene (Eq. 2) ratios were taken from each alkyl homolog group and normalized to the sum of alkylated chrysenes, more resistant to biodegradation.

\[
PWR = \frac{\Sigma C_{1}, C_{2}, C_{3}, C_{4} \text{ Phenanthrene}}{\Sigma C_{1}, C_{2}, C_{3}, C_{4} \text{ Phenanthrene} + \Sigma C_{1}, C_{2}, C_{3} \text{ Chrysene}} \quad \text{Eq. 1}
\]

\[
DWR = \frac{\Sigma C_{1}, C_{2}, C_{3} \text{ Dibenzothiophene}}{\Sigma C_{1}, C_{2}, C_{3} \text{ Dibenzothiophene} + \Sigma C_{1}, C_{2}, C_{3} \text{ Chrysene}} \quad \text{Eq. 2}
\]

2.2.4 Statistical Analysis

Statistical analysis to compare sample sets was performed using SigmaPlot software. First, the Shapiro-Wilk test was employed on paired samples to check for normality. The chosen alpha level was 0.05. A p-value greater than 0.05 was indicative of a normally distributed population. The population was not normally distributed if p-values were lower than 0.05. A two tailed t-test was then run to test for differences between two sets of normally distributed data.
resulting p-value of less than 0.05 indicated significant difference between data sets. The Mann Whitney Rank Sum test was run for data not normally distributed. A p-value of less than 0.001 was indicative of statistical significance.

2.2.5 Oil Weathering Rates

Oil samples were grouped using the classifications surface, subsurface and buried oil. Reactions were assumed to be first order. A linear regression analysis was performed for phenanthrene and dibenzothiophene ratios for each sample group. The equation used is as follows:

\[ \ln \frac{C}{C_0} = -kt \]

Where: 
\( C = \) Weathering ratio  
\( C_0 = \) Initial weathering ratio  
\( k = \) Reaction rate coefficient (days\(^{-1}\))  
\( t = \) Time (days)

The left side of the equation is unit-less. Regression analysis was performed using SigmaPlot.

2.3 Results and Discussion

2.3.1 Oil Weathering During Natural Attenuation

A total of 187 samples collected from 2013 to 2016 were extracted and analyzed for PAH concentrations which were subsequently used to create the weathering ratios described above. Samples collected across this spatial and temporal gradient at Breach 1 demonstrated significant differences in weathering of 3-ring PAHs relative to the more recalcitrant alkyl chrysenes. (Figure 4). Weathering is indicated by movement of the phenanthrene and dibenzothiophene ratios towards the origin. Ratios constructed from oil data collected at the surface near the wellhead in 2010 were used as a reference point for comparison (phenanthrene=0.935, dibenzothiophene=0.798) (Diercks et al. 2010). When compared to this reference point, changes
in the weathering ratios on Fourchon Beach represent 2 changes: weathering that occurred at sea between the wellhead and the shoreline and weathering that occurred on the beach since oil arrived in April 2010.

Figure 4- Weathering ratios of Breach 1 SRB and soil samples from 2013-2016. Ratios are taken from each alkyl homolog group (phenanthrenes and dibenzothiophenes) and normalized to the sum of chrysenes.

Overall, weathering ratios ranged from 0.168-0.972 (0.731±0.22) for phenanthrenes and 0.028-0.86 (0.48±0.22) for dibenzothiophenes (Table 1). The lowest ratios were found for subsurface samples, the category of oil that was beneath the sand but above the water table. Subsurface oil above the groundwater level had phenanthrene and dibenzothiophene ratios 5 and 6 percent lower than surface oil. Confirmed by t-tests using SigmaPlot software, weathering ratios for surface and subsurface oil above groundwater level (SRBs and loose sand) experienced
significantly more phenanthrene and dibenzothiophene weathering than buried oil below groundwater level. Values for each weathering ratio with differing superscripts represent statistical difference.

Table 1- Average phenanthrene and dibenzothiophene weathering ratios by sample type

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>ΣPhen/Σ(Phen+Chry)</th>
<th>ΣDiben/Σ(Diben+Chry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>0.668±0.19</td>
<td>0.418±0.19</td>
</tr>
<tr>
<td>Subsurface above groundwater level</td>
<td>0.632±0.23</td>
<td>0.373±0.21</td>
</tr>
<tr>
<td>Buried below groundwater level</td>
<td>0.903±0.04</td>
<td>0.664±0.09</td>
</tr>
<tr>
<td>All Samples</td>
<td>0.731±0.22</td>
<td>0.48±0.22</td>
</tr>
</tbody>
</table>

2.3.2 Rates of Oil Weathering

Weathering ratios for surface oil samples (n=44) averaged 0.668±0.19 for phenanthrene and 0.418±0.19 for dibenzothiophene (Table 2). The lowest phenanthrene and dibenzothiophene ratios were both seen in May and August 2015. These sampling events were when the last surface oil samples were taken. Total concentrations of ranged from 32.1 to 762 mg/kg. A general trend of lowered total PAH concentrations over the sample period was seen, with 3 samples from January 16 and 26, 2015, as outliers. Lower weathering ratios are generally coupled with relatively lower total concentrations. A general trend of weathering ratio reduction was seen over the sampling period. This trend was confirmed by a regression analysis, performed as described above. Weathering rate constants were found to be -0.0018 day⁻¹ and -0.0001 day⁻¹ for phenanthrene and dibenzothiophene, respectively.

Subsurface oil samples from above groundwater level (n=79) were analyzed for total PAHs (Table 3). A general trend of decreasing phenanthrene and dibenzothiophene ratios was seen over time. The last two data sets from August 2015 and January 2016 show substantial
weathering of both phenanthrenes and dibenzothiophenes. Total PAH concentrations ranged from 32.1 to 346 mg/kg. Total PAH concentration appeared loosely directly correlated to phenanthrene and dibenzothiophene ratios. Weathering rate constants found during regression analysis were -0.0007 day\(^{-1}\) and -0.0014 day\(^{-1}\) for phenanthrene and dibenzothiophene, respectively.

Table 2- Surface oil phenanthrene and dibenzothiophene weathering ratios and absolute concentrations. Total PAH given by mg PAH per kg soil.

<table>
<thead>
<tr>
<th>Year</th>
<th>Date</th>
<th>n</th>
<th>ΣPhen/Σ(Phen+Chry)</th>
<th>ΣDiben/Σ(Diben+Chry)</th>
<th>Total PAH (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014</td>
<td>23-Apr</td>
<td>3</td>
<td>0.815±0.050</td>
<td>0.584±0.035</td>
<td>163±157</td>
</tr>
<tr>
<td></td>
<td>19-Jun</td>
<td>4</td>
<td>0.891±0.050</td>
<td>0.671±0.050</td>
<td>220±110</td>
</tr>
<tr>
<td></td>
<td>6-Aug</td>
<td>1</td>
<td>0.889</td>
<td>0.631</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>8-Oct</td>
<td>4</td>
<td>0.785±0.050</td>
<td>0.416±0.052</td>
<td>111±22.0</td>
</tr>
<tr>
<td></td>
<td>7-Nov</td>
<td>4</td>
<td>0.548±0.17</td>
<td>0.275±0.078</td>
<td>59.4±34.7</td>
</tr>
<tr>
<td></td>
<td>21-Nov</td>
<td>6</td>
<td>0.709±0.060</td>
<td>0.422±0.075</td>
<td>35.4±8.55</td>
</tr>
<tr>
<td>2015</td>
<td>16-Jan</td>
<td>1</td>
<td>0.852</td>
<td>0.531</td>
<td>762</td>
</tr>
<tr>
<td></td>
<td>26-Jan</td>
<td>2</td>
<td>0.871±0.012</td>
<td>0.587±0.024</td>
<td>650±90.9</td>
</tr>
<tr>
<td></td>
<td>30-Jan</td>
<td>4</td>
<td>0.813±0.12</td>
<td>0.634±0.20</td>
<td>32.1±13.9</td>
</tr>
<tr>
<td></td>
<td>14-May</td>
<td>10</td>
<td>0.474±0.115</td>
<td>0.282±0.149</td>
<td>38.5±7.36</td>
</tr>
<tr>
<td></td>
<td>10-Aug</td>
<td>5</td>
<td>0.440±0.13</td>
<td>0.207±0.034</td>
<td>54.3±26.3</td>
</tr>
</tbody>
</table>

Table 3- Subsurface oil above groundwater level phenanthrene and dibenzothiophene weathering ratio and absolute concentrations by date. Total PAH given by mg PAH per kg soil.

<table>
<thead>
<tr>
<th>Year</th>
<th>Date</th>
<th>n</th>
<th>ΣPhen/Σ(Phen+Chry)</th>
<th>ΣDiben/Σ(Diben+Chry)</th>
<th>Total PAH (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>9-May</td>
<td>4</td>
<td>0.794±0.031</td>
<td>0.567±0.036</td>
<td>53.5±17.0</td>
</tr>
<tr>
<td></td>
<td>7-Jun</td>
<td>7</td>
<td>0.883±0.029</td>
<td>0.640±0.048</td>
<td>346±94.3</td>
</tr>
<tr>
<td></td>
<td>11-Nov</td>
<td>2</td>
<td>0.868±0.060</td>
<td>0.676±0.040</td>
<td>116±113</td>
</tr>
<tr>
<td>2015</td>
<td>9-Jan</td>
<td>3</td>
<td>0.758±0.1</td>
<td>0.422±0.14</td>
<td>92.3±63.8</td>
</tr>
<tr>
<td></td>
<td>16-Jan</td>
<td>8</td>
<td>0.783±0.14</td>
<td>0.509±0.15</td>
<td>152±85.7</td>
</tr>
<tr>
<td></td>
<td>26-Jan</td>
<td>8</td>
<td>0.823±0.06</td>
<td>0.560±0.085</td>
<td>171±121</td>
</tr>
<tr>
<td></td>
<td>30-Jan</td>
<td>8</td>
<td>0.614±0.25</td>
<td>0.374±0.20</td>
<td>114±117</td>
</tr>
<tr>
<td></td>
<td>10-Aug</td>
<td>2</td>
<td>0.287±0.056</td>
<td>0.0826±0.055</td>
<td>36.0±2.18</td>
</tr>
<tr>
<td>2016</td>
<td>25-Jan</td>
<td>37</td>
<td>0.492±0.18</td>
<td>0.228±0.13</td>
<td>32.1±17.8</td>
</tr>
</tbody>
</table>
PAH concentrations of buried oil samples below groundwater level (n=64) ranged from 16.5 to 557 mg/kg (Table 4). Total PAH concentrations were highest in samples from November and December 2013. Omitting these dates gives a Total PAH average of 16.9 mg/kg for buried oil samples. While total PAH concentrations appear to be relatively low in some samples, particularly throughout 2015, the phenanthrene and dibenzothiophene ratios are higher than those found in surface and subsurface oil, shown in Tables 2 and 3. This is indicative of diluted oil in samples and not of oil weathering. The phenanthrene ratio average was 18 and 22 percent higher than surface and subsurface oil above groundwater level, respectively. Surface and subsurface oil dibenzothiophene ratios were 27 and 31 percent lower, respectively. Weathering rates were low for buried oil. The phenanthrene rate constant was 0.00002 day\(^{-1}\), and the dibenzothiophene rate constant was -0.00003 day\(^{-1}\).

Table 4- Buried oil below groundwater level phenanthrene and dibenzothiophene weathering ratios and absolute concentrations. Total PAH given by mg PAH per kg soil.

<table>
<thead>
<tr>
<th>Year</th>
<th>Date</th>
<th>n</th>
<th>ΣPhen/Σ(Phen+Chry)</th>
<th>ΣDibenΣ(Diben+Chry)</th>
<th>Total PAH (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>13-Nov</td>
<td>12</td>
<td>0.888±0.26</td>
<td>0.649±0.48</td>
<td>557±131</td>
</tr>
<tr>
<td></td>
<td>1-Dec</td>
<td>1</td>
<td>0.858</td>
<td>0.575</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>2-Dec</td>
<td>3</td>
<td>0.913±0.017</td>
<td>0.681±0.039</td>
<td>493±626</td>
</tr>
<tr>
<td></td>
<td>6-Dec</td>
<td>2</td>
<td>0.842±0.0026</td>
<td>0.622±0.58</td>
<td>41.3±30.0</td>
</tr>
<tr>
<td>2015</td>
<td>9-Jan</td>
<td>10</td>
<td>0.954±0.02</td>
<td>0.738±0.11</td>
<td>11.7±11.2</td>
</tr>
<tr>
<td></td>
<td>16-Jan</td>
<td>16</td>
<td>0.925±0.41</td>
<td>0.706±0.098</td>
<td>8.70±7.41</td>
</tr>
<tr>
<td></td>
<td>10-Jun</td>
<td>20</td>
<td>0.880±0.029</td>
<td>0.614±0.53</td>
<td>16.5±15.2</td>
</tr>
</tbody>
</table>

Surface oil and subsurface oil above groundwater level weathering ratios lowered significantly as a function of time. To determine the significance of weathering, two-tailed student t-tests and the Mann Whitney Rank Sum test were employed using Sigma Plot. Surface oil was weathered significantly from 2014 to 2015, found using a t-test (P<0.05) (Table 5).
Likewise, the subsurface oil above groundwater level dibenzothiophene weathering ratio from 2013 to 2015 was significantly different (P<0.05), however the decrease in phenanthrene ratio was not (P>0.05). Using the Rank Sum test, phenanthrene and dibenzothiophene ratios were found to have decreased significantly (P<0.001) in subsurface oil above groundwater level between 2015 and 2016. Weathering of buried oil below groundwater level between 2013 and 2015 was not significant.

Table 5- Statistical analysis of oil weathering (phenanthrene and dibenzothiophene ratios) by sample type and year. Numbers indicate P values found from Mann Whitney Rank Sum Test and two-tailed student t-test.

<table>
<thead>
<tr>
<th></th>
<th>Surface 14 vs 15</th>
<th>Subsurface above groundwater level 13 vs 15</th>
<th>13 vs 16</th>
<th>15 vs 16</th>
<th>Buried below groundwater level 13 vs 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phen</td>
<td>0.006</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.998</td>
</tr>
<tr>
<td>Dibenz</td>
<td>0.036</td>
<td>0.003</td>
<td>0.001</td>
<td>0.001</td>
<td>0.634</td>
</tr>
</tbody>
</table>

The results suggest that dibenzothiophenes are preferentially weathered during initial processes. Past research has found that dibenzothiophenes can be converted by bacteria to biphenyl under sulfate reducing conditions (Armstrong 1995), such as those found at Breach 1. The phenanthrene weathering rate for surface oil was 2.6 times larger than subsurface oil. The dibenzothiophene weathering rate constants for surface oil was much lower than subsurface oil above groundwater level (0.0001 day⁻¹ vs -0.0014 day⁻¹). Dibenzothiophenes weathered very little in buried oil below groundwater level, and phenanthrene appeared to not weather at all with time. Rate constants for all groups match the data presented in the double ratio plots (Figure 4), in which non-buried oil was preferentially weathered, as were dibenzothiophenes. Overall, dibenzothiophene weathering appeared slightly more prevalent than phenanthrene weathering for surface samples and subsurface samples above groundwater level, particularly in samples closest
to the un-weathered reference point. Phenanthrene degradation appeared lower than
dibenzothiophene degradation in buried samples.

2.3.3 Oil Weathering in Response to In Situ Bioremediation

In July 2015, an active bioremediation project began at Breach 1 (discussed in detail in
Chapter 3 of this paper). Its goal was to provide oxygen to microbes in the anaerobic zone
beneath Breach 1 to enhance oil degradation. From July 22 to September 30, compressed air was
diffused into groundwater at Breach 1 through Waterloo emitters installed in groundwater wells.
From October 1, 2015 to April 27, 2016, compressed pure oxygen was used in lieu of
compressed air.

Three 2” diameter soil cores (a, b, c) were taken downgradient of 3 emitter wells (A1, B2, B3), for a total of 9 94” deep cores. Each core within each set was roughly a meter apart. Cores “a” were closest to their respective emitter well, and cores “c” were furthest, with cores “b” between them. Segments from each core were using the method detailed previously. Weathering ratios developed following GC-MS analysis are presented in Figures 5, 6 and 7. 2015 samples represent samples from the September 30, 2015 coring, following 2 months of compressed air addition. Three background cores were also taken during this event. 2016 samples represent samples from the May 5, 2016 coring, following an additional 7 months of pure oxygen addition.

Weathering ratios were lowest for samples taken from the unoiled reference location. Samples from the A1 well series showed primarily dibenzothiophene weathering during 2015, although phenanthrene weathering was seen in a few samples (Figure 5). Samples from 2016 indicated that only dibenzothiophene was weathering. The B2 well series samples from 2015 saw weathering of primarily phenanthrenes, particularly in core b (Figure 6). Cores a and c
experienced primarily dibenzothiophene weathering in 2016. Weathering seemed similar in all 3 B3 cores from 2015 (Figure 7). Phenanthrenes weathered preferentially compared to dibenzothiophenes. Samples from 2016 had weathering ratios closer to unweathered MC252 oil.

Figure 5- Weathering ratios of Breach 1 soil core samples (A1 well series) from 2015 and 2016. Ratios are taken from each alkyl homolog group (phenanthrenes and dibenzothiophenes) and normalized to the sum of chrysenes.
Figure 6- Weathering ratios of Breach 1 soil core samples (B2 well series) from 2015 and 2016. Ratios are taken from each alkyl homolog group (phenanthrenes and dibenzothiophenes) and normalized to the sum of chrysenes.
2.4 Conclusions

The hypothesis that oil weathering under natural environmental conditions differs by location on a beach was generally corroborated by results presented in this paper. Weathering ratios were significantly higher in buried samples below groundwater level than SRB samples above the groundwater table. This result has been previously found in other oil fate work (Elango et al., 2014; Lemelle et al., 2014; OSAT-II, 2011; Urbano et al., 2013) However, a statistical difference was not found between surface oil and subsurface oil above groundwater level. This finding of insignificance may have been a result of sampling. The morphology of Fourchon Beach is very dynamic, and SRBs are constantly covered and unsurfaced. The length of time...
SRB were exposed, even partially, before collection was unknown. However, the lack of statistical difference is likely due to the fact that while buried SRBs are covered by sand, they are generally shallowly buried, above the groundwater surface. Oxygen levels in this zone are lower due to poor diffusion through beach sands (OSAT-2 2011) but are still higher than in anoxic groundwater. Sufficient oxygen is available for biodegradation by native microbes.

Weathering rates of SRBs agreed with previous work and general hypotheses. Dibenzothiophenes were preferentially degraded over time, particularly in the preliminary stages of weathering, versus phenanthrenes. This weathering preference was also found in Curtis et al. 2014. Surface SRBs had weathering rates over twice that of subsurface SRBs above groundwater level. This preferential weathering in zones of higher oxygen was expected (Atlas 2011; Beazley 2012; OSAT-2 2011; Xu 2003). R-squared values were not high. Since all of this data was collected as part of field analysis, perfect linear regressions were not expected, as they may be in laboratory studies. Fourchon Beach is very dynamic. Under such conditions, SRBs can be buried which affects weathering. As discussed above, while results from some sampling dates fluctuated, expected trends in weathering ratios were seen over time.

Buried oil persists at depth, where oxygen is limited, even 5 years later. During manual attempts to clean the site in 2013, it was likely that the soil portions with the highest PAH concentrations were indeed removed. Samples from December 2 and 6, 2013, however, were from oil that was returned to the hole after pad screening. These samples had among the highest total PAH concentrations of all buried samples (Table 4). These high concentrations illustrate that active attempts to manually clean oiled sands are perhaps not extremely effective by their nature, and a passive remediation approach is desirable.
Results from 2015 and 2016 core samples at Breach 1 indicated that MC252 buried oil showed signs of weathering after the in-situ bioremediation field trial. Dibenzothiophene weathering was greater than phenanthrene weathering, except in the B3a series where phenanthrene weathering was dominant. These indications of oil weathering were likely due to the introduction of oxygen into anaerobic groundwater. While difficulties in continuously delivering oxygen were faced in the latter part of the experiment, the ability to introduce oxygen was successfully demonstrated. This will aid future response efforts in coastal environments.
CHAPTER 3: IMPACT OF BURIED MC252 OIL ON COASTAL HEADLAND BEACH GROUNDWATER PRE AND POST OXYGEN INJECTION

3.1 Introduction

The British Petroleum (BP) Deepwater Horizon (DWH) oil platform exploded and began burning on April 20, 2010 (McNutt 2011). Over the next 87 days, roughly 4.9 million barrels of crude oil were released into the Gulf of Mexico (Henaff 2012). Fourchon Beach, a dynamic 14.5 km stretch of coastal headland beach in Lafourche Parish, LA, was oiled in the following months (Michel, Owens et al. 2013). In May 2010, an oil-water emulsion began washing ashore (Urbano, Elango et. al 2013). Several hard structures were installed at breaches and low areas along the beach prior to the oil making landfall. This was an attempt to deter oil migration to the sensitive marsh areas behind the beach. One hard structure, a rock wall, was used to close a breach at Bayou Ferblanc, located on the easternmost portion of Fourchon Beach. The breach, hereafter referred to as Breach 1, filled with sand and emulsified oil in the following months following oil landfall. During response, several mechanical attempts were made to remove the buried oil, however supratidal buried oil is still found at Breach 1. Bioremediation of buried crude oil is one remedial option for crude oil remaining on the beach.

Bacteria can completely transform PAHs into organic matter in the form of microbial biomass, with CO₂ and H₂O as byproducts (Atlas 2011). Rates of hydrocarbon microbial degradation are much higher in aerobic conditions compared to anaerobic conditions (Atlas 2011; Beazley 2012; Odu 1970; Xu 2003). While anaerobic transformation of 2- and 3-ring PAHs has been reported (Coates, Woodward et al. 1997, Tang, Carpenter et al. 2005, Tang, Carpenter et al. 2006), the alkylated 3-4 ring PAHs in weathered MC252 crude oil are not amenable to these processes. At Breach 1, the extent of PAH weathering, which includes
microbial degradation, was minimal in buried oil beneath the water table at the Breach 1 site (Romaine et al., 2016, in prep, Chapter 2 of this thesis). In contrast, oil at the surface or buried above the water table, significant weathering of PAHs was observed. Limitation of oxygen and nutrients in beach groundwater were reported on residual oil from the Exxon Valdez spill in (Boufadel, Sharifi et al. 2010). Injection of nutrients or other amendments was demonstrated feasible. With the introduction of oil, oxygen demand increases in the system, and the groundwater is pushed into a sulfidic redox state. Factors such as inorganic nutrients, including nitrogen and phosphorus, salinity, pH and temperature are also crucial to successful hydrocarbon degradation (Beazley 2012). Oil-degradation rates are closely and positively related to the concentration of nutrients in beach groundwater (Oh et al. 2001). The optimal pH for oil degradation in estuarine sediments is roughly 8, with decreasing oil mineralization rates as pH decreases (Hambrick III et al. 1980). Westrick showed via lab studies that there can be optimal conditions for oil degradation on a beach. Favorable groundwater conditions include DO > 5 mg/L, > 6 mg-N/L, and > 0.6 mg-P/L (Westrick 2014). Groundwater on Fourchon beach is naturally anaerobic. Oil degradation of buried oil is typically very slow in oxygen-deprived areas, such as the supratidal, subsurface zone of fine grained Louisiana beaches (OSAT 2 2011).

The objective of this paper is to understand the geochemistry of groundwater characteristics at Fourchon Beach and how it responds to bioremediation practices, such as oxygen amendment. Geochemical indicators of anaerobic and aerobic metabolism were sampled before and after.

3.2 Materials and Methods

3.2.1 Site Description and Well Installation
The study was located on the easternmost segment of the 14.5 km coastal headland beach, Fourchon Beach, in Port Fourchon, LA. Groundwater samples were taken from Breach 1 using several series of groundwater monitoring wells and piezometers. Groundwater sampling of 8 existing piezometers began in June 2014. These piezometers were 25 mm in diameter and were installed using a Geoprobe at a depth of 2.4 m. A second set of twelve injection wells were also sampled. These wells were 100 mm in diameter also to a depth of 2.4 m. These wells were installed in January 2015 and were used to deliver oxygen to the subsurface using the Waterloo emitters described below. Thirdly, a third set of ten 50 mm monitoring wells were sampled for groundwater characteristics. These monitoring wells were installed north (marshside) of the 100 mm wells in June 2015 to a depth of 2.4 m. Finally, during a soil coring event in September 2015, eight additional 50 mm piezometers were installed north (marshside) of the wells containing the Waterloo emitters.

The 100 mm wells were equipped with 1.3 m Waterloo emitters in July 2015. Solinst Waterloo emitters (Solinst, Inc., Ontario, Canada) were used to amend Fourchon Beach with oxygen (Figure 8). Waterloo emitters work on the principle of diffusion (Fick’s Law of Diffusion). Gas flux from the silicon tubing on the emitter into the anaerobic groundwater is based on differences in concentration between the gas stream and the groundwater concentration. Small amounts of gases, such as hydrogen sulfide, can also back-diffuse into the tubing, which can affect the rate of diffusion. This can cause the partial pressure of oxygen to drop, affecting the long term performance of oxygen delivery. As a result, these gases are vented from the system using small valves at the end of each emitter series.

The fully assembled 1.2 m Waterloo emitters were hung by braided Kevlar cord from the well cap in the 100 mm wells, such that the center of the emitter was 1.2 m below ground
surface. A 25 mm PVC riser pipe was screwed onto the top of the emitter as per manufacturer instructions, to allow for sample tubing to be fed through the center of the emitter. Three separate series of emitters consisting of 4 wells each, A (1-4), B (1-4) and C (1-4), were installed. The emitters in each 4 well series were connected by 6.35 mm OD low density polyethylene (LDPE) tubing, encased by 25 mm PVC conduit. All three emitter series were fed by a single LDPE tubing gas source line that was fitted with a pair of T fittings to branch the air delivery to each set. The LDPE tube was connected to a regulator that was fed by gas cylinders stored in a locked cylinder cabinet approximately 20 meters northeast of injection well A1. Regulator pressure was set at 20 psi.

![Figure 8- Example schematic of a 3 Waterloo Emitter gas injection series](image-url)
From July 22, 2015 to September 30, 2015, compressed breathing air was fed into the
emitters. From October 1, 2015 to April 27, 2016 compressed pure oxygen was used. Tanks were
changed as needed to ensure constant supply. Each series of emitters was vented slightly (1-2
mL/min) to avoid hydrogen sulfide buildup in the tubing. This small venting did not significantly
increase gas usage.

3.2.2 Field Groundwater Sampling

Water samples were taken from selected piezometers, monitoring wells and oxygen
injection wells using battery powered Geopump Easyload II High Performance peristaltic pumps
and 6.35 mm OD LDPE tubing. Samples were taken from the bottom foot of the piezometers and
monitoring wells. To ensure the sample was indicative of groundwater surrounding the well,
groundwater was purged from the well into a 19 L bucket before sample collection. Purge was
equivalent to at least one volume of water in the well. In oxygen injection wells, sample tubing
was fed down through the center of the Waterloo Emitter assembly, and samples were taken just
below the emitter. Samples were taken after ten seconds of pumping. This was to ensure that the
measurement of representative of water in the well itself and not groundwater around the well.
Water samples to be taken to the laboratory were stored on ice in labeled 40mL clear Voa (EPA)
vials and 125mL glass jars. Once in the lab, samples were kept at 4 degrees Celsius until
analysis.

3.2.3 Nutrient and Electron Acceptor Analysis

Nutrients (NH$_4^{+}$, PO$_4^{3-}$) and an electron acceptor (SO$_4^{2-}$) in Breach 1 groundwater were
measured in the laboratory with a SmartChem 170 Discrete Analyzer (Unity Scientific Inc.)
using the EPA methods #365.1, 350.1 and 375.4, respectively. QA/QC consisted of blanks and
continuing calibration samples before each run. Field measurements for sulfate, sulfide, nitrate,
nitrite, iron ferrous and iron total were taken using a DR 2700 Portable Spectrophotometer. Lower detection limits were 0.018 mg/L for nitrate, 0.019 mg/L for nitrite, 0.28 mg/L for ferrous iron, 0.06 mg/L for total iron and 3.66 mg/L for sulfate. Field measurement was chosen particularly for sulfide and iron, as oxidation occurs quickly in these compounds. Samples were analyzed immediately after collection in a field laboratory constructed for that purpose.

3.2.4 pH, Redox, Conductivity, TSS, temp

Field measurements for salinity, temperature, pH, total dissolved solids (TDS) and oxidation reduction potential (ORP) were taken using a Myron L Ultrameter. Oxygen was originally measured in the field using the Winkler method. Beginning in June 2015, a Hach HQ30D Dissolved Oxygen Meter equipped with a luminescence sensor was used in lieu of the Winkler method. The Winkler method was coupled with the DO meter on the first day of analysis to ensure consistency between the two measurements. Alkalinity was measured using acid titration (Hach).

3.2.5 Groundwater Flow Monitoring

Groundwater level (MSL), temperature and conductivity were continually analyzed from July 2015 to May 2016 in monitoring wells at Breach 1 using Solinst Data Loggers installed in monitoring wells 3 and 9 (Figure 9). The loggers were hung 1.2 m below ground surface by braided Kevlar cord tied to the well caps. The datalogger in well 3 measured water level, conductivity and temperature while the well 9 datalogger measured only temperature and water level. A Barologger Edge Model 3001 was also hung just below the well cap in monitoring well 3 with braided Kevlar cord to allow for compensation for atmospheric pressure fluctuations when measuring water level. A survey using a level was used to establish the relative height of each datalogger to each other. This allowed for an estimate of the slope of the groundwater
surface between well 3 and well 9. Individual measurements of elevation using a water level indicator were used to confirm that the groundwater slope was parallel to the slope between wells 3 and 9.

Figure 9- Map of groundwater wells at Breach 1

3.3 Results and Discussion

3.3.1 Groundwater dissolved oxygen concentrations

Dissolved oxygen was measured during 3 phases of a bioremediation study at Breach 1: pre-oxygen addition, oxygen addition using compressed breathing air in the emitters and oxygen addition using compressed oxygen in the emitters. Average dissolved oxygen concentrations in
selected emitter wells were less than 0.02 mg/L pre-oxygen delivery, 3.03±2.3 mg/L during air delivery and 16.4±4.9 mg/L during pure oxygen delivery (Table 6). Dissolved oxygen concentrations were routinely highest in Well A1.

Table 6- Dissolved oxygen concentrations (mg/L) in selected emitter wells

<table>
<thead>
<tr>
<th>Phases</th>
<th>A1</th>
<th>A3</th>
<th>B2</th>
<th>B3</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-aeration</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Air</td>
<td>7.06</td>
<td>0.44</td>
<td>2.50</td>
<td>0.94</td>
<td>2.39</td>
<td>4.85</td>
</tr>
<tr>
<td>Oxygen</td>
<td>24</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>11</td>
<td>19</td>
</tr>
</tbody>
</table>

In the monitoring wells downgradient of the emitter wells, dissolved oxygen concentrations increased with each change in remediation phase. Average dissolved oxygen concentrations in selected monitoring wells were less than 0.02 mg/L before aeration, 0.16±0.04 mg/L during air delivery, 1.51±1.97 mg/L during pure oxygen delivery (Table 7). Monitoring wells B2A and B2C were installed during the coring event on September 30, 2015. Results from these wells only come from the oxygen delivery phase.

Wells 4, B2A and B2C should be noted. Due to the slow groundwater movement at Breach 1, certain monitoring wells remained anaerobic even following oxygen amendment. To combat this issue, a recirculation strategy was used whereby aerobic groundwater was added directly to monitoring wells. Briefly, a 946 L tote was elevated on blocks near the aforementioned wells and filled with groundwater from emitter wells B2, B3, C3 and C4. Air
stones connected to pure oxygen compressed gas were used to aerate the water to ~18 mg/L. Once full, water was gravity drained from the tank valve into monitoring wells 4, B2A and B2C using 6.35 mm LDPE tubing. The wells supplied with oxygen had higher dissolved oxygen concentrations than those not directly supplied (Table 7). Average dissolved oxygen concentrations were 2.8 and 0.19 mg/L, respectively.

Table 7- Dissolved oxygen concentrations (mg/L) in selected monitoring wells

<table>
<thead>
<tr>
<th>Phase</th>
<th>Monitoring Wells</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Pre-aeration</td>
<td>&lt;&lt;0.02</td>
</tr>
<tr>
<td>Air</td>
<td>0.23</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.15</td>
</tr>
</tbody>
</table>

3.3.2 Groundwater nutrient and electron acceptor concentrations

Groundwater sampling occurred before Waterloo emitter installation in order to determine typical geochemical characteristics of beach groundwater. The wells sampled included selected emitter wells and downgradient monitoring wells. Wells sampled during the air delivery phase included the monitoring wells 1-6 closest to the emitter wells. Data is presented for monitoring wells 1, 2 and 7 downgradient of the emitter wells and monitoring wells 4, B2A and B2C, which were supplied with aerobic water as previously described.

Groundwater nutrient concentrations were measured during each phase of the study (Table 8). Concentrations of nitrogen compounds (nitrate, nitrite and ammonia) remained
relatively constant in monitoring wells 1, 2 and 7 over the course of the study, as did phosphorus concentrations. While ammonia concentrations in monitoring wells amended with oxygenated groundwater differed little from that of monitoring wells 1, 2 and 7, nitrate concentrations were 60 percent higher on average. Nitrite concentrations were more than an order of magnitude higher. Phosphorous concentrations were nearly double in wells amended with oxygenated groundwater.

Table 8- Nitrogen (nitrate, nitrite & ammonia) and phosphorus concentrations (mg/L) of Fourchon Beach groundwater

<table>
<thead>
<tr>
<th>Phase</th>
<th>Nitrate (mg/L)</th>
<th>Nitrite (mg/L)</th>
<th>Ammonia (mg/L)</th>
<th>Phosphorus (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-oxygen</td>
<td>2.71</td>
<td>0.06</td>
<td>29</td>
<td>10.4</td>
</tr>
<tr>
<td>Breathing air</td>
<td>1.85</td>
<td>0.01</td>
<td>37</td>
<td>7.7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.67</td>
<td>0.03</td>
<td>36</td>
<td>8.4</td>
</tr>
<tr>
<td>Recirculation</td>
<td>3.89</td>
<td>0.63</td>
<td>31</td>
<td>16</td>
</tr>
</tbody>
</table>

In downgradient monitoring wells 1, 2 and 7, ferrous iron concentrations decreased with each phase (Table 9). Ferrous Iron increased to over 4 mg/L in wells amended with oxygenated groundwater. Total iron concentrations increased in all wells during each phase. Sulfate increased in monitoring wells 1, 2 and 7 and remained relatively unchanged in wells receiving oxygenated groundwater, compared to natural conditions. Sulfide decreased in those same wells.

Increases in nitrite and nitrate were consistent with nitrification in response to oxygen addition. Elevated phosphorus was observed throughout the beach groundwater as few iron
oxyhydroxides were present. P did not decrease upon aeration as expected despite decreases in ferrous iron and increases in ferric iron. Results, particularly for iron concentrations, may have been higher than in actuality due to a large amount of pyrite in groundwater. This was possibly due to the fact that water was not filtered prior to analysis in the spectrophotometer. Despite these chemical transformations, elevated N and P exist in beach groundwater to support microbial biodegradation of the crude oil components. The presence of elevated sulfide may have contributed to some iron remaining reduced.

Table 9- Electron acceptor and sulfide concentrations (mg/L) of Fourchon Beach groundwater

<table>
<thead>
<tr>
<th>Phase</th>
<th>Iron Ferrous (mg/L)</th>
<th>Iron Total (mg/L)</th>
<th>Sulfate (mg/L)</th>
<th>Sulfide (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-oxygen</td>
<td>0.80</td>
<td>0.65</td>
<td>1568</td>
<td>312</td>
</tr>
<tr>
<td>Breathing air</td>
<td>0.52</td>
<td>0.32</td>
<td>239</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.37</td>
<td>1.63</td>
<td>5399</td>
<td>373</td>
</tr>
<tr>
<td>Recirculation</td>
<td>4.09</td>
<td>2.78</td>
<td>1683</td>
<td>277</td>
</tr>
</tbody>
</table>

Groundwater temperature ranged from 24-30°C Celsius (Table 10). The optimum temperature range of bioremediation process is 20–38°C for the majority of bacteria (Zhou and Crawford 1995). Temperature was expectedly highest from July to September 2016 during the breathing air delivery phase. pH was roughly neutral and constant throughout the study. Total dissolved solids averaged 183 ppt. Oxidation reduction potential (ORP) averages were below -300 mV in monitoring wells 1, 2 and 7 and increased to -146 mV in wells after amendment with
oxygenated groundwater. Alkalinity was reduced by roughly half in monitoring wells 1, 2 and 7 but was nearly constant in wells receiving oxygenated groundwater.

Table 10- Chemical characteristics of Fourchon Beach groundwater

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>TDS (ppt)</th>
<th>ORP (mV)</th>
<th>Alkalinity (mg/L CaCO3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-oxygen</td>
<td>24.5</td>
<td>7.1</td>
<td>190</td>
<td>-304</td>
<td>1854</td>
</tr>
<tr>
<td>Breathing air</td>
<td>29.4</td>
<td>7.2</td>
<td>165</td>
<td>-307</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>26.4</td>
<td>7.3</td>
<td>223</td>
<td>-344</td>
<td>987</td>
</tr>
<tr>
<td>Recirculation</td>
<td>25.7</td>
<td>7.2</td>
<td>155</td>
<td>-146</td>
<td>1787</td>
</tr>
</tbody>
</table>

Seawater has a conductivity of 55,000 uS/cm. Results from data loggers in monitoring wells at Breach 1 suggest that groundwater is hypersaline. The conductivity of groundwater at Breach 1 was nearly 50 percent higher on average (Figure 10). When overwash occurs, the supratidal portion of the beach was submerged by seawater. High temperatures led to evaporation, leaving behind “salt pans” (Grotzinger 2006). Very little groundwater flushing occurred, due to low hydraulic conductivity in subsurface sands. This led to hyper-accumulation of salt in supratidal groundwater.

Groundwater temperature, taken with a data logger in groundwater, was generally stable compared to air temperature, taken with a data logger installed above water (Figure 11). Temperature variation was roughly 10 times less in groundwater than in air. While the results presented are slightly below the optimal range previously noted, they represent the coldest portion of the year (January 26-March 7).
Figure 10- Conductivity (uS/cm) of groundwater at Breach 1

Figure 11- Air (light blue) and water (dark blue) temperature (Celsius) at Breach 1
3.3.3 Groundwater Flow

Groundwater flow rates (in the direction of beach to back-marsh) were calculated using two data loggers. First, the difference in corrected elevations between the two sensors was set as the delta. The gradient was the delta divided by the distance between the loggers. Finally, the groundwater velocity was the gradient multiplied by the hydraulic conductivity. A hydraulic conductivity of 60 µm/sec was selected based on previous measures of hydraulic conductivity in Fourchon sands using a falling head permeameter. From January to March 2016, flow rate increased from roughly 0.05 to 0.25 meters per day (Figure 12). This is coincidental with increasing ocean water levels during spring months, which increases delta.

![Figure 12](image_url)

Figure 12- Flow rate (meters per day) of ground water at Breach 1, 2016
Groundwater level was nearly stable from day to day. From February 25 to 26, 2016, the groundwater level changed only 0.05 meters (Figure 13). Likewise, from March 1 to 2, 2016 a 0.06 meter change was seen (Figure 14). The two time periods presented represent time of low and high tidal ranges, respectively. This indicates that tidal forcings play little role in groundwater levels at Breach 1.

Groundwater level did appear to be affected by storm events, however. A sharp increase of 0.25 meters was seen on January 26 (Figure 15). This was potentially caused by a period of particularly high southerly winds.

Figure 13- Groundwater level at Breach 1 February 25-26, 2016
Figure 14- Groundwater level at Breach 1 March 1-2, 2016

Figure 15- Groundwater level at Breach 1 January 26-29, 2016
3.4 Conclusions

Temperature and pH of groundwater at Fourchon Beach were relatively constant and conducive to biological activity. However, salinity was much higher than seawater and was a likely cause of poor biodegradation (Oren 1992) of oil. Sulfide concentrations were also elevated, which is undesirable in a remediation setting. While nutrient concentrations were high enough to sustain biological growth, groundwater at the site was naturally anaerobic. The ability to amend groundwater with oxygen was demonstrated. Groundwater level fluctuation was fairly minimal, as tidal forces were shown to affect it very little. Groundwater movement was slow enough such that only low concentrations of oxygen were detected in downgradient wells. Groundwater flow rates were highest in spring months, yet still moved less than a third of a meter per day during this time. A recirculation strategy proved to be most effective in increasing oxygen concentrations at great distance from emitter wells. This suggests that an alternative oxygen amendment strategy may be preferable.
CHAPTER 4: SUMMARY AND OUTLOOK

4.1. Experimental Findings and Implications

Results indicate that oil weathers significantly differently based on location in the beach vertical profile. Oil above the groundwater table was significantly more weathered than buried oil below the groundwater table. Dibenzothiophenes weathered preferentially to phenanthrenes in nearly all samples. The poor weathering of oil below the groundwater surface was due to natural groundwater conditions. Nutrient concentrations, pH and temperature are sufficient for microbial function; however the hypersaline nature of the groundwater may limit pollutant degradation by microbes (Oren 1992). Most importantly however, anaerobic conditions are likely controlled the lack of weathering of oil below the groundwater surface. A field trial of in situ bio-stimulation from 2015-2016 demonstrated the ability to amend anaerobic groundwater with oxygen. Weathering was seen in buried samples below the groundwater surface. However, dissolved oxygen results suggest that oxygenated groundwater was confined locally to emitter wells due to slow groundwater movement.

4.2. Future Research

A continued bioremediation project at Breach 1 could potentially show greater weathering rates of supratidal buried oil below the groundwater level over time. An alternative, more consistent and more dependable oxygen delivery source, such as oxygen releasing compounds (ORCs), could be utilized. At sites in the future, alternative well layout and construction, using directional drilling, should be considered for optimum oxygen delivery to anaerobic groundwater. Oxygen was most successfully delivered to groundwater at Breach 1 through a temporary recirculation technique. This could be replicated on a continuous, larger scale. Renewable energy could be harnessed to minimize environmental impact. While this may
be more costly than utilization of strictly Waterloo emitters, the direct impact to the beach habitat will be much less and the cost will likely be less than current practices such as manual oil removal.
REFERENCES


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VITA

Zachary Joseph Romaine was born in Shreveport, Louisiana and was raised in a farming family in Abbeville, Louisiana. He graduated from Vermilion Catholic High School in 2010. Having always felt a strong connection with the land and, understanding the need to protect it, he pursued a bachelor’s degree in environmental engineering at Louisiana State University. After graduating in 2014, he began working towards a master’s degree in Coastal and Ecological Engineering at LSU. He will graduate in December 2016 and pursue a career in coastal restoration or remediation.