Biodegradation of MC252 crude oil after mobilization by washover events on coastal headland beaches

David Nelson Curtis

Louisiana State University and Agricultural and Mechanical College, david_curtis_@hotmail.com

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses

Part of the Civil and Environmental Engineering Commons

Recommended Citation

https://digitalcommons.lsu.edu/gradschool_theses/2617

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master's Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
BIODEGRADATION OF MC252 CRUDE OIL AFTER MOBILIZATION BY WASHOVER EVENTS ON COASTAL HEADLAND BEACHES

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 Masters of Civil Engineering

in

The Department of Civil and Environmental Engineering

by

David N. Curtis
B.S., University of Southern Mississippi, 2011
May 2014
ACKNOWLEDGEMENTS

A special thanks to the Edward Wisner Donation, for allowing the research team access to the sampling sites and for their cooperation throughout the whole process. I am especially grateful to Dr. John Pardue for giving me the opportunity to be in graduate school and direction as my major professor throughout the entire process. Likewise, I would like to thank my committee members and professors: Dr. Ronald Malone and William Moe. I would like to thank my family and fiancé who gave me the support that was needed to complete this thesis and graduate school.

In addition to these people I would like to thanks of the Pardue lab Group. To post-doctoral Vijaikrishnah “Vijai” Elango, for all his advice, help and overall guidance over these past two years and Ph.D. candidate Leslie Pipkin. To my fellow graduate students: Matthew Rodrigue and Autumn Westrick for all the help while in the field and experiments in the lab, thank you for your support and friendship. And last but not least, the great student workers: Matthew Decel and Mark Holman, for all their help in the lab and running experiments. I am forever thankful to all these people for their support in the pursuit of this degree.
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS........................................................................................................ii

LIST OF TABLES.....................................................................................................................v

LIST OF FIGURES...................................................................................................................vi

ABSTRACT..............................................................................................................................vii

1. CHAPTER 1: INTRODUCTION AND OUTLINE.................................................................1
   1.1. Background..................................................................................................................1
   1.2. Research Objectives...................................................................................................5
   1.3. Environmental Relevance of the Study.......................................................................5
   1.4. Organization of Thesis...............................................................................................6

2. CHAPTER 2: WASHOVER TIDAL EVENTS AS A SOURCE OF OIL PERSISTENCE ON
   COASTAL HEADLAND BEACHES....................................................................................7
   2.1 Introduction..................................................................................................................7
   2.2 Material and Methods...............................................................................................9
      2.2.1 Study Location and Sampling Events .................................................................9
      2.2.2 Washover survey ...............................................................................................10
      2.2.3 Depth distribution of oil compounds in washover channels............................10
      2.2.4 Washover scenario sampling ...........................................................................11
      2.2.5 Oil Extraction and Analysis .............................................................................11
      2.2.6 Weathering Ratios ............................................................................................13
   2.3 Results and Discussion..............................................................................................14
      2.3.1 Washover Channel Survey .................................................................................14
      2.3.2 Depth distribution in Washover Channels .........................................................15
      2.3.3 Individual Areas and Scenarios with weathering ratios ....................................23
   2.4 Conclusions................................................................................................................25

3. CHAPTER 3: FATE OF MC252 CRUDE COMPONENTS IN THE WASHOUT FANS ON
   A COASTAL HEADLAND BEACH..................................................................................30
   3.1 Introduction................................................................................................................30
   3.2 Materials and Methods.............................................................................................32
      3.2.1 Site Description and SRB sampling ...................................................................32
      3.2.2 Microcosm Study ..............................................................................................33
      3.2.3 Field porewater sampling ..................................................................................34
      3.2.4 Oil Extraction and Analysis .............................................................................35
      3.2.5 Nutrient and Electron Acceptor Analysis .........................................................36
   3.3 Results and Discussion.............................................................................................37
      3.3.1 Microcosm Results ............................................................................................37
      3.3.2 Porewater concentrations of nutrients in washover areas ...................................39
   3.4 Conclusions................................................................................................................45
LIST OF TABLES

Table 1. Concentrations of selected PAHs, biomarkers and weathering indices in composite washover channel samples .......................................................................................................................... 17

Table 2. Concentrations of selected PAHs, biomarkers and weathering indices in SRBs sampled within washover channels during the washover survey ................................................................. 18
LIST OF FIGURES

Figure 1. Caminada Headland– (Fourchon, Beach, Lafourche Parish, LA)..........................1

Figure 2. Shoreline Zones........................................................................................................2

Figure 3. Cross Section of an SRB found on Fourchon Beach..............................................3

Figure 4. Map of washover sample (Zone 1 – 3) sampled from Fourchon Beach...............16

Figure 5. Cores collected at washover channel adjacent to Bay Champagne (BC) in Zone 5.....20

Figure 6. Map of Sediment Cores collected at large washover channel in Zone 1 Breach Site....21

Figure 7. Sediment Cores collected from a large washover channel in Zone 1 Breach site.....22

Figure 8. PAH concentrations found within the three washover events..............................26

Figure 9. n-Alkanes concentrations found within the three washover events......................26

Figure 10. Double Weathering Ratio indicating the fate of the oil over time.........................27

Figure 11. Microcosm data from the anaerobic treatment containing intact SRBs.................40

Figure 12. Microcosm data from the aerobic treatment containing intact SRBs with killed control......................................................................................................................................41

Figure 13. Microcosm data from the aerobic and anaerobic nitrogen amended treatment containing crushed SRBs..........................................................................................................................42

Figure 14. Nutrient concentration examined from the flooded anaerobic microcosm study....43

Figure 15. Nutrient concentrations from the peeper analysis from the Breach Site in Zone 1...46
ABSTRACT

Washover events on coastal headland beaches occur when storm surge from cold fronts, high tides, tropical storms, and hurricanes move across the beach, reworking and depositing sand in the back marshes and shallow mudflat areas. On Fourchon Beach, Louisiana, a 9-mile coastal headland beach impacted by the Deep Water Horizon oil spill, these washover events have intermittently moved oil from the subtidal and intertidal portion of the beach to the supratidal mudflats and marsh areas. In order to determine the impacts of washover events on oil fate, 3 complementary studies were undertaken. First, washover areas (N=59) have been mapped and sampled for PAHs and n-alkanes in the most heavily impacted area at the eastern end of Fourchon Beach. Samples indicate the most heavily impacted segments were in areas where a physical breach of the beach developed. Second, characteristics of specific washover events and depth distribution were to establish typical categories of events (i.e., breaches, remobilization of oil on the beach and mobilization of subtidal oil mats) as well as the characteristics of oil mobilized by each category. Field measurements of washover event samples were analyzed by several weathering ratios including C30-hopane ratios, ΣPhenanthrene/ΣChrysenes and ΣDibenzothiophene/ΣChrysenes double ratio plotting. Third, a laboratory microcosm study was conducted to understand the biogeochemical controls on oil biodegradation in the new environment (washover mudflat) and how these controls impact its ability to degrade naturally. The study used intact surface residue balls (SRBs) that were deposited on the beach and marsh from various Washover events. Anaerobic and aerobic treatments consistent with the flooded mudflat areas were amended with nitrogen to determine if nutrients were limiting in the washover environment. Treatments were established for both crushed and intact SRBs. Results to date indicate that PAHs degrade optimally when the SRB’s are crushed up and are placed under non-flooded conditions with C1-C4 phenanthrenes, C1-C3 dibenzothiophenes and C1-C2
chrysenes all showing a large decrease in concentration over 150 days. These studies were discussed in the context of remedial measures during the emergency response phase used on Fourchon Beach to prevent washover impacts.
CHAPTER 1: INTRODUCTION AND OUTLINE

1.1. Background

On April 20, 2010, the Deepwater Horizon oil rig exploded off the coast of south Louisiana releasing MC252 oil into the Gulf of Mexico causing a widespread phenomenon that has affected the coast of Louisiana, Mississippi, Alabama and parts of Florida. During the spill, it is estimated that nearly 60,000 barrels per day of crude oil was released into the Gulf of Mexico (McNutt et al., 2011a). Being that the spill took place in the deep, open water of the Gulf of Mexico, the wind and underwater currents aided in the spreading of the oil from the area around the well to the area of the coastal headland beaches and bays (Le Henaff et al., 2012). One of the areas that was heavily impacted on the coastal headland beaches of Louisiana were the coastal marshes and a mangrove site located behind Port Fourchon beach which is not protected by dunes as seen on beaches located in other states. The coastal headland beaches are vulnerable to catastrophic events due to the lack of dunes or barriers that protect the back bay areas and marshes that are adjacent to the headland beach. One thing that makes Louisiana beaches unique is events that we term “Washovers.”

Figure 1. Caminada Headland– (Fourchon, Beach, Lafourche Parish, LA) Zones 1-9
A washover event on the Louisiana coastal headland beaches occurs when storm surge from cold fronts, high tides, tropical storms, and hurricanes move across the beach, reworking and depositing sand and oil deposits in the back marshes and shallow mudflat areas (Georgiou et al., 2005). Events such as hurricanes and tropical storms prevent a more catastrophic scenario as the tidal surge rises above the beach zones and allows for the SRBs and SOMs to make their way directly into marsh and mudflats bypassing the washover channels. On Fourchon Beach, Louisiana, a 9-mile coastal headland beach impacted by the Deepwater Horizon oil spill, these Washover events have intermittently moved oil or Surface Reside balls (SRBs) from the subtidal and intertidal portion of the beach to the supratidal mudflats and marsh areas throughout the 9 zones (Figure 1) located within the beach. The Fourchon headlands and mangrove sites were contaminated when a floating water and oil emulsion mixture washed over the headland beach during a tropical storm and high tides events (Lin and Mendelssohn, 2012; Urbano et al., 2013). During these washover events caused by cold fronts, high tides, tropical storms, and hurricanes, MC 252 was deposited along the shoreline within the three different tidal zones: the subtidal, intertidal, and supratidal (Figure 2).

Figure 2. Shoreline Zones. Modified From J. Michael, pres. Comm. (OSAT-II, 2011)
Oil that remains in the subtidal zone is in the form of submerged oil mats (SOM) which are broken up during the heavy wave activity along the coast. Surface residual balls (SRBs) are most often a product of the SOMs, which break up during the weathering events and cause the oil to mix with sand and shell to form a sphere structure as seen in (Figure 3). SRBs may be found in all three of the tidal zones, however they may vary in the concentrations of PAHs and alkanes based on the position on the beach and exposure to natural elements.

![Image of SRB composition](attachment://SRBComposition.jpg)

**Figure 3. Cross Section of an SRB found on Fourchon Beach**

MC 252 Crude oil is comprised of many different compounds, however this thesis will focus only on 2 of the crude oil components. The first important component of crude oil is Polycyclic Aromatic Hydrocarbons (PAHs). PAHs are semi volatile organic compounds which are comprised of unsaturated compounds that have at least two benzene ring attached to the polycyclic aromatic compound. PAH’s represent a slight percentage of the over-all crude oil arrangement, yet they are considered one of the most toxic components present (Schein et al., 2009). PAHs are classified as persistent organic pollutants (POPs) which are families of chemicals that are typically hydrophobic, lipophilic, and have long half-lives in different environments such as air, sediments, soils, and biota (Jones and de Voogt, 1999). Since PAHs and alkanes endure long half-lives, degradation spans for decades after the oil reaches its final...
destination. Once PAHs are released into the environment from events such as the *Deep Water Horizon (DWH)* oil spill, they become trapped into the soil as the washover allow the water to breach the headland beaches and MC252 is placed in soils and sediments because of their high air partition coefficients and low vapor pressures (Wang et al., 2007). The higher molecular weight PAHs which are comprised of three- and four-ringed PAHs tend to degrade a slower rate than those of a smaller molecular weight under anaerobic and aerobic conditions (McNally et al., 1998). Since PAHs have the ability to remain in the soil or sediments for an extensive time period, they are high toxic substance that is a byproduct of crude oil and a harmful compound to the coastal environment.

In addition to PAHs, alkanes are another common functional group found within hydrocarbons that are toxic to the environment. Alkanes are saturated compounds consisting of carbon and hydrogen in the form of single bonds (Coates et al., 1997). The length of alkane chains is an important factor in assessing the biodegradation of crude oil (Mehdi and Giti, 2008). The longer lengthen alkanes tend to biodegrade slower than the short chain alkanes. However, intermediate length alkane chains may biodegrade more readily due to the fact that alkanes contain the enzyme hydroxylase, which is a key component in the biodegradation process for alkanes.

While many PAHs and n-alkanes are known to biodegrade under aerobic conditions, contaminated sediments containing oil are often trapped during washover events below the surface and experience anaerobic conditions (Rockne and Strand, 1998). The oil trapped under the soil in the anaerobic environment contains microbes which compete with the oxygen demand from cellular respiration and oxidation of sulfate resulting from the flooded conditions in a coastal salt marsh system (Jackson and Pardue, 1999). Biodegradation must use alternative
electron acceptors in the form of sulfate-reducing bacteria, since oxygen is a limiting factor in these different systems (Jackson and Pardue, 1999). In addition to sulfate, nitrogen and phosphorous can also be used as electron acceptor nutrients found within the soil of an oil contaminated environment as cell mass grows with the addition of the new carbon source from the PAHs and alkanes (Venosa and Zhu, 2003). It is through these various alternative forms of electron acceptors that the biodegradation of the MC 252 oil takes place during washover events from the gulf to the coastal headland beaches and tidal marshes.

1.2. Research Objectives

The objectives of this research were to:

1. Determine the weathering and quantification of the SRBs and SOMs that make their ways on the beach from the washover events
2. Determine the depths at which the MC 252 is found on various locations on the headland beaches
3. Determine whether SRBs and SOMs from the MC 252 crude oil are biodegrading under anaerobic or aerobic conditions
4. Assess the different nutrients and oxygen concentrations that are found below the surface

Objective 1 and 2 will be addressed in Chapter 2 and Objectives 3 and 4 will be addressed in Chapter 3.

1.3. Environmental Relevance of the Study

The research described in this thesis determined the fate of the oil spill on Fourchon Beach, Louisiana, with emphasis on the tidal, supratidal, mudflat areas, and mangrove areas. Specifically, this thesis examined how hydrocarbons, in particular PAH and n-alkanes, biodegradation can occur in troubling areas created by washover events to describe the conditions in which SRBs and SOMs are positioned on the coastal headland beaches in order to better understand the fate of MC252 Oil. Previous studies have been completed in this laboratory using the SRBs and SOMs found on Fourchon Beach, however, not many studies
have been done on them, and their fate is still largely unknown four years after the spill. Therefore, the continuing study of MC252 crude oil allows for further information to come to light which will be useful in the field of oil spill cleanup and response.

1.4. Organization of Thesis

Chapter 2 investigates the washover tidal events as a source of oil persistence in supratidal, intertidal, mudflats and mangrove areas located within beach environment on Fourchon Beach, LA. Chapter 3 presents the results from a microcosm study, which took place over the course of 150 days to determine the biodegradability of MC 252 crude oil on the supratidal beach environment along with investigating the nutrients and oxygen present beneath the surface. The final chapter, Chapter 4 recaps the results from this work and highlights some areas for future research.
CHAPTER 2: WASHOVER TIDAL EVENTS AS A SOURCE OF OIL PERSISTENCE ON COASTAL HEADLAND BEACHES

2.1 Introduction

Coastal headland beaches and barrier islands in Louisiana were impacted by the nearly 60,000 barrels per day of MC252 crude oil released into the Gulf of Mexico from April 20, 2010 to July 15, 2010 (McNutt et al., 2011b). These beaches are characterized by relatively low relief with a poorly developed dune system fronting a back bay area of mudflats, marshes and mangroves. Washover events on coastal headland beaches occur when storm surge from cold fronts, high tides, tropical storms, and hurricanes move across the beach, reworking and depositing sand in the back marshes and shallow mudflat areas (Georgiou et al., 2005). On Fourchon Beach, Louisiana, a 9-mile coastal headland beach impacted by the Deepwater Horizon oil spill, these washover events have the potential to move oil from the subtidal and intertidal portion of the beach to the supratidal mudflats and marsh areas. These events contribute to very rapid erosion which can occur at a rate of about 40 feet per year at Fourchon beach (McBride et al., 1992).

Washover events that take place on the headland beaches have the potential to mobilize DWH oil forms including surface residue balls (SRBs) and submerged oil mats (SOMs). An SRB is oil residue that is typically shaped in the form of a sphere several centimeters in diameter, consisting of a mixture of sand, shells and oil (OSAT-II, 2011; Urbano et al., 2013a). SRBs are essentially oil free at the surface as they are mixed with the sand. Upon breaking an SRB in half a darker, oily core can be found along with a smell of oil that is the characterization of the SRB aggregates indicated that the MC252 crude oil content is typically 5-10% (OSAT-II, 2011).

Another form of oil that can be found on the headland beaches is submerged oil mats (SOMs). SOMs exist in the inshore surf zone in troughs between sand bars and the buried underneath the
sand which appear during the washover events (OSAT-II, 2011). The Fourchon beach dynamics are constantly changing and causing more of these washover events to occur moving SRBS into the supratidal and intertidal system including ultimately to the mudflats and mangrove wetlands (Georgiou et al., 2005). Weathering of the oil may occur in different areas of the tidal zone due to many factors such as moisture, salinity, nutrient availability and the availably of different electron acceptors (Urbano et al., 2013).

Biodegradation is the process in which compounds, which in this case are the PAHs, are degraded through the use of bacteria or microbes. It is known though studies that have taken place that PAHs can be degraded under aerobic conditions (Cerniglia, 1993) however under anaerobic conditions PAH tend to have a more difficult time degrading (Coates et al., 1997). From recent studies, crude oil within the SRBs can be degraded by weathering that takes place while the SRBs are exposed to the environment under aerobic conditions. Oxygen, nitrogen and sulfate reducing bacteria must be present for the PAHs and alkanes to biodegrade in the soil in which the SRBs are placed (Rabus and Widdel, 1995; Rueter et al., 1994; Urbano et al., 2013). Weathering ratios were used in this chapter to determine the amount of degradation that occurs over time in this paper using the compounds that were heavily persistent in the MC 252 crude oil such as the C1 – C4 phenanthrenes, C1 – C3 dibenzothiophenes and C1 – C3 chrysenes. The sums of C1 – C4 phenanthrenes and C1 – C3 dibenzothiophenes were totaled separately and they placed into an equation in which they were compared to the sum of the chrysenes simultaneously. Using these equations, we can see how the composition of MC252 changes during each sampling event.

The overall objective of this paper was to understand the role of washover events in transporting and distributing crude oil across the headland beach from the gulf to the mudflat
along Fourchon Beach, LA. Over the course of two years, samples have been collected from Zones 1 - 3 that are present on the beach. Within each zone, samples were collected near areas of the washover channels that make their way from the gulf to the back marsh area. 59 different washover spots were sampled and quantified to help explain the amount of oil that was present within the specific zone. Once the SRBs reach the back marsh area they are overlooked by the crews that are on the beach due to the limitations brought by water levels, therefore they are left there to breakdown. Along with the samples collected in the washover zones, cores were taking at the Zone 1 Breach Site location along with the cores taken adjacent to Bay Champagne to illustrate the oil concentration at different depths along the washover channels as the oil was buried in the sand as it piled up from the different washover events. Three historic washover events were also studied. Using all of the data that was collected over the course of two years, weathering ratios were developed to examine the fate of MC252 as it buried underground and left to biodegrade.

2.2 Materials and Methods

2.2.1 Study Location and Sampling Events

The study locations for this field study were located on a 9 mile coastal headland beach in Port Fourchon, LA previously impacted by the Deepwater Horizon oil spill. The beach was divided into 9 operational zones approximately 1 mile in length, numbered 1-9 from east to west (Figure 1). Six sampling efforts were conducted over the course of the study to understand the impact of washover events. An overall survey of washover channels in Zones 1-3 represented the first sampling effort. Next, 2 sampling efforts were conducted to examine the depth distribution of MC252 crude oil components within specific washover channels. Finally, 3 sampling efforts
were conducted to look at specific scenarios from washover events that occurred from 2011-2013. Details on these sampling events are described below.

2.2.2 Washover survey

A complete survey of the washover channels in Zones 1-3 was conducted from February to May 2012. During the survey, sampling was conducted in every washover channel encountered across the approximate 3-mile distance for a total of 59 channels. At every channel, a core was taken using a 15 cm diameter metal core tubes approximately 30 cm in depth. The location of the core was at the approximate midpoint of the channel at the water-line of small bay bounding the beach on the north. The top 15 cm of the core was composited immediately after sampling and transported to the laboratory for analysis of crude oil components. During the survey, SRBs encountered within end of the washover channel (on the beach within 20 meters of the core location) were sampled. These would be representative of the oil forms that are transported into the channel.

2.2.3 Depth distribution of oil compounds in washover channels

Cores were removed from 2 washover channels to determine the depth distribution of MC252 crude oil components. First, cores were removed from a washover channel adjacent to Bay Champagne in Zone 5. Three 15 cm diameter cores were removed on 12/15/2011 and sectioned into 6.5 cm sections to a total depth of 70 cm. Samples were extracted and analyzed for crude oil components as described below. Second, sediment cores were collected from a large washover channel in Zone 1, which previously had opened as a breach during TS Lee in September 2011. This site will be termed the Zone 1 breach site for this study. Cores were removed using an AMS Multi-Stage soil core sampler consisting of a stainless steel extendable cylindrical sampler that collects 6.5cm diameter cores up to 60 cm deep. For the present study,
the cores that were taken with just one of the 30.5 cm section of the device. The coring took place during the winter months when the water level was lower and the mudflats were exposed. Cores were collected from 3 transects across the washover channel. Each core was collected in a plastic liner, capped and transported back to the lab once collected. The cores were sectioned into 5 cm sections, homogenized and extracted and analyzed for crude oil components as described below.

2.2.4 Washover scenario sampling

Along with the coring data, samples were taken over the course of a two year time period and over the course of multiple storm events mobilized oil during three specific washover events. Data from three specific events are presented here: the breakup and washover of an onshore SOM immediately after TS Lee in 9/2011 (Onshore SOM event), the breakup and washover of an offshore SOM during a strong cold frontal passage in 4/2013 and the repetitive washover events occurring at the Zone 1 Breach site described above. For each of these events, oil forms were sampled from the intertidal, supratidal and washover channels to assess the type, concentrations and weathering status of oil moving through the channel.

2.2.5 Oil Extraction and Analysis

Once the cores were collected and brought back to the lab, extractions were performed by thoroughly mixing the sample, weighing about 10 grams, and then mixing the sample with sodium sulfate and magnesium sulfate to remove any moisture that might be contained in the soil before it was extracted. Once the soil, sodium sulfate and magnesium sulfate were thoroughly mixed, they were transferred into individual sample stainless steel cells for accelerated solvent extraction. The cells are placed in a Dionex Accelerated Solvent Extractor (ASE) 350 (Thermo
Scientific), which extracts the oil elements from the samples using a 50:50 mixture of hexane and acetone under 1700 psi of pressure at a temperature of 100°C. Once the ASE extracts the oil from the sample, the solvent sample volume was reduced to 10 mL using a RapidVac N2 Evaporation System (Labconco, USA), and stored in a refrigerator. 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 (30m x 0.25mm 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, using internal standard within each sample and running a calibration check sample. The PAH method calculates the following compounds: naphthalene (C_{10}N), C1-naphthalenes (C_{1}N), C2-naphthalenes (C_{2}N), C3-naphthalenes (C_{3}N), C4-naphthalenes (C_{4}N), acenaphthylene (ACL), acenaphthene (ACE), fluorene (F), C1-fluorenes (C_{1}F), C2-fluorenes (C_{2}F), C3-fluorenes (C_{3}F) phenanthrene (C_{6}P), C1-phenanthrenes (C_{1}P), C2-phenanthrenes (C_{2}P), C3-phenanthrenes (C_{3}P), C4-phenanthrenes (C_{4}P), dibenzothiophene (C_{6}D), C1-dibenzo thiophenes (C_{1}D), C2-dibenzothiophenes (C_{2}D), C3-dibenzothiophenes (C_{3}D), fluoranthene (FAN), pyrene (PY), C1-pyrene/fluoranthene (C1-PY/FA), chrysene (C_{6}C), C1-chrysenes (C_{1}C), C2-chrysenes (C_{2}C), and C3-chrysenes (C_{3}C). The ALK methods calculates the following compounds: decane (C10), undecane (C11), tridecane (C13), tetrade cane (C14), pentadecane (C15), hexadecane (C16), heptadecane (C17), pristine, octadecane (C18), n-eicosane (C20), docosane (C22), n-tetracosane (C24), n-hexacosane (C26), n-octacosane (C28), n-triacontane (C30), n-dotriacontane (C32), and n-hexatriacontane (C36). C30-Hopane was also quantified in order to ratio the oil concentration (Urbano et al., 2013b). These compounds were quantified using the experimental data analysis
program in which the peaks are recognized and calculated based on the concentration of oil within the soil.

2.2.6 Weathering Ratios

For this experiment weathering ratios were developed in order to determine the fate of the oil once it is washed up on the shore during the washover events. Surface residue balls (SRB) deposited on the headland beaches may be left on the surface and exposed to direct sunlight and air. To account for the weathering aspects, three compounds were further examined: C1-C4 phenanthrenes, C1-C3 dibenzothiophenes, and C1-C3 chrysenes. The total amount of phenanthrenes, dibenzothiophenes that each sample contained were independently compared to the total amount chrysenes in each sample. The following formula was used to calculate the sum of C1 – C4 phenanthrenes over C1 - C3 chrysenes:

\[
\frac{(100 + \Sigma Phen)}{\Sigma Phen + \Sigma Chry}
\]

(Eq 2.6.1)

Using the same type equation, the same can be done but substituting the sum of C1 – C3 dibenzothiophenes in for the phenanthrenes:

\[
\frac{(100 + \Sigma DBZ)}{\Sigma DBZ + \Sigma Chry}
\]

(Eq 2.6.2)

The resulting data for these formulas can be seen in the weathering ratio graph (Figure 10) which illustrates the original weathering of the MC252 oil upon its arrival on the coastal headland beaches. The samples that are compared on the weathering ratio graph (Figure 10) are
Offshore SOM site (4/2013), Onshore SOM site (9/2011), Breach site (2012-2013) and the original calculated weather value for the MC525 oil.

2.3 Results and Discussion

2.3.1 Washover Channel Survey

Results of the washover survey are presented in Figure 4. Oil was detected in cores removed from the sampled washover channels at a frequency of 10/59 = ~17%. The actual frequency of contamination may be higher since they are based on single composite cores from the center of the channel. As an example, WO-7 from Zone 1 had no oil in the survey core but later more detailed sampling identified oil throughout the channel. Similar frequencies were observed in Zones 1 (4/23=17%) and 2 (5/25 = 20%). Zone 3 had washover channels in the easternmost ½ mile of the segment but not in the western end of the segment. Only 1 channel in Zone 3 (WO-11) had detectable oil. These results demonstrate that washover events are mobilizing oil from the intertidal to the washover channels. These channels represent the route of transport from the beach to the adjacent wetlands.

Concentrations of PAHs in the washover survey cores ranged from 19-238 mg/kg (Table 1). The highest concentrations were observed in WO-18, a relatively small channel in Zone 2. Dominant PAHs include the alkylated phenanthenes followed by the alkylated dibenzothiophenes, naphthalene’s and chrysenes in agreement with other studies (Diercks et al., 2010b; Liu et al., 2012; Urbano et al., 2013a). Weathering ratios, which track disappearance of lower molecular weight 3-ring PAHs, phenanthenes and dibenzothiophenes, relative to 4-ring PAH chrysenes, show that partial weathering has occurred in samples collected from the washover channels. The phenanthrene and chrysene weathering ratios ranged from 59-79 and 32-
49, respectively. This compares with weathering ratios from surface oil near the wellhead of 93 (phenanthrene) and 80 (dibenzothiophenes) (Diercks et al., 2010a).

In addition to the washover samples, SRBs, the oil-sand aggregates found on the beach surface, were removed from areas within the washover channels. Representative PAH concentrations from SRBs are presented in Table 2. Concentrations of total PAHs were higher than the channel samples ranging from 60-462 mg/kg. This was expected due to the dilution involved in taking a 15 cm composite sample. Weathering ratios for the phenanthrene and dibenzothiophenes were slightly higher than the channel ranging from 72-86 for phenanthrene and 51-63 for the dibenzothiophenes. Based on the observed position on the SRBs on the beach, the pattern of washover events and the weathering ratios and concentrations observed in the channels, movement of these SRBs during these storm surge washover events can explain the observed results.

2.3.2 Depth distribution in Washover Channels

Coring was performed at 2 locations (Bay Champagne in Zone 6 and a breach location in Zone 1 to determine the depth distribution of MC252 in washover channels. The results of the Bay Champagne coring can be found in Figure 5. This data consisted of 3 cores, 24 inches in depth, taken from the water’s edge of a small tidal bay (Bay Champagne). Two cores (BC-1 and BC-2) had detectable oil at various depths whereas core BC-3 did not contain any oil. The segments of the BC cores (Figure 5) in which oil was present ranged from the 0 – 20 cm and 30 – 45 cm segments in BC-1 and 0 – 10 cm and 10 – 25 cm segments in BC-2.
Figure 4. Map of washover sample (Zone 1 – 3) sampled from Fourchon Beach. The colored (red and green) dots represent reflect the locations on the beach that were sampled. The red dots indicate samples that contained elevated levels of MC 252 crude oil concentrations.
Table 1. Concentrations of selected PAHs, biomarkers and weathering indices in composite washover channel samples. Oil measured in units of mg/Kg

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C1N</td>
<td>0.01</td>
<td>0.01</td>
<td>0.21</td>
<td>0.25</td>
<td>0.21</td>
<td>0.207</td>
<td>0.22</td>
</tr>
<tr>
<td>C2N</td>
<td>0.15</td>
<td>0.07</td>
<td>0.29</td>
<td>0.27</td>
<td>1.43</td>
<td>&lt;0.01</td>
<td>0.10</td>
</tr>
<tr>
<td>C3N</td>
<td>0.01</td>
<td>0.01</td>
<td>0.88</td>
<td>1.37</td>
<td>7.60</td>
<td>1.76</td>
<td>1.20</td>
</tr>
<tr>
<td>C4N</td>
<td>0.50</td>
<td>0.30</td>
<td>1.20</td>
<td>1.22</td>
<td>5.59</td>
<td>0.86</td>
<td>1.35</td>
</tr>
<tr>
<td>C0P</td>
<td>0.41</td>
<td>0.18</td>
<td>1.03</td>
<td>0.73</td>
<td>2.10</td>
<td>0.68</td>
<td>1.31</td>
</tr>
<tr>
<td>C1P</td>
<td>1.03</td>
<td>4.09</td>
<td>0.12</td>
<td>2.59</td>
<td>26.53</td>
<td>1.01</td>
<td>3.08</td>
</tr>
<tr>
<td>C2P</td>
<td>1.78</td>
<td>3.09</td>
<td>1.99</td>
<td>3.46</td>
<td>35.63</td>
<td>2.19</td>
<td>4.07</td>
</tr>
<tr>
<td>C3P</td>
<td>1.97</td>
<td>3.85</td>
<td>3.43</td>
<td>4.83</td>
<td>29.01</td>
<td>4.41</td>
<td>1.12</td>
</tr>
<tr>
<td>C4P</td>
<td>1.66</td>
<td>4.74</td>
<td>2.45</td>
<td>2.28</td>
<td>17.07</td>
<td>3.84</td>
<td>4.17</td>
</tr>
<tr>
<td>CoD</td>
<td>0.86</td>
<td>1.00</td>
<td>0.88</td>
<td>&lt;0.01</td>
<td>1.50</td>
<td>0.55</td>
<td>2.01</td>
</tr>
<tr>
<td>C1D</td>
<td>0.97</td>
<td>1.83</td>
<td>1.00</td>
<td>2.50</td>
<td>5.39</td>
<td>0.91</td>
<td>3.30</td>
</tr>
<tr>
<td>C2D</td>
<td>0.75</td>
<td>1.58</td>
<td>0.88</td>
<td>1.87</td>
<td>14.25</td>
<td>1.18</td>
<td>1.32</td>
</tr>
<tr>
<td>C3D</td>
<td>0.40</td>
<td>1.64</td>
<td>0.98</td>
<td>1.78</td>
<td>8.49</td>
<td>1.10</td>
<td>1.27</td>
</tr>
<tr>
<td>C1F</td>
<td>1.83</td>
<td>0.39</td>
<td>0.94</td>
<td>0.95</td>
<td>3.37</td>
<td>0.75</td>
<td>0.23</td>
</tr>
<tr>
<td>C2F</td>
<td>0.01</td>
<td>0.01</td>
<td>1.02</td>
<td>0.42</td>
<td>7.22</td>
<td>0.72</td>
<td>0.89</td>
</tr>
<tr>
<td>C3F</td>
<td>0.01</td>
<td>0.01</td>
<td>0.13</td>
<td>0.31</td>
<td>7.08</td>
<td>1.29</td>
<td>1.05</td>
</tr>
<tr>
<td>C0C</td>
<td>1.95</td>
<td>2.89</td>
<td>1.94</td>
<td>3.56</td>
<td>10.38</td>
<td>1.13</td>
<td>3.59</td>
</tr>
<tr>
<td>C1C</td>
<td>1.99</td>
<td>4.42</td>
<td>1.12</td>
<td>2.63</td>
<td>13.91</td>
<td>2.24</td>
<td>5.82</td>
</tr>
<tr>
<td>C2C</td>
<td>1.40</td>
<td>2.47</td>
<td>1.31</td>
<td>2.63</td>
<td>9.60</td>
<td>1.67</td>
<td>2.54</td>
</tr>
<tr>
<td>C3C</td>
<td>1.08</td>
<td>2.73</td>
<td>1.01</td>
<td>1.78</td>
<td>6.11</td>
<td>0.98</td>
<td>2.29</td>
</tr>
<tr>
<td>C30-Hopane</td>
<td>2.57</td>
<td>8.17</td>
<td>3.42</td>
<td>4.95</td>
<td>10.50</td>
<td>4.72</td>
<td>5.38</td>
</tr>
<tr>
<td>Total PAH</td>
<td>19.2</td>
<td>36.0</td>
<td>26.9</td>
<td>38.8</td>
<td>238.1</td>
<td>47.1</td>
<td>52.96</td>
</tr>
<tr>
<td>WR - P - (100*ΣP)/(ΣP+ΣC)</td>
<td>59.00</td>
<td>62.15</td>
<td>69.91</td>
<td>77.27</td>
<td>78.52</td>
<td>70.09</td>
<td>63.46</td>
</tr>
<tr>
<td>WR - D - (100*ΣD)/(ΣD+ΣC)</td>
<td>32.18</td>
<td>34.46</td>
<td>45.44</td>
<td>48.64</td>
<td>48.68</td>
<td>39.41</td>
<td>35.03</td>
</tr>
</tbody>
</table>
Table 2. Concentrations of selected PAHs, biomarkers and weathering indices in SRBs sampled within washover channels during the washover survey. Oil measured in units of mg/Kg

<table>
<thead>
<tr>
<th>Compound</th>
<th>Zone 1 WO-12</th>
<th>Zone 1 WO-23</th>
<th>Zone 2 WO-8</th>
<th>Zone 2 WO-24</th>
<th>Zone 3 WO-7</th>
<th>Zone 3 WO-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1N</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.28</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>C2N</td>
<td>0.15</td>
<td>0.19</td>
<td>0.04</td>
<td>5.24</td>
<td>2.42</td>
<td>1.63</td>
</tr>
<tr>
<td>C3N</td>
<td>0.79</td>
<td>0.79</td>
<td>0.68</td>
<td>19.28</td>
<td>1.13</td>
<td>1.17</td>
</tr>
<tr>
<td>C4N</td>
<td>2.32</td>
<td>1.02</td>
<td>0.77</td>
<td>22.51</td>
<td>5.65</td>
<td>4.46</td>
</tr>
<tr>
<td>C0P</td>
<td>1.19</td>
<td>0.16</td>
<td>1.41</td>
<td>6.42</td>
<td>0.88</td>
<td>0.23</td>
</tr>
<tr>
<td>C1P</td>
<td>8.17</td>
<td>7.86</td>
<td>4.96</td>
<td>53.83</td>
<td>10.36</td>
<td>13.17</td>
</tr>
<tr>
<td>C2P</td>
<td>13.43</td>
<td>10.08</td>
<td>5.10</td>
<td>81.09</td>
<td>16.63</td>
<td>11.46</td>
</tr>
<tr>
<td>C3P</td>
<td>18.04</td>
<td>13.17</td>
<td>10.20</td>
<td>34.18</td>
<td>19.95</td>
<td>20.88</td>
</tr>
<tr>
<td>C4P</td>
<td>8.27</td>
<td>9.78</td>
<td>11.07</td>
<td>32.14</td>
<td>10.68</td>
<td>14.71</td>
</tr>
<tr>
<td>C0D</td>
<td>1.20</td>
<td>0.73</td>
<td>1.10</td>
<td>2.21</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>C1D</td>
<td>10.30</td>
<td>6.76</td>
<td>2.02</td>
<td>9.51</td>
<td>3.59</td>
<td>4.11</td>
</tr>
<tr>
<td>C2D</td>
<td>1.47</td>
<td>2.10</td>
<td>3.99</td>
<td>26.27</td>
<td>9.75</td>
<td>4.53</td>
</tr>
<tr>
<td>C3D</td>
<td>1.82</td>
<td>4.14</td>
<td>2.61</td>
<td>24.23</td>
<td>6.06</td>
<td>5.38</td>
</tr>
<tr>
<td>C1F</td>
<td>1.12</td>
<td>1.05</td>
<td>0.71</td>
<td>4.82</td>
<td>5.94</td>
<td>5.09</td>
</tr>
<tr>
<td>C2F</td>
<td>2.32</td>
<td>2.20</td>
<td>&lt;0.01</td>
<td>7.65</td>
<td>9.14</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>C3F</td>
<td>3.76</td>
<td>2.73</td>
<td>1.03</td>
<td>2.74</td>
<td>5.62</td>
<td>1.89</td>
</tr>
<tr>
<td>C0C</td>
<td>4.77</td>
<td>2.09</td>
<td>3.96</td>
<td>24.10</td>
<td>5.92</td>
<td>7.16</td>
</tr>
<tr>
<td>C1C</td>
<td>3.37</td>
<td>3.45</td>
<td>1.54</td>
<td>35.61</td>
<td>6.53</td>
<td>5.32</td>
</tr>
<tr>
<td>C2C</td>
<td>2.49</td>
<td>2.38</td>
<td>4.39</td>
<td>27.61</td>
<td>5.07</td>
<td>4.57</td>
</tr>
<tr>
<td>C3C</td>
<td>1.88</td>
<td>1.85</td>
<td>2.20</td>
<td>13.76</td>
<td>3.40</td>
<td>3.58</td>
</tr>
<tr>
<td>C30-Hopanes</td>
<td>6.02</td>
<td>5.25</td>
<td>7.10</td>
<td>55.06</td>
<td>7.81</td>
<td>12.80</td>
</tr>
<tr>
<td>Total PAH</td>
<td>101.56</td>
<td>90.09</td>
<td>60.22</td>
<td>462.31</td>
<td>149.75</td>
<td>127.79</td>
</tr>
<tr>
<td>WR - P - (100*ΣP)/(ΣP+ΣC)</td>
<td>86.08</td>
<td>84.18</td>
<td>79.39</td>
<td>72.33</td>
<td>79.34</td>
<td>81.73</td>
</tr>
<tr>
<td>WR - D - (100*ΣD)/(ΣD+ΣC)</td>
<td>63.71</td>
<td>62.84</td>
<td>51.49</td>
<td>43.81</td>
<td>56.40</td>
<td>51.00</td>
</tr>
</tbody>
</table>
Weathering ratios were computed from the data from oil detected in the individual segments: PAH/C30-hopane (10.2-12.4) ΣPhen/ΣChrysene (59-66) and ΣDibenz/ΣChrysene (47-49). The ΣPhen/ΣChrysene and ΣDibenz/ΣChrysene weathering indices were within the range of those in the washover survey (Table 1). PAH/C30-hopane values were at the low end of the samples in the survey (Table 1).

The results of the representative core data (Figure 6) from the Zone 1 Breach Site (Zone 1 WO-7 in the survey) can be found in Figure 7. This data consists of 21 cores that were 12” deep. Oil was detected in 6 cores with a detection frequency of 5/17 = ~29%. Three cores, Core A1, A4 and B4 (Figure 7) were examined in detail since they possessed the highest concentration of PAHs below the surface for the PAH/C30-hopane ratio ranged from 5.8 -12.6, at the low end of the range observed in the washover survey. ΣPhen/ΣChrysene (85-92) and ΣDibenz/ΣChrysene (45-95) ratios for Cores A1, A4 and B4 were higher than those in the BC cores and those in the washover survey, in general.

Given the results provided in Figure 5 and 7, a few things can be said about the two different coring events. First, oil is buried during the washover events due to the amount of sand that the water is able to carry with during the erosion of the beach. In each set of cores, the majority the oil is present within the first 10” beneath the surface. Given the weathering ratios that were calculated in Figures 5 and 7, the oil that was buried adjacent to Bay Champagne either had conditions that were more conducive to weathering than the Zone 1 breach site or it was contaminated with a different quality of oil. Oxygen limitations likely exist beneath the surface of these washover channels and this may contribute to persistence of the oil transported and deposited during washover events.
Figure 5: Cores collected from washover channel adjacent to Bay Champagne (BC) in Zone 5
Figure 6: Map of Sediment Cores collected at large washover channel in Zone 1 Breach Site
Figure 7: Sediment Cores collected from a large washover channel in Zone 1 Breach site
2.3.3 Individual Areas and Scenarios with weathering ratios

Three additional sampling events were conducted over the course of a two-year time period to measure the quality of oil mobilized from specific washover events that occurred on Fourchon Beach from 2011-2013. These events were selected to be representative of typical scenarios that occurred post-spill at this location. All of these events represented first, the breakup of an onshore SOM occurred during TS Lee whose storm surge impacted the beach in September 2011. In Ops Zone 7, a large mat located in the supratidal was exposed, broken up and pieces deposited in Bay Champagne during the storm. Samples of these pieces were removed for analysis immediately after the storm. Second, an offshore mat located off Breach 4, a breach closed by a hard structure on the border of Ops Zones 4 and 5, broke up and was deposited on the beach during a strong cold front passage in April 2013. Hereafter, this will be referred to as the offshore SOM site. Finally, oil reworked from offshore and onshore locations at the Breach 1 location, where coring activities described above were conducted, were sampled from 2012-2013 with a Large amount of oil were deposited in breach locations. During every storm and cold front new oil was mobilized from either onshore or offshore.

The averages of total PAH concentrations and individual PAH components present during each sampling event are present in Figure 8. The Zone 1 Breach 1 site had the highest PAH concentrations over the time period with a PAH/hopane Ratio of 75. The Zone 1 breach is constantly depositing new SRBs to the headland beach surface or reworking existing oil that has been previously deposited. The second highest concentration of total PAHs shown in Figure 8, came from the onshore SOM site from TS Lee which presented a PAH/hopane ratio of 35. The offshore SOM site had the lowest PAH/hopane ratio of approximately 15. PAH concentrations vary by approximately a factor of 5 between these different scenarios and events.
Upon further investigation based on the results, the individual PAH compounds shared similar results to the rest of the washover events studied in this paper. In consistent findings with (OSAT-II, 2011), the concentrations of the C1-C4 phenanthrenes, C1 – C3 dibenzothiophenes and C1–C3 chrysene tend to be heavier in concentration when broken down into individual compounds. The highest concentrations in each sample were in the form of C2 phenanthrenes based on Figure 8 and is consistent throughout all of the samples that were analyzed include the 59 washover zones and the two different coring surveys. The breach site contained the highest concentration of C2 phenanthrenes with a ratio of 17.5 followed by the 8.5 ratio from the onshore mat.

A similar graph was configured in order to show the n-alkanes that each samples event possessed using Figure 9. Like the results that can be seen for the PAH data, the breach site contained the highest concentrations of total alkanes over the course of the year and the onshore mat that was broken up during TS Lee follows the same order as seen with the matching PAH data. Based on the results that are shown in Figure 9, the consistency of the Alkanes and PAHs further prove that the breach site is always receiving new concentrations as seen by the ratio of about 300 of Total Alkanes/Hopanes of oil during the wash out zones during typical high tides due to its low lying channels and that TS lee was a force that broke up a significant on shore mat with a ratio of about 150 Total Alkanes/Hopanes during a storm event which lasted a short period of time. The winter storms moves new SRBs onto the beach based on the Total Alkanes/Hopanes ratio of about 50, however they are not as strong as the TS and constant daily washover locating in the low lying area along Fourchon Beach.

Weathering information for each of the sites was computed using a double weathering ratio plot which plotted 2 ratios in a 2-D space. (Figure 10). These ratios compared
concentrations of phenantrenes to chrysenes on the y-axis and dibenzothiophenes to chrysenes on the x-axis. As weathering proceeds, samples should proceed from the far right to the origin. The double weathering ratio plot is constructed using the weathering ratio equations (Eq 2.5.1 and Eq 2.5.2). Plotted on the graph is results from sample taken near the wellhead on the surface in 2010 (Diercks et al., 2010a) during their initial response to the oil spill. This point serves as a reference point for the weathering observed in the remaining samples. Based on all the samples analyzed here, the Zone 1 Breach site is more susceptible to weathering and had ratios distributed over the largest range. These represented SRBs that had been deposited on the beach and were therefore susceptible to weathering according to previous studies of these oil forms (Elango et al., 2014; Lemelle et al., 2014; OSAT-II, 2011; Urbano et al., 2013a). SOMs have the potential for conditions that encourage persistence including the potential for O₂ deficits and submergence offshore. These weathered at lower rates, even though the absolute amounts of oil in these samples was lower than the SRBs from Breach 1. Finally, if phenanthrene and dibenzothiophenes are weathering at equal rates they should decline along a 45 degree line towards the origin in Figure 10. This was not the case, however and dibenzothiophenes appeared to weather somewhat preferentially. Further research is needed to determine why, since both a 3-ring PAHs with similar structures.

2.4 Conclusions

Washover events that occur from cold fronts or high tides and catastrophic events such as tropical storms and hurricanes have been studied in this chapter and show the ability to transport oil across the tidal regions of the beach from subtidal to the mudflats. These reoccurring events place more sand on top of the existing oil-rich beach, pushing the oil further below the surface. During the Washover survey that took place from February thru May 2011,
Figure 8: PAH concentrations found within the three washover events

Figure 9: n-Alkanes concentrations found within the three washover events
59 washover sites from Zones 1 – 3 were sampled and 10 or 17% contained oil. Out of the 3 zones surveyed, Zone 2 had 5 or 20% of the sites that contained a presence of MC252 within the washover channels. These detection frequencies were based on single discrete points within each channel and demonstrate the proof-of-concept of the transport of MC252 crude oil across the beach to these channels.

Two of the washover channels were examined in more detail to determine distribution of oil with depth. In the channel adjacent to Bay Champagne, 2 of the 3 cores contained oil with maximum concentrations with depth observed within the first 20 cm while at the Zone 1 breach
site 5 of the 17 cores contained oil with the maximum concentrations within the first 10 cm. Each of the 5 cores showed a presence of oil with in the first 5 cm, along with various concentrations at depths deeper below the surface further illustrating that the oil is being buried below the surface.

Three scenarios were examined to determine the quality of oil based on the relative weathering observed in oil aggregates sampled on the beach that had either washed over the surface or had the potential to be transported. These scenarios included an onshore SOM that is broken up and distributed across the beach by storms, an offshore SOM affected by the same processes and a breach site where oil has been distributed throughout the beach in the breach channel. For the SOM samples these were samples taken after discrete washover events (offshore SOM in April 2013, onshore SOM in September 2011) while sampling at the breach occurred over a continuous 2-year period (2011-2013). During weathering, evaporation, dissolution and biodegradation of the PAHs and alkanes in the SRBs and SOMs occur are they are exposed to the natural elements of sun, wind, rain and tidal activity. All of the oil samples showed partial weathering of the 3-ring PAHs (phenanthrenes and dibenzothiophenes) when compared to surface oil from near the wellhead (Diercks et al., 2011). Samples from the SOMs were less weathered than those from SRBs from the Breach site 1 which is consistent with previous studies demonstrating the biodegradation on MC252 PAHs in these aggregates (Elango et al., 2014). Comparisons of weathering ratios from the samples directly from the washover channels and the oil sampled from the beach demonstrate that no additional weathering is occurring.

The primary conclusion from this chapter is that the MC252 oil is moving across the beach surface due to the low laying washover channels that allow the gulf water easy access to the mudflats and marshes. Once on the beach surface, weathering events can degrade the oil
slowly, however, movement into the wetter mudflat areas appears to reduce the weathering potential considerably. Biodegradation in this environment may be considerably slower which is the subject of experiments in the following chapter.
CHAPTER 3: FATE OF MC252 CRUDE COMPONENTS IN THE WASHOUT FANS ON A COASTAL HEADLAND BEACH

3.1 Introduction

Beach morphodynamics can dramatically influence the fate of spilled crude oil by burial, sequestration and other coastal processes that influence weathering (Bernabeu et al., 2006; Boufadel et al., 1999; Short et al., 2007). Coastal headland beaches, heavily impacted by the Deepwater Horizon spill, are impacted by storm-surge driven process which contribute to the burial of the oil in the intertidal area (Pardue et al., 2014). These storm events, termed washovers, are tidal events driven by cold fronts, tropical storms, hurricanes and high tides that drive waves and water over the beach crest (Georgiou et al., 2005). These events move oil from the intertidal to the back mudflats, marsh and mangrove wetlands that bound these beaches (Curtis et al., 2014). Since the oil is moved into environments that are typically anaerobic in nature, degradation of key oil components, such as polycyclic aromatic hydrocarbons (PAHs) and alkanes, may be limited causing the oil to persist over long time frames (Short et al., 2007).

Biodegradation of MC252 crude oil components has been shown to be an important fate process across the continuum from the wellhead to the shoreline (Hazen et al., 2010; Kostka et al., 2011). In studies conducted on Fourchon Beach biodegradation potential of oil in the intertidal and supratidal environment has been demonstrated using weathering ratios, measurement of biogeochemical characteristics, and microbial populations that include known PAH degraders (Elango et al., 2014; Urbano et al., 2013). Washovers, however, deposit oil in mudflats, marsh and mangrove areas north of the beach in environments that are permanently wet which creates the potential for anaerobic conditions. The biodegradation of MC252 oil may slow significantly in these habitats relatively to the beach environment.
Oil reaches the coastal region of Louisiana as a water-in-oil emulsion, mixed with sand and shell to form 2 types of oil forms, surface residue balls (SRBs) and submerged oil mats (SOMs). An SRB is typically spherical aggregate and is usually held together by a mixture of sand, shells and oil that is deposited on the beach (OSAT-II, 2011). On the balls surface, SRBs are essentially oil free since the surface is mixed predominantly with sand, but once they are broken in half a darker, oily core can be found along with a smell of oil that is characterized by SRB aggregates from the MC252 crude oil which has an oil content is typically in the range of 5-10% (OSAT-II, 2011). SOMs exist in the inshore surf zone troughs between sand bars and the buried underneath the surface which appear during washover events (OSAT-II, 2011). When the gulf is mixed up by hurricanes, tropical storms, cold fronts and high tides, Surface Residual Balls (SRBs) and submerged oil mats (SOMs) are redeposited behind by these events. It is estimated that the headland beaches are eroding at a rate of about 40 feet per year (McBride et al., 1992) which allows SRBs and SOMs the ability to move from the gulf, across the land and into the back bay areas. SRBs and SOMs that form on the surface are aggregates which create barriers to the flow of nutrients and electron acceptors such as nitrogen, sulfate and phosphorus by clogging the pores of the sandy headland beaches. In recent studies, the residence time of the aggregates at different positions on the beach demonstrate small disparity which can dictate the susceptibility of weathering (Urbano et al., 2013). However, regardless of location of the SRBs and SOMs, the lack of oxygen is associated with persistence of MC 252 crude oil due to the requirements of aerobic microbial populations and the inadequate biodegradation capabilities of anaerobic microbial to degrade PAHS and Alkanes.

In this study a microcosm experiment was conducted in the laboratory under anaerobic and aerobic conditions using intact SRBs that were collected from a site on Fourchon Beach, LA.
The weathered SRBs were collected along a transect from the intertidal to the supratidal. Once the SRBs were collected and weighed, each aerobic and anaerobic microcosm received intact or crushed SRBs. Degradation was followed in the SRBs over time. In addition to the laboratory study, field measurements were conducted using dialysis samplers to determine nutrient concentrations in the washover channels. The overall goal of the study is to determine the weathering potential, specifically focused on biodegradation of PAHs and alkanes that is found in the SRBs that make their way into the mudflat sediments as a result of these washover events.

3.2 Materials and Methods

3.2.1 Site Description and SRB sampling

The study location is the 9 mile coastal headland Fourchon Beach located in Port Fourchon, LA. It is part of the larger Caminda Headlands beach system consisting of Elmer’s Island and Fourchon Beach. The beach was heavily impacted by the Deepwater Horizon oil spill and from June 2011 to present, 64% of the total oiled material collected in the GoM was removed from this one beach. The specific site used for the current study was located on the eastern end of Fourchon Beach in Operational Zone 1. Fourchon Beach was divided into 9 operational cleanup zones numbered 1-9 from east to west. The study site was located in a low-lying area that is prone to washover events during storm surge events as seen in Chapter 2. For this study, SRBs were collected after Hurricane Isaac on 11/19/2012. The beach was broken up into three section for the beach survey 0-30’, 30 – 150’ and 150’ – mudflat. Within these section SRB’s were collected.
3.2.2 Microcosm Study

A MC252 oil biodegradation study was conducted using a laboratory serum bottle microcosm approach using mudflat sediment and SRB’s from the Breach 1 study site. Studies were conducted under both anaerobic and aerobic conditions. The study was conducted over a timeframe of 150 days with microcosms sacrificed for oil analysis every 30 days. For this study, seven different treatments (1-7) were used. Each treatment received 6 sets of bottles (A-F), prepared in triplicate, which served as the samples for analysis every 30 days. The microcosm contained 20 mL of seawater from study site, 10 g of mudflat sediment from the site and 10 g of SRB’s from various distances form the beach shore, as described above. Treatment 1 was a flooded anaerobic microcosm that contained an unbroken SRB from the 0’ – 30’ zone on the beach. Treatment 2 consisted of a fertilized flooded anaerobic microcosm containing an unbroken SRB from the 30’ – 150’ zone. Treatment 3 was comprised of a fertilized, flooded anaerobic microcosm that contained a crushed SRB from the 150’ – mudflat zone. Treatment 4 was a non-flooded aerobic microcosm that contained an unbroken SRB from the 0 - 30’ zone on the beach. Treatment 5 consisted of a fertilized, non-flooded aerobic microcosm containing an unbroken SRB from the 30-150’ zone. Treatment 6 was comprised of a fertilized, nonflooded aerobic microcosm that contained a crushed SRB from the 150’ – mudflat zone. The killed control was conducted using the SRB’s from the 0 – 30’ zone on the beach. The killed control involved autoclaving the microcosms at 15 psi, 121°C temperature, and then flooding with a water solution containing formaldehyde. The anaerobic environment was achieved through means of a Coy Laboratories anaerobic chamber that is feed Nitrogen and compressed (NOS) gases in which the samples were set up, sealed tight with a cap and stored in the chamber over the course of 150 days. The aerobic microcosm samples were placed in the open laboratory
environment, left uncapped and initially flooded with water. The water collected from the GoM for the experiment contained an initial sulfate concentration between 2700 mg/l – 3000 mg/l and a phosphorus concentration of 1 mg/l. 135 mg of ammonium chloride was added to gulf water to yield a N source present in the water at 35.3 mg/L. The seven treatments were monitored and shaken weekly. Every 30 days, samples from each of the 7 treatments extracted and analyzed using methods described in section 2.5. The water from the sample bottles was also removed and analyzed for nutrients and sulfate.

3.2.3 Field porewater sampling

Porewater from the Breach 1 study site was obtained using a set of 3 dialysis samplers or peepers (Hesslein, 1976; Jackson et al., 1996). The peeper is constructed of Plexiglas and machined to include ~75 sample cells along the length of the sampler. The sampler is filled with deionized water, and covered with a 0.4 µm pore size membrane. The peepers were implanted vertically into the mudflat sediment until all of the sample cells were submerged at the sediment: water interface. Three locations at the Breach 1 study site mudflat were used to study the ground water. The peeper was left in the sample location for the period of approximately 1 month for diffusion-driven equilibration to occur. The samplers were removed from the sediment and the water in the cells was recovered using a syringe. The sample in the syringe was then placed into 1.5 mL Agilent screw-top vials, and stored on ice until further analysis using the methods described below for nitrate (NO$_3^-$), nitrite (NO$_2^-$), orthophosphates (PO$_4^{3-}$), ammonium (NH$_4^+$), and sulfate (SO$_4^{2-}$).

In order to measure the amount of dissolved oxygen present in the shallow ground water, measurements were taken at the Breach 1 site using an AMS Retract-A-Tip gas vapor sampling probe (Charette and Allen, 2006). Once the tip was placed into the ground, a 20 ft. piece of rigid
tubing was placed on the inside the protective outer rod in order to draw the water from the ground. The rigid tubing was then connected to a peristaltic pump that was used to pump the groundwater to the surface. Samples were taken along a transect from the mudflat to the nearshore area. At each location, the AMS sampler was pumped for approximately 5 min to allow for a representative sample of water to be collected. Once the location was purged, 3-300 mL BOD bottles were filled to the top, capped off instantly and tested for dissolved oxygen using Winkler’s method. Along with measuring the DO, additional samples were collected and were stored in glass and transported back to the lab for additional salinity measurements.

3.2.4 Oil Extraction and Analysis

Once the microcosms were ready to be analyzed at the end of each cycle, extractions were performed by thoroughly mixing the sample, weighing about 10 grams, and then mixing the sample with sodium sulfate and magnesium sulfate to remove any moisture that might be contained in the soil before it is extracted. Once the soil, sodium sulfate and magnesium sulfate were thoroughly mixed, they were transferred into the individual sample stainless steel cells for accelerated solvent extraction. The cells are placed in a Dionex Accelerated Solvent Extractor (ASE) 350 (Thermo Scientific), which extracts the oil elements from the samples using with a 50:50 mixture of hexane and acetone under 1700 psi of pressure at a temperature of 100°C. Once the ASE extracts the oil from the sample, the solvent sample volume was reduced to 10 mL using a RapidVac N₂ Evaporation System (Labconco, USA), and stored in a refrigerator. 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 (30m x 0.25mm 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, 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). The ALK methods calculates the following compounds: decane (C₁₀), undecane (C₁₁), tridecane (C₁₃), tetradecane (C₁₄), pentadecane (C₁₅), hexadecane (C₁₆), heptadecane (C₁₇), pristine, octadecane (C₁₈), n-eicosane (C₂₀), docosane (C₂₂), n-tetracosane (C₂₄), n-hexacosane (C₂₆), n-octacosane (C₂₈), n-triacontane (C₃₀), n-dotriacontane (C₃₂), and n-hexatriacontane (C₃₆). C₃₀-Hopane was also quantified in order to ratio the oil concentration (Urbano et al., 2013b). These compound are quantified using the experimental data analysis program in which the peaks are recognized and calculated based on the concentration of oil within the soil.

3.2.5 Nutrient and Electron Acceptor Analysis

Nutrients (NO₂⁻, NO₃⁻, NH₄⁺, PO₄³⁻) and an electron acceptor, (SO₄²⁻) were measured using a SmartChem 170 Discrete Analyzer (Unity Scientific Inc.) using the EPA methods #353.2, 365.1, 350.1 and 375.4, respectively. QA/QC consisted of blanks and continuing calibration samples before each run.
3.3 Results and Discussion

3.3.1 Microcosm Results

The results of the anaerobic and aerobic microcosm study with the intact SRBs can be seen in Figure 11 & 12. Ratios of key PAH groups to the poorly biodegradable C30-hopanes are used to assess the relative rates of weathering, specifically focused on biodegradation. These treatments were constructed using SRBs that were collected from the intertidal (0-30’ from the shoreline) without any fertilization amendments. Based on the results from the Σ Phenanthrenes / Σ Chrysenes ratios, minimal amount of degradation occurred over the course of the 150 days. The only amount of degradation that can be inferred from the graph was using the Total amount of PAHs contained in the samples as the overall amount of the PAHs within the samples changed over the course of 150 days but individual alkylated groups the phenanthrenes (C₁P-C₄P), the dibenzothiophenes (C₁D-C₃D), and the chrysenes (C₁C-C₃C) did not decrease significantly at P>0.05. A killed control was constructed (Figure 12) using the intact SRBs from the same location as these treatments and the results were very consistent with the results displayed from Figure 11 & 12.

The results of the anaerobic and aerobic microcosm study that were fertilized can be seen in Figure 11 & 12. These treatments were constructed using SRBs that were collected from the 30 feet to 150 feet zone and they were left intact for the purposes of this study. Figure 11 & 12 was constructed using the ratios of Σ Phenanthrenes / Σ Chrysenes ratios concentrations as described above. Again, results indicate minimal loss of PAHs over the 150-day time frame and were similar to the results from Figure 11 & 12 for natural attenuation treatments. The results from the graphs indicate again that the only amount of degradation that can be inferred from the graph was using the Total amount of PAHs contained in the samples as the lower molecular
weight compounds such as \((\text{C}_1\text{N}-\text{C}_4\text{N})\) Napthalenes tend to degrade but there is not significant difference \((P>0.05)\) causing the overall amount of the PAHs within the samples to change over the course of 150 days.

The results from the anaerobic and aerobic treatments that used crushed SRBs and fertilization can be seen in Figure 13. These two sets of samples were constructed using SRBs that were collected from the ranges from 150’ to the rear mudflats along the headland beach surface. These SRBs were significantly weathered and had lower concentrations than the previous studies but are representative of the types of SRBs deposited in the washover channels. Figure 13 was constructed using the same graph formats from the previous two figures. However, the results from the crushed samples varied from the SRB that where left intact. Almost every compound saw a decrease with a statistical difference at \(P<0.05\) and the aerobic samples displayed the greatest amount of decrease at \(P<0.05\) in concentration and in some compound such as the \((\text{C}_1\text{D}-\text{C}_3\text{D})\) dibenzothiophene, and the phenanthrenes \((\text{C}_1\text{P}-\text{C}_4\text{P})\) the concentration was nearly extinct by the end of the test.

Changes in nutrient \((\text{N} \text{ and P})\) and sulfate concentrations are displayed in Figure 14 for the anaerobic treatments. Sufficient water was not recovered from the aerobic treatments to perform similar tests. The initial sulfate concentrations present in the water ranged from \(~2800 – 3000\) mg/L. The sulfate concentrations in Figure 14 declined after approximately 60 days suggesting that sulfate reduction was occurring at that time. Increases in sulfate over the first 60 days of the study have been observed previously using these sands and may results from dissolution of salts precipitated in the sands, themselves or oxidation of pyrite. The ammonium concentration was spiked to \(35\) mg/L in the fertilized treatments and within 60 days, the concentrations were reduced to less than \(10\) mg/L. Ammonium chloride was re-added to raise the
concentration to 20 mg/L which was also depleted within the next 60 days. Loss of ammonium from the porewater could be due to sorption or uptake into new microbial cells. No net nitrate or nitrite was produced and nitrification is unlikely given the flooded conditions. The concentration of nitrate initially present in the seawater 3.5 mg/L and nitrite was low throughout the experiment (Figure 14). The concentrations of nitrate were also consumed within the first 60 days likely due to denitrification under the anaerobic flooded conditions. In the anaerobic treatments it appears that nitrate reduction conditions were present in the first 60 days followed by sulfate reducing conditions. Phosphorus, was present at initial concentrations of 1 mg/L but were reduced to concentrations below 0.5 mg/L after 30 days. There appears to be sufficient P as it remained greater than 0.1 mg/l throughout the experiment after the initial uptake to support biodegradation, however.

3.3.2 Porewater concentrations of nutrients in washover areas

Three dialysis samplers were along the centerline of the washover fan at the Zone 1 breach site and incubated for a month. Concentrations of sulfate (SO$_4^{2-}$), phosphorous (P), ammonium (NH$_4^+$), nitrate (NO$_3^-$), and nitrite (NO$_2^-$) from top 75 cm from the surface are presented in Figure 15. Profiles of SO$_4^{2-}$, P and NH$_4^+$ showed changes at ~30 cm below the surface, consistent with a major redox transition in the mudflat sediments.

Sulfate concentrations at the surface ranged between 1500 and 1700 mg/L in the top 30 cm. for samplers 2 and 3 and the 50 cm mark on sampler 1. Sampler 1 was positioned on the washover fan closest to the gulf and at the beginning of the washover fan. Because of it position and elevation, this location would have received a larger tidal fluctuation, wetting and drying more frequently.
Figure 11: Microcosm data from anaerobic natural attenuation and nitrogen amended treatment containing intact SRBs. The ratio of each compound was calculated by dividing $\Sigma$Phenanthrenes / $\Sigma$Chrysenes.
Figure 12: Microcosm data aerobic natural attenuation, nitrogen amended and aerobic kill control treatment containing intact SRBs. The ratio of each compound was calculated by dividing ΣPhenanthrenes / ΣChrysenes.
Figure 13: Microcosm data from aerobic and anaerobic nitrogen amended treatment containing crushed SRBs. The ratio of each compound was calculated by dividing $\Sigma$Phenanthrenes / $\Sigma$Chrysenes.
Figure 14: Nutrient concentrations for the flooded anaerobic microcosm study.
Therefore, the impact of this fluctuation would be observed lower in the profile. Samplers 2 and 3 were located further back in the washover channel in areas that were flooded more often. In all 3 samplers, below the depth, sulfate decrease to 200-600 mg/L indicative of a completely anaerobic zone of sulfate reduction.

Phosphorus and ammonium showed the opposite trend (Figure 15). Concentrations of phosphorus and ammonia ranged from 1-2 mg/L and a 1-4 mg/L, respectively, in the upper zone (30-50 cm). At a similar transition when sulfate began to decline, P and NH$_4^+$ increased. P will increase under anaerobic conditions as the primary surfaces that sorb P, the iron oxyhydroxides, are reduced to soluble ferrous iron. Ammonium will increase as processes that convert ammonium to nitrite and nitrate cease to operate. The highest concentration of ammonia below the surface took place in sampler 2 at a distance of about 55 cm below the surface and a concentration of about 25 mg/L. Nitrate and nitrite were also measured but were consistently less than 0.1 mg/L over the length of the profile.

In addition to the nutrient data that was obtained from the washover zone dissolved oxygen (DO) concentrations were recorded at the washover fan beneath the surface in 2013 (Westrick et al., 2014). In the shallow groundwater ~30 cm beneath the washover channel at this location, DO concentrations were less than 0.5 mg/L. This confirms that the flooded zone has very low DO which could lead to oil persistence. Taken together the $O_2$ and dialysis sampler data indicate that sufficient N and P exist to support oil degradation. Data also indicate that very anaerobic conditions are observed below 30-50 cm, which is deeper than the presence of oil in these channels (Curtis et al., 2014). In this upper zone, temporal $O_2$ availability appears to be enough to keep the sulfate oxidized and likely the iron oxyhydroxides as well. Partial weathering
in the oil at depth at this location may indicate that some O\textsubscript{2} is available to drive PAH degradation but at rates substantially slower than other areas on the beach.

### 3.4 Conclusions

With all the information that is presented in this chapter, a few conclusions can be drawn. Previous studies (from Chapter 2) have demonstrate that washover events deposit oil on the coastal headland beaches and can move oil into mudflats and marshes which are tidal inundated. These previous studies also showed that this oil can, in some cases, be buried below the surface where weathering of the dominant 3-ring PAHs (phenanthrene and dibenzothiophenes) was observed to be slower. The key question is whether biodegradation is inhibited as a weathering process under these conditions.

Microcosm studies showed no weathering over 150 days when intact SRBs were incubated under anaerobic or aerobic conditions in mudflat sediments. These results confirm the slow weathering under these conditions as indirectly shown in previous studies. Unlike the intact SRBs, however, the microcosm experiment using crushed SRBs showed signs of weathering. Specifically, the weathering ratio of $\Sigma$Phenanthrenes / $\Sigma$Chrysenes show a significant difference ($P<0.05$) in the anaerobic and aerobic microcosms over the course of 150 days. Since the PAHs are not known to biodegrade anaerobically, the loss from the crushed SRBs may be due to other weathering processes, such as dissolution or evaporation, in addition to biodegradation. These processes could occur more readily when the SRB was crushed and the surface area was increased.
Figure 15: Nutrient Concentrations from the Peeper analysis from the Breach Site in Zone 1.
Nutrient and electron acceptor data from the field, coupled with the previous distribution of oil in the washover channels from data in Chapter 2, suggest that N and P are readily available. While O$_2$ was barely detected in the porewater from the washover channel, profiles of sulfate suggest that the upper part of the profile is not permanently inundated and sulfate is not being consumed by sulfate reduction. This suggests that the top ~30 cm of the mudflat is wetting and drying enough to prevent completely anaerobic conditions from developing. These conditions do not, however, seem sufficient to lead to significant weathering involving biodegradation once oil reaches these locations. These results suggest that oil reaching the washover channels will be persistent due to slow rates of biodegradation.
CHAPTER 4: SUMMARY AND OUTLOOK

4.1 Experimental Findings and Implications

From all of the information that is presented in these chapters a few conclusions can be made about the Deep Water Horizon Oil Spill. The washover event that are caused by high tides, tropical storms, winter storms and hurricanes are constantly reworking the gulf and depositing SRBs and uncovering SOMs located in the subtidal region placing the remnants in the intertidal and supratidal regions. When the SRBs and SOMs, make their way on shore they can be susceptible to weathering which aids in the breakdown of the concentration of oil. When the SRBs and SOMs are present on the beach, they are then susceptible to be buried by the reoccurring washover events that take place on the headland beaches. Based on the results from the coring study that took place, evidence shows that the oil does get buried during these events and which make it difficult for the oil to degrade due to the lack of oxygen present below the surface and limited nutrients.

Upon further investigation as seen through a microcosm study, SRBs that remain intact have a more difficult time degrading versus the SRBs which are crushed up as the crushed SRBs tend to dissolve within the water over time. The microcosm study under anaerobic conditions demonstrated that when there is an absence in oxygen, supplemental nutrients in the form of sulfate, ammonia and phosphorus can be consumed by the bacteria present within the SRBs. Given the information found from the peeper analysis, nutrients are present below the surface vary with depth and are typically found in the form for of sulfate, phosphorus and ammonia which work simultaneously with each other in order to aid in the degradation process. It can be concluded from all the information found within this thesis that SRBs are making their way on
the headland beaches however they are susceptible to weathering and degradation given by the
natural environment in which they are place along the different tidal zones in Fourchon Beach.

4.2 Future Research

For future research, more SRBs and washover sites should be collected either on different
coastal beaches or other washover events, to determine long term weathering and degradation
rates from the natural environment. Likewise the headland beaches ought to have more core
surveys done over other the numerous washover zones in order to determine the amount of oil
that is buried in other zones along the beach. It is hard to replicate what actually takes place in
the field within the lab. With that being said, a duplicate microcosm study could be conducted
using SRBs over a longer period of time and discovering a way to capture the CO$_2$ that could be
collected from the degradation of the microcosms along with adding microorganisms that are
known to degrade the oil to enhance the process and calculate rates. Consequently, additional
field experiments may be worth undertaking to confirm the laboratory results and help better
understand what is happening to the oil once it does degrade.
REFERENCES


VITA

David Nelson Curtis was born in Metairie Louisiana and was raised in Laplace, LA. His parents Mike Curtis, a Chemist, and Ginger Curtis run a small family business specializing in water and wastewater testing and consulting. After graduating High School in 2007 from Brother Martin High School in New Orleans, LA, he moved to Hattiesburg, MS to start his undergraduate education from the University of Southern Mississippi. He choose to major in Chemistry ACS Certified since it ran in the family. Upon graduating from USM, he decided to pursue a masters in environmental engineering since he always wanted to be an engineer. He will graduate in May of 2014 and pursue a career in something dealing with consulting in water and wastewater.