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The fate and transport of light petroleum hydrocarbons in the Lower Mississippi River Delta

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THE FATE AND TRANSPORT OF LIGHT PETROLEUM HYDROCARBONS IN THE LOWER MISSISSIPPI RIVER DELTA

A Dissertation

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 Doctor of Philosophy

in

The Department of Civil and Environmental Engineering

by

Samantha Nicole Danchuk
B.S., Florida State University, 2004
M.S., University of California, Berkeley, 2005
May 2009
DEDICATION

To my Mom and Dad,

The most supportive, amazing and inspiring people in the world,

you have helped me make my dream come true.

Thank you for being you and for making me, me.
ACKNOWLEDGEMENTS

A million thanks to my advisor, Dr. Clinton Willson, for allowing me to find my own way through my research. Oil spill modeling was probably not what he imagined I would be doing, yet he was the perfect guide on this journey. I am grateful for all the time he spent with me. As a mentor, he has shown me the benefits of patience when things are not working the way you want, focusing on the big picture and the ultimate goals and how to just say exactly what you mean. I also want to thank my committee members Dr. Gabrielle Allen, Dr. Chunyan Li, Dr. Zhi Qiang Deng and Dr. Elijah Ramsey for their support and helpful comments that pointed me in the right direction at key moments in this research. I am very appreciative of their time and willingness to serve on my committee.

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ABSTRACT

Important processes governing the fate and transport of light petroleum hydrocarbons in the Lower Mississippi River and other river delta systems are not adequately represented in existing oil spill models. In response, three methods were introduced to include the effects of dynamic annual discharges and variation of shoreline type on shoreline retention and re-floatation and the potential of oil- mineral aggregate formation based contributing environmental factors.

Parcel tracking was used, in conjunction with detailed shoreline types correlated to flow rate, to evaluate the benefits of using multiple shoreline re-floatation half lives correlated to shoreline type instead of a single half life for total shoreline. At low flow rates, simulations with detailed delineation of shoreline type and multiple re-floatation half lives predicted that ~35% more oil re-floated than when a single shoreline type was used. In addition to shoreline type, river geometry and the hydrodynamics significantly influenced the distribution of oil along the shoreline.

To evaluate the accuracy of mass balance estimates, potential oil- mineral aggregate (OMA) formation was quantified during four distinctly different states of the river during a year with different combinations of salinity, suspended sediments, discharge and temperature. The peak season for OMA formation in the river for the two lighter oils was found to be winter and spring when high sediment availability supports the process. The peak season for the dense, high viscosity oil was summer when the low flow rates and approaching salt wedge increased the river’s salinity. Typical dispersion modeling does not account for OMA providing inaccurate mass balances since as much as 36% of an oil spill has the potential to reach the Gulf of Mexico as OMA, depending on environmental conditions and spill characteristics.
The methodology and resulting conclusions were verified by implementing the methods introduced in previous chapters to hindcast the trajectory and assess the mass balance of the $DM932$ spill that occurred in New Orleans on July 23, 2008. The incorporation of the multiple half live method resulted in an improved model capable of replicating actual spill data.
CHAPTER 1

INTRODUCTION

1.1 Background

The demand for fossil fuels is driving the rapid expansion of its industry’s infrastructure. As the infrastructure grows across land and sea, more pipelines and tanker vessels will transport oil from offshore across greater areas inland to the storage facilities, refineries, and distributors. At any point in the process, releases can potentially occur, resulting in enormous environmental and economic impacts. Oil spill rates are likely to increase as the industry expands. Understanding the behavior of the oil and interactions with the natural environment is essential to a sustainable balance between industry, the public and the environment.

Oil spill storage facilities, pipelines, and tankers are responsible for frequent, costly, environmentally destructive oil spills in inland waterways. Inland oil spills occur more frequently but in smaller volumes than ocean spills; they have a higher potential to contaminate drinking water supplies, affect fisheries and wetland areas and recreational areas (Owens et al., 1992). For most countries, shipping via rivers is the cheapest or only possible method of transportation. Major spills have occurred along all of the major transport routes in the world including the Amazon, Niger, and Mississippi River deltas. Although these spills occurred in very different parts of the world, the incidents share similarities: critically important environmental and social resources were put at risk and/or damaged, large stretches of shoreline were oiled, and all would benefit from new approaches and improved methods for predicting and responding to the fate and transport of oil in inland areas.

Louisiana hosts a large portion of the nation’s oil infrastructure. Crude oil is pumped continuously from offshore and inland wells through pipelines that run underground across most of the state. Oil storage facilities and refineries are located along waterways for ease of transport
and proximity to water supply. The risk of spillage at fixed locations being served by vessels is the highest of all types of spill incidents (International Tanker Owners Pollution Federation Ltd., 2005). One of the world’s busiest port complexes, the Lower Mississippi River is the main supply route for the ports of New Orleans, Baton Rouge, and South Louisiana. Over 6,000 ocean vessels move through the Port of New Orleans, yearly, carrying 11.4 million tons of cargo (Meselhe, 2003). Conveniently, the refineries in Louisiana are primarily located along the Lower Mississippi River. From Convent (RM 159) to Belle Chasse (RM 76), seven refineries produce about 1.5 million barrels per day (bpd). These refineries are located on the Mississippi River, near New Orleans. An additional seven refineries and terminals stretch from Pont a la Hache (RM 49) to the Gulf of Mexico. In the Bird’s Foot Delta, these refineries would be in the region most likely to be near proposed diversions that open to wetlands. The Delta supplies the public and industry with a water supply, natural resources, agriculture, recreation, tourism, wetland protection and wildlife habitat. The public and industry use 11 billion gallons of surface water each day. As a result, the abundance of oil and massive transportation system coincide as uniquely beneficial, but seriously risky resources for the adjacent communities and environment within the Lower Mississippi River Delta.

The need for contingency plans for the Louisiana’s coastal areas is obvious. Numerical modeling of possible spill scenarios to investigate the fate, transport and impact of oil through waterways, wetlands, and possible diversions is an essential predictive and decision-making tool. Government agencies and research institutions have developed models capable of modeling inland oil spills; however, the uniqueness of each spill location prevents a code from being universally applied. A model needs to be capable of simulating the specific characteristics of the environment to accurately predict the transport and behavior of a spill. The Lower Mississippi
River has several specific characteristics that must be accurately represented in an oil spill model.

1.2 Inland Oil Spill Modeling

The development of inland river oil spill models was motivated by the frequency of river spills and potential to contaminate drinking water. Numerical modeling allows the opportunity to investigate scenarios and the sensitivity of a system without an actual spill occurring. The detrimental impacts of oil spills have led government agencies, private industry and academia to develop empirical and numerical spill models with a range of capabilities. These models can be used to study possible spill scenarios, to assist in the development of contingency plans for containment and recovery, and to aid in environmental impact analyses.

The purpose and capability of oil spill models range from simple trajectory, particle tracking models, to two and three dimensional fate and transport models able to predict distribution on the surface, water column, and shorelines and quantify biological response and environmental impact (Reed et al., 1999). Initial oil spill models were simple empirical first order models used to describe the spreading and travel time of surface oil slicks. Over the past three decades, the understanding of processes occurring beyond gravity and advection has improved. The shape of the assumed slick has evolved from circular to elliptical to a plume with a tail. However, recent models still use variations of the early spreading and dispersion models. In most cases, empirical relationships yield better results when compared to analytical solutions derived from the understood physics. The domain of the model has grown as well, from the floating surface slick only to a layered slick with exchange between the suspended particles mixed in the water column, atmosphere and bottom sediments. Advanced oil spill models consist of weathering algorithms for evaporation, dissolution, degradation, and vertical mixing, in addition to the transport processes of advection and diffusion (Figure 1.1).
Figure 1.1 Fate and Transport of Light Petroleum Hydrocarbons in Surface Water

The value of a model depends on its ability to simulate the processes occurring in a specific environment not just its complexity. Most oil spill models have been developed for the ocean and coastal areas, but rivers have different processes and physics than ocean spills. The variation and large magnitude of river velocities across the river width along with flow obstructions i.e. islands or structures require the flow velocities to be modeled accurately. River models need a computational scheme that can detect the parcels of oil interacting with the complex shoreline shapes and model the physics occurring. The need to control rivers requires the model to be able to handle increases or decreases in flow, unsteady conditions. Changes in water levels will affect the slick area and its position relative to the shoreline (Yapa et al., 1994).

Furthermore, the Lower Mississippi River Delta requires consideration of processes that are still under research including shoreline retention and oil-mineral aggregate (OMA) formation. These processes have little or no importance in offshore spills, but the meandering nature of the Mississippi River increases the potential of shoreline retention as a removal
process. Shoreline retention is specific to shoreline type and dependent on sediment characteristics, the presence of vegetation and the adhesiveness of the oil. Shoreline retention is usually either left out of calculations or modeled in a limited capacity, not sufficient for an environment like the Mississippi River so prone to shoreline oiling. Sediment-oil interaction is also an important removal process within the water column. The sediment load of the Mississippi River is primarily comprised of high concentrations of fine sediments. These fine sediments can interact to form neutrally buoyant OMAs that can remove significant amounts of oil from the surface and discourage shoreline oiling. OMA formation has never been included in a mass balance estimate for the Lower Mississippi River. The lack of inclusion of these significant processes in previous modeling of the Lower Mississippi River motivated the work presented in this dissertation.

1.3 Motivation

The overall goal of this research was to include fate and transport processes specific to the Lower Mississippi River into a model that could provide improved trajectory predictions and mass balance estimates for contingency planners. In case studies of previous spills, the majority of oil always ended up on the shorelines of the river due to the meandering nature of river and/or wind forces. The levee banks of the Lower Mississippi River varies between rip rap, mud flats, sand bars, and vegetated areas such as swamp, freshwater marsh, and scrub-shrub wetlands (Michel et al. 2002; NOAA 2008a; LOSCO 2008). Over the period from January 20, 1999 to July 20, 2008, annual river discharge in the lower Mississippi River varied from 3,900 cubic meters per second (m$^3$/s) to 41,200 m$^3$/s, with an average discharge of 13,400 m$^3$/s. The maximum discharge can correlate to a stage level 4.6 meters greater than the minimum (USACE 2008). As a result, river flow and potential oil slicks will interact with different shoreline types at
different flow rates, over a year. This dependence of shoreline type on flow rate needs to be recognized and incorporated into trajectory models and contingency plans.

If shoreline interactions are included in a model, usually one of two approaches is taken. The first is calculating the shoreline’s maximum holding capacity. The maximum holding capacity determines how much oil a sediment type can retain per unit length or area. When the oil exceeds the holding capacity it will be released back to the river. Reed et al. (1999) computed holding capacity from oil viscosity, sediment permeability, porosity, and water level. Darcy’s Law was used to determine the penetration depth, accounting for the change in water level while residual oil remains on the surface of the sediments (Reed et al., 1999). However, this equation does not account for beach type. Porosity is the only parameter characterizing the beach. Maximum capacity may not be reached for a long time. Furthermore, maximum beach capacity is not applicable for the Mississippi River shoreline, often characterized by vegetation and rip rap. The alternative is to predict the mass of oil remaining onshore as a first order process (Reed et al, 1999). Re-floatation half-life values describing the ability of the shore to hold oil were provided by Torgrimson (1980). Based on observations of removal rates from previous spills, the half life method does not represent the detailed physics of the process, but is commonly used due to the complexity of trying to model shoreline-oil interactions at large scales. In the General NOAA Operational Modeling Environment (GNOME), a spill trajectory model, a single shoreline half life is assumed for the entire study area. Thus, a method of tracking oil parcels using multiple shoreline half lives was implemented in Chapter 2 to evaluate the sensitivity of the shoreline to the half life parameter and more accurately model the trajectory of oil by including the multiple shoreline types found along the Lower Mississippi River.

The second major focus of this dissertation is developing a method of accounting for OMA formation after spills in the Lower Mississippi River. The first evidence of OMAs forming
in freshwater (salinity of 1.5 ppt) was found during the investigation of the Rio Desaguadero spill, concluding OMAs were an important removal process, responsible for 27-37% of unaccounted for oil (Lee et al. 2001, 2002). The presence of OMAs after a freshwater oil spill prompted this investigation of OMA potential in the Lower Mississippi River. Furthermore, review of past spills in the Lower Mississippi River suggests OMA formation may have affected the fate of the spill. During a high discharge period, after the Tank Barge LB960 spill, no shoreline oiling was found. Trajectory modeling predicted some shoreline oiling would have occurred despite fast currents, suggesting another process was preventing the oil from adhering to the shoreline (NOAA 2001). In other post spill summaries, a percentage of the oil remained unaccounted for in the environment such as after the MIT Westchester spill, 11% (Michel et al. 2002) and the T/B LBT 62, 27% unrecovered (NOAA 1995).

The third component of this dissertation was motivated by the need to test and validate maps, theories and methods used in the early chapters of this dissertation. The DM932 river spill occurred near New Orleans on July 23, 2008. The DM932 was split in half, releasing some portion of the 9,983 barrels of no. 6 fuel oil it contained into the river. On Approximately 220 km of the shoreline was oiled to varying degrees coating vegetation, rip rap, structures, and debris and pooling in rip rap and low lying areas. The post spill assessment provided a large amount of shoreline oiling data for weeks after the spill. The spill also provided an opportunity to hindcast the trajectory of the spill using re-floatation half lives used in the second chapter and calculates an estimate of OMA formation to compare to the mass balance.

In an effort to support the conclusions made in this dissertation, an analysis of the relationship between mesh resolution and spill trajectory results was conducted. The trajectory simulations can only be as accurate as the hydrodynamics used to drive the model. Thus, three
meshes of increasing resolution were utilized in hydrodynamic and trajectory modeling to determine if any inaccuracies could result from the mesh not having adequate resolution.

1.4 Organization of Dissertation

The dissertation is organized into six chapters following the central theme of the fate and transport of light petroleum hydrocarbons in the Lower Mississippi River. Chapter 1 begins with an introduction into the risk of oil spills in the study area of the Lower Mississippi River and the need for contingency plans with accurate oil spill models. In the following section, the basics and inadequacies of inland oil spill modeling are discussed. Finally, the motivation and scope of this dissertation details the need for modeling of the Lower Mississippi River that includes shoreline retention, OMA formation, the most recent case study data from the DM932 spill and an investigation of mesh resolution as related to trajectory modeling.

Within Chapter 2, the investigation of the effects of shoreline sensitivity on oil spill trajectory modeling is discussed. The beginning outlines the characteristics of the Lower Mississippi River, its discharge and the shoreline. A discussion of using re-floatation half lives to model shoreline retention is followed by the methodology for generating shoreline maps using remote imagery. A hydrodynamic model and an oil spill trajectory model were used to investigate the relationships between shoreline type and river flow rate and oil retention due to flow rate, river geometry and shoreline type. The conclusions and recommendations comment on the shoreline oil distributions from the simulations and use of the re-floatation half life.

The third chapter examines the seasonal variability of OMA potential. The limiting factors were outlined, followed by calculations for each one. The results were summarized to determine an estimate of OMA potential for each season and the impact of including OMA in a mass balance.
The fourth chapter describes the incident of the *DM932* spill and the shoreline oil distribution from the actual spill. Hindcast modeling results were compared to shoreline survey data from the spill. The estimate for OMA formation based on spill conditions was calculated and compared to the spill mass balance.

The fifth chapter details previous modeling of the Lower Mississippi River. Then, the mesh requirements for the finite element method were discussed. The hydrodynamic model used a finite element to solve the two dimensional shallow water equations for the river. The velocity profiles were checked for convergence for the three mesh resolutions. Finally, the impact of mesh resolution of trajectory simulations was analyzed and summarized.

Chapter 6 provides a summary of the modeling, results, and conclusions, followed by future recommendations. The successes of modeling multiple shoreline types and predicting shoreline oiling accurately compared to a real spill are highlighted, as well as the importance of including OMA calculations in future mass balance estimates.
CHAPTER 2

EFFECTS OF SHORELINE SENSITIVITY ON OIL SPILL TRAJECTORY MODELING OF THE LOWER MISSISSIPPI RIVER

2.1 Introduction

Quantifying the sensitivity of shorelines to floating oil is critical to oil spill fate and trajectory modeling, especially in rivers with a highly meandering path like the lower Mississippi River where shoreline contact is likely. The longevity of oil on the shoreline varies by shoreline characteristics and morphology, as shown in studies of the shoreline retention and weathering after oil spills such as the Exxon Valdez, Braer, Prestige, Arrow, and Amoco Cadiz (Hofer 2003; Michel and Hayes 1999; Owens et al. 2008; Mille et al. 1998).

The lower Mississippi River provides convenient access for oil transport between refineries, storage facilities and production sites on and offshore of the coast. An oil spill could seriously damage the riverine resources and already rapidly degrading coastal wetlands, pollute the water supply, destroy wildlife habitat and cause detriment to other economic, social and natural resources. Spills in this section of the river threaten to contaminate the main drinking water source for many communities in Southern Louisiana. Figure 2.1 shows the location of the study area, as well as the locations of the refineries and drinking water intakes (LDHH 2006).

The shoreline area within the levee banks of the Lower Mississippi River study varies between rip rap, mud flats, sand bars, and vegetated areas such as swamp, freshwater marsh, and scrub-shrub wetlands (Michel et al. 2002; NOAA 2008a; LOSCO 2008). Over the period from January 20, 1999 to July 20, 2008, annual river discharge in the lower Mississippi River varied from 3900 cubic meters per second (m$^3$/s) to 41,200 m$^3$/s, with an average discharge of 13,400 m$^3$/s. The maximum discharge can correlate to a stage level 4.6 meters greater than the minimum (USACE 2008). As a result, river flow and potential oil slicks will interact with different
shoreline types at different flow rates, over a year. This dependence of shoreline type on flow rate needs to be recognized and incorporated into trajectory models and contingency plans.

Using a Geographic Information System, shoreline maps can be created that vary spatially and over time (Fisher 1997; Tortell 1992). For the study area, detailed shoreline maps based on recent remote sensing imagery were generated to improve the ability of models to simulate the oil-shoreline interactions possible in the lower Mississippi River. To demonstrate the importance of developing and updating shoreline maps that detail the specific characteristics of the local area, spill trajectory modeling is presented using multiple shoreline specific re-floatation half lives for a 125.5 km reach of the lower Mississippi River, from Convent, LA to West Pointe a la Hache, LA. The goal of this study is to identify the important factors affecting shoreline oil distribution, evaluate the sensitivity of the model to the re-floatation half life parameter and improve the representation of the actual shoreline types existing along the river and the oil-shoreline interactions in the simulations.

Figure 2.1 Lower Mississippi River Study Area
2.2 Methodology

2.2.1 Description of Study Area

Nine refineries are located along the study reach of the Lower Mississippi River as well as the highly trafficked Port of New Orleans (LDNR 2007). Modeling of this area is critical due to the high risk of spills from accidents with tankers or at fixed locations. In the last three years, there have been four spills from vessels and refineries, ranging in volume from 900 to 11,000 barrels and four major potential threats, caused by grounded barges, have required US Coast Guard response and cleanup (NRC 2008).

The Lower Mississippi River is a highly meandering river, as a result of the delta morphology, presently controlled by engineering that has impacted the spatial variability of the shoreline. The Lower Mississippi River flows through the Bird’s Foot Delta of Louisiana into the Gulf of Mexico. The delta lobes were formed by the fine grained sediments carried and deposited by the river. When sediments accreted in the bed or the sea level changed, the river gradient would decline, forcing the river to find a steeper path to the Gulf of Mexico and resulting in the formation of a new lobe. The Bird’s Foot Delta was the last delta lobe to form during the Holocene epoch, and flow control structures and dredging maintain the river’s course. (Aslan and Autin 1999; Meade 1995). During floods, the river would flow over banks, slow, and deposit silts and clays, forming natural levees adjacent to the river. To prevent flooding into adjacent communities, artificial levees were constructed on the floodplain on both sides of the river. Cypress trees and grasses act as natural stabilizers of the banks and levees along the shoreline.

The study area includes a 125.5 km reach of the river, its natural levees, and the portion of the floodplain contained inside the artificial levees. As the river rises, it flows over the natural levees, across the floodplain, flooding the vegetation including grasses and cypress trees, until it reaches the artificial levees. Figure 2.2a depicts a typical shoreline including the beach and low
vegetation present at low flow rates; Figure 2.2b shows the levee bank at an approximate flow rate of 22,650 m$^3$/s, 60-80% of the maximum flow rate. This research examines how detailed classification of the shoreline types in the study reach allows type-specific re-floatation half-lives to be used, impacting the amount of oil predicted to stick to the shoreline.

Figure 2.2 (left) Depiction of typical shoreline (right) Photograph of levee within study area at a discharge of 22,650 m$^3$/s

**2.2.2 Shoreline Oil Retention and Re-floatation Half-Lives**

Oil retention by the shoreline depends on the degree to which oil penetrates the substrate, the extent of mechanical washing occurring, water level variability, and the adhesiveness of the oil. The depth of oil penetration is dependent upon the viscosity of the oil and shoreline sediment characteristics including grain size, surface area, and the porosity (Owens et al. 2008). Once the maximum amount of oil has penetrated the substrate, the oil pools at the surface and can be refloated by the river more easily if accessible. The river has continuous longitudinal flow past the shoreline and no wave action, similar to a sheltered coastal environment without tides. Flooding or other changes in discharge could result in the water level rising and then, afterwards, stranding oil out of reach of natural physical removal forces. Shoreline capacity cannot be modeled using the trajectory model in this study, instead oil retention was based on the process
of re-floatation. In order to account for the amount of oil removed by these processes, a single empirical parameter, the shoreline re-floatation half life is derived for each shoreline.

A re-floatation half life represents the adhesiveness of the oil to the shoreline as a function of substrate porosity, oil properties, vegetation, and environmental processes. Oil re-floatation half lives are different for each shoreline type depending on substrate, vegetation and oil type (NOAA 2002a; Torgrimson 1980). The study area has five shoreline types visible 1) mud with clay and organics, from overbanking and deposition of suspended sediments 2) sand bars, where coarser bed sediments deposit around bends 3) man- made rip rap 4) low vegetation including grass and shrubs (freshwater marsh and swamp) 5) high vegetation including cypress trees (scrub shrub wetlands). These shoreline type classifications are for illustrational purposes, the specific shoreline type may be more descriptive of vegetation, habitat, and accessibility. The following re-floatation half lives were chosen assuming a medium crude oil was interacting with the shoreline along the Mississippi River. At low flow rates, the river would be contained within the natural levees and potential oil slicks would interact with muddy banks, sand bars or rip rap. Very fine, consolidated muddy sediments have low permeability and tend to be saturated, limiting oil penetration. Furthermore, the formation of oil mineral aggregates, which remain suspended in the water column, reduces the adhesion of oil to shoreline sediments (Owens and Lee, 2003). The re-floatation half life was chosen as 1 hour to reflect the impermeable nature of the mud sediments. The re-floatation half life of the sand flats was chosen as 24 hours based on the Baffin Island Oil Spill (BIOS) experiment at Cape Hatt, Canada. After 24 hours of the experiment, 60% of a medium crude oil that was stranded on a low energy mixed coarse sediment beach was refloated and removed (Owens et al., 1994). Oil coats the surface, penetrates into the crevices, and pools within rip rap as evidenced after the M/T Westchester spill on the lower Mississippi River (Michel et al. 2002). As a result of the persistence of oil in rip rap, the
oil re-floatation half life was chosen as 1 year. The re-floatation half life of the vegetated areas was also chosen as 1 year. Wang et al. (2000) studied the long term persistence of light Arabian crude oil from the Metula spill (1974) in a salt marsh environment, finding only 25-55% of the oil had been removed after 24 years. The density and characteristics of vegetation including plant height, stem diameter, and leaf density impacts how much and how long oil can be retained. By choosing 1 year as the re-floatation half life during 3 day simulations, the long term persistence of oil in vegetation is sufficiently represented even if some variation between types of vegetation exists. The vegetation of the study area was still categorized by height and density into low and high vegetation, providing additional information that may be useful in future research. The re-floatation half lives were assigned to segments of the shoreline delineated by the new shoreline maps created for this study.

2.2.3 Shoreline Mapping Using Remote Sensing Imagery

Remote sensing data makes detailed and complete shoreline mapping possible (Jensen et al. 1990; Populus et al. 1995). Forty-five Digital Orthophoto Quarter Quandrangle (DOQQ) images were obtained for the study area from U.S. Geological Survey, National Wetlands Research Center, published in 2005, distributed by http://atlas.lsu.edu. DOQQs are color infrared aerial photographs taken at 6096 m above average ground, that cover an area of 6.44 km by 7.24 km. Each pixel on the photograph represents one meter on the ground (Atlas, 2008). In color infrared images, vegetation is visible in shades of red and pink (Coulter et al. 2000). Dark red identifies the dense- leafed cypress trees; light red and pink colors the grass and low vegetation. Buildings and roads appear white. Water appears dark blue or black. Barren ground appears green/brown. Sand bars appear white. The base layer of the shoreline map was generated using Geographic Information Systems (GIS) techniques. Shoreline types are depicted as color-coded polygons identifying either sand (yellow), mud flat (purple), low vegetation (light green), or high
vegetation (dark green). Section 2.4 describes how this base layer was integrated with results from the hydrodynamic model to produce the final maps.

2.2.4 Hydrodynamic Model

A hydrodynamic model provides the current vectors required for oil slick trajectory model. The velocity field was modeled using the ADaptive Hydraulics (ADH) modeling system. ADH was developed by the Coastal Hydraulics Laboratory, Engineering Research and Development Center, US Army Corps of Engineers as a finite element model capable of solving two dimensional, 3-dimensional Navier-Stokes equations, saturated and unsaturated groundwater flow and overland flow. The program has mesh adaption capabilities, where error is determined for each element, prompting the element to be split only if needed, increasing refinement while maintaining computational efficiency. For the 2-dimensional shallow water simulations used for the study, the finite element formulation used linear Lagrange basis continuous functions with first or second order temporal terms to reduce numerical dissipation (Berger and Tate 2007).

The bathymetry and elevation data used in the simulations were obtained from a high resolution mesh (SL15RV3_2005) developed at the University of Notre Dame, under contract to the USACE for use in surge probability evaluation, hurricane protection planning, and coastal restoration planning (Westerink et al. 2006). Simulations were run with inflow rates of 8,500 m$^3$/s, 14,000 m$^3$/s, 25,000 m$^3$/s and 28,750 m$^3$/s to represent the range of annual discharge. A tailwater elevation boundary condition at Pointe a la Hache was forced for each flow rate based on historical stage-discharge data provided by the New Orleans District US Army Corps of Engineers. Calibration included adjusting the eddy viscosity and roughness parameters to match the historical stage levels at eight river gage locations (USACE 2008). Stage levels within calibrated model were within 0.15 m for all discharges. Additionally, velocity measurements, at
the surface and at 60% depth, from the Carrollton gage in New Orleans were compared to depth averaged velocities output from the model. Velocities at the surface of the river, at the Carrollton gage, range from 0.7 to 2.1 m/s for stages between 0.91 m and 4.6 m. At 60% depth, the velocities range from 0.61 to 2 m/s, for stage levels of 0.91 m and 4.6 m. The depth averaged modeled velocities fell within the range of the two available measurements, and within 10% of the surface velocity. Following validation, water surface level elevations were used in shoreline mapping and the currents were used as input files for the oil spill trajectory model. The observed data undergoes quality control by the USACE. If the data did contain errors, the calibration of the hydrodynamic model could result in inaccuracies in predicted velocities and stage levels, thus affecting the travel time of the slick and the shoreline mapping that relies on stage level. If the wrong shoreline types were predicted to be interacting with the oil during the trajectory simulations, the amount of shoreline retention and re-floatation occurring would be inaccurate.

2.2.5 Shoreline Characteristics along the Mississippi River

The spatially detailed shoreline type maps and water surface elevations (Figure 2.3a) for each of the four discharges were imported as layers into GIS to create quasi-two dimensional maps that represent the temporal changes in shoreline type with river discharge (Figure 2.3b). The final product allows the user to identify what shoreline type should be input into the oil spill trajectory model based on location and flow rate. A field survey was conducted for most of the study area to verify the correct shoreline types were assigned on the map. The study region between the river at low discharges and the levees was found to have 97.9% high vegetation (74.1 square kilometers), 1.32% low vegetation (0.8 square kilometers), 0.2% rip rap (0.15 square kilometers), 0.85% beach with no vegetation, including mud and sand (0.64 square kilometers) based on areas calculated for this study using GIS and the DOQQ images. The percentage was calculated from the ratio of total area of one shoreline type to the total area of shoreline within
the levees. Using the most recent DOQQ images and the field survey allows the most accurate shoreline information to be used in the model.

![Image of Elevation Contours and Shoreline Mapping Overlay]

Figure 2.3 (left) Elevation Contours (right) Contours and Shoreline Mapping Overlay

### 2.2.6 Oil Spill Trajectory Model

The spill trajectories were modeled using the diagnostic mode of the General NOAA Operational Modeling Environment (GNOME). GNOME uses the Lagrangian Element (LE) approach to model the movement of individual oil parcels based on wind and current fields. Horizontal mixing is simulated using a random walk method. GNOME uses a simple three phase evaporation algorithm. A re-floatation half life can be set to represent the adhesiveness of the oil to the shoreline as a function of substrate porosity, oil properties, vegetation, and environmental processes. The re-floatation half life, \( \lambda \), is used to determine the probability of an parcel of oil refloating, \( p_{\text{refloat}} \), after a time, \( t \), in hours since deposition in the following equation.

\[
p_{\text{refloat}} = 1 - e^{-\frac{t \ln(2)}{\lambda}}
\]

Refloating for an individual LE is determined by choosing a random number on the interval (0, 1), \( R_{(0,1)} \) for the parcel. If \( R_{(0,1)} < p_{\text{refloat}} \), the parcel is refloated. The refloated parcel is placed at its last water position before beaching. The trajectory can be modeled as a “best guess” with the given input parameters or account for uncertainty within a 90% confidence interval.
using the minimum regret feature. The mass balance of the oil spill is tracked throughout the simulation accounting for the oil’s location and weathering (Beegle-Krause 2001; NOAA 2002b).

Spill scenarios were simulated for each of the four flow rates using currents from ADH. Wind was not included in the simulations, in order to focus on shoreline retention resulting from currents, river structure and shoreline sensitivity. The lack of winds reduces the evaporation which is strongly correlated to the oil type; on the order of 28% of the mass will evaporate for the oil tested. A large spill, 1000 barrels of medium crude oil, was simulated as an instantaneous release and was run for 3 days. The random diffusion coefficient was input as 1.69 m$^2$/s based on measurements in the river (Rathban and Rostad 2004; Waldon 1998). The time step used in the trajectory simulations was 72 s. The spill locations were chosen so that oil would interact with a variety of shoreline types when possible. The two spill locations and eight sampling sites are shown in Figure 2.1. The sampling sites mark areas where the shoreline type variability may have the most impact on beaching and where a bend in the river may have an impact. The travel time between spill site 1 and sampling location 8 is approximately 2 days at 8,500 m$^3$/s and 1.25 days at 28,750 m$^3$/s. The first set of simulations set the baseline for the maximum shoreline retention possible that occurs when vegetation interacts with the oil, correlating to a re-floatation half life of 1 year.

The second set of simulations were intended to highlight the effects of using the re-floatation half lives assigned to each shoreline segment and flow rate. The re-floatation half life assigned to mud was 1 hour; the half life for sand was 24 hours; high vegetation, low vegetation and rip rap had half lives of 1 year. Some models have incorporated methods to model spatial variability in shoreline retention (Reed et al. 1989; Yapa and Shen 1994; Reed et al. 1999). At present, GNOME only allows the assignment of one re-floatation half life for all of the shoreline.
Therefore, to improve the representation of the various shoreline types in the model, a post-simulation bookkeeping approach was applied to account for parcel re-floatation from each shoreline type present. First, the re-floatation half life was set as 1 hour in GNOME. The parcel locations were exported at 1 hour time steps and tracked from one segment of shoreline type to another. Then, the ratio of the mass of oil refloated to mass of oil retained was compared to the probability of re-floatation from equation 2.1 to determine if the correct mass of oil in each shoreline segment was retained. For example, if after one day since deposition, the mass ratio for a given sand segment is greater than 0.5, suggesting more oil refloated from the sand than the half life predicted, the fraction of oil overestimated to refloat was removed from the downstream segment and replaced on the upstream sand segment. This approach and its results are referred to as the multiple shoreline type method or multiple in shoreline distribution results. This method was repeated for Day 2 and Day 3 of the simulation and for each of the shoreline segments. Since this method is not interactive with the GNOME program in real time, the assumption is made that current vectors will deposit a refloated parcel adjacent to its previous location on shore. Thus, potential error exists if parcels are swept downstream more than one shoreline segment. The amount and distribution of oil beached between each sampling sites were compared for GNOME simulations using the multiple half life method and a one year half life for four river discharges.

2.3 Results and Discussion

2.3.1 Relationship of Shoreline Type and River Flow Rate

By overlaying the water level contours on top of the shoreline maps, the shoreline types along the study reach were determined for each flow rate (Table 2.1). The areas covered by each shoreline type were summed, then, divided by the total area at a given flow rate and multiplied by 100 to attain percentages of shoreline type interacting with the river by flow rate. At the
lowest flow rate, the river is mostly interacting with the muddy clay sediments and organic matter on the banks. As the river flow rate increases, the majority shoreline type changes to high vegetation for flow rates of 14,000 m$^3$/s and above. For most of the flow rates, the shoreline type changes along reaches of the study area, suggesting incorporating shoreline detail would impact the location and amount of oil retained in a trajectory model.

Table 2.1 Shoreline Type Interacting with the River by Flow Rate Based on Shoreline Maps

<table>
<thead>
<tr>
<th>Flow Rate (m$^3$/s)</th>
<th>Mud (% of shore)</th>
<th>Sand (% of shore)</th>
<th>Low Vegetation (% of shore)</th>
<th>High Vegetation/Rip rap (% of shore)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8,500</td>
<td>82.7</td>
<td>1.5</td>
<td>0</td>
<td>15.8</td>
</tr>
<tr>
<td>14,000</td>
<td>18.2</td>
<td>1.5</td>
<td>7.3</td>
<td>73</td>
</tr>
<tr>
<td>25,000</td>
<td>3.5</td>
<td>0</td>
<td>5</td>
<td>91.5</td>
</tr>
<tr>
<td>28,750</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

2.3.2 Oil Retention Due to Flow Rate and River Geometry

Current velocities increase with flow rate, affecting the shape of the slick, its movement through the river, and the time it interacts with the shoreline. Downstream from spill site 1, the 28,750 m$^3$/s flow rate has the least amount of oil sticking to the shore initially, evidence of the faster velocities affecting the slick shape and reducing the time passing through the bend; the slick is carried past the first sampling point before 38% of the oil is retained by the second sampling site (Figure 2.4a). After the bends, slow currents allow more shoreline interaction closer to the site of the spill; the difference in oil retained by each sampling point at 8,500 m$^3$/s is greater than the differences at 25,000 m$^3$/s or 28,750 m$^3$/s, by 10-17% (Figure 2.4a, b). The variability in currents by flow rate impacts the distribution of oil along the shoreline, concurrently with the effects of river geometry and shoreline type. River geometry significantly affects shoreline retention in conjunction with flow rate and shoreline variability. The fast moving, elongated slick moved through the straight section
between spill site 1 and sampling point 2. However, through the bend, vegetation retains and holds a significant amount of oil between sampling points 1 to 2 (Figure 2.4a). At low flow rates, the slick spreads laterally and sticks to the shoreline on both sides of the river. As currents moved the slick to the outside of the bend where velocities decrease, heavy oiling occurred along the shoreline. By sampling site 2, 47% of the oil is beached at 8500 m$^3$/s and 35% is beached at 25,000 m$^3$/s after the first day. Similarly, for Spill Site 2, after the bend (between sampling sites 5 and 7) approximately 59% of the oil slick is beached from spill site 2 at 8500 m$^3$/s; at a flow rate of 25,000 m$^3$/s, 44% of the oil is beached (Figure 2.4b). Reports from the 1999 T/V Hyde Park spill that occurred south of New Orleans indicated heavy oiling from mile markers 55 to 49, the same reach as sample sites 5 to 7 (NOAA 2001). In contrast, straight sections retain less oil, especially at high flow rates, as shown by the small amounts of oil on shore between sample points 3 to 4 and 7 to 8. The meandering nature of the river causes parts to be prone to heavy oiling and priorities for contingency plans of the area.

2.3.3 Oil Retention by Shoreline Type

To highlight the importance of modeling shoreline type, two spill scenarios were analyzed for each flow rate using the new shoreline maps and coordinating re-floatation half lives. The new shoreline maps account for the various types of shoreline present along the river and the relationship of shoreline type to river flow rate variability. The greatest shoreline variability occurs at the lower flow rates (Table 2.1). At 8,500 m$^3$/s, the percentage of oil beached decreases at all sampling points between Days 1, 2 and 3, as a result of the short re-floatation half lives of the mud and clay (Figures 2.5a, b). After Day 1, the percentage of oil beached is very similar to results from the one year half life and, even though re-floatation is occurring, enough of the oil has not moved past the sampling point to be evident. By Day 2, retained oil continues to re-float and move until beached again. By Day 3, even more of the oil
Figure 2.4 (a, left) Oil on shoreline after Day 1 for Spill Site 1 for four river discharges (b, right) Oil on shoreline for Spill Site 2 after Day 1
originally stuck close to the point of release detaches and reattaches further down river (Figure 2.5a, b). The percentage of oil beached decreases more by day at 8,500 m³/s than at 14,000 m³/s. For example, at sampling site 4, the percentage of oil beached at 8,500 m³/s decreased from 67% to 32% (Figure 2.5a); at the same point, the percentage of oil beached at 14,000 m³/s only decreased from 68% to 60% (Figure 5c). This difference between the percentages beached at the two flow rates is due to shoreline type and the presence of vegetation. Below spill site 2, the oil-vegetation interaction dominates, preventing significant shifts in distribution (Fig 2.5b, d).

All changes in the distribution of oil at these two lower flow rates would not be evident without the use of multiple re-floatation half lives. At higher discharges, the dominant shoreline type is dense vegetation and changes in oil distribution are less significant than in previous cases. The shoreline distribution of oil at 25,000 m³/s and 28,750 m³/s are within 5.5% of the distributions predicted using the one year half life. At lower flow rates, more variability in shoreline exists; thus, incorporating shoreline type into modeling provides a more accurate description of the location and distribution of beached oil. Very significant differences in distribution of oil along the shoreline were evident among the lower flow rates, which would not have been captured if only one shoreline type were used. The re-floatation half lives used for shorelines significantly impacts the distribution of oil on time scales critical to oil spill trajectory simulations.

2.4 Conclusions

In this study, five shoreline types were identified along the Mississippi River and mapped with respect to flow rate. A method for including multiple shoreline types in the GNOME trajectory model was applied. After analyzing the resulting distributions of oil, the following was determined (1) the shoreline of the Mississippi river has distinct shoreline types at different flow rates that will retain oil differently, (2) using re-floatation half lives that correlate to shoreline type in trajectory modeling highlighted the sensitivity of GNOME to this parameter, (3) different
Figure 2.5 Oil retained on shoreline by sampling site comparing 3 days of simulation using a single and multiple half lives (a) Spill Site 1, Discharge of 8,500 m$^3$/s (b) Spill Site 2, Discharge of 8,500 m$^3$/s (c) Spill Site 1, Discharge of 14,000 m$^3$/s (d) Spill Site 2, Discharge of 14,000 m$^3$/s [figures in order from left to right, top to bottom]
combinations of flow rate, river geometry and shoreline type will lead to significantly varying degrees of oiling (4) it is important when modeling any environment containing multiple shoreline types to represent each type or else significant error in the predicted distribution of oil will result.

2.5 Recommendations and Perspectives

Implementing shoreline maps that reflect the influence of flow rate on shoreline type significantly impacted the distribution of oil after a spill; thus, we recommend developing similar detailed maps for any study area with large flow rate variability or shoreline characteristics similar to the Lower Mississippi River. Using a single half life does not sufficiently describe the sensitivity of the shoreline to oil retention. The results showing the impact of shoreline variability also highlight the need for more research on the parameters of oil retention by vegetation to further improve the ability of oil spill trajectory models to simulate shoreline-oil interactions. Developing a model and its tools based on the specific characteristics of the study area, instead of applying a generic model or method, provides more realistic results useful for contingency planning. Finally, trajectory models should include the capability to model multiple shoreline types simultaneously.
CHAPTER 3

INFLUENCE OF SEASONAL VARIABILITY OF RIVER DISCHARGE, TEMPERATURE, AND SUSPENDED SEDIMENTS ON OIL-MINERAL AGGREGATE FORMATION

3.1 Introduction

Vertical mixing can cause oil from a surface slick to disperse into the water column as suspended droplets. Once in the water column, under certain conditions, suspended material coats the oil droplets forming oil-mineral aggregates (OMA), a process different from sediment adsorption of oil. The formation rate of the aggregates depends on suspended particulate characteristics and concentration (Delvigne et al., 1987; Payne et al., 1989; Delvigne, 2002; Guyomarch et al., 1999), droplet size and number (Khelifa et al., 2005a), temperature (Khelifa et al., 2002), salinity (Payne et al., 1989; Le Floch et al., 2002; Khelifa et al., 2005b), mixing energy (Cloutier et al., 2002), and oil properties (Khelifa, 2002). Droplets stabilize within the first 24 to 48 hours (Hill et al., 2002) and, once stable, OMA does not recoalesce with the slick or adhere to surfaces. The subsurface current transports OMA away from the slick until finally settling (Lee et al., 2003).

Oil-mineral aggregates reduce the mass of oil in surface slicks, enhance biodegradation rates in the water column, reduce the amount of oil adhered to the shoreline and contribute to contaminant transport through sedimentation (Lee, 2002). Evidence of oil-mineral aggregate formation was documented after the Sea Empress spill (South Wales, UK) (Lee et al., 1997), in laboratory investigations (Payne et al., 2003; Ma et al., 2008), in post-spill contaminated sediments after the Braer, Tsesis, and Exxon Valdez spill (Johansson et al., 1980; TESGOOS, 1994; Bragg and Owens, 1994) and field studies on the shoreline cleaning effects of OMA formation (Bragg and Owens, 1994; Bragg and Yang, 1995; Lee et al., 1997). The first evidence of OMAs forming in freshwater (salinity of 1.5 ppt) was found during the investigation of the
Rio Desaguadero spill, where it was concluded OMAs were an important removal process, responsible for 27-37% of unaccounted for oil (Lee et al., 2001; 2002). A review of past spills in the Lower Mississippi River suggests OMA formation may have affected the fate of the spill. During a high discharge period, after the Tank Barge 1B960 spill, no shoreline oiling was found. Trajectory modeling predicted some shoreline oiling would have occurred despite fast currents, suggesting another process was preventing the oil from adhering to the shoreline (NOAA, 2001). In other post spill summaries, a percentage of the oil remained unaccounted for in the environment such as after the MIT Westchester spill, 11% (Michel et al., 2002) and the T/B LBT 62, 27% unrecovered (NOAA, 1995). OMA was not sampled for after either of the above mentioned spills; therefore, OMA cannot be concluded to account for the unrecovered oil. However, the Lower Mississippi River has favorable characteristics suggesting OMA formation may occur after a spill, which would significantly impact the mass balance calculations, shoreline impacts, and the amount of oil carried into the Gulf of Mexico.

The Lower Mississippi River is subject to spills due to its role as a major transportation route for commercial goods and petroleum products to and from refineries, storage facilities, and production sites on and offshore. The annual river discharge varies considerably, from 3,900 cubic meters per second (m$^3$/s) to 41,200 m$^3$/s, resulting in current speeds of 0.6 m/s to over 2.2 m/s (USACE, 2008). During times of low discharge, the salt wedge advances upriver from the Gulf of Mexico, increasing salinity within the river. Suspended sediment concentrations vary seasonally from 50 to 760 mg/L, with high silt and clay content (USGS, 1987). The annual temperatures in Louisiana vary from 5°C in winter to 28°C in summer (USACE, 2008). The combination of these characteristics has the potential to encourage OMA formation. Their variation in magnitude suggests the OMA formation potential would vary on a seasonal basis.
The principal aim of this study is to quantify estimates of potential OMA formation within the Lower Mississippi River Delta during four distinctly different states of the river during a year. The potential for OMA formation is examined for four seasons and the associated different combinations of salinity, suspended sediments, discharge and temperature along the river. Empirical relationships from laboratory and field studies were applied to calculate the percentage of OMA that could form under the seasonal conditions.

1. Investigate the potential for OMA to form based on each of the influencing factors including temperature, suspended sediment concentrations, salinity, and mixing energy
2. Determine the limiting factors for OMA formation on a seasonal basis
3. Investigate the impact of accounting for OMA and its impact on other fate and transport processes that occur following a river spill

3.2 Methodology

3.2.1 Limiting Factors

The study area extends from Luling (river mile 119) to the Head of Passes (river mile 0) (Figure 3.1). Four cases were chosen to represent the extremes in magnitude of the potential limiting factors influencing OMA formation within the reach. Suspended sediment concentrations were obtained from a USGS study of the lower 295.6 miles of the river (USGS, 1987). The USGS took monthly samples at eight fixed sites and during six steady-flow conditions every 5 to 10 river miles, then analyzed for particle size distributions. The suspended sediment concentrations were averaged for each season. Winter has cold temperatures, high discharge, high suspended sediment concentrations and low salinity. Spring has warm temperatures, the highest discharge, high suspended sediment concentration, and low salinity. The initial period in summer is similar to spring except summer has warmer temperatures. The
rest of summer has low discharge, high salinity and typically low suspended sediments. Fall has cool temperatures, the lowest discharge, very low suspended sediment concentrations and relatively high salinity. The OMA potential of three oils was calculated for each season using empirical relationships for each of the limiting factors: suspended sediments, temperature, and salinity. The three types of oil, Arabian Medium Crude, BAL110, and IF30, were chosen based on their common use in previous experiments, similarities to oils transported on the lower Mississippi river and for differences in the properties. Finally, the percentages of oil potentially in OMA as a result of each factor were compared for each season to determine the limiting factor (Table 3.5).

Figure 3.1 Lower Mississippi River with sampling locations and river mile increments from Luling (RM 119) to Head of Passes (RM 0). (Base map: USGS, 2009)
3.2.1.1 Mixing Energy

Shear forces exerted by the banks and bed of a river act against the pressure and gravity forces acting on the flow. When nonlinearities in the flow dominate, turbulence results, forming an energy dissipating network of eddies, known as the Kolmogorov cascade, that can mix parcels across the depth and width of the river (Fischer, 1979). Changes in river depth, direction and velocity, as around bends, enhance the amount of turbulence in the river (Logan, 1999). Turbulence causes collisions between suspended particles and oil droplets and the further break up of large droplets dispersed from an oil slick. More small droplets lead to more collisions and more flocculation.

The Delvigne and Sweeney (1988) model, typically used in oil dispersion modeling, is based on the process of breaking waves driving droplets into the water column. By measuring the number and size distributions of oil droplets in the water column after a passing breaking wave, they determined the dissipation of wave energy is proportional to the vertical entrainment of oil. Rivers do not have breaking waves, with the exception of large ship wakes; therefore, the model cannot be applied. However, turbulence generated shear forces can be theorized to entrain oil into the water column.

The Reynolds number, Re, measures the magnitude of the nonlinear (inertial) term in the Navier- Stokes equation divided by the effect of the viscous dissipation in a fluid flow.

\[
Re = \frac{\rho_w ud}{\nu}
\]  

where \( Re \) is the Reynolds number, \( \rho_w \) is the density of water, \( u \) is the longitudinal velocity, \( d \) is the river depth, and \( \nu \) is the kinematic viscosity of water (Fischer, 1979).

In this form, the Reynolds number describes the amount of mixing energy in a river system. In rivers, \( Re \) can be very large, thus highly turbulent. For example, the Reynolds number
for the lower Mississippi River can be calculated to be on the order of \(10^7\)-\(10^8\), with maximum river depths of 24 m and 56 m, along straight sections and bends, respectively, and a range of velocities from 0.6 m/s to 2.1 m/s (Equation 3.1). Comparatively, the open ocean has Reynolds numbers on the order of \(10^7\) (Soloviev and Lukas, 2006). The turbulence in the river caused by shear stress is similar to the amount of turbulence in the ocean caused by breaking waves, when comparing Reynolds numbers; therefore, for the purpose of this study, enough mixing energy was assumed to exist in the river to generate droplets. Thus, under favorable conditions, OMAs could form. However, direct measurement of the mixing energy of the Mississippi River and its effect on droplet formation is needed. Furthermore, Khelifa et al. (2002) suggested in rivers where high concentrations of fine sediment are expected, formation of OMAs could be much higher and require less dissipation energy. The high concentrations of fine suspended sediments available in the lower Mississippi River could stabilize large droplets (formed with less dissipation energy) and prevent recoalescence into the slick.

### 3.2.1.2 Suspended Sediments

During OMA formation, solid particles adsorb at the oil-water interface creating a strong film that reduces interfacial tension and stabilizes OMAs. The more solids adsorbed, the less free oil-water interface is available for potential contact between droplets, preventing coalescence. OMA formation depends on suspended sediment concentrations, grain size and the mineralogy and organic content of the sediments (Lee, 2002; Khelifa et al., 2005). Studies have found OMA potential to increase with suspended sediment concentration (Ajijolaiya et al., 2006; Payne et al., 1989; Wood et al., 1998; Guyomarch et al., 1999), increase as sediment size decreases (Ajijolaiya et al., 2005) and increase with organic content (Khelifa et al., 2008).

Previous experiments have yielded empirical relationships that depend on oil and sediment properties to estimate the amount of oil trapped in OMAs. Yan and Masliyah (1993)
investigated the potential of demulsifying oil-in-water emulsions by adding fresh oil to asphaltene-treated clay. In their study, the maximum number of particles that can exist on the oil-water interface of a droplet, in a hexagonal packed arrangement, was found to relate to the ratio of the droplet size and particle size. Ajijolaiya et al. (2006) validated the Yan and Masliyah (1993) particle number vs. size ratio relationship

\[ C_{550} = \frac{\alpha \rho_s D_s}{\rho_o D_o} C_o \]  

(3.2)

where \( C_{550} \) is the critical sediment concentration (kg/m\(^3\)), \( \alpha \) is a dimensionless packing factor, \( \rho_s \) is the sediment density (~2600 kg/m\(^3\)), \( D_s \) is the sediment mean diameter (m), \( \rho_o \) is the oil density, \( D_o \) is the oil droplet mean diameter (m), and \( C_o \) is the oil mass concentration (kg/m\(^3\)). Note: a single droplet size is assumed.

The critical sediment concentration is reached when all of the droplets in suspension are coated by a film of sediment particles and is dependent on the oil and sediment densities, droplet and particle sizes, and the oil concentration present. After the critical sediment concentration has been reached and all droplets are coated by a monolayer, the amount of OMA approaches a maximum.

Ajijolaiya et al. (2006) confirmed the validity of the critical sediment concentration concept and equation by quantifying the amount of OMAs formed as a function of sediment concentration and sediment size. They conducted two sets of experiments in seawater, with oil of density 829 kg/L. One experiment used a range of sediment concentrations varying from 10 mg/L to 100 mg/L for sediments for one grain size with mean diameter of 1 \( \mu \)m. The second experiment used one concentration, 223 mg/L, for sediment diameters ranging from 0.5 to 16 \( \mu \)m. The experiments found that trapping efficiency (the percentage of oil in OMAs) increased with sediment concentration and decreased with grain size, and depended on the amount of oil.
available for interaction. To compare this trend to a similar one documented previously by Guyomarch et al. (1999) and account for the differences in oil concentrations used in both sets of experiments, the trapping efficiency was plotted against a normalized concentration, \( \frac{C_S}{C_{S50}} \). The normalized concentration represents the ratio of the concentration of sediments, \( C_S \), present in the experiment versus the critical sediment concentration. In the Ajijolaiya et al. (2006) study, the critical sediment concentration was assumed as the concentration at 50% trapping efficiency. The data of Ajijolaiya et al. (2006) and Guyomarch et al. (1999) were both found to follow the equation of the form

\[
E = \frac{E_{\text{max}} \left( \frac{C_S}{C_{S50}} \right)^n}{1 + \left( \frac{C_S}{C_{S50}} \right)^n}
\]

(3.3)

where \( E \) is the fraction of oil trapped in OMA, \( E_{\text{max}} \) is the maximum possible trapping efficiency and \( n \) is the shape of the trapping efficiency versus sediment concentration curve. The least squares fit of the data presented by Ajijolaiya et al. (2006) and Guyomarch et al. (1999) yields \( E_{\text{max}}=85\% \) and \( n=3 \).

The sediment concentration at which 50% of BAL110 oil is trapped is approximately 280 mg/L (Guyomarch et al. 1999). Assuming the dimensionless packing factor, the sediment density, the sediment mean diameter, and the oil concentration are the same for the other two oils; equation 3.2 can be used to find the critical sediment concentration of a different oil

\[
C_{S50,\text{Arabian Med}} = \frac{(\rho \cdot D_0)_{\text{BAL110}}}{(\rho \cdot D_0)_{\text{Arabian Med}}} \cdot C_{S50,\text{BAL110}}
\]

(3.4)

Values of \( C_{S50} \) for Arabian Medium Crude and IF30, were found by solving equation 3.4 using \( C_{S50} \) for BAL110 and the measurements of oil droplet diameter and density for the respective oils (Table 3.1). The critical sediment concentrations were 280 mg/L, 240 mg/L, and 119 mg/L for BAL110, Arabian Medium Crude and IF30, respectively. IF30 has the lowest
critical sediment concentration since fewer and larger droplets from denser, more viscous oil, thus, requiring less sediment to coat them.

Finally, the fraction of oil potentially trapped in OMA can be calculated equation 3.3 by inputting the sediment concentrations observed in the river and the $C_{550}$ determined for Arabian Medium Crude, BAL110 and IF30. Suspended sediment concentrations were measured at Luling (RM 119), Belle Chasse (RM 77), West Point a la Hache (RM 48) and Venice (RM 11) over a two year period (USGS, 1987). The sediment concentrations were similar at the four locations with a standard deviation of 44 mg/L; thus, an average concentration was calculated for the river during each season. The average sediment concentrations in the river used were 350, 347, 550, 145 and 54 mg/L for winter, spring, summer peak, summer and fall. The potential OMA percentages were calculated using equation 3.3 and compared to the estimates generated by the other contributing factors in this study.

Table 3.1 Oil Properties (ESTC, 2009)

<table>
<thead>
<tr>
<th>Oil Type</th>
<th>Oil Density (at 0°C) (kg/m$^3$)</th>
<th>Oil Density (at 20°C) (kg/m$^3$)</th>
<th>$W_{ar}$ (weight % ARC)</th>
<th>Droplet Mean Diameter (m)$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAL110</td>
<td>878</td>
<td>864</td>
<td>16</td>
<td>3e-6</td>
</tr>
<tr>
<td>Arabian Med</td>
<td>890</td>
<td>876</td>
<td>13</td>
<td>3e-6</td>
</tr>
<tr>
<td>IF30</td>
<td>955</td>
<td>944</td>
<td>18</td>
<td>5.5e-6</td>
</tr>
</tbody>
</table>

$^1$ Droplet size is a function of the viscosity ratio and thus specific to oil type (Khelifa et al. 2002).

3.2.1.3 Temperature

Droplet formation is critical to OMA formation (Khelifa et al., 2005). Oil droplet size and concentration are affected by temperature, viscosity, and asphaltene- resin content (ARC) of the oil. Oils with a higher ARC require more turbulence to break up into droplets and have a higher viscosity than oils with less ARC (Khelifa et al., 2002). As the temperature increases, the
viscosity of an oil droplet decreases leading to the generation of smaller droplets at larger number concentrations, if adequate mixing energy is present. Warmer temperatures also prevent droplets from coagulating due to the increased long range repulsive forces and reduced adhesion forces between droplets (Liu et al., 2006). The following calculations are made to estimate the potential OMA formed as a function of temperature, viscosity and ARC, assuming enough sediment and mixing energy is available.

Khelifa et al. (2002) performed a series of experiments to investigate the OMA formation as related to ARC content and temperature. Eight different oils (~250 mg/L samples), including Arabian Medium Crude and IF30, were shaken with 100 mg/L of 0.9 μm size minerals at 0° C and 20° C to form OMAs by Khelifa et al. (2002). Experimental results showed oil droplet viscosity was dependent on temperature and ARC content

\[ \frac{\mu_d}{\mu_c} = \beta e^{\gamma W_{ar}} \]  

(3.4)

where \( \beta \) and \( \gamma \) are functions of temperature, at 0° C, \( \beta=0.168, \gamma=0.35 \); at 20° C, \( \beta=0.085, \gamma=0.29 \) (Khelifa et al. 2002) and \( W_{ar} \) is the weight percent of asphaltenes and resins in the oil, \( \mu_d \) is the viscosity of a droplet and \( \mu_c \) is the viscosity of the continuous phase.

To find a correlation between high and low viscosity and ARC content oils, the mass concentration of oil droplets, \( W_o \), was normalized by the weight percent of ARC (\( W_{ar} \)) resulting in a function not explicitly dependent on temperature

\[ \frac{W_o}{W_{ar}} = 0.3e^{3.23 \left( \frac{\mu_d}{\mu_c} \right)^{-0.22}} \]  

(3.5)

where \( W_o \) is the ratio between the mass of oil stabilized by OMA and the initial mass of the oil introduced in the system. The above relationship was valid for eight different oils and two temperatures including two oils used in the present study, IF30 and Arabian Medium Crude.
Using the ARC content and the empirical constants referenced from Khelifa et al. (2002), a viscosity ratio for each of the three oils was calculated from equation 3.4 at 0° C and 20° C. Then, equation 3.5 was solved using each viscosity ratio. Values of the viscosity ratio in between or above 0° C and 20° C were linearly interpolated from $\beta$ and $\gamma$. Some error may result from assuming the empirical constants vary linearly with temperature but the effect is not significant. The temperatures for each season used in calculations were 9, 15, 28, and 24 for winter, spring, summer and fall. Finally, the percentage of oil trapped in OMAs, $W_o$, due to temperature was determined for each season by multiplying the ratio from equation 5 by $W_{ar}$.

To further understand the impact of accounting for OMA and temperature effects, evaporation rates at different seasonal temperatures were calculated using ADIOS2 with and without the inclusion of OMA as a removal process. NOAA’s ADIOS2 program calculates evaporation using a pseudo-component model, where each component evaporates based on its own vapor pressure and relative mole fraction. The total rate is then determined as the sum of the individual rates (Lehr et al., 2002). ADIOS2 was run for an instantaneous release of 10,000 gallons of each type of oil for a period of five days at 5° C and 20° C and 4.5 m/s wind speed. The current speed was varied by season from 0.5 to 2 m/s. To investigate the effect of OMA formation, the minimum and maximum OMA percentages, calculated using the above methodology, were each added by using the removal tool in ADIOS2 to apply dispersant over the entire spill area to remove the desired percentage immediately after the spill. The percentage of the spill evaporated without OMA was compared to the evaporation percentages with the minimum and maximum amounts of OMA formed.

### 3.2.1.4 Salinity

For OMA to form, an oil droplet and mineral particle must come within a few nanometers of each other. Surface chemistry affects whether this interaction will occur (Stoffyn-Egli and
Lee, 2002). In rivers, mineral particles are well dispersed (Le Floch, 2002), and most particles and oil droplets repel each other (Schramm, 1992) as a result of their negative surface charges counteracting the van der Waals attraction forces (Huang & Elliot, 1977). As salinity increases, attraction forces remain constant; however, the repulsive forces on the surface of particles decrease (Friberg, 1976). At low salinity levels, OMA formation is strongly dependent on salinity (Le Floch, 2002). In a similar fashion, salinity affects the flocculation of clay particles in the river when interacting with salt water.

The Lower Mississippi River flows into a salt wedge estuary (Pritchard, 1955). The elevation of the bottom of the river is lower than the water surface level of the Gulf of Mexico up to 15 miles downstream of Natchez, Mississippi. As river discharge decreases, the toe of the saltwater wedge moves upriver; as river discharge increases, the wedge moves seaward. Over time, interfacial waves break along the river water/saltwater interface, moving saltwater upward into the overlying freshwater and slowly increasing the salinity of the surface layer. Typically, the lower river has salinities averaging 0.1, 0.015, 0.1, 0.35 and 0.4 ppt for winter, spring, summer, summer peak and fall, respectively (McAnally and Pritchard, 1997).

The effects of salinity on OMA formation are different for each oil and sediment type. However, a typical OMA vs. salinity profile shows linear increase before reaching a maximum fraction of oil in OMAs at the critical salinity, $S_{cr}$ (Le Floch et al., 2002). The percentages of oil in OMA were calculated based on the following,

$$\begin{align*}
  \text{if} & \quad S < S_{cr}, & \quad E = cS \\
  S \geq S_{cr}, & \quad E = E_{\text{max}}
\end{align*}$$

(3.6)

where $E$ is the percentage of oil trapped in OMA, $S$ is the salinity at the surface, $S_{cr}$ is the critical salinity, $c$ is the slope before reaching $S_{cr}$, and $E_{\text{max}}$ is the maximum percentage of OMA possible.
Previous experiments (Le Floch et al., 2002) and field observations (Lee et al., 2001) have documented OMA formation at salinity levels that include those found in the Mississippi River for certain oils. In experiments by Le Floch et al. (2002), the amount of OMA formed reached $E_{\text{max}}$ at a salinity of 0.15 ppt for BAL110 ($E_{\text{max}} = 80\%$) and 1.5 ppt for IF30 ($E_{\text{max}} = 40\%$). Due to the strong correlation of OMA formation with salinity and oil type, the potential OMA formation due to salinity effects will not be estimated for Arabian Medium Crude.

The potential amount of OMAs formed due to salinity was calculated based on an average salinity for each season. The OMA percentages were also calculated for the month of July at 5 points along the river to show the downstream variation in OMA potential due to salinity. Unless the observed data was significantly inaccurate, the averaging should minimize the resulting errors in the calculations and provide useful estimates that accomplish the objective of the study.

### 3.3 Results

#### 3.3.1 Effects of Suspended Sediments on OMA Formation

The maximum OMA potential occurred during the seasons with the highest suspended sediment concentrations (Figure 3.2). Winter and spring had the same OMA potential due to sediments, close to 56%, 65%, and 82% for BAL110, Arabian Medium Crude and IF30, respectively. During the summer peak, the high suspended sediment concentration led to the highest OMA potential of 75%, 79%, and 84% for BAL110, Arabian Medium Crude and IF30, respectively. During fall, when the least amount of sediment was available, negligible amounts of OMA formed except for IF30 oil, which had a potential 7% in OMAs. IF30 oils, the densest oil in the study, formed the highest percentages of OMAs as a result of having the lowest critical sediment concentration. A sharp increase in OMA potential occurs after the critical sediment concentration has been reached. The critical sediment concentration was not present during the
summer for Arabian Medium Crude and BAL110 and was not present during the fall for any of the oils.

Figure 3.2 OMA formation potential by season for three oils due to suspended sediments, temperature and salinity

3.3.2 Temperature Effects

During the winter season, the cold temperatures limit the potential amount of oil taken up by OMAs to 25, 30, and 23% for BAL110, Arabian Medium Crude, and IF30, respectively
Summer had the most potential for OMA formation as a result of temperature with 63%, 83%, and 54% possible for BAL110, Arabian Medium Crude and IF30. Increasing temperature reduced the viscosity ratio of the oils, thereby increasing the OMA potential. The spring had similar OMA potential to winter. Fall had OMA potential half way in between percentages for spring and summer. In all cases, the oil with the highest ARC and viscosity, IF30, had the least OMA potential due to its tendency to form fewer and larger droplets.

During the initial days after a spill, evaporation and OMA formation occur simultaneously. For the lighter oils, BAL110 and Arabian Medium Crude, evaporation amounts were 16-17% higher in warm temperatures during summer and fall compared to colder temperatures during winter and spring (Table 3.3). IF30, denser than the other oils, evaporates 36% more in warmer temperatures than colder temperatures. At all temperatures, the amount evaporated from the IF30 spill was 29-40% less than BAL110 or Arabian Medium Crude. Denser oils evaporate more slowly than lighter oils. Less oil is evaporated when OMAs form than when no dispersion occurs (Table 3.3). Oil removal by evaporation decreased by 2 to 11% for BAL110, 1 to 13% for Medium Arabian Crude, and 1 to 5% for IF30, when the minimum and maximum OMA formation occurred.

The temperature included in the trajectory and weathering models was obtained from the daily 8am reading at the river gages. Daily variation is not included in NOAA emergency response forecasting and was not included in this study. The evaporation rates and OMA formation would decrease as the temperature decreases over the course of the day. The daily variation in temperature increases with the further distance away from the Gulf of Mexico. The daily variation of temperature may be as much as 7° C this variation could result in variation of OMA formation on the order of 10% and evaporation on the order of 5%.
Table 3.2 Temperature-OMA Calculation Input Parameters and Results

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>β</th>
<th>γ</th>
<th>Viscosity Ratio</th>
<th>OMA (% of spilled oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>BAL110 AMC IF30</td>
<td>BAL110 AMC IF30</td>
</tr>
<tr>
<td>0</td>
<td>0.168</td>
<td>0.35</td>
<td>45.43 15.90 91.49</td>
<td>19 23 18</td>
</tr>
<tr>
<td>5</td>
<td>0.147</td>
<td>0.33</td>
<td>31.32 11.47 61.21</td>
<td>22 26 20</td>
</tr>
<tr>
<td>10</td>
<td>0.126</td>
<td>0.32</td>
<td>21.17 8.11 40.14</td>
<td>25 30 23</td>
</tr>
<tr>
<td>15</td>
<td>0.106</td>
<td>0.31</td>
<td>13.92 5.58 25.62</td>
<td>29 36 26</td>
</tr>
<tr>
<td>20</td>
<td>0.085</td>
<td>0.29</td>
<td>8.80 3.69 15.72</td>
<td>36 44 31</td>
</tr>
<tr>
<td>25</td>
<td>0.064</td>
<td>0.28</td>
<td>5.23 2.29 9.07</td>
<td>45 58 39</td>
</tr>
<tr>
<td>28</td>
<td>0.044</td>
<td>0.26</td>
<td>2.79 1.28 4.69</td>
<td>63 83 54</td>
</tr>
</tbody>
</table>
Table 3.3 Percentages of OMA and Evaporation

<table>
<thead>
<tr>
<th>Oil Type</th>
<th>No Dispersion</th>
<th>Minimum OMA Dispersion</th>
<th>Maximum OMA Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Evaporation</td>
<td>Remaining</td>
<td>Evaporation</td>
</tr>
<tr>
<td>BAL110</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan</td>
<td>26</td>
<td>74</td>
<td>22</td>
</tr>
<tr>
<td>April</td>
<td>31</td>
<td>69</td>
<td>23</td>
</tr>
<tr>
<td>Nov</td>
<td>31</td>
<td>69</td>
<td>29</td>
</tr>
<tr>
<td>Dec</td>
<td>26</td>
<td>74</td>
<td>22</td>
</tr>
<tr>
<td>Arabian</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan</td>
<td>29</td>
<td>71</td>
<td>24</td>
</tr>
<tr>
<td>April</td>
<td>35</td>
<td>65</td>
<td>25</td>
</tr>
<tr>
<td>Nov</td>
<td>34</td>
<td>65</td>
<td>33</td>
</tr>
<tr>
<td>Dec</td>
<td>29</td>
<td>71</td>
<td>24</td>
</tr>
<tr>
<td>Medium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nov</td>
<td>14</td>
<td>86</td>
<td>10</td>
</tr>
<tr>
<td>Dec</td>
<td>14</td>
<td>83</td>
<td>13</td>
</tr>
<tr>
<td>IF30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan</td>
<td>9</td>
<td>91</td>
<td>8</td>
</tr>
<tr>
<td>April</td>
<td>14</td>
<td>86</td>
<td>10</td>
</tr>
<tr>
<td>Nov</td>
<td>14</td>
<td>83</td>
<td>13</td>
</tr>
<tr>
<td>Dec</td>
<td>9</td>
<td>91</td>
<td>8</td>
</tr>
</tbody>
</table>
3.3.3 Effects of Salinity

As the salt wedge moves upstream during times of low discharge, the salinity in the river increases downstream as the river approaches the Gulf of Mexico. The increase in salinity downstream suggests OMA potential increases downstream. By extrapolating the results of the LeFloch et al. (2002) experiment to the salinity levels present in the river, estimates of OMA potential in the river due to salinity were calculated (Table 3.4).

Table 3.4 Hypothetical Salinity Effects on OMA Formation along the River at One Time (calculations based on equations in Le Floch et al. 2002)

<table>
<thead>
<tr>
<th>Location (river miles)</th>
<th>Salinity (ppt)</th>
<th>Oil in OMAs (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAL110</td>
<td>IF30</td>
<td></td>
</tr>
<tr>
<td>92</td>
<td>0.09</td>
<td>48</td>
</tr>
<tr>
<td>81</td>
<td>0.12</td>
<td>64</td>
</tr>
<tr>
<td>71</td>
<td>0.2</td>
<td>80</td>
</tr>
<tr>
<td>68</td>
<td>0.25</td>
<td>80</td>
</tr>
<tr>
<td>65</td>
<td>0.28</td>
<td>80</td>
</tr>
</tbody>
</table>

Additionally, the potential OMA was calculated for average salinity values for each season as described in section 2.1.4 (Table 3.5). The maximum amount of OMA was formed during summer and fall when the critical salinity was reached for BAL110 oil. In winter, a potential 53% of oil could be taken up by OMA due to salinity. The minimum OMA potential occurred in spring for both IF30 and BAL110 due to the high discharge preventing the encroachment of the saltwater wedge. For all seasons, the OMA potential for IF30, the most viscous oil, was below 11% and the critical salinity was not reached.

3.4 Discussion

Comparing the estimates of OMA formation for each of the oils subject to the different limiting conditions of the seasons, excluding the summer peak, suggests 0 to 36 percent of the spilled oil could be taken up by OMAs (Table 3.6). The limiting factor depends on oil type and
Table 3.5 Salinity Effects on OMA Formation by Season (calculations based on equations in Le Floch et al. 2002)

<table>
<thead>
<tr>
<th>Season</th>
<th>Salinity (ppt)</th>
<th>Oil in OMAs (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td>0.1</td>
<td>53 3</td>
</tr>
<tr>
<td>Spring</td>
<td>0.015</td>
<td>8 0</td>
</tr>
<tr>
<td>Summer</td>
<td>0.35</td>
<td>53 11</td>
</tr>
<tr>
<td>Summer Peak</td>
<td>0.1</td>
<td>80 3</td>
</tr>
<tr>
<td>Fall</td>
<td>0.4</td>
<td>80 9</td>
</tr>
</tbody>
</table>
season. Due to the sometimes drastic impact of the limiting factor on the OMA potential, an average percentage of all factors was also presented for each oil type/season combination to show the potential OMA formation if the process was not limited by the one dominant factor (Table 3.6). The potential minimum percentage for dense, high viscosity oil, such as IF30, occurs during the summer and fall months when critical salinity has not been reached and the suspended sediment concentrations are low. For IF30, salinity was the limiting factor for all seasons, except fall. The minimum percentage for BAL110 and Arabian Medium Crude occurs during the fall when the suspended sediments are limited. During the fall, the lack of suspended sediments was the limiting factor for all oils. Suspended sediment concentrations would have to reach 250 mg/L to negate sediment availability as a limiting factor. During the winter and spring, the conditions are beneficial for OMA formation for BAL110 and Arabian Medium Crude since the average suspended sediment concentrations are much larger than the critical sediment concentration.

During the summer peak flood event, the maximum OMA potential for the three oils occurred due to the high suspended sediment availability and warm temperatures. The calculations for the summer peak result in overestimation of potential OMAs that could form in the natural environment. These estimates are based on the assumption enough droplets are dispersed into the water column. The rate of vertical mixing could further limit the formation of OMAs. Furthermore, the equations used in this study are derived from laboratory experiments. Natural conditions, sediments and simultaneously occurring fate and transport processes will have an impact that will either enhance or inhibit the OMA potential discussed in this study.

Adding OMA formation into a weathering model such as ADIOS2 affects the mass balance by reducing evaporation. Despite the non-complimentary relationship of the evaporation and OMA formation, both processes contribute to the reduction of available oil that could be beached or transported in the slick. OMAs remain buoyant in the water column, further reducing
the potential for oil to be beached. By examining the distribution of suspended sediments across the channel and at bends, the potential for more OMA to form exists in the center of the channel through straight sections and to the outside of the bend where the highest suspended sediments exist. If more OMA is forming at the outside of the bend, less can be deposited as typically occurs on the shoreline along the bend. Depending on the location of the spill, the OMAs could remain buoyant through Head of Passes, allowing some amount of the spill to be dispersed into the Lower Mississippi River passes and out to the Gulf of Mexico.

Table 3.6 Comparison of OMA Potential and Limiting Factors by Season

<table>
<thead>
<tr>
<th></th>
<th>Winter</th>
<th>Spring</th>
<th>Summer (peak)</th>
<th>Summer</th>
<th>Fall</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BAL110</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limiting Factor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OMA (%)</td>
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<td><strong>Arab Med</strong></td>
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<tr>
<td>Limiting Factor</td>
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<td>OMA (%)</td>
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<td>SS</td>
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</tbody>
</table>

3.5 Conclusions

Based on the assumptions and calculations made in this work, high sediment availability and low critical salinity resulted in winter and spring being the peak seasons for BAL110 and Arabian Medium Crude OMA formation in the lower Mississippi River. Due to the relatively higher critical salinity concentration for IF30, the peak season for OMA formation is in the
summer when low flow rates allow for the salt wedge to migrate upriver and create higher salinity conditions.

OMA estimates should be added in the mass balance of an oil spill, since typical dispersion modeling does not account for the process. As much as 36% of an oil spill has the potential to reach the Gulf of Mexico as OMAs, depending on environmental conditions and spill characteristics. As a result, potential environmental consequences are underestimated including the transport and stabilization of oil into the water column, biodegradation and the prevention of shoreline oiling. Additionally, alternative responses and remediation approaches may be required.

The mixing energy of the river is another important factor in OMA formation that was difficult to include in this study. Physical measurements of the turbulence and entrainment of oil droplets in rivers are needed to develop an applicable dispersion model. Additionally, experiments using Mississippi River sediments and different oils at a range of salinities are needed to quantify formation rates.
CHAPTER 4

HINDCAST MODELING OF THE DM932, NEW ORLEANS OIL SPILL: SHORELINE AND OIL-MINERAL AGGREGATES

4.1 Riverine Oil Spill Modeling and the Lower Mississippi River

The simplest models of the lower Mississippi river were time of travel studies developed as early warning systems for protecting drinking water intakes from spills. In the late 1960’s, Stewart (1967) and Everett (1971) conducted separate fluorescent dye studies at low discharges between Baton Rouge and New Orleans, Louisiana to examine the travel time and dispersion of the river. Graphs were generated for travel time versus discharge, travel time and concentration, and peak concentration. Additionally, lateral dispersion studies were conducted by monitoring dye movement through meanders. However, the conclusions from these studies could not be applied to non-solutes or spills with different initial locations. Martens (1974) also performed dye studies from Baton Rouge to West Point a la Hache but at a much higher discharges, almost three times the discharge of the previous studies. The high discharge was chosen because of its relatively linear relationship with travel time compared to low discharges that are subject to tidal influence and fluctuation. In the Martens (1974) study, samples were taken at the surface and 50 feet below the surface at three locations to investigate vertical dispersion. Within 11 to 18 miles downriver from the injections site, the surface contaminant concentration, initially double the concentration at 50 feet, was reduced to concentrations similar to as the lower sample. The last travel time study was conducted by Calandro (1976, 77) for solutes traveling from the Arkansas-Louisiana state line to Plaquemine Parish and from Belle Chasse to Head of Passes. A tracer was injected to provide calibration data for a model that would generate curves to predict the leading edge, the peak, and the trailing edge of a tracer cloud for the annual range of discharges in the
A similar model is still available; Waldon (1998) developed the River Time of Travel (RTOT) model based on a stream flow relationship that predicts the velocities of the leading edge, peak, and trailing edge and integrates velocities along a given reach of river for travel time estimates. Discharge, predicted duration and the mass of the spill are used to calculate the peak concentration. The model was calibrated using nine time-of-travel dye studies and has been used as an early warning system for river water users.

The purpose and capability of oil spill models range from simple trajectory, particle tracking models, to two and three dimensional fate and transport models able to predict distribution on the surface, water column, and shorelines and quantify biological response and environmental impact (Reed et al., 1999). If shoreline interactions are included in a model, usually one of two approaches is taken. The first is calculating the shoreline’s maximum holding capacity. The maximum holding capacity determines how much oil a sediment type can retain per unit length or area. When the oil exceeds the holding capacity it will be released back to the river. Reed et al. (1999) computed holding capacity from oil viscosity, sediment permeability, porosity, and water level. Darcy’s Law was used to determine the penetration depth, accounting for the change in water level while residual oil remains on the surface of the sediments (Reed et al., 1999). However, this equation does not account for beach type. Porosity is the only parameter characterizing the beach. Maximum capacity may not be reached for a long time. Furthermore, maximum beach capacity is not applicable for the Mississippi River shoreline, often characterized by vegetation and rip rap. The alternative is to predict the mass of oil remaining onshore as a first order process (Reed et al, 1999). Re-floatation half-life values describing the ability of the shore to hold oil were provided by Torgrimson (1980). Based on observations of removal rates from previous spills, the half life method does not represent the
detailed physics of the process, but is commonly used due to the complexity of trying to model shoreline-oil interactions at large scales.

In the General NOAA Operational Modeling Environment (GNOME), a spill trajectory model, a single shoreline half life is assumed for the entire study area. Thus, a method of tracking oil parcels using multiple shoreline half lives was implemented in Danchuk and Willson (2009) to evaluate the sensitivity of the shoreline to the half life parameter and more accurately model the trajectory of oil by including the multiple shoreline types found along the Lower Mississippi River. GNOME continues to be used by NOAA’s Office of Response and Restoration to model trajectories in the Mississippi River.

4.2 Incident Summary

On July 23, 2008, at 1:30 am (CDT), the M/V Tintomara, a 200 meter chemical tanker loaded with styrene and biodiesel collided with the DM932, a 66 meter fuel barge on the Mississippi River near downtown New Orleans (MM 98.2) (Figure 4.1) (NOAA 2008). The DM932 was split in half, releasing some portion of the 9,983 barrels of no. 6 fuel oil it contained into the river (Figure 4.2a). The barge came to rest, partially submerged near the Crescent City Connection Bridge (MM 95.7). The barge continuously leaked, forming a long slick of black oil with a silver sheen covering 90% of the river, 14 miles from the barge within the first 6 hours (Figure 4.2b, c). Within a few days, patches of oil reached the Head of Passes (MM 0) forming tar patties and rainbow sheens. The high viscosity of the oil caused the oil to persist in the environment rather than evaporate. Approximately 220 km of the shoreline was oiled to varying degrees coating vegetation, rip rap, structures, and debris and pooling in rip rap and low lying areas (Figure 4.3). On July 30, 2008, a second discharge from the barge occurred, approximately 59.5 barrels. Additional small releases of oil from the barge occurred during the salvage operation. As a result, multiple shoreline types within each shoreline segment were oiled due to
the significant 2 m decrease in river stage level that occurred simultaneously to the releases. In addition, contamination of the river bed occurred as the weathered oil interacted with suspended sediments forming oil-sediment aggregates and small tarballs, causing concern to dredging and drinking water intake operations. Emergency response began at daylight on the day after the incident in effort to contain, remove and assess the extent of the damage of the spill.

Figure 4.1 DM932 Spill Locations (Final Barge Position: 29° 54.75' N, 90° 5.50' W)

Primary concern was for the drinking water intakes along the river which were blocked with booms and monitored. Overall, 47,000 meters of containment boom and sorbent boom were deployed to contain the spill, protect shorelines, and block cuts in the river. In an effort to protect the booms from ship wakes, more than 187 km of the river was closed to marine traffic for several days. Assessment of cleanup concerns and removal of contaminated began thereafter. Approximately 3,929 barrels of an oil and water mixture were removed from the sunken barge on August 6, 2008, reducing the initial estimate of oil released into the river. Then, the barge was
cut and lifted in sections during the salvage operation. Over 3,309 barrels of an oil/water mix was recovered from the river. Cleanup crews removed about 4,900 cubic meters of oily debris.

Figure 4.2 Photos from the DM932 spill (Source: NOAA 2008b) (a) Barge split in half near Crescent City Connection Bridge, New Orleans, Louisiana (b) Oil streamers along the river (US Coast Guard Overflight on July 25, 2008) (c) Oil patches cover entire width of river (d) Streamers indicate turbulent diffusion causes significant spreading towards shorelines of river
Figure 4.3 Types of Shoreline Oiled

(a) Banding along rip rap after water level decreases (NOAA 2008b)

(b) Heavy oiling of low vegetation (“Burnt grasses”) (c) Pooling in Batture lands (high vegetation areas) (NOAA 2008b)

(d) Mud flats clean due to rapid re-floatation of oil
from the river banks. The debris included dead branches, thin willow roots known as shaggy beard, trash and other removable material. The overall fate of the spilled oil is estimated as

Volume spilled: 5,925 barrels;
Lost via evaporation (11%): 651 barrels;
Recovered as free oil (average 50% water in recovered liquids): 3619 barrels
Recovered as oiled sediment: 125 tonnes (862 barrels)
Recovered as debris: 645 barrels
Remaining in the environment: 148 barrels

The purpose of this study was to analyze the distribution of oil retained by shorelines after the DM 932 spill, to hindcast the trajectory of the spill and evaluate the sensitivity of the shoreline oil distribution to the re-floatation half life parameter, and to investigate the potential of oil-mineral aggregate formation as the process responsible for removing the remaining oil in the environment.

4.3 Shoreline Types Affected By Spill

The Shoreline Cleanup Assessment Team (SCAT) surveyed the lower 99 miles of the river to assess and quantify the degree of shoreline oiling from 7/29/08 to 8/14/08 (NOAA, 2008). The SCAT surveys include descriptions of the character of the oil, the length and width of segments of oiled shoreline by shoreline type, and the distribution of the oil within the segment. The river was divided into 5 to 10 mile survey segments identified as Divisions A- S. For this study, the raw data from the SCAT surveys of each reach of shoreline were assimilated and analyzed to compute the areas of oiled shorelines by type, validate the shoreline types present, and evaluate the relationship of shoreline type and degree of oiling. The area of oil retained by the shoreline was calculated by multiplying the area of an oiled shoreline segment by the percentage of oil distributed within the segment. Then, the individually calculated areas were
compiled by shoreline type (Table 4.1). Heavy oiling describes a band of oil at least 1 m wide with more than 50% distribution (Michel et al. 2002). Moderate oiling defines shoreline with 10 to 50% distribution. Light oiling distribution is less than 10%. Very light oiling is less than 5%.

Table 4.1 Total shoreline oiling by shoreline type and degree of oiling (in hectares)

<table>
<thead>
<tr>
<th>Shoreline Type</th>
<th>All</th>
<th>Very Light</th>
<th>Light</th>
<th>Moderate</th>
<th>Heavy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scrub Shrub</td>
<td>6.96</td>
<td>0.50</td>
<td>1.52</td>
<td>0.79</td>
<td>4.15</td>
</tr>
<tr>
<td>Rip Rap</td>
<td>4.57</td>
<td>0.19</td>
<td>0.55</td>
<td>2.07</td>
<td>1.76</td>
</tr>
<tr>
<td>Mud/Sand Structures/</td>
<td>3.71</td>
<td>0.05</td>
<td>0.79</td>
<td>1.11</td>
<td>1.75</td>
</tr>
<tr>
<td>Pilings</td>
<td>0.14</td>
<td>0.04</td>
<td>0.07</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>0.20</td>
<td>0.01</td>
<td></td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>15.57</td>
<td>0.79</td>
<td>2.92</td>
<td>4.19</td>
<td>7.67</td>
</tr>
</tbody>
</table>

The five types of shoreline oiled by the spill and identified in the SCAT data include scrub shrub, rip rap, mud/ sand, man-made structures and other. Scrub shrub describes the vegetated low lying shoreline consisting of willow trees, grasses and shrubs. In these areas, the oil coated leaves, formed bands around tree trunks, and pooled on the sediments. Rip rap is a shoreline erosion protection structure made of rocks that lines the majority of shoreline near New Orleans. The spilled oil coated the rock surfaces and pooled in the crevices within the rip rap, and multiple bands of stranded oil were formed as a result of stage level decrease. The fine, consolidated mud areas have low permeability and are typically saturated, limiting oil penetration. The sand flats consist of fine grained sand that is exposed at low river stage levels. Water saturation prevents oil penetration in both types of sediment, resulting in the formation of pools on top of the sediments in areas not subject to refloating or light stains in areas where natural physical removal occurred. Pilings, piers, and other man- made structures were coated by bands of oil indicating the water level at time of deposition. The category of other includes shorelines that overlap such as rip rap and pilings that were grouped in the SCAT survey.
The majority of shoreline oiled was scrub shrub, followed closely by rip rap (Table 4.1). These shoreline types are areas where oil persists and is slow to be removed naturally. The distribution of oil on scrub shrub shoreline segments was mostly heavy due to the pooling within the low lying areas after its initial oiling and the lack of natural removal or re-floatation after the water level dropped. The rip rap was subject to mostly heavy and moderate oiling as a result of pooling and coating that occurred when the river and floating oil was contained by the rip rap, the re-floating of deposited oil across the rip rap as stage level decreased and the additional releases that occurred from the barge at lower stage levels. The amount of oil pooled in the mud/sand areas was dependent on the elevation of the area. In areas where possible, oil was refloated, then, contained by the booms in the river.

4.4 Trajectory Modeling

Hindcasting an oil spill allows the predictive ability of a particular trajectory model to be assessed and identifies weakness or sensitivity in the model, so that improvements can be made in the future. Since shoreline retention was the dominant process affecting the fate and transport of oil from DM932 spill, this hindcast study focuses on the parameter representing the adhesiveness of the oil to the shoreline as a function of substrate porosity, oil properties, vegetation, and environmental processes, the re-floatation half life.

A re-floatation half life can be set to represent the adhesiveness of the oil to the shoreline as a function of substrate porosity, oil properties, vegetation, and environmental processes. The re-floatation half life is used to determine the probability that a parcel of oil will refloat some time after deposition. Re-floatation half lives vary for each shoreline type. Values typically used for mud, sand and vegetation (or rip rap) are 1 hr, 24 hrs, and 8760 hrs (Torgrimson, 1980). In NOAA’s General NOAA Operational Modeling Environment (GNOME), the re-floatation half life is set as a single constant value during a trajectory simulation and assumes a single shoreline
type is present. As seen in the SCAT survey of the DM 932 spill, multiple shoreline types exist along the Mississippi river. The occurrence of water level variation, shoreline type changes, and stranding of oil are also not represented in this trajectory model. Nonetheless, GNOME is the model used by the NOAA HAZMAT Scientific Support Team to predict the trajectory of oil after a spill. Thus, evaluating the predictive ability of GNOME when applied to the Mississippi river is important.

 GNOME uses the Lagrangian Element (LE) approach to model the movement of individual oil parcels based on wind and current fields. Horizontal mixing is simulated using a random walk method. GNOME uses a simple three phase evaporation algorithm. The mass balance of the oil spill is tracked throughout the simulation accounting for the oil’s location and weathering (Beegle-Krause 2001; NOAA 2002b).

 The diagnostic mode of GNOME was used to simulate 1) 5870 barrels of fuel no. 6 continuously released from the DM 932 over a period of five days and 2) 60 barrels instantaneously on July 30, 2008. The velocity field was modeled using the ADaptive Hydraulics (ADH) modeling system, developed by the Coastal Hydraulics Laboratory, Engineering Research and Development Center, US Army Corps of Engineers. The bathymetry and elevation data used in the simulations were obtained from a high resolution mesh (SL15RV3_2005) developed at the University of Notre Dame, under contract to the USACE for use in surge probability evaluation, hurricane protection planning, and coastal restoration planning (Westerink et al. 2006). A tailwater elevation boundary condition at Pointe a la Hache was forced based on the stage-discharge data provided by the New Orleans District US Army Corps of Engineers for the period of study.

 The input parameters used in GNOME were similar to those used by NOAA to predict the trajectory of the spill from New Orleans to West Pointe la Hache (NOAA 2008b). The lower
boundary was chosen as West Pointe a la Hache, since most of the shoreline oiling occurred by this location and tidal influence was not significant. The random diffusion coefficient input was 1.69 m$^2$/s. The time step used in the trajectory simulations was 72 s. Wind speed varied from 5 to 10 mph, typically from the southwest or west direction.

### 4.5 Travel Time Analysis

By 6:30 CDT the following morning after the initial spill, NOAA had forecasted the trajectory for multiple scenarios as part of the emergency response. The stage level input into the simulations went from 10.5 feet on Wednesday to 9.8 feet on Sunday. The diffusion coefficient used by NOAA was 1 m$^2$/s. The re-floatation half life used was 1.5 hours. The time step used was 72 s. The river velocity was scaled according to the stage height at New Orleans, using a rating curve. With winds from the S and SE, most of the oiling was predicted to be on the South facing shoreline (USCG 2008). Within 6 hours of the accident, the arrival time of the leading edge was observed at RM 80, forecasted by NOAA to reach Belle Chase (RM 78) and hindcasted to reach RM 80 (Figure 4.4). The leading edge was observed to reach Venice (RM 20) 26.5 hours after the initial spill, forecasted at 33 hours, and hindcasted (based on trendline) at 30 hours. The hydrodynamics used for the hindcasting correctly approximate the travel time of the leading edge of the slick.

### 4.6 Shoreline Oiling

The distribution of oil by shoreline type was hindcast using three re-floatation half lives, 1 hr, 24 hrs, and 8760 hrs, individually. An additional hindcast was run using the multiple shoreline type and re-floatation half life method discussed in (Danchuk and Willson, 2009). The distribution of oil for each segment of shoreline was categorized as heavy, moderate, or light. These distributions were correlated to shoreline type using shoreline maps developed for the specific stage level from DOQQ images and the hydrodynamic results. The distributions of oil
Figure 4.4 Travel Time of Spill as observed, forecasted by NOAA and hindcasted for present study
Table 4.2 Total shoreline oiling from hindcasting by shoreline type and degree of oiling using various re-floatation half lives (in hectares)

<table>
<thead>
<tr>
<th>Half Life</th>
<th>Shoreline Type</th>
<th>All</th>
<th>Light*</th>
<th>Moderate</th>
<th>Heavy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1hr</td>
<td>Scrub Shrub</td>
<td>3.81</td>
<td>0.79</td>
<td>0.43</td>
<td>2.59</td>
</tr>
<tr>
<td></td>
<td>Rip Rap</td>
<td>3.28</td>
<td>0.36</td>
<td>1.48</td>
<td>1.44</td>
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<tr>
<td></td>
<td>Mud/Sand Structures/</td>
<td>3.71</td>
<td>2.34</td>
<td>0.77</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>Pilings</td>
<td>0.27</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td>11.07</td>
<td>3.49</td>
<td>2.95</td>
<td>4.63</td>
</tr>
<tr>
<td>24 hrs</td>
<td>Scrub Shrub</td>
<td>7.21</td>
<td>1.78</td>
<td>1.19</td>
<td>4.24</td>
</tr>
<tr>
<td></td>
<td>Rip Rap</td>
<td>4.03</td>
<td>0.99</td>
<td>1.73</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>Mud/Sand Structures/</td>
<td>4.17</td>
<td>1.52</td>
<td>0.95</td>
<td>1.7</td>
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<tr>
<td></td>
<td>Pilings</td>
<td>0.40</td>
<td>0.07</td>
<td>0.33</td>
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<td></td>
<td><strong>Total</strong></td>
<td>15.81</td>
<td>4.36</td>
<td>4.2</td>
<td>7.25</td>
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<tr>
<td>8760 hrs</td>
<td>Scrub Shrub</td>
<td>7.09</td>
<td>1.30</td>
<td>0.55</td>
<td>5.24</td>
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<tr>
<td></td>
<td>Rip Rap</td>
<td>5.36</td>
<td>1.22</td>
<td>1.78</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td>Mud/Sand Structures/</td>
<td>4.7</td>
<td>0.20</td>
<td>1.86</td>
<td>2.64</td>
</tr>
<tr>
<td></td>
<td>Pilings</td>
<td>0.40</td>
<td>0.07</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td>17.15</td>
<td>2.72</td>
<td>4.19</td>
<td>10.24</td>
</tr>
<tr>
<td>Multiple</td>
<td>Scrub Shrub</td>
<td>6.8</td>
<td>0.00</td>
<td>1.55</td>
<td>5.25</td>
</tr>
<tr>
<td></td>
<td>Rip Rap</td>
<td>4.7</td>
<td>0.00</td>
<td>2.7</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Mud/Sand Structures/</td>
<td>3.6</td>
<td>1.6</td>
<td>2</td>
<td>0.00</td>
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<td></td>
<td>Pilings</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td>15.1</td>
<td>1.6</td>
<td>6.25</td>
<td>7.25</td>
</tr>
</tbody>
</table>

Light represents an area with an oil distribution of less than 10% and includes very light oiling.

Comparing the distributions of oil by shoreline type for each of the three re-floatation half lives tested were compared to the SCAT survey data (Table 4.2).

4.7 Hindcasting of Shoreline Oil Distribution

4.7.1 Use of Single Re-floatation Half-Life

Comparing the distributions of oil by shoreline type provides evidence of which re-floatation half life most accurately represents the shoreline oiling documented by the SCAT data.

The shortest re-floatation half life of 1 hr under predicted the amount of oil retained by the
These predictions suggest the 1 hour half life overestimated the re-floatation occurring, allowed too much oil to continue to float within the river, thereby overestimating the amount of free product that could be recovered, and moving more oil past the lower boundary than was observed. Areas of scrub shrub and rip rap that tend to retain oil longer were significantly under represented by this half life. The 24 hour half life over predicted the retention by scrub shrub by 3.6% and mud/sand by 12%; the rip rap retention was under predicted by 12.4%. The reduced re-floatation that occurs for the 24 hour hal life compared to the 1 hour half life allows for a better approximation of retention for the shoreline types that tend to hold oil for long terms. The longest half life, \( \lambda = 8760 \) hours, over predicted heavier oiling in scrub shrub and rip rap areas closer to the release site and then, under predicted oil retention further down river. Overall, the 8760 half life over predicted oiling in the scrub shrub, rip rap and mud/sand areas by 2%, 17%, and 3%, respectively. Each of these half lives result in a deviation from the degree of observed oiling in the SCAT data of more than 10% for at least one shoreline type.

### 4.7.2 Use of Multiple Re-floatation Half Lives

The differences between the hindcast modeling and the SCAT survey data are a result of the limitations of the model. Although using a single half life provided relatively good results, the use of multiple half lives for each shoreline type was expected to increase the ability to model the degree of oiling in each shoreline segment more accurately. Using multiple shoreline re-floatation half lives resulted in similar areas of oiled shoreline by type as the SCAT survey data (Table 4.2). Less variation in the degrees of oiling was observed in multiple re-floatation half life hindcast. For example, the scrub shrub and rip rap areas were only oiled in heavy to moderate degrees. Meanwhile, mud and sand shorelines had mostly light or moderate oiling. Since scrub shrub and rip rap are assigned the longest re-floatation half life, almost all of the oil
deposited on these shorelines will remain for the duration of the simulation. Conversely, any oil deposited in a mud or sandy area will re-float and redistribute along another stretch of shoreline, resulting in mostly light and moderate oiling as the concentration of oil along shoreline reaches is reduced and redistributed. At the time of the spill, the majority of the shoreline interacting with the oil was scrub shrub and rip rap (74% in total), which both were assigned a re-floatation half life of one year. As a result, most of the oil did not refloat and the distribution remained the same in the days following the spill. Using multiple re-floatation half lives approximated the shoreline oiling within 8%, 6.5% and 5.5% for scrub shrub, rip rap and mud/sand. All deviations from the observed data were less than 10%, justifying the use of the multiple re-floatation half life to represent the shoreline interactions most accurately according to specific shoreline type.

Using a re-floatation half life of one hour under-predicted the area of oiled shoreline for all shoreline types when compared to the observed SCAT data. (Figure 4.5) A 24 hour re-floatation half life provides results that are similar to scrub shrub, less oiled rip rap, and an over-prediction of mud/sand. When the 1 year (8760 hours) re-floatation half life was used in GNOME, similar oiled shoreline areas resulted for scrub shrub when compared to the SCAT data, the oiled area of rip rap and mud/sand was over-predicted. The multiple re-floatation half life resulted in oiled areas for each shoreline type that were within 5% of the observed SCAT shoreline areas.

Although the multiple re-floatation half life resulted in areas of oiled shoreline that were very similar to the SCAT observational data, scrub shrub had areas that were under-predicted and examples of over-predicted areas of oiled rip rap occurred (Figure 4.6). One possible theory for these differences from the observed data could be that once a river bend is saturated, GNOME does not allow the parcels to be retained, thus they must continue to float. After the
Figure 4.5 Shoreline oiled resulting from simulations using single half lives of 1 hr, 24 hours, and 8760 hours, the multiple re-floatation half life method and the observed SCAT data from the spill.

Figure 4.6 Shoreline oiled when the multiple re-floatation half life method was used in simulations.
actual spill, the SCAT data documented pooling occurring in low lying scrub areas, however, the model does not capture the phenomena of pooling. Oppositely, the re-floatation half life assigned to rip rap assumes rip rap has area or volume available for deposit, the possibility that the SCAT data reflect rip rap reaching capacity causes oil to refloat, thus an over prediction by the model.

Some issues with shoreline segments could still not be resolved, as unexpected obstructions blocked the shoreline, such as a ship or barge. Over 400 ships were inspected and washed during the cleanup process; a few areas of shoreline were completely protected from oiling as a result of the stationary barges. Furthermore, booms deployed along shorelines blocked oil floating in the river channel while retaining oil that refloated from the shoreline. Thus, the SCAT survey data does not exactly represent the distribution of oil that would occur naturally.

Finally, the most difficult aspect of modeling the DM932 spill was the decrease in river stage level that led to oiling at multiple elevations of rip rap, over banking and pooling in batture (low lying) areas behind rip rap, and stranding of oil not accessible for re-floatation. The dynamic and complex nature of the shoreline oiling across multiple shoreline types prevents very precise analysis of oil distribution and would insert error into any re-floatation half life implemented.

4.7.3 Influence of Other Input Parameters

Although the re-floatation half life allows for a certain amount of oil to be redistributed, the current and wind fields are the most important factors of initial deposition. Heavy to moderate oiling occurred on the outside of the bends in Divisions C and D and the south/ south east facing shorelines in Divisions E and F, as expected (Figure 4.7). Large lateral velocity vectors move oil parcels to the outside of bends where velocities slow and oil is retained on the shoreline. Specific to the conditions of this spill, winds from the South/ Southwest direction were additional forces moving oil towards south facing shorelines. The same wind and velocity fields
were used in each test of the re-floatation half life; however, the distribution of oil by location was best represented by the simulations run with multiple re-floatation half lives (Figure 4.7), suggesting redistribution by re-floatation is a dominant process in the Mississippi river at the flow rate at the time of the spill.

Figure 4.7 (a) SCAT survey data for August 8, 2008 (USCG, 2008) (b) Shoreline oil distribution from hindcast trajectory for multiple re-floatation half lives implemented in one simulation

Additionally, model parameters affected the distribution of oil along the shoreline. The diffusion coefficient was varied from 0.5, 1, 1.69 and 5 m²/s. As the diffusion coefficient is increased, the slick spreads radially, eventually causing shoreline oiling when the slick expands to the shoreline. The peak concentration has the same travel time in each simulation; however, a few parcels are diffused ahead of the slicks with the higher diffusion coefficients. When the diffusion coefficient is increased, heavier oiling occurs closer to the spill release location and as a result, less oiling occurs further downstream. The diffusion coefficient of 5 m²/s causes a
considerable amount of shoreline oiling due to the slick spreading to both sides of the shoreline. The percentage of total oiling was the same for each simulation, but the location and degree of oiling varied depending on the diffusion coefficient. Without wind, the river geometry and diffusion are the only causes of shoreline oiling. The results show the diffusion coefficient has a significant impact on the slick shape and shoreline oiling. The diffusion coefficient must be chosen carefully; an overestimation of diffusion within the confines of the river banks can result in a major over prediction of oiling of the shoreline. Calibrating the coefficient based on actual spill data is the best method for selection. The value used in the studies of re-floatation half life was $1.69 \text{ m}^2/\text{s}$. Since this value is based on observations of the river and provided results that matched survey data from the DM932 spill, it should be considered to be an acceptable value. The effect of the time step was also examined. The results were similar for all time steps, the largest time step resulted in more shoreline oiling in areas where the channel curved and current vectors moved oil straight into the shoreline. At a time steps smaller than or of 50 s, the degree of oiling by location approaches a constant pattern.

4.8 Oil Mineral Aggregates

Oil interacting with suspended sediments can form aggregates that are positively or negatively buoyant. Evidence of sinking aggregates was found in the dredging hopper, as a layer of thick foam on top of dredged sediments with patchy small droplets of brown oil and a slight rainbow and silver sheen. Oil mineral aggregates (OMA) form when oil droplets are coated by fine grained particles. Sediment size, sediment concentration, temperature, salinity, droplet number concentration, and oil properties impact the potential for OMA to form. These positively buoyant aggregates do not adhere to shorelines and can transport oil within the water column into the Gulf of Mexico. The amount of OMA that could potentially form under the conditions
present during the spill, with respect to temperature, suspended sediments and salinity, was calculated using empirical equations from previous studies.

To calculate the OMA potential as a result of temperature and the weight of asphaltene and resin (ARC) content of the oil, the following equation was used,

\[ W_o = W_{ar} 0.3e^{3.23\left(\frac{\mu_d}{\mu_c}\right)^{-0.22}} \]  \hspace{1cm} (4.1)

where \( W_o \) is the ratio between the mass of oil stabilized by OMA and the initial mass of the oil introduced in the system; \( W_{ar} \) is the weight percent of asphaltenes and resins in the oil; \( \mu_d \) is the viscosity of a droplet and and \( \mu_c \) is the viscosity of the continuous phase (Khelifa et al. 2002). The viscosity ratio of an oil droplet is given by

\[ \frac{\mu_d}{\mu_c} = \beta e^{\gamma W_{ar}} \]  \hspace{1cm} (4.2)

where \( \mu_d \) is the viscosity of a droplet and \( \mu_c \) is the viscosity of the continuous phase; \( \beta \) and \( \gamma \) are functions of temperature, at 20° C, \( \beta=0.064, \gamma=0.275 \) (extrapolated from values in Khelifa et al. 2002) and \( W_{ar} \) is the weight percent of asphaltenes and resins in the oil, \( W_{ar} =21 \) for Fuel oil no. 6 (ESD 2000).

From this calculation, an estimated 31% of oil could form OMAs as a result of temperature. Since the mass balance of the spill states less than 5% of the oil remained in the environment, the estimate based on temperature is too high and one of the other factors must have limited OMA formation.

The effect of suspended sediments on OMA was determined by first calculating the critical suspended sediment concentration for fuel oil no. 6. The sediment concentration at which 50% of BAL110 oil is trapped according to the Guyomarch et al. (1999) data is approximately 280 mg/L. Assuming the dimensionless packing factor, the sediment density, the sediment mean
diameter, and the oil concentration are the same for fuel oil no. 6; an equation can be derived for calculating the critical sediment concentration of a fuel oil no. 6,

\[ C_{S50_{Fuel\ oil\ no.\ 6}} = \frac{(\rho_0 D_0)_{BAL110}}{(\rho_0 D_0)_{Fuel\ oil\ no.\ 6}} C_{S50_{BAL110}} \]  \hspace{1cm} (4.3)

where \( C_{S50} \) is the critical sediment concentration (kg/m\(^3\)), \( \rho_0 \) is the oil density, \( \rho_0 = 860 \) km/m\(^3\) for BAL110 and 978 for Fuel no. 6; \( D_0 \) is the oil droplet mean diameter (m), \( D_0 = 3e^{-6} \) m for BAL110 and 5.5e-6 for Fuel oil no. 6. Note: a single droplet size is assumed.

Then, using the following equation to calculate OMA potential,

\[ E = \frac{E_{\text{max}} \left( \frac{C_S}{C_{S50}} \right)^n}{1 + \left( \frac{C_S}{C_{S50}} \right)^n} \]  \hspace{1cm} (4.4)

where \( E \) is the fraction of oil trapped in OMA, \( E_{\text{max}} \) is the maximum possible trapping efficiency, \( C_S \) is the mass concentration of sediment per volume (kg/m\(^3\)), \( C_S = 0.2 \); \( C_{S50} \) is critical sediment concentration (kg/m\(^3\)), and \( n \) is the shape of the trapping efficiency versus sediment concentration curve. The least squares fit of the data presented by Ajijolaiya et al. (2006) and Guyomarch et al. (1999) yield \( E_{\text{max}} = 85\% \) and \( n = 3 \).

Again the OMA estimate is too high, 63\% of oil could be trapped by OMA based on suspended sediment availability. Salinity is typically the limiting factor for viscous oils such as fuel oil no. 6. The effect of salinity is very specific to oil type; an empirical relationship has not yet been developed. However, some insight can be gained by looking at the OMA potential of a similarly viscous oil, IF30, at a salinities of 0.09 to 0.2. Based on the data from Le Floch et al. 2002 for IF30, OMA can potentially trap 2 to 5\% of the total oil spilled. This estimate of OMA formation would explain the fate of oil remaining in the environment, not accounted for in the mass balance.
4.9 Summary

The total area of oiled shoreline from the DM932 spill was calculated for each shoreline type from the SCAT data and the distribution was analyzed. The SCAT data oil distributions were compared to results from hindcast modeling that varied the re-floatation half life parameter. The simulations using multiple re-floatation half lives yielded the most accurate results when the actual spill SCAT data was used for comparison. The variation of the diffusion coefficient and time step was also found to affect the shoreline oil distribution. Stage level variation and the presence of ships that are not included on shoreline maps also limit the predictive performance of the model. Despite some small variations from the spill data, GNOME was found to provide accurate hindcast trajectories for the spill, suggesting if the input parameters used in the study were implemented in a forecast, accurate results would be yielded. Finally, the potential of oil-mineral aggregate formation was estimated to remove 2 to 5% of the total oil spilled, explaining the fate of oil remaining in the environment, and completing the mass balance.
5.1 Background

Mesh refinement is generally assumed to improve the accuracy of a numerical simulation within a particular domain. However, the accuracy is only improved to the extent that the refinement strategy is based on representing the discrete features and flow characteristics found in the simulated field i.e. shallow areas around reefs, tidal wave propagation, or ship wakes. The Lower Mississippi River contains several discrete features where mesh size is relevant to the accuracy of hydrodynamic simulations. For example, current fields around bends or shallow sand bars are characterized by small recirculation eddies. Additionally, the non-uniform bathymetry leads to significant variations between currents traveling through the shallow areas adjacent to the shoreline and the deepest part of the river. The importance of mesh refinement goes beyond an interest in accurately simulating the hydrodynamics of the Mississippi River. Contingency plans and response operations are critically dependent on transport modeling of chemicals and petroleum products released on the river, whose accuracy also depends on the underlying mesh. Thus, in this chapter, the following background information is presented 1) previous hydrodynamic modeling of the Mississippi River 2) the relationship between finite element modeling and mesh design and 3) the Lagrangian element and random walk methods. Following the literature review, a study of the velocity fields generated from three meshes of increasing degrees of refinement and the resulting oil parcel trajectories is presented and analyzed.

5.1.1 Previous Modeling of the Mississippi River

The simplest models of the lower Mississippi river were time of travel studies developed as early warning systems for protecting drinking water intakes from spills. In the late 1960’s,
Stewart (Stewart 1967) and Everett (1971) conducted separate fluorescent dye studies at low discharges between Baton Rouge and New Orleans, Louisiana to examine the travel time and dispersion of the river. Graphs were generated for travel time versus discharge, travel time and concentration, and peak concentration. Additionally, lateral dispersion studies were conducted by monitoring dye movement through meanders. However, the conclusions from these studies could not be applied to non-solutes or spills with different initial locations. Martens (1974) also performed dye studies from Baton Rouge to West Point a la Hache but at a much higher discharges, almost three times the discharge of the previous studies. The high discharge was chosen because of its relatively linear relationship with travel time compared to low discharges that are subject to tidal influence and fluctuation. In the Martens (1974) study, samples were taken at the surface and 50 feet below the surface at three locations to investigate vertical dispersion. Within 11 to 18 miles downriver from the injection site, the surface contaminant concentration, initially double the concentration at 50 feet, was reduced to concentrations similar to the lower sample. The last travel time study was conducted by Calandro (1976, 77) for solutes traveling from the Arkansas- Louisiana state line to Plaquemine Parish and from Belle Chasse to Head of Passes. A tracer was injected to provide calibration data for a model that would generate curves to predict the leading edge, the peak, and the trailing edge of a tracer cloud for the annual range of discharges in the river. A similar model is still available, Waldon (1998) developed the River Time of Travel (RTOT) model based on a stream flow relationship that predicts the velocities of the leading edge, peak, and trailing edge and integrates velocities along a given reach of river for travel time estimates. Discharge, predicted duration and the mass of the spill are used to calculate the peak concentration. The model was calibrated using nine time of travel dye studies and has been used as an early warning system for river water users.
The first one dimensional model of the river used a weighted, four point, implicit finite difference approximation to solve the unsteady open channel flow equations with convective diffusion for the reach from Tarbert Landing, Mississippi to Venice, Louisiana (Curwick, 1988). An explicit finite difference method was chosen to solve the mass continuity equation from a Lagrangian perspective. The model was calibrated and validated using stage, discharge and dye tracer data. The study concluded flow was mostly unidirectional, turbulent and pulsating. Bi-directional flow occurs during extended periods of low flow and hurricane surges. The pulsations derive from turbulence within local eddies. Mean velocities were found to vary by as much as 20% within short time spans on the order of 15 minutes.

The United States Army Corps of Engineers (USACE) has used CH3D to simulate the three dimensional hydrodynamics and sediment transport in the lower Mississippi River in several studies. CH3D uses finite difference approximation in the horizontal and sigma stretched approximation in the vertical (Chapman, 1996). In 1998, CH3D-SED was used to simulate sediment behavior at the Old River Control Complex (ASCE 2007). The study found CH3D could not reproduce flow over and around a clay shelf or secondary currents due to an oversimplified horizontal turbulence model. Secondary currents occur in river bends as a result of the centrifugal acceleration that carries high velocity surface currents outward and low velocity near bed currents inward. In 2000, USACE used the code to model 5 flow rates, including a peak flow of 37,000 m$^3$/s, to investigate the dredging and shoaling impacts of building a 1,400 m$^3$/s diversion. In 2001, the effects of the angle of the West Bay diversion on the sediment diverted were studied using CH3D. Each of the scenarios run with the code were short sections of the river.

Barbe et al. (2000) developed a model to investigate the long term effects of dredging due to freshwater diversions along the Mississippi River for more than 306 miles of the river. HEC-6
was used to predict the river bed profiles from Tarbert Landing to Southwest Pass. HEC-6 is a 1D model that does not simulate eddies or secondary currents associated with a meandering river and varying bathymetry. Although the model incorporated discharge hydrographs into its simulations, the hydrodynamics of the river were not effectively simulated.

Most recently, Meselhe (2004) developed a two and three dimensional hydrodynamic model that reaches from Tarbert Landing to the Gulf of Mexico using TELEMAC-2D and H3D. TELEMAC-2D solves the de Saint-Venant equations through a finite element method and can perform particle tracking and computation of Lagrangian elements. H3D is a finite difference numerical model, similar to the Princeton Ocean Model that solves the three dimensional Reynolds averaged Navier Stokes equations on an orthogonal curvilinear grid. Several grids were used in the study. The coarsest grid covered Tarbert Landing to Bonnet Carre with 16,634 nodes and 31,359 elements (130.5 m to 657 m element length). The finest TELEMAC grid had 56,644 nodes and 109,918 elements (52 m to 357 m element length). Using H3D, the grid had 67,060 nodes and 130,789 elements with node spacing of 90 to 130 m across the river and 300 m in the longitudinal direction. The model was calibrated using Acoustic Doppler Current Profiler data from cross-sections south of Venice and stage level data from gages along the river (Meselhe 2004). Although the models were developed to be part of contingency plans for oil spills in Louisiana, the results of trajectory simulations were not available. The purpose of the Meselhe (2004) study was to determine the most appropriate model and grid size to use for the task of modeling the hydrodynamics of the river. A similar purpose exists for this chapter of my dissertation, except the goal was to progress one step further by determining the grid size that is necessary to most accurately simulate the hydrodynamics, within the limitations of two-dimensional modeling, and furthermore, to examine the impact grid size has on the trajectory simulations.
5.1.2 Finite Element Method and Mesh Design

The hydrodynamic code uses the finite element method to solve the two-dimensional shallow water equations. The finite element method requires the discretization of a spatial domain with finite elements, in the case of two dimensions, triangles. The resolution of the finite element mesh is determined by the smallest feature occurring in the solution. In the case of the river, the maximum element size should not be larger than any eddies or the length required to represent changes in the bathymetry. In the Lower Mississippi River, eddies are elliptical with a major axis on the order of a few hundred meters and the minor axis on the order of one hundred meters or less. With respect to the shallow areas near shorelines, the slope can change laterally from as much as 30% in 80 m or 7% in 250 m. Additionally, elements should not have large differences in size locally and ideally should have equilateral sides (Legrand et al. 2006).

5.1.3 Lagrangian Element Algorithm and the Random Walk Method

The Lagrangian frame of reference specifies a parcel’s position in time, rather than a concentration as a function of space and time (Eulerian). Approaching oil spill modeling from the Lagrangian perspective simplifies and reduces the computational requirements and eliminates potential numerical error since the advection-diffusion equation does not need to be solved.

Oil spill trajectory models typically use a Lagrangian Element method to split the oil slick area into a given number of equal mass parcels, known as Lagrangian elements (Beegle-Krause 2001; Wang et al. 2008). External forces, including wind, currents, and diffusion, are responsible for moving each parcel from its initial location to a new one over one time step. The trajectory model used in this study separates the physics of advection, random walk diffusion and wind forcing into “mover” objects and assumes the theory of linear superposition of mechanics to move individual Lagrangian elements (LE). During each time step of the trajectory simulation, each LE has a known initial position and then, each mover determines the distance and
magnitude the LE should move in that time step. The steps are then added in a vector sum and the result is used to move the LE to its new position. The trajectory model simulates horizontal mixing by a random walk method described by Csanady (1973). A diffusion coefficient is input to calculate random step lengths in the x and y directions from a uniform distribution. A uniform distribution results in a more conservative estimate for the spreading of the oil compared to another alternative, a standard normal distribution.

Application of the random walk technique as explained by Csanady (1973) begins by assuming a parcel forgets its initial velocity for a small period of time, $\beta^{-1}$ (much smaller than the time step). The total displacement due to diffusion is divided up into a number of independent steps over a period of time, $\Delta t$. The x-component of the $j$-th step can be represented as,

$$x_j = \int_{j\Delta t}^{(j+1)\Delta t} u(t') dt'$$  \hspace{1cm} (5.2)

The parcel velocities due to advection and wind only affect each step at the beginning and end for a period of $\beta^{-1}$, and the effect can be negligible if the $\Delta t$ is long enough. As a result, the parcel is said to be taking a random walk, as each step is taken at random, independent of any previous step.

A parcel has an equal probability of moving forward or backward, the probability being 1/2. The probability a parcel will be at $m$ after $N$ steps of a random walk is described as

$$P(m, N) = \frac{2}{\pi N} \exp \left( -\frac{m^2}{2N} \right)$$  \hspace{1cm} (5.3)

Over time and a series of random steps, a concentration distribution develops. If the individual step length is $l$, then $m$ can be represented as

$$m = \frac{x}{l}$$  \hspace{1cm} (5.4)
In a diffusing cluster of independently moving parcels and total mass $Q$, the material contained within the range $\Delta x$, would be

$$\Delta M = QP(m, n) \cdot \frac{\Delta x}{2l}$$  \hspace{1cm} (5.5)$$

Then, the concentration distribution would be

$$\chi = \frac{\Delta M}{\Delta x} = \frac{Q}{2l} \cdot \sqrt{\frac{2}{\pi N}} \exp \left(-\frac{x^2}{2Nl^2}\right)$$  \hspace{1cm} (5.6)$$

The concentration distribution can be transformed into the 1-D classical diffusion equation.

$$\chi(x, t) = \frac{Q}{2\sqrt{\pi Dt}} \exp \left(-\frac{x^2}{4Dt}\right)$$  \hspace{1cm} (5.7)$$

If the diffusion coefficient is

$$D = \frac{1}{2} nl^2 = ul$$  \hspace{1cm} (5.8)$$

The above equation is true based on the assumption that the parcels are moved $n$ displacements per unit time, so that the total number of steps $N$ can be related to the diffusion time, $t$; then, $t = N/n$ and $u = 1/2nl$ (where $u$ is a diffusion velocity).

As mentioned previously, the diffusion coefficient is used by the trajectory model to calculate random step lengths, $l$, in the x and y directions. Then, the random step length and direction is combined with vectors from currents and wind to move an element to its new position. The Lagrangian element and random walk techniques are applied by the trajectory model used in this study of mesh refinement. Mesh resolution can play a part during the spatial interpolation of velocity fields, affecting oil parcel trajectories even if the nodal velocities are the same as observed velocities (Pokrajac and Lazic 2002). In an effort to better understand this relationship, the impact of mesh refinement on trajectory simulations was evaluated.
5.2 Methodology

The objective of the study was to compare the velocity fields generated from three meshes of increasing degrees of refinement and the resulting oil parcel trajectories. The reach of the river modeled extends from Convent to Venice, Louisiana (Figure 5.1). The coarse mesh was obtained directly from a mesh (SL15RV3_2005) developed at the University of Notre Dame, under contract to the USACE for use in surge probability evaluation, hurricane protection planning, and coastal restoration planning (Westerink et al. 2006). The coarse mesh had an average mesh size of $\Delta x=100$ m and $\Delta y=100$ m, 65480 elements. The mesh included the area within the levees and of the Mississippi River from Convent, Louisiana to Venice, Louisiana. The medium mesh was refined from the coarse mesh using the refine function of the Surface Water Modeling System 9.2.4, which splits a single element into four elements (Figure 5.2); on average, mesh size was $\Delta x=50$ m and $\Delta y=50$ m. The fine mesh had $\Delta x=25$ m and $\Delta y=25$ m.

![Figure 5.1 Study area including locations of cross-sections across a bend (A-A’;C-C’) and a straight (B-B’)](image)
Figure 5.2 Refinement of a triangular element

Each mesh provided detailed bathymetry and elevation data used in the hydrodynamic simulations. Cross-sections of the meshes were compared to USACE survey data and found to reproduce the bathymetry and topography well (Figures 5.3 and 5.4). When the mesh was refined using SMS, the elevations of the new nodes were interpolated based on a linear interpolation scheme. The surface is assumed to vary linearly across each triangle; the equation of the plane defined by the three vertices is used to compute the elevation at any point on the triangle. Bends of the river had the most non-uniformity in bathymetry. As a result, the bends were the areas where refining the mesh was intended to enhance the ability to reproduce the bathymetry. In Figure 5.3a, the ledge near the bottom of the bend is more defined by the medium and fine mesh. In Figures 5.3b and 5.3c, refining the mesh provides a better approximation of the slope, especially on the steeper slopes. The bathymetry of the straight sections is well represented by all of the meshes; only small differences exist among the cross-sections of each mesh (Figure 5.4a, 5.4b).

The velocity field was modeled using the ADaptive Hydraulics (ADH) modeling system. ADH was developed by the Coastal Hydraulics Laboratory, Engineering Research and
Development Center, US Army Corps of Engineers as a finite element model capable of solving two dimensional, 3-dimensional Navier-Stokes equations, saturated and unsaturated groundwater flow and overland flow. The program has mesh adaption capabilities, where error is determined for each element, prompting the element to be split only if needed, and increasing refinement while maintaining computational efficiency. For the 2-dimensional shallow water simulations used for the study, the finite element formulation used linear Lagrange basis continuous functions with first or second order temporal terms to reduce numerical dissipation (Berger and Tate 2007). ADH also has the capability to correct 2-dimensional simulations for 3-dimensional vorticity effects by including vorticity as a constituent that moves with the model.

In an effort to decrease the numerical dissipation in ADH, second order accurate temporal terms are available to the user as well as the first order accurate temporal terms. Terms in the form

\[
\frac{dh}{dt} \approx \frac{h^{n+1}-h^n}{dt} \quad (5.9)
\]

can be replaced by approximations in the form:

\[
\frac{dh}{dt} \approx \left(\frac{3}{2}h^{n+1}-\frac{1}{2}h^n\right) - \left(\frac{3}{2}h^n-\frac{1}{2}h^{n-1}\right) \quad (5.10)
\]

In the case where the horizontal length scale is much greater than the vertical length scale, the shallow water equations can be derived from depth-integrating the Navier-Stokes equations. Conservation of mass implies the vertical velocity is small and the vertical pressure gradients are hydrostatic. The approximation assumes the velocity field is nearly constant throughout the depth of the water column. By setting the vertical velocity component and variations throughout the water column to zero, the shallow water equations can be derived. The assumption of a single vertical level prevents the capability of including any factor that varies with height.
An enhanced version of the numerical scheme was developed for ADH by the USACE to allow the user to choose between the two schemes or a fractional amount of each.

\[
\frac{dh}{dt} \approx \alpha \left( \frac{\frac{3}{2}h^{n+1} - \frac{1}{2}h^n - \frac{1}{2}h^{n-1}}{dt} \right) + (1 - \alpha) \frac{h^{n+1} - h^n}{dt}
\]  

(5.11)

The possible range of values for \( \alpha \) are from 0 to 1. When \( \alpha \) is input as zero, the scheme is first order accurate. When \( \alpha \) is 1, the scheme is second order accurate. The conservative form of the shallow water equations are derived from the Navier Stokes equations of conservation of momentum and mass, which will remain true even when the shallow water assumptions are invalid. The two dimensional shallow water equations can be written in conservative form as

\[
\frac{\partial Q}{\partial t} + \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + H = 0
\]  

(5.12)

where \( Q = \begin{bmatrix} h \\ uh \\ vh \end{bmatrix} \)

(5.13)

\[
F_x = \begin{bmatrix}
uh \\
u^2h + \frac{1}{2}gh^2 - \frac{h}{\rho}\sigma_{xx} \\
uvh - \frac{h}{\rho}\sigma_{yx}
\end{bmatrix}
\]  

(5.14)

\[
F_y = \begin{bmatrix}
vh \\
v^2h + \frac{1}{2}gh^2 - \frac{h}{\rho}\sigma_{yy} \\

\end{bmatrix}
\]  

(5.15)

\[
H = \begin{bmatrix}
0 \\
gh \frac{\partial z_0}{\partial x} + ghS_x \\
gh \frac{\partial z_0}{\partial y} + ghS_y
\end{bmatrix}
\]  

(5.16)

The Reynolds’ stresses due to turbulence plus the molecular stresses are represented by \( \sigma \),
\[ \sigma_{xx} = 2\rho v \frac{\partial u}{\partial x} \] (5.17)

\[ \sigma_{xy} = \sigma_{yx} = \rho v \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \] (5.18)

\[ \sigma_{yy} = 2\rho v \frac{\partial v}{\partial y} \] (5.19)

The friction slope, \( S \), can be calculated as

\[
S_x = \left\{ \frac{u}{\frac{n^2}{gh} \sqrt{u^2 + v^2}} \right\} \frac{n^2}{c_o^2 \sqrt{h}} \] (5.20)

\[
S_y = \left\{ \frac{v}{\frac{n^2}{gh} \sqrt{u^2 + v^2}} \right\} \frac{n^2}{c_o^2 \sqrt{h}} \] (5.21)

where \( C_f \) = coefficient of friction; \( n \) = Manning’s roughness coefficient; and \( C_0 \) = a dimensional conversion coefficient (1 for SI units, 1.486 for U.S. units)

The linear Lagrange basis functions that are \( C^0 \), the functions are continuous, are used for the finite element formulation

\[ Q(x, y, t) \approx \sum_j \Phi_j(x, y) Q_j(t) \] (5.22)

In non-conservative form, the equations are written in terms of velocities instead of momentum. The velocities are not subject to a conservation equation, thus, the equations will not hold across a hydraulic jump or shock. This condition is not an issue for the river. If the shallow water equations are considered in a shallow water equations in non-conservative form,

\[ M \frac{\partial q}{\partial t} + A \frac{\partial q}{\partial x} + B \frac{\partial q}{\partial y} + h = 0 \] (5.23)
\[ q = \begin{pmatrix} h \\ u \\ v \end{pmatrix} \quad (5.24) \]

\[ M = \begin{pmatrix} 1 & 0 & 0 \\ 0 & h & 0 \\ 0 & 0 & h \end{pmatrix} \quad (5.25) \]

\[ A = \begin{pmatrix} u & h & 0 \\ c^2 & uh & 0 \\ 0 & 0 & uh \end{pmatrix} \quad (5.26) \]

\[ A = \begin{pmatrix} v & 0 & h \\ 0 & vh & 0 \\ c^2 & 0 & vh \end{pmatrix} \quad (5.27) \]

and \( C = (gh)^{1/2} \)

The following test function was based on the shallow water equations

\[ \psi_{\xi}^T = \phi_{\xi}^T + \alpha (\Delta x \frac{\partial \phi_{\xi}^T}{\partial x} MP^{-1} \Lambda_x PM^{-1} + \Delta y \frac{\partial \phi_{\eta}^T}{\partial y} MR^{-1} \Lambda_y RM^{-1}) \quad (5.28) \]

Or

\[ \psi_{i}^T = \phi_{i}^T + \phi_{i}^T \quad (5.29) \]

where \( \alpha \) is a coefficient between 0 and 0.5,

\[ \Delta x = 2 \left[ \left( \frac{\partial x}{\partial \xi} \right)^2 + \left( \frac{\partial x}{\partial \eta} \right)^2 \right]^{1/2}, \Delta y = 2 \left[ \left( \frac{\partial y}{\partial \xi} \right)^2 + \left( \frac{\partial y}{\partial \eta} \right)^2 \right]^{1/2} \quad (5.30) \]

\( \xi \) and \( \eta \) are local variables with values between 0 and 1.

\[ P = \begin{pmatrix} 0 & 0 & 1 \\ 1 & -\frac{c}{g} & 0 \\ 1 & \frac{c}{g} & 0 \end{pmatrix} \quad (5.31) \]

\[ R = \begin{pmatrix} 0 & 1 & \frac{1}{c} \\ 1 & 0 & -\frac{c}{g} \\ 1 & 0 & \frac{c}{g} \end{pmatrix} \quad (5.32) \]
The weak form finite element approximation is

\[ \Lambda_x = \frac{1}{a} \begin{pmatrix} u & 0 & 0 \\ 0 & u - c & 0 \\ 0 & 0 & u + c \end{pmatrix} \]  \hspace{1cm} (5.33) \\

\[ \Lambda_y = \frac{1}{a} \begin{pmatrix} v & 0 & 0 \\ 0 & v - c & 0 \\ 0 & 0 & v + c \end{pmatrix} \]  \hspace{1cm} (5.34) \\

\[ \alpha = (u^2 + v^2 + c^2)^2 \]  \hspace{1cm} (5.35)

The weak form finite element approximation is

\[ \sum_e \left[ \int_{\Omega_e} \left( \psi_i^T \frac{\partial Q}{\partial t} - \frac{\partial \phi_i^T}{\partial x} F_x - \frac{\partial \phi_i^T}{\partial y} F_y + \phi_i^T \left( \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} \right) + \psi_i^T H \right) d \Omega_e + \right. \\
\left. \phi_{i,e}^T (F_x n_x + F_y n_y) d \Gamma_e \right] = 0 \]  \hspace{1cm} (5.36)

where the subscript e identifies a particular element; and \((n_x, n_y) = \mathbf{n}\) is the unit vector outward and normal to the boundary \(\Gamma_e\).

The Courant condition is not explicitly used in ADH. An initial time step is set as an input parameter. For the simulations presented in Chapter 5, this value was set as 100s. Then, a specified number of linear and nonlinear iterations are performed until the program converges to a solution within a set tolerance. If a solution is not reached by the number of specified iterations, the time step is reduced, and ADH performs the assigned number of iterations again until a solution is reached. The time step will also be increased if a solution is converged upon in quickly.

The default values were used in this study, which are empirical coefficients based on measured values from previous river studies. In flow around bends, helical vortices move deep water towards the inside of a bend and surface water towards the outside of bends. The secondary current is a result of an imbalance between the mean centrifugal forces and the lateral
Figure 5.3. Cross sections of three different bends in the river from USACE survey data, the coarse mesh, the medium-refined mesh and the fine mesh [figures in alphabetical order from left to right, top to bottom].
Figure 5.4 Cross sections of two different straight sections of the river from USACE survey data, the coarse mesh, the medium-refined mesh and the fine mesh [figures in alphabetical order from left to right, top to bottom].

hydrostatic pressure gradient. As a result, fast surface currents move towards the outside of the bend while a large secondary flow accumulates fluid moving at low velocities on the inside of the bend. If these 3-dimensional effects are not accounted for the mean flow path would remain in the center of the channel and the river stage level may be inaccurately represented. These potential impacts would affect the trajectory and shoreline oil distribution of the simulations. For example, less oiling could occur on the inside of the bends due to the lack of slower velocities or on the outside of bends due to the lack of lateral currents to push oil into the banks. Additionally,
if the stage level is misrepresented, the wrong shoreline type could be simulated affecting the amount of oil retained.

Simulations were run with inflow rates of 12,750 m$^3$/s, 18,200 m$^3$/s, and 28,000 m$^3$/s to represent the range of annual discharge in the Mississippi river and highlight potential differences between current vectors at the three mesh sizes. A tailwater elevation boundary condition at Venice, Louisiana was forced for each flow rate based on historical stage-discharge data provided by the New Orleans District US Army Corps of Engineers. Calibration included adjusting the eddy viscosity and roughness parameters to match the historical stage levels at eight river gage locations (USACE 2008). The eddy viscosity is calculated within the model as it runs. The eddy viscosity equation includes a user given weighting factor, the average depth, the manning’s n parameter, and the average velocity. The roughness parameter, Manning’s n, was determined based on a trial and error approach. The Lower Mississippi River has the condition where Manning’s n decreases as discharge increases (Fread 1992). Initial values tested were between 0.02 for discharge above 28,000 m$^3$/s and 0.03 for discharges near 6,000 m$^3$/s. However, the values that provided the best results were much lower varying between 0.0125 and 0.015.

Stage levels within calibrated model were within 0.15 m for all discharges. Additionally, velocity measurements, at the surface and at 60% depth, from the Carrollton gage in New Orleans were compared to depth averaged velocities output from the model. The solution accuracy was evaluated based on the convergence of solutions from the refined meshes.

The spill trajectories were modeled using the diagnostic mode of the General NOAA Operational Modeling Environment ( GNOME) (NOAA, 2002b). GNOME uses the Lagrangian Element approach to model the movement of individual oil parcels based on wind and current fields. The ADH hydrodynamic simulations provided the current fields for GNOME. Horizontal mixing is simulated using a random walk method. GNOME uses a simple three phase
evaporation algorithm. A re-floatation half life can be set to represent the adhesiveness of the oil to the shoreline as a function of substrate porosity, oil properties, vegetation, and environmental processes. The mass balance of the oil spill is tracked throughout the simulation accounting for the oil’s location and weathering (Beegle-Krause 2001; NOAA 2002). The output of the GNOME model reports the distribution of oil along the shoreline, which is used to analyze the effect of mesh refinement on trajectory modeling. The input parameters used are summarized in Table 5.1.

Table 5.1. Input Parameters for GNOME

<table>
<thead>
<tr>
<th>Input Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Currents</td>
<td>from ADH</td>
</tr>
<tr>
<td>Wind</td>
<td>None</td>
</tr>
<tr>
<td>Diffusion Coefficient</td>
<td>1.69 m²/s</td>
</tr>
<tr>
<td>Refloatation Half Life</td>
<td>24 hrs</td>
</tr>
<tr>
<td>Computational Time</td>
<td>see Table 2</td>
</tr>
<tr>
<td>Oil Type</td>
<td>Medium Crude</td>
</tr>
<tr>
<td>Amount Released</td>
<td>100 barrels</td>
</tr>
<tr>
<td>Number of parcels</td>
<td>1000</td>
</tr>
</tbody>
</table>

Spill scenarios were simulated for nine experiments that were combinations of mesh size, discharge and spill location (Table 5.2). Experiments 1 and 2 tested two spill locations for three mesh resolutions at 18, 200 m³/s. Experiments 3 and 4 tested two spill locations for three mesh resolutions at 12, 750 m³/s. Experiments 5 and 6 tested two spill locations for three mesh resolutions at 28,000 m³/s. A re-floatation half life of 24 hours was used as a result of the conclusions made in Chapter 3, even though the use of multiple half lives correlating to shoreline Rostad 2004; Waldon 1998). The dispersion coefficient accounts for horizontal mixing and affects the shape and concentration distribution of the slick. As the mesh is refined and the accuracy of current paths are improved, parcels dispersed to the outside of the slick are less
Table 5.2 Description of the Experiments

<table>
<thead>
<tr>
<th></th>
<th>Experiment 1, 2</th>
<th>Experiment 3, 4</th>
<th>Experiment 5, 6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial Parcel Coordinates</strong></td>
<td>(29 44.72 N, 90 0.83 W); (29 54.65 N, 90 7.79 W)</td>
<td>(29 44.72 N, 90 0.83 W); (29 54.65 N, 90 7.79 W)</td>
<td>(29 44.72 N, 90 0.83 W); (29 54.65 N, 90 7.79 W)</td>
</tr>
<tr>
<td><strong>River Location Description</strong></td>
<td>Straight, Bend</td>
<td>Straight, Bend</td>
<td>Straight, Bend</td>
</tr>
<tr>
<td><strong>Flow rate (m³/s)</strong></td>
<td>18,200</td>
<td>12,750</td>
<td>28,000</td>
</tr>
<tr>
<td><strong>Tracking time (days)</strong></td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Coarse Mesh</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Element size (Δx x Δy) (m)</td>
<td>110 x 110</td>
<td>110 x 110</td>
<td>110 x 110</td>
</tr>
<tr>
<td>Number of elements</td>
<td>65485</td>
<td>65485</td>
<td>65485</td>
</tr>
<tr>
<td>Number of nodes</td>
<td>35134</td>
<td>35134</td>
<td>35134</td>
</tr>
<tr>
<td><strong>Medium Mesh</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Element size (Δx x Δy) (m)</td>
<td>54 x 54</td>
<td>54 x 54</td>
<td>54 x 54</td>
</tr>
<tr>
<td>Number of elements</td>
<td>261940</td>
<td>261940</td>
<td>261940</td>
</tr>
<tr>
<td>Number of nodes</td>
<td>135753</td>
<td>135753</td>
<td>135753</td>
</tr>
<tr>
<td><strong>Fine Mesh</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Element size (Δx x Δy) (m)</td>
<td>27 x 27</td>
<td>27 x 27</td>
<td>27 x 27</td>
</tr>
<tr>
<td>Number of elements</td>
<td>1047760</td>
<td>1047760</td>
<td>1047760</td>
</tr>
<tr>
<td>Number of nodes</td>
<td>533446</td>
<td>533446</td>
<td>533446</td>
</tr>
</tbody>
</table>
By choosing a single re-floatation half life to simulate shoreline oiling, the trajectory simulations are simplified while still including the re-floatation process. The dispersion coefficient was chosen as 1.69 m$^2$/s based on observations of the river (Rathban and likely to be moved off on an inaccurate path. The time step used in the trajectory simulations was 36 s which is small enough so that a parcel will not move past an element in error. Shoreline oiling was compared for each of the experiments. Heavy oiling occurred if more than 15 parcels deposited on the shoreline within 100 m. Medium oiling sections contained 5 to 15 parcels in 100 m. Light oiling sections had 1 to 5 parcels in 100 m of shoreline.

5.3 Results

5.3.1 Mesh Resolution and Velocity Fields

Increasing the mesh resolution improved the model’s ability to reproduce known hydrodynamic features in the river. The medium and fine meshes visibly delineated the size and pattern of eddies around the bends more distinctly than the coarse mesh (Figure 5.5, a,b,c). The magnitudes of the currents, visible in the deepest part of the channel, are much larger in the fine and medium mesh, note the coarse mesh did not reproduce the ledge within the bend (Figure 5.3a). Similarly, the slow currents near the sides of the river are graded more accurately, resulting in current vectors that do not overestimate the flow in shallow areas. The velocity vectors within the straight section for the three meshes are almost identical (Figure 5.5, d,e,f). Simple bathymetry and lack of meanders reduces the need for increased mesh resolution, the coarse mesh is sufficient. The value added by increased mesh resolution was also analyzed by comparing the velocity profiles within a bend and a straight section for different flow rates.

The similarities between the velocity profiles for the coarse, medium and fine mesh indicate the current field is well represented even with the coarse mesh (Figure 5.6 a,b). The coarse mesh hydrodynamic results have a smoother velocity profile across the river within the
bend and the straight at all tested flow rates. More nodes lead to the calculation of more nodal velocities and less of an averaging effect. The coarse mesh underestimates the velocity at 18,500 m$^3$/s by as much as 0.09 m/s, at 700 m from the river bank, and 0.15 m/s in the center of the channel at 12,750 m$^3$/s. An underestimated velocity can result in as much as a 20% error in travel time and increase the time for potential shoreline interaction. The slower velocities indicate the coarse mesh has elements that stretch from the deepest part of the river to a much shallower area.
Figure 5.6. Velocity Profiles for coarse, medium and fine mesh size across a bend (cross section A-A’) and a straight (cross section B-B’) for 18,500 m$^3$/s (top) and 12,750 m$^3$/s (bottom)
Figure 5.7 Velocity profile across a bend with re-circulating eddies (cross section C-C’)
creating an average velocity that inaccurately represents the actual velocities in the steeper
sloped areas in the river’s bathymetry. Although the cross-sectional average velocity is the same
for each mesh within 5% for 18,500 m$^3$/s and 12%, for 12,750 m$^3$/s, the local variations near the
shorelines are more likely to impact trajectory results. The currents nearest to the shoreline seem
to be overestimated by the coarsest mesh at all flow rates. Additionally, the coarse mesh lacked
did not reproduce re-circulating eddies as well as the fine and medium mesh (Figure 5.7).

The Galerkin Least Squares method employed in ADH minimizes the error of the
approximating functions by employing a central difference scheme that uses weighted residual
formulations for momentum equations. The conservation equations maintain stability, locally on
the elements and globally across the mesh. ADH provides second order accuracy spatially and
temporally. As the grid is refined and the time step is reduced, the spatial and temporal errors
should asymptotically approach zero. Since the grid size was divided by 2 for each refinement of
the mesh and the accuracy of the method is of second order spatially, the error was expected to
be divided by 4 at each refinement. When the mesh is refined and the error is reduced, the
solution converges to a constant solution. Grid convergence is related to the rate that the
difference between the exact and numerical solution approaches zero as the grid size approaches zero. To evaluate the order of convergence, \( p \), three solutions, \( u_1 \), \( u_2 \), \( u_3 \) (taken from the velocity profile where the maximum difference occurs between grid sizes) and a constant grid refinement ratio of 2 was used.

\[
p = \frac{\ln\left(\frac{u_3 - u_2}{u_2 - u_1}\right)}{\ln(2)} = 1.92
\]  

(5.37)

The sampled velocity profiles demonstrate convergence with refinement within the expected range based on the order of accuracy (Figure 5.6) and refinement additionally increased the available information about bathymetry producing results that converge to a solution that captures observed river features.

### 5.3.2 Mesh Refinement and Oil Trajectory Simulations

Mesh resolution did impact on the oil distribution along the shoreline (Figure 5.8). Although the heaviest oiling occurred in the same locations the majority of the time, the length of shoreline that experienced heavy oiling was approximately 4.5 km less in the fine mesh as compared to the coarse mesh. However, the concentration of heavily oiled areas in the coarse mesh increased by as much as 15% of their original concentration. Medium oiled areas decreased in length by 3.7 km in the fine mesh compared to the coarse mesh. Coincidentally, the amount of light oiling in the fine mesh increased by 23% as compared to the coarse mesh. Overall, only a 3.4% decrease was found in the length of shoreline that was oiled in the fine mesh, but the oiling patterns were similar for all three meshes. The mass balance showed similar trends, the amount of oil retained by the shoreline at the end of the 3-day simulations was greatest for the coarse mesh, yet the percentages were very similar for all of the mesh resolutions (Table 5.3). More oil was transported out of the study area using the fine and medium resolution meshes, possibly as a result of the higher predicted velocities by these two meshes.
Figure 5.8 Shoreline oil distribution along the Mississippi River after a spill near New Orleans, at 18,500 m³/s for coarse, medium and fine mesh resolutions (in alphabetical order from top). (Red line represents heavy oiling (more than 15 parcels in 100 m); Orange represents medium oiling (5 to 15 parcels in 100 m); Green represents light oiling (1 to 5 parcels in 100 m))
Table 5.3 Mass Balance of Spills after 3-day simulation by discharge and mesh resolution

<table>
<thead>
<tr>
<th>Discharge (m³/s)</th>
<th>Initial Spill Location (degree minutes)</th>
<th>Coarse Mesh</th>
<th>Medium Mesh</th>
<th>Fine Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Evaporated (%)</td>
<td>Retained by Shoreline (%)</td>
<td>Floating in River (%)</td>
</tr>
<tr>
<td>12,750</td>
<td>29 54.65 N, 90 7.79 W</td>
<td>36.1</td>
<td>48.8</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>29 44.72 N, 90 0.83 W</td>
<td>37.5</td>
<td>49.6</td>
<td>12.9</td>
</tr>
<tr>
<td>18,200</td>
<td>29 54.65 N, 90 7.79 W</td>
<td>36.3</td>
<td>62.7</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>29 44.72 N, 90 0.83 W</td>
<td>35.3</td>
<td>61.4</td>
<td>0.6</td>
</tr>
<tr>
<td>28,000</td>
<td>29 54.65 N, 90 7.79 W</td>
<td>37.6</td>
<td>53.2</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>29 44.72 N, 90 0.83 W</td>
<td>34.8</td>
<td>49.1</td>
<td>5.4</td>
</tr>
</tbody>
</table>
Refining the mesh more accurately delineated current paths and thus, affected the slick shape traveling down river. Faster velocities tend to elongate the slick, keeping it centered in the channel and away from shorelines. As the mesh was refined the fastest velocities in the deepest parts of the channel were more accurately defined (Figure 5.5a). As a result, the slick was more likely to remain in the channel during the trajectory simulations using the medium and fine resolution meshes. The averaged current vectors calculated in the coarse mesh that may have pushed oil on the shoreline were better represented in the medium and fine mesh resulting in more of the oil transported along the direct path of the main current.

5.4 Discussion

Since the hydrodynamic results converged to a more accurate solution, it was assumed that increasing the mesh resolution would also improve the accuracy of the trajectory simulations. However, the hydrodynamics only affect the advection of the parcels. The diffusion of the parcels adds a random effect that prevents a simple analysis of trajectory simulations. Changing the diffusion coefficient will alter the shape of the slick and alter the location of shoreline oiling (Discussion of the impact of the dispersion coefficient is discussed in the Appendix). The similar patterns in degree and distribution of oil on the shoreline between the three meshes are a good indicator that the trajectory is accurate based on the input parameters or that the mesh resolution does not have a major impact on the trajectory. However, the variation in the degree of oiling by location, less heavy and medium oiling and more light oiling with the fine mesh, provides evidence that the mesh resolution is significant.

The presence of oil in more concentrated distributions suggests the coarse mesh may overestimate the lateral currents around bends, carrying more oil to the shoreline than is accurate. Additionally, the direction and overestimation of current magnitudes in the shallow areas near the shorelines appears to be a function of element size, since the coarse mesh had the most oiled
shoreline overall. However, the greater details in the finer mesh allowed for capturing of the recirculating eddies in the bends and resulted in a redistribution of oil in the inner and outer bends with more oiling occurring over shorter shoreline lengths specific to more descriptive current paths. These smaller scale features were not captured in the coarse mesh. Overall, the mesh resolution was determined to impact the mass balance and shoreline oil distribution. The similarities between the fine and medium mesh in patterns and distribution do not justify requiring a fine mesh. Computational efficiency is important for emergency response forecasting trajectory models, thus, the extra time required to run the fine mesh is not justified by the minimum amount of variation from the medium mesh results (Table 4). Using the fine mesh requires between 40 to 45% more CPU time than the coarse mesh. Incorporating multiple re-floatation lives would further improve the accuracy of the shoreline oil distribution, as was concluded in the comparisons of the trajectories and shoreline survey data after the DM932 spill in Chapter 4. It would have been very difficult to extract the effects of shoreline variation from the impact of mesh resolution in this study, now that the variation in patterns and degree of oiling has been observed in this study.

Table 5.4 CPU Time for ADH and GNOME Simulations (in seconds)

<table>
<thead>
<tr>
<th>Mesh Resolution</th>
<th>Coarse</th>
<th>Medium</th>
<th>Fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td># Total Iterations</td>
<td>ADH</td>
<td># Total Iterations</td>
<td>ADH</td>
</tr>
<tr>
<td>Experiment 1 &amp; 2</td>
<td>8.65E+04</td>
<td>2.5E+04</td>
<td>3.40E+05</td>
</tr>
<tr>
<td>Experiment 3 &amp; 4</td>
<td>1.21E+05</td>
<td>2.7E+04</td>
<td>4.75E+05</td>
</tr>
<tr>
<td>Experiment 5 &amp; 6</td>
<td>2.17E+05</td>
<td>3.18E+04</td>
<td>8.48E+05</td>
</tr>
</tbody>
</table>

5.5 Conclusion

The accuracy of the hydrodynamic solutions for three mesh resolutions was assessed based on the convergence of velocity profiles to a single profile. The hydrodynamic results were used in a Lagrangian element trajectory model that included the random walk method to define
the relationship between mesh refinement and parcel tracking. River features were well
represented and velocity accuracy was improved by refining the mesh, highlighting the presence
of eddies in the bends, the strong correlation of velocity magnitude to the bathymetry, and the
need for increased mesh resolution to model the slope in the shallow areas. Also, oil trajectory
simulations were impacted by the differences in velocities between meshes. Calculating
improvement in accuracy of trajectory simulations due to refined mesh and improved velocity
accuracy was difficult since other processes such as diffusion were acting simultaneously.
Finally, the medium mesh is preferred for its ability to capture river features, while maintaining
computational efficiency. However, the similarities in the trajectory model results suggest the
coarse mesh provided acceptable results and would be sufficient for future studies.
Important processes governing the fate and transport of light petroleum hydrocarbons in the Lower Mississippi River are not adequately represented in existing oil spill models. In response, this dissertation introduced three methods to include the effects of dynamic annual discharges on the type of shoreline interacting with floating oil, the impact of shoreline type variation on shoreline retention and re-floatation, and the potential of oil-mineral aggregate formation that results from the high suspended sediment concentrations in the river and other contributing environmental factors. The methodology and resulting conclusions were verified by implementing the methods introduced in previous chapters to hindcast the trajectory and assess the mass balance of the DM932 spill that occurred in New Orleans on July 23, 2008. To further investigate the validity of the methods and resources used in this dissertation, a final study examined the impact of mesh resolution on hydrodynamic and trajectory simulations. The following chapter summarizes the work and conclusions of this dissertation.

Spatially detailed maps of the shoreline were established in between the levee structures of the Lower Mississippi River. The maps represented the shoreline type interacting with the river by flow rate. Depending on the elevation of shoreline and stage level, shoreline type varied from mud/sand or rip rap to high and low vegetation, as the river overtopped the natural levees or rip rap. To include the most accurate shoreline representation, multiple re-floatation half lives were implemented in the trajectory model to represent the change in shoreline type and the coinciding change in shoreline re-floatation and retention.

The behavior of oil in the natural environment is complex and many competing factors determine the extent of shoreline oiling. As river velocities increase with flow rate, the time oil
interacts with the shoreline is minimized. The oil slick elongates, tends to stay in the middle of
the channel, and moves quickly past shoreline. However, if oil does reach the shoreline, it most
likely will be retained due to the increased presence of vegetation at high flow rates; vegetation
will retain oil for long periods of time due in part to the adhesiveness of the oil to organics, the
large surface area exposed by leaves and stems, and the characteristic low elevation within
vegetated areas behind the natural levees or rip rap. Thus, river geometry becomes an important
factor as way for oil to reach the shoreline. As current vectors change direction around the bend,
oil parcels are moved towards the outside where velocities decrease and heavy oiling can result.
The above instance represents one result of the trajectory simulations and illustrates the
dependence of shoreline oiling on flow rate, shoreline type and river geometry.

At low and medium discharges, the shoreline type varies substantially down river. The
presence of mud shorelines and sand bars, both with short re-floatation half lives, encourage the
distribution of oil to shift downstream over time. Re-floatation is a significant transport process
in the Lower Mississippi River, assuming oil is permanently retained after deposition is false.
These simulations highlighted the need to incorporate multiple re-floatation half lives in a single
simulation. This conclusion is critical for future contingency planners for two reasons, (1)
considering most post-spill surveys are conducted within a week of the spill and clean-up
operations continue into the following months, there would be plenty of time for oil
redistribution on the shoreline and (2) modeling shoreline retention with a single re-floatation
half life for an area with multiple shoreline types will result in significant errors in the degree
and location of oil predictions.

Ocean oil spill models utilize a breaking wave theory to describe the process of the
vertical dispersion of oil and droplet formation. An additional algorithm is used to predict the
amount of the oil that will combine with sediment and fall out of suspension. This sedimentation
calculation is based on the energy dissipation rate in breaking wave conditions, the concentration of sediments and oil droplet concentration. After the Rio Desaguadero spill in freshwater and experimental research, the formation of oil-mineral aggregates was documented as a significant removal process, expanding the need to model suspended particle-oil interactions to rivers. Unfortunately, the breaking wave theory is not applicable to rivers. In response to this issue, the potential for OMA formation was examined for four seasons based on the different combinations of salinity, suspended sediments, discharge and temperature along the river. Empirical relationships from laboratory and field studies were applied to calculate the percentage of OMA that could form under the existing conditions. These estimates are based on the assumption enough droplets are dispersed into the water column. The rate of vertical mixing could further limit the estimates of OMA. Natural conditions, sediments and simultaneously occurring fate and transport processes will have an impact that will either enhance or inhibit the OMA potential discussed in this study.

The potential OMA formation ranged from 0 to 36 percent, indicating a strong dependence on oil type and season. For the denser, more viscous oil, IF30, salinity was the limiting factor for all seasons, except fall. During the fall, the lack of suspended sediments was the limiting factor for all oils. Both salinity and suspended sediments had a critical level that had to be reached before OMA formation would accelerate rapidly. Suspended sediment concentrations would have to reach 250 mg/L to negate sediment availability as a limiting factor. During the winter and spring, the conditions are beneficial for OMA formation for BAL110 and Arabian Medium Crude since the average suspended sediment concentrations are much larger than the critical sediment concentration. During the summer peak flood event, the maximum OMA potential for the three oils occurred due to the high suspended sediment availability, warm temperatures and retreating salt wedge. The calculations for the summer peak result in
overestimation of potential OMAs that could form in the natural environment. This assumed overestimation prompts the necessity of validating OMA formation with real spill data.

By adding OMA formation into a weathering model such as ADIOS2, the effects on the mass balance were examined. Although adding OMA reduces the amount of evaporation that occurs, both processes contribute to the reduction of available oil that could be beached or transported within the river system. OMAs remain buoyant in the water column, further reducing the potential for oil to be beached. By examining the distribution of suspended sediments across the channel and at bends, the potential for more OMA to form exists in the center of the channel through straight sections and to the outside of the bend where the highest suspended sediments exist. If more OMA is forming at the outside of the bend, less can be deposited as typically occurs on the shoreline within the bend. Depending on the location of the spill, the OMAs could remain buoyant through Head of Passes, allowing some amount of the spill to be dispersed into the Gulf of Mexico. Overall, including OMA as an important process in fate and transport modeling in the Lower Mississippi River offers a way to explain a lack of shoreline oiling documented after previous spills and/ or completes the mass balance by accounting for all sources of oil removal.

The DM932 incident provided the opportunity to validate the methods of including multiple shoreline types and re-floatation half lives and of including OMA in mass balance estimates. The total area of oiled shoreline from the DM932 spill was calculated for each shoreline type from the SCAT data and the distribution was analyzed. The SCAT data oil distributions were compared to results from hindcast modeling that varied the re-floatation half life parameter. This parameter must be chosen carefully, especially when only one half life value is implemented. The re-floatation half life of 24 hours most accurately simulated the
shoreline oiling present in the SCAT data when the oil distribution by shoreline type and location were compared. Overall, the shortest re-floatation half life of 1 hr under predicted the amount of oil retained by the shoreline, suggesting more oil was floating in the river at the end of the simulation or had exited past the lower boundary. Areas of scrub shrub and rip rap that tend to retain oil longer were significantly under represented by this half life. This observation is important since a re-floatation half life of 1.5 hours was used for initial trajectory forecast by NOAA.

The differences between the hindcast modeling and the SCAT survey data are a result of the limitations of the model. Although using a single half life provided relatively good results, the use of multiple half lives for each shoreline type increased the ability to model the degree of oiling in each shoreline segment more accurately. Some issues with shoreline segments were still not resolved, as unexpected obstructions blocked the shoreline, such as a ship or barge. Over 400 ships were inspected and washed during the cleanup process; a few areas of shoreline were completely protected from oiling as a result of the stationary barges. Finally, the most difficult aspect of modeling the DM932 spill was the decrease in river stage level that led to oiling at multiple elevations of rip rap, over banking and pooling in batture (low lying) areas behind rip rap, and stranding of oil not accessible for re-floatation. The dynamic and complex nature of the shoreline oiling across multiple shoreline types prevents very precise analysis of oil distribution and would insert error into any re-floatation half life implemented.

In addition, the potential of oil- mineral aggregate formation was estimated to remove 2 to 5% of the total oil spilled, explaining the fate of oil remaining in the environment, and completing the mass balance. In calculating an OMA estimate for the DM932 spill, the approach for assuming the most conservative estimate of OMA formed based on the limiting factor was determined accurate. Calculating OMA based only on suspended sediments provided an estimate
that was too high to fit in the mass balance from the spill. Based on the ARC content of the fuel oil spilled and the temperature during the spill, the second estimate was for 31% of oil to be taken up by OMA. However, the estimate based on salinity was much lower and approximated the amount of oil missing from the mass balance for the spill.

The accuracy of the hydrodynamic solutions for three mesh resolutions was assessed based on the convergence of velocity profiles. The hydrodynamic results were used in a Lagrangian element trajectory model that included the random walk method to define the relationship between mesh refinement and parcel tracking. River features were well represented and velocity accuracy was improved by refining the mesh, highlighting the presence of eddies in the bends, the strong correlation of velocity magnitude to the bathymetry, and the need for increased mesh resolution to model the slope in the shallow areas. Since the hydrodynamic results converged to a more accurate solution, it was assumed that increasing the mesh resolution would also improve the accuracy of the trajectory simulations. However, the hydrodynamics only affect the advection of the parcels. The diffusion of the parcels adds a random effect that prevents a simple analysis of trajectory simulations. The similar patterns in degree and distribution of oil on the shoreline between the three meshes are a good indicator that the trajectory is accurate based on the input parameters.

By affecting parcel path and slick shape, the mesh refinement did alter the trajectory results, but not enough to justify requiring a fine mesh. The presence of oil in more concentrated distributions suggests the coarse mesh may overestimate the lateral currents around bends, carrying more oil to the shoreline than is accurate. Additionally, the direction and overestimation of current magnitudes in the shallow areas near the shorelines appears to be a function of element size, since the coarse mesh had the most oiled shoreline overall. However, by delineating the recirculating eddies in the bends, more oil was distributed in fine meshes on the adjacent shoreline
when compared to the coarse mesh with less distinct eddies. Based on the above observations, the medium mesh was preferred for its ability to capture river features, while maintaining computational efficiency. However, the similarities in the trajectory model results suggest the coarse mesh provided acceptable results and would be sufficient for future studies.

In conclusion, this dissertation demonstrates and validates methods to incorporate variability in discharge, diversity in shoreline, and the formation of OMAs into existing models used by spill responders that improved the accuracy of fate and transport modeling in the Lower Mississippi River.
REFERENCES


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APPENDIX

MODEL SENSITIVITY TO DIFFUSION COEFFICIENT AND TIME STEP

Horizontal mixing or horizontal dispersion includes the processes of molecular diffusion and mechanical dispersion. Both are modeled by a constant diffusion coefficient. As discussed in Chapter 5, diffusion is added to the drift velocity as a fluctuation component calculated by a random walk method.

The horizontal mixing coefficient can be estimated reasonably well in flow through straight channels based on the hydraulic properties of the channel (Overstreet and Galt 1995). The accuracy decreases for straight irregular sided rivers. In meandering rivers with sharp bends, the lateral turbulent mixing is much greater than in straight sections, with a rule of thumb of bend diffusion coefficients being six times greater than straight sections. Due to the high variability of the coefficient in rivers, direct observation is the best option.

Previous modelers have taken the approach of testing a range of diffusion coefficients and comparing the results to available data from previous spills. In the application of OILMAP to Prince William Sound, Alaska, the horizontal diffusion coefficient was varied from 10 to 100 m$^2$/s, an acceptable range for storm and open water conditions within the coastal area (French-McCay 2004). The value of 50 m$^2$/s provided results that were the most similar when compared to observations after the Exxon Valdez spill. In this hindcast, wind and localized dispersion was responsible for shoreline oiling over a wide area. In another study by French-McCay, a spill within a shipping channel, inland of Narragansett Bay, was modeled using a constant diffusion coefficient of 0.1 m$^2$/s (French-McCay et al. 2006). French-McCay also calculated the dispersion coefficient in the Narragansett Bay study. The coefficients were calculated according to the following equations, reflecting the local depth and current speed at each time step.
\[ D_{xx} = 14.2 \left( \frac{2g}{c_h} \right)^{\frac{1}{2}} UH \]  
(A.1)

\[ D_{yy} = 14.2 \left( \frac{2g}{c_h} \right)^{\frac{1}{2}} VH \]  
(A.2)

where \( g \) is gravity, \( H \) is local depth (m), \( U \) and \( V \) are the velocities in the x and y directions and \( C_h \) is the Chezy coefficient \( (C_h=(8*f/g)^{1/2}, \text{where } f \text{ is the friction coefficient.} \) In the above equation, the bottom friction does not have a significant effect on the diffusion coefficient. Current speed has the most impact on the diffusion.

Copeland et al. 2006 used values of 0.1, 1, and 10 m\(^2\)/s for the diffusion coefficient, \( D_x \) in the application of a trajectory model to the offshore Brunei Shell Platform and surrounding coastal area. These values were scaled according to the following equation

\[ \text{step size} = (2 * D_x t)^{0.5} \]  
(A.3)

The smallest value was chosen to allow the wind and current effects to be clearly seen in the results. The smaller diffusion coefficient accounted for the lack of variation in the trajectory and small amount of particle dispersion. The comparison of diffusion coefficients showed an expected widening of the plume as the dispersion coefficient increased. Copeland et al. 2006 observed only minimal changes in total shoreline deposition (less than 10 ppt), even though the diffusion coefficient was varied by a factor of 100. In this application, the wind and advection effects dominated, so that diffusion had little overall impact. Note that the diffusion coefficient used in each of the above studies was a constant and isotropic, operating in the same capacity in the x and y directions.

To observe the impact of the diffusion coefficient on slick shape and trajectory as well as shoreline deposition, a simple study was conducted using four diffusion coefficients of 0.5, 1, 1.69 and 5 m\(^2\)/s. ADH was used to simulate the current field for a discharge of 18,500 m\(^3\)/s for a stretch of the Lower Mississippi River that contains both bends and straights. Then, GNOME
was used to simulate a spill amount of 100 barrels, using 1000 parcels, no wind effects, and a 0.01 hour time step. The simulation length was 10 hours. The re-floatation half life used was 24 hours, thus, re-floatation is limited and the effect of the diffusion coefficient can be the focus. All other methods and input parameters were the same as those discussed in the main chapters of this dissertation.

The following images are from the simulations using different diffusion coefficients after 1, 2, and 10 hours. The one and two hours simulations highlight the changes in slick shape (Figure A1 a-d; Figure A2 a-h). As the diffusion coefficient is increased, the slick spreads radially, eventually causing shoreline oiling when the slick expands to the shoreline. The peak concentration has the same travel time in each simulation; however, a few parcels are diffused ahead of the slicks with the higher diffusion coefficients (Figure A1 b-d). When the diffusion coefficient is increased, heavier oiling occurs closer to the spill release location and as a result, less oiling occurs further downstream (Figure A1 i-l). The diffusion coefficient of 5 m$^2$/s causes a considerable amount of shoreline oiling due to the slick spreading to both sides of the shoreline (Figure A1 d). The percentage of total oiling was the same for each simulation, but the location and degree of oiling varied depending on the diffusion coefficient.

Without wind, the river geometry and diffusion are the only causes of shoreline oiling. The results show the diffusion coefficient has a significant impact on the slick shape and shoreline oiling. The diffusion coefficient must be chosen carefully; an overestimation of diffusion within the confines of the river banks can result in a major over prediction of oiling of the shoreline. Calibrating the coefficient based on actual spill data is the best method for selection. The value used in the studies of the Lower Mississippi River in this dissertation was 1.69 m$^2$/s. Since this value is based on observations of the river and provided results that matched survey data from the DM932 spill, it should be considered to be an acceptable value.
Figure A.1. Trajectory simulations around a bend using diffusion coefficients for 0.5, 1, 1.69, and 5 m²/s (in columns from left to right respectively). Results after 1 hour (a - d); Results after 2 hours (e – d); Results after 10 hours (i – l).
Figure A.2. Trajectory simulations through a straight using diffusion coefficients for 0.5, 1, 1.69 and 5 m²/s (in columns from left to right respectively). Results after 1 hour (a - d); Results after 2 hours (e – d); Results after 10 hours (i – l).
In an additional study, the choice of time step was evaluated. Trajectories were simulated using four time steps of 200 s, 100 s, 36 s, and 25 s. Although the results were similar for all time steps, the largest time step resulted in more shoreline oiling in areas where the channel curved and current vectors moved oil straight into the shoreline. The time steps of 36 s and 25 s had the same locations and degree of shoreline oiling, suggesting 36 s is sufficient.
VITA

Samantha Danchuk was born and raised in South Florida. From an early age, she has dedicated her time towards environmental causes and promoting the preservation of natural coastal resources. She graduated from Florida State University with a Bachelor of Science degree in civil and environmental engineering in 2004. The following year, she received her Master of Science degree in environmental engineering from the University of California, Berkeley. In the fall of 2005, she began her pursuit of the Doctoral degree in civil engineering at Louisiana State University. After graduating in the spring of 2009, she will continue to develop and implement effective solutions to coastal problems worldwide.