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RELATIONSHIPS BETWEEN PARTICLE PROPERTIES AND SCATTERING IN COASTAL WATERS OF THE NORTHERN GULF OF MEXICO INFLUENCED BY THE MISSISSIPPI RIVER

by

Bruce Alan Spiering

Abstract of a Dissertation Submitted to the Graduate School of The University of Southern Mississippi in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

May 2010
ABSTRACT

RELATIONSHIPS BETWEEN PARTICLE PROPERTIES AND SCATTERING IN COASTAL WATERS OF THE NORTHERN GULF OF MEXICO INFLUENCED BY THE MISSISSIPPI RIVER

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This study was conducted to determine how the characteristics of an assemblage of suspended particles, including their composition and size affect the relationship between the optical scattering coefficient \( b (\text{m}^{-1}) \), and the dry mass of the particles in suspension. Knowledge of the scattering to total suspended matter (TSM) ratio, i.e. the mass specific scattering coefficient \( b^* (\text{m}^2/\text{g}) \), is important because the light detected by optical imaging sensors used for remote sensing is the light that has been scattered by particles back through the water surface. If this ratio is not known or varies within the region of interest, accurate estimates of TSM using remotely sensed data will not be accurate. The hypothesis of this study is that \( b^* \) is not constant in the study area, and that change in \( b^* \) within the study area can be attributed to change in particle composition and change in the number concentration of particles relative to their diameters (i.e. the particle size distribution function, PSD) for the range of particle sizes important to light scattering (approximately 0.01 to 250 µm for this study).

The primary objective of this study was to determine the variability in \( b^* \) within the study area, i.e. the region where the main channel of the Mississippi River enters the Gulf of Mexico and mixes with marine water of the Louisiana continental shelf, and to characterize the change in \( b^* \) relative to change in the percent organic fraction (%OM) of
TSM and the slope parameter $\xi$ of the assumed power law PSD. Additional objectives were to determine if $b^*$ and particle characteristics remained consistent within prescribed geographic regions within the study area. These regions included the location just outside the river mouth at Southwest Pass, main sediment plume extending from the river mouth, shelf waters not directly in the main plume and the region surrounding the Birdfoot Delta that receives river water through the myriad of outflows of the main channel. This characterization was done using statistical regression analysis of measured particle properties and through the use of modeling of particle optical properties using the Mie theory for homogeneous spheres.
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14. Original and Adjusted Values of Average $\xi$, O2, and Comparison Between Modeled $b_m$ and Measured $b_r$, and the New $b_{r/b}$. The First 3 Rows Represent Original Data, the Next Three Rows Represent Adjustments to $\xi$ Made in Chapter III and the Final 2 Rows Represent the Final Adjustments in Chapter IV that Best Matched Measured Data.......................... 153
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Equation

1. \[ R_{rs}(\lambda) \approx T \frac{f}{Q} \frac{b_{p}(\lambda)}{a(\lambda) + b_{x}(\lambda)} \] .................................................................................. 40

2. \[ mass_{total} = \sum_{i} mass(D_i) = \sum_{i} kD_i^{-\frac{6}{5}} \pi \left( \frac{D_i}{2} \right)^3 (\rho_M (1 - OM) + \rho_{OM} OM) \] ..........92
CHAPTER I

RELATIONSHIPS BETWEEN PARTICLE PROPERTIES AND SCATTERING IN COASTAL WATERS OF THE NORTHERN GULF OF MEXICO INFLUENCED BY THE MISSISSIPPI RIVER

Introduction

Particles suspended in marine waters both influence and are influenced by a wide variety of important biogeochemical processes. Currently, researchers utilize both \textit{in situ} and remote sensing methods to investigate characteristics of these particle suspensions. One important characteristic is the mass concentration of the particle assemblage (i.e. Total Suspended Matter or TSM (mg/l or g/m$^3$)). To obtain such a measurement using remotely sensed images the relationship between the optical properties of the particle assemblage and its mass concentration must be known or predictable throughout the observed region. Much of the current understanding of remote sensing of marine particle suspensions is based on relationships developed from investigations in the open ocean where optical properties are assumed to be primarily controlled by phytoplankton. In coastal regions, where there may be a wide range in the composition and size distributions of particle assemblages, variability in the relationships between biogeochemical properties and optical properties is not as well understood. Common filtering techniques used to investigate suspended particles do not account for important characteristics of TSM such as numbers of particles, sizes, densities and refractive indices. Without this additional information it is difficult to estimate the true cause of variability in the optical scattering and absorption relative to the variability in mass concentration.
Light scattering and absorption by an assemblage of particles is a function of the integrated scattering and absorption over the entire range of sizes and refractive indices present (Bohren and Huffman 1983). Similarly the dry mass of the assemblage is a function of all particle sizes (i.e. volume) and densities present. The study of the relationship between optical scattering and particle mass must consider the influence of all these parameters. Studies of optical properties and suspended particles in other coastal regions have confirmed the scattering to TSM ratio, or mass specific scattering coefficient $b^*$ ($m^2/g$), is not constant (e.g., Babin et al. 2003; Binding et al. 2005; Loisel et al. 2007).

The remote sensing reflectance is proportional to particle backscattering in the relationship $R_{rs}(\lambda) = G b_b(\lambda)/(a(\lambda)+b_b(\lambda))$, where $\lambda$ is wavelength and $G$ represents the two-way transmission of light through the water’s surface, illumination and observation angles, the volume scattering function and sea-state (Gordon 1975; Mobley 1994). Because of the importance of backscattering in the remote sensing relationship, particle scattering and backscattering will be the focus of this work.

Analysis of particle composition and optical scattering have demonstrated that the variability in the scattering to TSM ratio accounts for errors in TSM estimates obtained from modeled and measured remotely sensed reflectance values (Stumpf and Pennock 1989; Binding et al. 2005). Studies in coastal waters of Europe demonstrate that the scattering and backscattering to TSM ratios vary with change of assumed particle density and refractive index, and further, the ratios vary with change in the particle size distribution (PSD) function (Babin et al. 2003; Loisel et al. 2007). This observed variability in particle characteristics also appears to follow local trends in spatial
variability, e.g. near-shore particles differ from off-shore particles (Babin et al. 2003; Loisel et al. 2007). However, trends observed in the Baltic Sea were not consistent with observations in other European coastal locations (Babin et al. 2003). In a multi-year study at nine locations in near shore (depth < 30 m) U. S. coastal waters of the Atlantic, Pacific and Gulf of Mexico, Sullivan et al. (2005) found distinctive regional patterns in both bulk index of refraction and the particle size distribution function.

There is clearly a need to have a regional understanding of particle assemblage composition and size distribution characteristics, and of the variability in optical scattering and absorption relative to TSM. Knowledge of the spatial variability in particle assemblage, or bulk, particle density relative to bulk index of refraction, and characteristics of the particle size distribution function will provide greater insight into developing algorithms that will increase the accuracy of TSM estimates obtained using remote sensing methods.

This research aims to increase the understanding of the cause or major influences on the observed variability in optical properties relative to TSM in the coastal waters influenced by the Mississippi River plume where there is expected to be a wide range of TSM concentrations and optical conditions. Specifically, this work addresses the issue of how the optical scattering to TSM ratio ($b^*$) varies relative to variation in particle composition and size distribution. The area for this study was chosen because it is a region of highly variable particle characteristics where complex mixing between river water and unbounded marine waters occurs. Because the mixing can occur over a relatively large area, the synoptic views provided by remote sensing methods can potentially provide an increased understanding of the biogeochemical processes.
throughout the entire area. It is therefore important to know the spatial variability in the relationship between optical and particle properties.

The current study was conducted in the Northern Gulf of Mexico and the Louisiana Shelf where the Mississippi River supplies an average of 18,400 m$^3$/s of fresh water and 94,000 tons/yr of suspended matter, including minerals, organic matter, nutrients, metals, salts and other material through the main channel at Southwest Pass and the myriad outlets of the Birdfoot Delta (Milliman and Meade 1983; USGS NASQAN 1996-2005, St. Francisville, LA). Numerous researchers have studied the impact of suspended sediments on a variety of biogeochemical processes including primary production (Lohrenz et al. 1999, Green et al. 2008), eutrophication and hypoxia (Walker and Rabalais 2006), sediment transport (Corbett et al. 2004; Dagg et al. 2008), and carbon flux (Del Castillo and Miller 2008). To interpret the variability in the scattering to TSM ratio relative to the processes noted above, knowledge of the concentrations of suspended particles, their sizes, densities, and refractive indices is necessary.

One common method currently used to study the transport and fate of river supplied suspended particles is to collect in situ water samples to obtain the dry mass of the total suspended matter (e.g. USGS NASQAN; Walker 1996; Corbett 2004; Dagg et al. 2008). These results are then utilized by many researchers to monitor or track the sediment laden river effluent. Similar observations are also made with remotely sensed images, using algorithms derived from the in situ samples to estimate TSM throughout the region of interest (Stumpf 1988; Walker 1996; Walker et al. 2005; Salisbury et al. 2004; Miller and McKee 2004).
However, determinations of mass concentrations of TSM by filtration provides no information about the number of particles, their size, density or optical scattering and absorption characteristics, except for the minimum particle size captured by the filter used. In order to obtain information about the bulk particle density and index of refraction, TSM obtained from the filtration process can be further characterized by its relative amounts of particulate organic matter (POM) and particulate inorganic matter (PIM) (i.e. percent organic matter or %OM). Two approaches for obtaining this information are often used. The first is the loss-on-ignition technique to remove volatile POM, leaving only PIM to be gravimetrically measured (e.g. Binding et al. 2005; Stavn and Richter 2008). The second method uses locally established relationships between the particulate organic carbon (POC) content and TSM to estimate the %OM (e.g. Redalje et al. 1994; Trefry et al. 1994; Babin et al. 2003; Loisel et al. 2007).

The majority of river supplied particles are clay and quartz minerals (Johnson and Kelly 1984) along with terrigenous organic detritus (Parker and Hedges 1976; Goni et al. 1997). Shelf particle suspensions also include large numbers of phytoplankton (e.g. Liu et al. 2004). Minerals have higher refractive indices relative to water (Lide 2005) than organic matter and phytoplankton (Aas 1996; Stramski et al. 2001). Minerals also have a much higher density (Lide 2005) than organic matter (Aas 1996). Studies using assumed particle densities and refractive indices derived from the methods above demonstrated that the scattering to TSM ratio increased with low density, low refractive index particles and decreased with high density, high refractive index particles (Babin et al. 2003; Loisel et al. 2007). In these previous studies, one or more of the parameters of interest were
obtained from theoretical modeling or from observed relationships between parameters reported in other studies.

In this study a comprehensive set of measurements not previously available for this region were used to conduct a systematic evaluation of both optical and particle variability and the inter-relationships between them in this dynamic region. The particle composition, i.e. bulk density and bulk index of refraction were evaluated in terms of the %OM present in TSM samples. The particle size distribution function was measured using a profiling optical particle size analyzer along with optical scattering, backscattering and absorption measurements. Mie theory modeling using bulk particle index of refraction and the particle size distribution function was used to explain how particle properties are influencing the relationship between optical scattering and TSM. Mie theory modeling was be used to evaluate the performance of the particle size analyzer and optical methods for determining the bulk particle index of refraction (Twardowski et al. 2001) and particle size distribution function parameters (Boss et al. 2001b). These methods have been used previously to evaluate the relationships between particle scattering and composition and were used here for comparison with methods in this study (e.g. Twardowski et al. 2001; Boss et al. 2004; Sullivan et al. 2005; Loisel et al. 2007). In this study the assumed particle size distribution (PSD) function is the power law function, \( N(D) = kD^{-\xi} \), where \( N \) is the volume concentration (i.e. the number of particles of a given diameter \( D \), in a volume of water) of all the particles in a given diameter range \( D \), \( \xi \) is the slope parameter of the log transformed values of \( N(D) \) vs. \( D \), and \( k \) is a scaling factor. This size distribution function has been used for many years to represent marine particle suspensions (e.g. Bader 1970; Stramski et al. 2001; Boss et al.
2001b) although others, such as two component gamma distributions have been identified (e.g. Peng and Effler 2007; Risovic 1993).

The hypothesis of this study is that the relationship between optical scattering and TSM varies within the study area and this variability can be attributed to the variability in %OM, and particle size distribution parameters, \( k \) and \( \xi \), of the particle suspensions.

The objectives are:

1. Determine the magnitude and variability of TSM, PIM, POM, %OM, bulk particle density and index of refraction, and the PSD parameters \( \xi \) and \( k \) in the study area.

2. Determine the magnitude and variability of optical scattering, backscattering and absorption in the study area.

3. Determine the magnitude and variability in the scattering to TSM ratio in the study area due to variability in derived bulk index of refraction, bulk density and PSD parameters.

4. Use the Mie theory for homogeneous spheres to model scattering and absorption coefficients using calculated bulk refractive index and the slope parameter from parts one and two above to evaluate the performance of the methods developed in parts one and two and to help explain the relative importance of the bulk refractive index and particle size distribution function on the scattering to TSM ratio and the remote sensing reflectance calculated from \( Rrs \propto b_p/(a+b_p) \).

It is noted here that the use of %OM to partition bulk particle density and index of refraction does not account for the potential differences in relative numbers of organic
and inorganic particles. Obtaining an estimate of the relative numbers of organic and inorganic particles may be possible with the measurements made here, however this type partitioning was not attempted in this study.

Organization of the Dissertation

This dissertation is organized in three parts (Fig. 1). The first part presents the TSM and optical absorption and scattering coefficients measured in the study area and investigates their variability as a function of variability in %OM. Because optical coefficients vary as a function of particle index of refraction and TSM varies as a function of particle density, methodologies will be developed to determine bulk particle index of refraction and bulk particle density using %OM and published values of density and refractive index for particles expected in the study area. Because different particle assemblage characteristics are expected to be found in the study area relative to potential differences in regional mixing of river water from the main channel at Southwest Pass vs. river water diffused through the Birdfoot Delta, a water classification scheme will be developed for grouping stations based on proximity to the Birdfoot Delta, the main plume and surrounding shelf waters. Variability in TSM and optical coefficients relative to variability in %OM will be investigated for these groupings as well as for the study area as a whole.

The second part of the dissertation presents the coefficients $\xi$ and $k$ of the power law particle size distribution function, $N(D) = kD^{-\xi}$, as determined from measurements made with a particle size analyzer (LISST-100b). Using the methods developed in the first part for determining bulk particle refractive index and density, and water class groupings, the variability between TSM and optical scattering and absorption coefficients
relative to variability in $\xi$ and $k$ were investigated. Alternative methods for estimating bulk particle index of refraction and the power law slope parameter have been used to investigate marine particle characteristics in coastal waters of the U.S. and Europe (e.g. Twardowski et al. 2001; Boss et al. 2001a; Sullivan et al. 2005; Loisel et al. 2007). The method for computing bulk particle index of refraction from the $b_b/b$ ratio (Twardowski et al. 2001) and the method for computing the slope parameter from the spectral beam attenuation coefficients (Boss et al. 2001b) were employed here for comparison with methods developed in part one. Variability in TSM and optical coefficients relative to variability in $k$, $\xi$ and the alternative bulk particle index of refraction were investigated for the study area as a whole and the for groupings described above.

The final part of the dissertation utilized the Mie theory for homogeneous spheres to model scattering and absorption coefficients using calculated bulk refractive index and the slope parameter from parts one and two above. These results were used to evaluate the performance of the methods developed in parts one and two and to help explain the relative importance of the bulk refractive index and particle size distribution function on the scattering to TSM ratio and the remote sensing reflectance calculated from $R_{rs} \propto b_b/(a+b_b)$. 


Figure 1. Data analysis flow diagram.
CHAPTER II

CHARACTERISTICS AND SPATIAL DISTRIBUTION OF SUSPENDED PARTICLES IN MARINE WATERS INFLUENCED BY THE MISSISSIPPI RIVER

Abstract

The objectives of this study were to measure TSM, optical scattering, backscattering and absorption coefficients, and the particle size distribution in the marine waters of the Louisiana Shelf where mixing occurs with Mississippi River water from the main channel at Southwest Pass, and from the myriad of outlets of the Birdfoot Delta. Measurements were organized into regional groups depending on their proximity to the Birdfoot Delta, the main sediment plume, and shelf waters. The purpose of the regional groupings was to determine if there were regional differences in $b^*$ (m$^2$/g) i.e., the ratio between the optical scattering coefficient $b$ (m$^{-1}$) and TSM (g/m$^3$, or mg/l). The values of $b^*$ obtained from measured data were compared to the bulk particle refractive index as determined using the percent organic matter (%OM) of TSM to weight the relative contribution of high refractive index mineral particles and low refractive index organic particles. The purpose of this comparison was to determine if changes in $b^*$ could be attributed to changes in bulk particle index of refraction. Variability in $b^*$ relative to variability in the particle size distribution function is considered separately in subsequent chapters below. The separate analysis is intended to allow for the comparison of the relative individual impacts of bulk particle index of refraction and size distribution on $b^*$. Data for the study were collected during four cruises between October 2001 and May 2004. Two cruises occurred during below average river flow at stations within 20 km of the river mouth at Southwest Pass. Two cruises were conducted west of Southwest Pass.
and south of the Louisiana Bight with stations ranging to about 70 km from Southwest Pass, one during a period of below average river flow and one during a period when flow was near the annual average.

ANOVA indicated average values of measured variables in the different water classes were significantly different, but there was much overlap in data values due to high standard deviations. When average mass specific optical coefficients obtained from the entire study were used to estimate TSM by water class, differences of up to 70% were found between estimates and measured TSM in each of the classes.

In stations identified as being in the main sediment plume extending from the river mouth at Southwest Pass, TSM decreased in surface waters in inverse proportion to distance from the mouth. Similar relationships were found in optical coefficients at 650 nm but remote sensing reflectance at 650 nm calculated from the relationship $R_{rs} \propto b_b/(a+b_b)$ decreased with only a weak non-significant trend. The $b_b/b_{650}$ ratio decreased linearly with increasing %OM in plume stations as expected.

Optical coefficients at 650 nm were weakly correlated (p < 0.01) with bulk index of refraction estimated from weighting by %OM. However, mass specific coefficients were not significantly correlated with bulk index of refraction. Regression relationships between bulk density vs. TSM and bulk index of refraction vs. $b_b/650$, were best described by power law functions. In each case there was very little change in either TSM or $b_b/650$ as density or refractive index increased from their lowest values to about halfway between maximum and minimum values. Above the midpoint in the range of density and refractive index both TSM and $b_b/650$ increased dramatically. This indicates that both TSM and $b_b/650$ are much more sensitive to lower %OM particle suspensions. Because
mass specific coefficients are based on the ratio of these two parameters, their co-
variance based on the presence of river supplied mineral particles throughout the study
area appears to have diminished any regional variation within this study area.

Introduction

Light scattering and absorption by particles suspended in marine waters is
dependent on the bulk particle index of refraction and the numbers and size ranges of
particles in suspension. The total dry mass or total suspended matter (TSM) of the
particle assemblage is dependent on the bulk particle density and numbers and sizes of
particles. In this chapter variability in the relationship between particle scattering and
TSM due to variability in particle composition will be investigated. The scattering to
TSM ratio, or mass specific scattering coefficient is represented by $b^*$ with units of $m^2/g$.

In the region west and south of the Mississippi River mouth at Southwest Pass,
sediment laden river water from the main channel and river water diffused through the
passes and outlets of the Birdfoot Delta mix with Louisiana shelf waters. The spatial
extent of the mixing of both the main plume and water diffused through the delta is
influenced by several independent factors including river flow rate, prevailing winds,
tidal currents and other shelf currents. The uncertainty in spatial distribution of mixing
and the high spatial variability in suspended particle concentration and composition make
the relationships between in situ samples and remotely sensed measurements difficult to
interpret. It is therefore important to determine if there are differences in the scattering to
TSM ratios in different mixing regimes. A regional approach was used to group sample
stations based on proximity to the Birdfoot Delta, the main river plume and surrounding
shelf waters. The coastal region of the Northern Gulf of Mexico receives an annual
average 18,400 m$^3$/s of fresh water and 94,000 tons/yr of dissolved and suspended matter, including minerals, organic matter, nutrients, metals, salts and other material from the Mississippi River (Milliman and Meade 1983). Approximately 30% is discharged through the Atchafalaya River and 70% is discharged via the Birdfoot Delta directly onto the continental shelf (Milliman and Meade 1983; USGS NASQAN 1996-2005, St. Francisville and Melville, LA). The myriad of outlets and passes of the Birdfoot Delta are mostly un-gauged but estimates of other researchers (e.g. Walker 1996) and anecdotal observations from satellite imagery of the largest channels indicate only about a third of the river water exits directly through the main shipping channel at Southwest Pass. The remaining two thirds enters shelf waters throughout the Birdfoot Delta. The sediment laden plume extending from the mouth of Southwest Pass is usually quite distinct in satellite imagery but the outflows from the other outlets appear as variable mixtures in the waters surrounding the Birdfoot Delta (e.g. Salisbury et al. 2004).

This study was conducted in the largely un-bounded open water west and south of the Birdfoot Delta where both the main plume and the surrounding water mix with shelf water. The extent and position of the main plume and the distribution of the diffused water are strongly influenced by prevailing winds (Walker 1996; Salisbury et al. 2004; Walker et al. 2005).

Particle characteristics in the study area represent extremes in composition with high relative proportions of mineral particles supplied by the river and high relative proportions of organic particles naturally occurring in shelf waters. River supplied mineral particles have both high densities and high refractive indices (Johnson and Kelly
1984; Lide 2005), while organic particles are much lower in density and refractive index (e.g. Aas 1996; Stramski et al. 2001).

Both scattering and TSM are functions of particle composition. Particle index of refraction affects light scattering and particle density affects TSM. To relate changes in particle composition to scattering and TSM, TSM samples were partitioned into Particle Inorganic Matter (PIM) and Particle Organic Matter (POM). This partitioning allowed the calculation of the percent organic matter (%OM) in the samples.

Optical properties, TSM, and chlorophyll fluorescence are spatially and temporally variable throughout the study area (D’Sa et al. 2003; Yuan et al. 2005; D’Sa et al. 2006; D’Sa et al. 2007). Variability in $b^*$ in coastal waters of Europe has been attributed to the relative proportion of organic matter in TSM (Binding et al. 2005; Babin et al. 2003; Loisel et al. 2007; Stavn and Richter 2008). Similarly the backscattering to total scattering ratio $b_b/b$ has also been shown to vary with relative proportions of organic matter (Loisel et al. 2007) and bulk particle index of refraction (Twardowski et al. 2001). It has also been shown via Mie theory modeling (Ulloa et al. 1994) that the ratio of backscattering (i.e. scattering at angles 90 to 180) to total scattering (i.e. angles from 0 to 180) varies in proportion to the index of refraction in the presence of small particles with diameters $D$, in the range $0.01 < D < 10 \mu m$.

Because river water enters the study area in two essentially different modes, i.e. about one third through the main shipping channel Southwest Pass and the remaining two thirds through much lower volume and therefore lower energy passes and channels, the mixing of the two sources occurs in different regions of the study area (Walker 1996; Salisbury et al. 2004). Water from Southwest Pass is often observed beyond the farthest
extent of this study area while mixing of water from the Birdfoot Delta occurs in closer proximity to the delta. However, satellite images of the study area show sediment plumes from the delta driven far off shore by prevailing winds (e.g. Walker 1996; Walker et al. 2005). Because of these two potentially different mixing modes, particle characteristics may be different, thereby resulting in different scattering to TSM ratios.

The hypothesis of this chapter is that mass specific optical coefficients vary relative to different mixing regimes throughout the study area. The variability in the mass specific optical coefficients is expected to be attributable to variability in the %OM. The objective of this study was to determine the magnitude and spatial variation in the optical scattering to TSM ratio in the study region. Further, the variability of the mass specific optical coefficients in and between the different mixing regions and shelf waters was investigated. Lastly, the contribution to variability in the mass specific optical coefficients by variability in bulk density and index of refraction determined as a function of %OM was investigated. Because particle sizes are not routinely measured, this chapter does include variability due to particle size distributions.

For this chapter, TSM, %OM, and optical properties were measured, and a water classification process was developed for grouping stations by shelf, plume and ambient water characteristics. Methods were developed for calculating bulk particle density and bulk refractive index using %OM and published values of mineral and organic densities and refractive indices. The ratio of optical scattering to TSM, $b^*$, was calculated from measurements made in the study area. Differences in mean parameter values for all water classes were evaluated using ANOVA and regression analysis. Variability in the optical scattering to TSM ratio was evaluated relative to variability in %OM, and bulk
density and index of refraction for the entire study area and between regional water classes.

Methods

Satellite Image Processing

The satellite images presented here are used for two purposes. The first is to simply provide a map to locate the cruise stations. The second is to assist in placing stations in water classes described below. Images were obtained from the NASA MODIS sensor (MODerate resolution Imaging Spectrometer). There is a MODIS sensor on each of two polar orbiting satellites, Aqua and Terra.

Satellite images in Figs. 2 - 5 are false color composites of NASA MODIS Aqua and Terra red and near infrared (NIR) 250 m bands and green 500 m band. Images were obtained from the NASA MODIS website, http://ladsweb.nascom.nasa.gov/. Image swaths for cruise dates were selected and downloaded for processing. MODIS bands are assigned to the red, green and blue image colors as NIR, red, and green respectively. Initial processing was done using MRT_Swath (NASA) to obtain scan angle corrected and geographically referenced images for the study area. Geographic resolution was chosen to match the spatial resolution of the 250 m resolution bands. Images were saved in GeoTIFF format. Matlab (The Mathworks) image processing and mapping toolboxes were used to create the image figures and plot the station locations. Image digital numbers have been stretched to improve the contrast between plume water and surrounding water.

TSM concentrations have been estimated from empirical relationships with remote sensing signals in red wavelengths for many years (e.g. Stumpf 1988; Stumpf and
Pennock 1989; Miller and McKee 2004). These relationships have been used previously to indicate the presence and movement of freshwater plumes in coastal waters (e.g. Dinnel et al. 1990; Stumpf et al. 1993; Walker 1996; Salisbury et al. 2004). The MODIS 250 m red band has been used to measure TSM with only a dark pixel subtraction for atmospheric correction and a simple 1st order regression equation to convert pixel values to TSM (Miller and McKee 2004). Because there were few and in some cases no cloud free images for cruise dates, the images presented here were not atmospherically corrected or converted to TSM. Identification of the sediment plume and waters surrounding the Birdfoot Delta is based only on the observed brightness of pixels in the red band. In these images there is usually a distinct transition between bright pixels with presumed high TSM and darker pixels surrounding them. The NIR band is used to highlight the land-water interface (note the land is red in the images). The green band is simply to balance the image colors.

**Cruises**

Data were collected on 4 cruises of opportunity from 2002 to 2004 (Table 1). Two different programs supported the cruises, allowing collection of data in three seasons and two distinct locations relative to the river mouth at Southwest Pass. At each station a profile of water optical properties was collected from near surface to within approximately 2 m of the local bottom. At stations with bottom depths greater than 100 m, optical casts were stopped around 100 m depending on conditions. Subsequent to optical profiles, water samples were collected from Niskin bottles near the surface, near the bottom and at an intermediate depth at the lower extent of the mixed layer indicated by increased chl \( a \) or change in transmittance.
Table 1

*Cruise Dates and Locations*

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Vessel</th>
<th>Dates</th>
<th>Upper Left Coordinates</th>
<th>Lower Right Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE2</td>
<td>R/V Pelican</td>
<td>10/7–10/15/2002</td>
<td>29.1 N, 91.1 W</td>
<td>28.0 N, 89.4 W</td>
</tr>
<tr>
<td>A3</td>
<td>R/V Acadiana</td>
<td>07/29–08/02/2003</td>
<td>29.0 N, 89.6 W</td>
<td>28.7 N, 89.3 W</td>
</tr>
<tr>
<td>A4</td>
<td>R/V Acadiana</td>
<td>10/14-10/15/2003</td>
<td>29.0 N, 89.6 W</td>
<td>28.7 N, 89.3 W</td>
</tr>
<tr>
<td>NE3</td>
<td>R/V Pelican</td>
<td>04/24-05/03/2004</td>
<td>29.1 N, 91.1 W</td>
<td>28.0 N, 89.4 W</td>
</tr>
</tbody>
</table>

Cruises A3 and A4 were conducted in seasonally low flow periods during summer (July 29 – August 2) and fall (October 14 – 15) of 2003 within a 20 km radius mostly south and southeast of Southwest Pass (Figs. 2 and 3). Station locations were randomly selected based on plume location estimated from the most recent satellite images prior to each cruise. Sampling strategy consisted of positioning the vessel near the mouth and allowing it to drift with wind and current until such time as it was decided to return to the vicinity of the mouth.
Figure 2. Cruise A3 station locations. Image is from MODIS TERRA 7/29/2003. Symbols represent sampling stations.
Figure 3. Cruise A4 station locations. Image is from MODIS AQUA 10/16/2003.

Cruises NE2 and NE3 were moderate range (<75 km from Southwest Pass) cruises in fall 2002 and spring 2004 respectively, within an area west of Southwest Pass extending southward below the Louisiana Bight (Figs. 4 and 5).

Cruise NE2 occurred during a seasonally low flow period (October 10 – 17) of 2002. The cruise was conducted over a period of 8 days at 12 pre-defined stations in a grid pattern (Fig. 4). Extreme endpoint stations were selected in the river at Head of Passes (mr) and at an offshore station (blue). Intermediate stations near the mouth (br, bg, bgb) were also added. Stations were occupied in north-south and east-west transects
as well as somewhat randomly. All stations were occupied at least once and some three times.

Cruise NE3 was conducted in the spring (April 24 – May 3) of 2004 when river flow is typically high due to seasonal snow melt and spring rains (Fig. 5). This cruise was conducted in the same region as NE2 however the fixed grid of stations was abandoned for a somewhat random approach similar to that of cruises A3 and A4. Satellite images were obtained prior to and during the cruise and stations were selected based on the presumed position of the plume. A number of stations were selected near the river mouth and one station was selected far offshore, 72 km south of the mouth at Southwest Pass.
Figure 4. Cruise NE2 station locations. Image is from MODIS AQUA 10/16/2002.
Figure 5. Cruise NE3 station locations. Image is from MODIS AQUA 4/27/2004.

Mississippi River Data

River flow rate and TSM were obtained from the USGS monitoring station at St. Francisville, LA, (USGS NASQAN) for the period of 1996 to 2005. TSM and flow data were plotted along with the corresponding cruise periods (Fig. 6).

Winds

Wind speed and direction were obtained from the NOAA C-MAN station BURL1 located at the mouth of Southwest Pass (28.905 N, 89.428 W) for cruise dates and six
days prior to each cruise. Average wind speed and predominant directions were extracted from the hourly data.

Classification of Water Types

To help understand the spatial variability of TSM, %OM and optical properties of particle suspensions, cruise stations were grouped into seven different classes using several criteria. The seven station groupings include River, (there was only one up-river station at Head of Passes, NE2 Station mr), River Mouth (within the plume a few km from the mouth), Ambient water (water surrounding the Birdfoot Delta but not in the main plume (Wright and Coleman 1971)), Plume water (water down stream of the mouth still in the sediment plume), Shelf water ( water not in the plume or ambient water), and Blue water (there was only one blue station, NE3 Station 12). The seventh group is called Shore and includes two samples from NE2 Station 9 which is about 2 km from the shore near Grand Isle, LA. This station had high TSM values but did not appear to be influenced by plume or ambient waters. High TSM values were likely due to bottom resuspension and local run-off.

The term “ambient water” used in this classification scheme is based on the description by Wright and Coleman (1971) in their study of the river effluent at South Pass approximately 33 km east of Southwest Pass. They identified three distinct water masses, (their Fig. 3), described as:

a. the South Pass effluent of fresh, sediment-laden water emanating from the mouth; b. a slow-moving, shallow and highly stratified band of ambient fresh to brackish turbid water, supplied by outlets to the northeast; and c. slightly diluted (salinity 25-30 ‰) gulf water. (p. 8654)
The objective of creating these water classes was to segregate waters of the main plume flowing from Southwest Pass, the ambient water surrounding the Birdfoot Delta and the shelf waters that receive and mix with the river water. Each of these groupings was expected to represent regions where particle suspension characteristics were significantly different from each other. Particle suspension characteristics in the main plume were expected to have a continuous transition between river mouth and shelf waters along the length of the plume. The selection criteria for grouping stations was somewhat subjective but was primarily dependent on measured surface TSM, proximity to the Birdfoot Delta, the open Gulf, the river mouth and the position of the plume from Southwest Pass as interpreted from satellite images. During multi-day cruises some stations occupied multiple times had both high and low TSM values. These stations were treated as separate stations and grouped accordingly.

The use of satellite images for the selection process was based on observed brightness of the pixel values as described above. The interpretation of the images was based in part on the findings of Salisbury et al. (2004), who used satellite images to describe the distinct pattern of the plume surrounded by lower TSM water masses. Salisbury et al. (2004) also identified water masses as contiguous features. In the current study plume waters were interpreted as bright pixels that formed a contiguous array extending away from the river mouth. Ambient waters were interpreted as bright pixels that formed a contiguous feature surrounding the delta. In some cases prevailing winds had driven the ambient water far from land. Stations within these waters were classified as Ambient. Shelf waters were interpreted as darker pixels over the shelf not in the plume.
or ambient water. Each station was evaluated based on satellite images available for the days closest to the sample date.

Surface data from each cruise was segregated by water classification as described above. Parameter values in classes River Mouth, Ambient, Plume, and Shelf were averaged and differences in means between classes were tested for significance using the single factor ANOVA. Classes MR, Blue and Shore were not included in the ANOVA because there was only one sample each for MR and Blue and two samples for Shore.

**TSM and %OM from Gravimetric and Loss on Ignition (LOI) Analysis**

Suspended sediment samples were processed following Franson (1995). Water samples were filtered through 47 mm glass fiber filters (Whatman glass microfiber filter, Grade GF/F), with a nominal pore size of 0.7 μm. Filters were baked at 550 C for 15 minutes, weighed and placed in filter holders prior to each cruise. Sample volume was adjusted based on material observed on filters. Volume ranged from 200 ml to greater than 2000 ml. After completion of sample filtering, three 100 ml aliquots of Nanopure (Barnstead) water were run through the filter to remove salt. After filtration, filters were replaced in holders and kept refrigerated. All samples were filtered at sea, between stations. Samples were drawn from Niskin bottles as soon as possible to mitigate effects of settling. When large volumes were required, the entire Niskin sample was stored in a carboy and mixed prior to extracting samples as filtering progressed.

Filters were refrigerated or placed in a desiccator until processed after each cruise. Filters were dried at 103 C for at least 2 and up to 24 hrs and kept in an electronic desiccator until weighed. They were then ashed in a furnace at 550 C for 15 min, returned to the desiccator and re-weighed. TSM was obtained by subtracting pre-filtered weight
from dried weight, PIM was obtained by subtracting pre-filtered weight from ashed weight. POM was obtained by subtracting PIM from TSM. Weights were volume normalized to units of mg/l. Drying and ashing cycles were repeated up to three times. Concentrations reported here are from the final cycle.

To test the variability in sample processing, one station included sample replication. Filtration was replicated three times at each of three depths. The three depths provided a range of suspended particle concentrations that included low to moderately high values of TSM. For each sample depth, three filters were obtained, all using equal amounts of water from the same niskin bottle.

Values of TSM, PIM, and POM presented in this work were not corrected for salt retention or loss of clay structural water. Salt retention on glass fiber filters has been addressed in the literature as a potential source of error in final TSM weights (e.g. Trees 1978; Stavn et al. 2009). Many researchers dismiss the salt retention issue by washing filtered samples with various volumes of de-ionized water (e.g. Walker 1996; Binding et al. 2005). Stavn et al. (2009) found that salt retention after rinsing with de-ionized water was a function of sample salinity but was not statistically correlated with total volume filtered. A correction factor for water of hydration related to retained salt was also reported by Stavn et al. (2009). Further investigation of salt retention is clearly necessary to determine the applicability of correction factors such as those reported by Stavn et al. (2009) to a given data set.

Error associated with ashing of clay minerals is somewhat more complicated and is a function of specific clay types and their relative concentrations as well as ashing time and temperature (Barille-Boyer et al. 2003). Overestimates of POM in samples with low
concentrations of organic matter can be as high as 300% in some cases (Barille-Boyer et al. 2003). No similar analysis was attempted using a Mississippi River water assessment of suspended clay minerals.

**Bulk Particle Density**

In order to understand the relationships between particle composition and the scattering to TSM ratio $b^*$, sampled TSM was separated into particle inorganic matter (PIM) and particle organic matter (POM) components as described above. The separation of TSM into PIM and POM components allows for an assessment of the role of particle density in the variability of $b^*$. Since only two particle types can be identified using the loss on ignition technique, an average or bulk value of density for each particle type was developed. A simple weighting scheme for combining the two particle types based on the %OM was developed to calculate a bulk density for each sample. It should be noted that the simple weighting scheme described below does not take into account the relative numbers of each type of particle. The use of this weighting scheme therefore includes the implicit assumption that there are equal numbers of each particle type. In a preliminary analysis performed after the defense of this dissertation, it was determined that segregating the particle assemblage by relative numbers of each particle type could be accomplished using the measured %OM and the size distribution data obtained from the LISST-100b. This new ratio describing relative numbers of particles was likely a better approach to determining the bulk particle density and the bulk particle refractive index discussed below. However, this preliminary analysis did not negate the results presented here nor did it dramatically impact the overall conclusions described in this work. It does appear that this alternate method of partitioning the particle assemblage
would result in a better understanding of the relationship between optical coefficients and TSM and therefore represents an area for further investigation.

Bulk particle density was calculated using %OM to estimate proportions of high density mineral particles and low density organic particles. To create such a calculation a characteristic density was determined for both mineral $\rho_{\text{MIN}}$, and organic particles $\rho_{\text{OM}}$. Specific particle densities used are provided in Table 2 (See Bulk Index of Refraction below for a detailed explanation of expected mineral proportions).

The mineral particle density was assumed to be an average of the mineral particle densities found in the study area (Kelly and Johnson 1984). Mineral specific densities (Lide 2005) were averaged by expected proportions (Kelly and Johnson 1984) resulting in an average mineral density defined here as $\rho_{\text{MIN}} = 2.65 \text{ g/cm}^3$.

To create a bulk density for organic particles, organic detritus (OD) and living phytoplankton cells (PH) were considered to be separate particle types with densities of $\rho_{\text{OD}}$, and $\rho_{\text{PH}}$, respectively. Dry organic matter has a density of about 1.4 g/cm$^3$ (Aas 1996). To create density estimates for organic detritus and phytoplankton, estimates of water content of each particle type were considered. Estimates indicate that the volume of phytoplankton cells can consist of up to 80 % water (e.g. Aas 1996). There is no specific knowledge of the water content of detrital particles in the study area. Some researchers estimate detrital particles also consist of as much as 80 % water (c.f. Aas 1996; Babin et al. 2003). However in this work in order to create a contrast between organic detritus and phytoplankton densities, organic detritus will be assumed to consist of 20 % water. To obtain an estimate for phytoplankton density $\rho_{\text{PH}}$, the dry organic matter density (1.4 g/cm$^3$) was combined with the estimated water density (~1.0 g/cm$^3$),
in proportion to the assumed relative volumes of each, i.e. 20% dry mass and 80% water, to get $\rho_{PH} = 1.4 \text{ g/cm}^3 \times 0.2 + 1.0 \text{ g/cm}^3 \times 0.8 = 1.08 \text{ g/cm}^3$. Similarly for organic detritus with an assumed water content of 20%, $\rho_{OD} = 1.4 \text{ g/cm}^3 \times 0.8 + 1.0 \text{ g/cm}^3 \times 0.2 = 1.38 \text{ g/cm}^3$.

In natural marine water particle assemblages there is expected to be found a combination of phytoplankton cells and their associated organic detritus present because of incomplete feeding by zooplankton, fecal pellets excreted by zooplankton and natural cell lysis. The relative concentrations of phytoplankton cells and organic detritus are not known but it is assumed in this work that up to 25% of the total number of organic particles consist of organic detritus. Two approaches were used here to estimate the relative contribution to total organic matter density by organic detritus. The first assumes that both organic detritus and phytoplankton densities are the same, each having a water content equal to that of phytoplankton, i.e. 80%, and therefore there is no distinction between the two particle types. This assumption results in the simple weighting scheme where there is as single density for mineral particles $\rho_{MIN} = 2.65 \text{ g/cm}^3$, and a single density for organic particles $\rho_{PH} = 1.08 \text{ g/cm}^3$. The bulk particle density is then $\rho_{1} = \rho_{MIN} \times (1-\text{OM}) + \rho_{PH} \times \text{OM}$.

In the second approach, the organic detrital particles represent a third particle type having a water content of only 20% as described above. In the river water, where %OM is lowest in this study, organic particles are assumed to consist of 100% organic detritus due to light limitation in the turbid river water preventing phytoplankton growth. Phytoplankton blooms within the river channel have been observed (Dagg et al. 2008) but none were reported during the times of the cruises reported here. In shelf and blue water,
organic particles are assumed to consist of both phytoplankton and organic detritus. The relative proportion of organic detritus within the overall organic matter present is assumed to vary linearly between river water and shelf water with 100% organic detritus at the river mouth and 25% organic detritus and 75% phytoplankton in shelf water. For the following calculations OM = %OM/100. As OM varies from about 0.1 at the river mouth to near 1.0 in shelf waters, the relative concentration between organic detritus (OD) and phytoplankton cells was assumed to vary inversely with OM (i.e. OD = 100% when OM = 0.1 and 25% when OM = 1.0). The relative proportion of OD is then represented by the equation of the line between these two conditions as OD = (-0.75/0.9) * (1 – OM) + 0.25. This proportion is then used to vary the density between organic detritus and phytoplankton to get an average particle density of \( r2 = \rho_{MIN} \times (1-\text{OM}) + \text{OM} \times (\rho_{OD} \times \text{OD} + \rho_{PH} \times (1-\text{OD})). \)

It should be noted here that after the defense of this dissertation it was discovered that the calculations of the dry mass of suspended particles included the density of water in the estimate of bulk particle density. Water was not included in the measured values of TSM, PIM and POM and therefore calculations using these reported bulk densities are incorrect. However the inclusion of water in the calculation resulted in a maximum overestimate in density of less than four times when %OM was 100%. While this error skews the subsequent mass calculations it does not change or negate the overall approach, results or conclusions of this work.

**Bulk Particle Index of Refraction**

Bulk index of refraction at a given station was computed using a process based on published (e.g. Lide 2005; Aas 1996) individual particle characteristics, measured
relative fractions of PIM and POM and some assumptions about the relative contributions between river and marine supplied organic matter. The particle index of refraction relative to seawater consists of a real part and an imaginary part, \( m_r(\lambda) = n_{\text{re}}(\lambda) + \text{in}(\text{im})(\lambda) \). The real part, \( n_{\text{re}} \), is associated with scattering and the imaginary part, \( n_{\text{im}} \), is associated with absorption (Van de Hulst 1957; Bohren and Huffman 1983). Each part is wavelength (\( \lambda \))-dependent. Throughout this work, the notation \( \text{re} \) and \( \lambda \) is dropped unless required for understanding. The un-subscripted \( n \) is the real part of the computed bulk particle index of refraction without a wavelength reference. Because published values vary only slightly with wavelength (e.g. Lide 2005), \( n \) used in this work is assumed to be wavelength independent. Subscripted \( n \) is used only for defining specific particle types below.

All refractive indices described in this work refer to particles only and are relative to seawater which is slightly temperature and salinity dependent. The index of refraction of seawater is chosen to be \( n = 1.34 \) based on a review of ranges of salinity and temperature found in the study area (Mobley 1994, his Table 3.4 and Fig. 3.5).

To characterize the range and spatial variability of the bulk index of refraction of particles in the study region a numerical value of \( n \) was calculated for each station. Bulk particle index of refraction is dependent on the community composition of particles found in each water sample. River supplied particles consist of predominantly clay minerals, some quartz minerals and terrigenous organic detritus (Kelly and Johnson 1984). Marine particles include marine organic detritus and living cells ranging in size from heterotrophic bacteria and cyanobacteria to large phytoplankton. (Liu 2004; Redalje et al. 1994). It should be noted that phytoplankton blooms have been observed upstream of the
river mouth (Dagg et al. 2008) however no effort was made during the cruises of this study to detect such a bloom.

Four particle types were defined and specific values of \( n \) (Table 2) were calculated based on characteristics described below for mineral only particles, \( n_{\text{min}} \), river supplied organic matter, \( n_{\text{rom}} \), Gulf supplied organic matter, \( n_{\text{gom}} \), and a combined river particle, \( n_{\text{riv}} \), which assumes constant proportions of mineral and terrigenous organic matter of 0.8 and 0.2 respectively. The final bulk \( n \) is calculated by simple summation of proportions of the four particle types defined below.

Table 2

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>( n )</th>
<th>( n(\text{im})(440) )</th>
<th>( n(\text{im})(530) )</th>
<th>( n(\text{im})(650) )</th>
<th>( n(\text{im})(675) )</th>
<th>Density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{\text{min}} )</td>
<td>1.175</td>
<td>0.00045</td>
<td>0.00024</td>
<td>0.00010</td>
<td>0.00008</td>
<td>2.65</td>
</tr>
<tr>
<td>( n_{\text{riv}} )</td>
<td>1.171</td>
<td>0.00045</td>
<td>0.00024</td>
<td>0.00010</td>
<td>0.00008</td>
<td>2.4</td>
</tr>
<tr>
<td>( n_{\text{rom}} )</td>
<td>1.157</td>
<td>0.00045</td>
<td>0.00024</td>
<td>0.00010</td>
<td>0.00008</td>
<td>1.4</td>
</tr>
<tr>
<td>( n_{\text{gom}} )</td>
<td>1.040</td>
<td>0.00653</td>
<td>0.00024</td>
<td>0.00010</td>
<td>0.00414</td>
<td>1.08</td>
</tr>
</tbody>
</table>

*River supplied inorganic particles, \( n_{\text{min}} \).* In an analysis of surface suspended particles in the Mississippi River near New Orleans, Johnson and Kelly (1984) reported mineral composition was significantly correlated with grain size and that clay minerals made up greater than 90 % of the smallest size fractions (< 2 um), with quartz increasing to 30 % in sizes between 2 and 7.8 um and nearly 50 % in larger size fractions (> 7.8 um). Predominant clay minerals are montmorillonite, illite and kaolinite, with relative concentrations of each variable across the sampling transect and between seasonal samples (Johnson and Kelly 1984). For this work a constant proportion of clays is used consisting of 40 % montmorillonite, 40 % illite, and 20 % kaolinite based loosely on
values reported by Johnson and Kelly (1984). The index of refraction for clay is found from the weighted sum of the individual indices for each of the three clay species (Lide 2005), \( n_{\text{clay}} = 0.4 \times 1.172 + 0.4 \times 1.187 + 0.2 \times 1.167 = 1.177 \). Total mineral composition used in this work includes 90 % clay (\( n = 1.177 \)) and 10 % quartz (\( n = 1.152 \) [Lide 2005]). This combination results in a mineral refractive index of \( n_{\text{min}} = 1.175 \).

*River supplied organic matter*, \( n_{\text{rom}} \). The index of refraction of dry marine algal mass based on metabolite analysis ranges from 1.146 to 1.167 with a density of about 1.4 \( g/cm^3 \) (Aas 1996). A mean value of \( n_{\text{rom}} = 1.157 \) will be used in this work. It is understood that river born organic matter contains lignin not present in marine phytoplankton. It is assumed that the refractive index of lignin does not differ significantly from the range observed by Aas (1996).

*Gulf supplied organic matter (marine phytoplankton)*, \( n_{\text{gom}} \). Metabolite analysis and estimates of the volume fraction of water in living cells indicates a refractive index for marine phytoplankton ranging from 1.03 to 1.06 (Aas 1996). Averaging the refractive index from 26 marine phytoplankton species (Stramski et al. 2001, and references within) results in a value of \( n_{\text{gom}} = 1.04 \).

*Combined river particle*, \( n_{\text{riv}} \). In order to facilitate comparisons between various water classes (see results and discussion below), a characteristic river particle has been created assuming a constant ratio of mineral to organic matter of 0.8 \( n_{\text{min}} \) and 0.2 \( n_{\text{rom}} \) respectively, resulting in \( n_{\text{riv}} = 1.171 \). This ratio is based on samples taken directly in the river and directly in the plume near the mouth. Samples taken during different cruises show a similar characteristic of low (< 20 %) organic fraction in river water.
Particle Absorption. Wavelength specific values of $n_{\text{im}}(\lambda)$ for marine phytoplankton are taken to be the mean of 26 species used by Stramski et al. (2001) where $n_{\text{im}}(440 \text{ nm}) = 0.0065$ and $n_{\text{im}}(675 \text{ nm}) = 0.0041$. Values for minerals and organic detritus are computed from the equation developed by Stramski et al. (2001) based on data collected by Iturriaga and Siegal (1989) as $n_{\text{im}}(\lambda) = 0.010658 \exp(-0.007186 \lambda)$, where $\lambda$ is in nm. This equation will also be used to calculate values for phytoplankton at wavelengths where pigment absorption is low and few measurements exist. Much higher values of $n_{\text{im}}(\lambda)$ for minerals have been reported (Patterson 1977; Stramski et al. 2007) and these differences will be addressed when appropriate. The same proportions of mineral and organic fractions described for n are used for $n_{\text{im}}(\lambda)$ (Table 2).

Five schemes have been devised to determine the proportions used in calculating bulk n (Table 3). There are three primary particle types are present, mineral, organic detritus and organic marine phytoplankton, each having a distinct index of refraction (see below). However, the loss on ignition technique used here does not differentiate between organic sources. The first scheme, $n_1$, uses %OM to determine the proportions of only $n_{\text{min}}$ and $n_{\text{gom}}$ (Table 2). The second scheme, $n_2$, uses %OM to determine the proportions of $n_{\text{riv}}$ and $n_{\text{gom}}$. The third scheme, $n_3$, uses same weighting scheme as the density calculation $r_2$, to determine the proportion of $n_{\text{min}}$ and an organic n determined from the same assumptions about the relative contribution by organic detritus to total organic matter to determine the proportions of $n_{\text{gom}}$ and $n_{\text{rom}}$ (see density calculation above). The fourth scheme, $n_4$, uses the same method as $n_3$ except that the organic n proportions are determined directly from %OM. The fifth scheme, $n_5$, uses the same method as $n_4$ with
the exception that when POM falls below 20 %, the entire organic n contribution is defined as \( n_{\text{rom}} \).

Table 3

**Bulk Index of Refraction Equations**

<table>
<thead>
<tr>
<th>Type Index</th>
<th>Combination Logic</th>
</tr>
</thead>
<tbody>
<tr>
<td>n1</td>
<td>( n_{\text{min}} ) * (1-OM) + ( n_{\text{gom}} ) * OM</td>
</tr>
<tr>
<td>n2</td>
<td>( n_{\text{riv}} ) * (1-OM) + ( n_{\text{gom}} ) * OM</td>
</tr>
<tr>
<td>n3</td>
<td>( n_{\text{min}} ) * (1-OM) + OM * (( n_{\text{rom}} ) * OD + ( n_{\text{gom}} ) * (1-OD)) * OM</td>
</tr>
<tr>
<td>n4</td>
<td>( n_{\text{min}} ) * (1-OM) + (( n_{\text{rom}} ) * (1-OM) + ( n_{\text{gom}} ) * OM) * OM</td>
</tr>
<tr>
<td>n5</td>
<td>( n_{\text{min}} ) * (1-OM) + (( n_{\text{rom}} ) * 0.2 + ( n_{\text{gom}} ) * (OM-0.2)) * OM</td>
</tr>
</tbody>
</table>

† OD = (-0.75/0.9) \* (1 – OM) + 0.25
‡ for OM<0.2 n5=\( n_{\text{min}} \) \* (1-OM)+(\( n_{\text{rom}} \) \* OM)

**Optical Measurements**

On all cruises except NE2, optical property profiles were measured simultaneously using instruments attached to a steel frame. On cruise NE2 the LISST-100 was deployed separately and data was merged with other measurements as described below. Measurements of spectral absorption, \( a(\lambda) \) and beam attenuation, \( c(\lambda) \), were obtained with an ac-9 (WET Labs, Philomath, OR). Absorption, \( a(\lambda) \) (m\(^{-1}\)), beam attenuation, \( c(\lambda) \) (m\(^{-1}\)) were obtained at 9 discrete wavelengths, 412, 440, 488, 510, 532, 555, 650, 676, 715 nm. Scattering, \( b(\lambda) \) (m\(^{-1}\)), was obtained at each wavelength by subtraction, \( b(\lambda) = c(\lambda) - a(\lambda) \). Backscatter, \( b_{\theta}(\lambda) \), was obtained with an ECO-VSF3 (WET Labs, Philomath, OR). Particle backscattering \( b_{\theta}(\psi, \lambda) \), was obtained from the ECOVSF3 at 3 angles (\( \psi = 100, 125, 150 \) degrees) and 3 wavelengths (\( \lambda = 450, 530, 650 \) nm). Total spectral backscatter was obtained after applying an absorption correction and integrating a second order linear regression fit of \( b_{\theta}(\lambda) \) obtained at 3 measured angles (WETLabs application note). Salinity, temperature and depth were obtained from an
SBE-49 CTD (Sea-Bird Electronics, Inc, Bellevue, WA). Particle size distribution (PSD) in 32 size bins from 1.0 to 250 μm was obtained at 660 nm from the LISST-100B (Sequoia Scientific, Bellevue, WA). The LISST-100B was zeroed with de-ionized water before and after each cruise and found to be highly stable. LISST-100B data were converted to number of particles per size bin using the methods described in Chapter III. All optical data except the LISST-100 were integrated with an ac-9 Plus (WET Labs) data logger.

Optical windows of all instruments and the absorption and attenuation tubes of the ac-9 were cleaned at least once per day. An on-deck clear water measurement from the ac-9 was made at least once per day. These measurements were applied to all casts made on that day. Each cast included deploying the optical instruments at a depth of either 5 or 10 m, depending on bottom depth, for a period of at least 10 minutes prior to the start of the downcast. This procedure allowed bubbles to escape the optical surfaces as well as the absorption and scattering tubes of the ac-9.

After each cast, data were downloaded and converted from digital numbers to optical units using scale and offset coefficients provided by WETLabs. Data from each instrument were merged into a single file using time tags for each sample. Data from the ac-9 were temperature, salinity, and offset-corrected via on-deck clear water corrections (also temperature-corrected) and subsequently scatter corrected using techniques described in the ac-9 Protocol Document, Rev. H, 2003. ECO-VSF3 data were corrected for in-situ absorption before computing total spectral \( b_b \) (WETLabs application note: “Computing \( b_b \) with ECO-VSF Beta Data”).
Merging of LISST data and WETLabs data was accomplished by matching depths recorded by the LISST and the CTD. Because instruments were operated independently, the depth profiles were matched using statistical correlation. An offset determined by the CTD depth at the start of the downcast was applied and a common depth profile was added to the LISST data file. This depth profile was used for subsequent depth binning.

For each optical cast, data collected from profiling instruments is binned into 0.5 m depth bins, starting at \( z = 0.25 \) m by averaging values collected at 0.25 m above and below specified depths. Only downcast data are reported in this work. Optical measurements taken at the depth of the start of the downcast are used as surface samples. The typical start of the downcast is usually between 1 and 2 m below the surface. When no data was collected between the surface \((z = 0 \text{ m})\) and the start of the downcast the data at the upper most depth bin in the profile is used to fill in depth bins to the surface. Propagation of optical data to the surface assumes constant values between the actual surface and the start of the downcast.

Particle absorption \( a_p(\lambda) \), and attenuation, \( c_p(\lambda) \), were obtained by subtracting filtered \((0.2 \mu\text{m}) a_{CDOM}(\lambda) \) and \( c_{CDOM}(\lambda) \) from unfiltered, \( a_t(\lambda) \) and \( c_t(\lambda) \) measurements after binning. The ac-9 calibration process includes removing the response due to water. For the remainder of this work the subscript \( t \) describes the ac-9 derived coefficients with the water component removed. The subscript \( p \) describes the ac-9 derived coefficients with both water and CDOM components removed, i.e., \( c_t(\lambda) = c_p(\lambda) + c_{CDOM}(\lambda) \).

Filtered measurements often contained large spikes which were likely due to release of bubbles trapped in the filter. Negative values or extremely large values were also obtained, likely due to the spatially variable water conditions and time between
casts. When negative values of $a$ were obtained, the samples were excluded from the data set. At 650 nm the difference between the means of $b_t$ and $b_p$ is not significantly different in this data set ($p << 0.01$). The regression slope between $b_t$ and $b_p$ was 0.996 ($r^2 = 0.999$). Because some values of $b_p$ were excluded due to negative values of $a_p$ it was decided to report only $b_t$.

Only optical coefficients at 650 nm will be used in this study. The wavelength 650 nm was chosen for two reasons. The first is that both particle absorption and absorption by colored dissolved organic matter (CDOM) are very low at this wavelength (Mobley 1994). The second is that instruments available at the time of this study provide for measurements of both scattering and backscattering at 650 nm. An additional consideration is that TSM is often estimated from the red bands of remote sensing instruments.

*Remote Sensing Reflectance*

An often cited relationship between reflectance observed by satellite imaging sensors and *in situ* optical scattering and absorption originally described by Gordon (1975, 1988) and further summarized from Mobley (1994) is

\[
R_s(\lambda) \approx T f \frac{b_p(\lambda)}{Q a(\lambda) + b_p(\lambda)}
\]  

(1)

The term $T*f/Q$ considers the two-way transmission of light through the water’s surface, illumination and observation angles and sea-state. Because of the difficulty in obtaining accurate values for this term under all conditions in a study area it is often represented by a constant value, e.g. 0.0513 (Ladner et al. 2002). Ladner et al. (2002) examined this value in a study using data from Mobile Bay and surrounding Gulf of Mexico water and reported values of 0.0502 at 565 nm and 0.0476 at 665 nm.
Computing $R_{rs}$ using these values versus an assumed constant value of 0.0513, results in a maximum difference of only about 7%. Therefore in this study the $T^*f/Q$ term will be considered constant and not included in further analysis. Therefore only the ratio of the backscatter and absorption coefficients will be considered using the following notation, $R_{rs} \propto b/(a + b)$.

Data Processing

All statistical and modeling analysis was done using commercial software packages including Excel (Microsoft, Inc.) and Matlab (The Mathworks, Inc.). Image processing was done using Matlab, MRT_Swath (NASA) and ENVI (RSI).

Results

Mississippi River Data

Flow rate and TSM were obtained from the USGS monitoring station at St. Francisville, LA, (USGS NASQAN) for the period of 1996 to 2005 (Fig. 6, Table 4). Flow rate and TSM were positively correlated ($r = 0.46$, $n = 108$) for the 9 year period of available station data but the regression does not provide any predictive capability. Flow rate and silt and clay size fraction were inversely correlated ($r = -0.59$) for the same period indicating that lower flows were insufficient to keep larger particles in suspension (Mossa 1996). No correlation was found between TSM and percent silt and clay size fraction measured at the St. Francisville station.

Winds

Prevailing wind direction was estimated from the 24 hour time series on the dates prior to and during the cruise (Table 4). Wind direction recorded is the direction of the source of the wind. Winds during each of the cruises were within seasonal expectations
and appeared to be the dominant factor in directing the position of the plume and the movement of ambient water around the Birdfoot Delta. Similar observations between wind direction and position of the river plume have been reported (Walker 1996; Walker et al. 2000; Walker et al. 2005).

Table 4

*Mississippi River Flow and Total Suspended Matter at St. Francisville, LA (USGS NASQAN), Prevailing Wind Speed and Direction at Southwest Pass (NOAA BURL, 28.905 N, 89.4283 W)*

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Dates</th>
<th>River Flow (m$^3$/s)</th>
<th>Total Suspended Matter (mg/l)</th>
<th>Wind Speed (m/s)</th>
<th>Prevailing Wind Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE2</td>
<td>10/7– 10/15/2002</td>
<td>8906</td>
<td>130</td>
<td>5 - 10</td>
<td>N - NE</td>
</tr>
<tr>
<td>A3</td>
<td>07/29 – 08/02/2003</td>
<td>10534</td>
<td>82</td>
<td>2 – 7</td>
<td>SW - W</td>
</tr>
<tr>
<td>A4</td>
<td>10/14-10/15/2003</td>
<td>7263</td>
<td>77</td>
<td>5 – 15</td>
<td>NW - NE</td>
</tr>
<tr>
<td>NE3</td>
<td>04/24-05/03/2004</td>
<td>17726</td>
<td>154</td>
<td>5 - 10</td>
<td>SE - NE</td>
</tr>
<tr>
<td>9 yr. average</td>
<td>1995-2005</td>
<td>16442</td>
<td>178</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TSM Filter Replications and Error Analysis

TSM replicates were performed at only one station but were obtained from three different depths representing a range of concentrations (Table 5). At most stations in the study area there was a strong pycnocline within a few meters of the surface. Transmissometer data on the CTD profiler usually indicated higher turbidity in surface waters, lower turbidity below the pycnocline, and high turbidity near the bottom. At the station selected for replication of samples, turbidity at the surface was actually the lowest in the profile, however the range of turbidity indicated by the transmissometer at this station was similar to the range observed at other locations and was chosen for replication because it was representative of many other stations. The coefficient of variation (COV) was highest for the lowest TSM < 1.0 mg/l at the 2.2 m depth. Standard deviation was
higher for higher values of TSM but COV was lower when TSM was highest at the depth of 33 m. Results for PIM follow the same trends as for TSM but COV is much higher at the 2.2 m depth where a very low concentration was measured. This is not surprising since PIM is obtained in the second sequence of filter processing. The average difference in actual dry vs. ashed filter weights at depth 2.2 m was 1.3 mg and the standard deviation was 0.1 mg which is within the lower limit of the electronic balance (0.1 mg). This suggests that the ashing step adds the greatest uncertainty to the measurements for low concentration samples. Derived parameter %OM had standard deviations at each depth that reduced accuracy in the ten’s digit and created the greatest uncertainty in samples with the highest range of %OM.

Table 5

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>TSM (mg/l)</th>
<th>PIM (mg/l)</th>
<th>POM (mg/l)</th>
<th>%OM</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>0.68</td>
<td>0.03</td>
<td>0.65</td>
<td>95.8</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>stddev</td>
<td>0.10</td>
<td>0.06</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>cov</td>
<td>0.15</td>
<td>1.73</td>
<td>0.1</td>
</tr>
<tr>
<td>22.7</td>
<td>1.42</td>
<td>0.55</td>
<td>0.87</td>
<td>61.8</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>stddev</td>
<td>0.15</td>
<td>0.18</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>cov</td>
<td>0.11</td>
<td>0.33</td>
<td>0.1</td>
</tr>
<tr>
<td>33.9</td>
<td>11.47</td>
<td>9.07</td>
<td>2.40</td>
<td>20.9</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>stddev</td>
<td>0.21</td>
<td>0.31</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>cov</td>
<td>0.02</td>
<td>0.03</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Bulk Density Weighting Analysis**

The two methods for computing bulk particle density were compared over the range of 0.1 < OM < 1.0 and the percent increase from r1 was computed (Table 6). The percent increase in r2 over r1 is less than 1 % at OM = 0.1, increasing to a maximum difference of 5.82 % at OM = 0.9.
Table 6

*Bulk Density Calculations Using Methods for r1 and r2 With Percent Difference. OM is Organic Fraction, OD is Fraction of OM Due to Organic Detritus, PH is Fraction of OM Due to Phytoplankton.*

<table>
<thead>
<tr>
<th>OM</th>
<th>0.10</th>
<th>0.20</th>
<th>0.30</th>
<th>0.40</th>
<th>0.50</th>
<th>0.60</th>
<th>0.70</th>
<th>0.80</th>
<th>0.90</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-OM</td>
<td>0.90</td>
<td>0.80</td>
<td>0.70</td>
<td>0.60</td>
<td>0.50</td>
<td>0.40</td>
<td>0.30</td>
<td>0.20</td>
<td>0.10</td>
<td>0.00</td>
</tr>
<tr>
<td>OD</td>
<td>1.00</td>
<td>0.94</td>
<td>0.89</td>
<td>0.83</td>
<td>0.78</td>
<td>0.72</td>
<td>0.67</td>
<td>0.61</td>
<td>0.56</td>
<td>0.50</td>
</tr>
<tr>
<td>PH</td>
<td>0.00</td>
<td>0.06</td>
<td>0.11</td>
<td>0.17</td>
<td>0.22</td>
<td>0.28</td>
<td>0.33</td>
<td>0.39</td>
<td>0.44</td>
<td>0.50</td>
</tr>
<tr>
<td>r1</td>
<td>2.49</td>
<td>2.34</td>
<td>2.18</td>
<td>2.02</td>
<td>1.87</td>
<td>1.71</td>
<td>1.55</td>
<td>1.39</td>
<td>1.24</td>
<td>1.08</td>
</tr>
<tr>
<td>r2</td>
<td>2.52</td>
<td>2.38</td>
<td>2.24</td>
<td>2.10</td>
<td>1.96</td>
<td>1.81</td>
<td>1.66</td>
<td>1.51</td>
<td>1.36</td>
<td>1.20</td>
</tr>
<tr>
<td>%increase</td>
<td>0.96</td>
<td>1.88</td>
<td>2.75</td>
<td>3.56</td>
<td>4.29</td>
<td>4.92</td>
<td>5.42</td>
<td>5.74</td>
<td>5.82</td>
<td>5.56</td>
</tr>
</tbody>
</table>

TSM was compared to densities r1 and r2 to evaluate the impact on TSM due to differences in methods (Fig. 7). One hypothesis of this work was that variability in both TSM and optical coefficients can be explained in part by variability in particle composition as determined by the %OM. In this study area where the Mississippi river supplies large amounts of mineral particles, particle density appears to be the greatest contributor to variability in TSM. Up to 70 % of the variability in TSM can be explained by the change in particle density computed using the %OM weighting methods (Fig. 7).

As noted previously, the assumption that organic detritus differs in water content from organic matter associated with living phytoplankton does not appear to be the case. The percent difference between r1 and r2 is a maximum of about 6 % when %OM is 90 %. This small difference is further borne out in the regressions between bulk density and TSM where there is a very small difference in the regression equation coefficients and in \( r^2 \). In this study area, where there is a high percentage of mineral particles, this issue represents only about 1 % of the variability in TSM (Fig. 7). When the regression equations are used to calculate TSM from r1 and r2 there is only 1.03 % difference between them.
Figure 7. r1 and r2 vs. TSM. The upper equation is the regression between TSM and r1, the lower equation is for r2. The solid lines are the regression lines.

**Bulk Particle Refractive Index Weighting Analysis**

As noted above, five schemes were used to determine the range of possible values of bulk n. The intent was to evaluate the possible impact on calculated values of n resulting from the unknown relative concentrations of low index phytoplankton derived organic matter and the much higher index organic detritus. To evaluate the relative differences between the five methods of computation of n, each was compared to n1 as %OM was varied from 10 % to 100 %. The percent difference from n1 was computed over the range of %OM (Table 7). Methods n2, n4, and n5 were less than 2.65% different than n1 at any level of OM. The difference using method n3 was 1.01 % when OM was 0.1, increasing to 5.63 % when OM was 1.0.

It is observed in the data of Table 7 that the choice of methods for calculating bulk particle refractive index can produce very different results relative to specific values of %OM. In the following statistical analysis the choice of methods makes little or no
difference due to the dependence of all methods on %OM. Only n1 and n3 were used in statistical analyses because they represent the lowest and highest ranges of values respectively.

Table 7

**Bulk Index of Refraction Using Five Methods. Percent Difference is Relative to n1. OM is the Fraction of Organic Matter.**

<table>
<thead>
<tr>
<th>OM</th>
<th>0.10</th>
<th>0.20</th>
<th>0.30</th>
<th>0.40</th>
<th>0.50</th>
<th>0.60</th>
<th>0.70</th>
<th>0.80</th>
<th>0.90</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>n1</td>
<td>1.161</td>
<td>1.147</td>
<td>1.134</td>
<td>1.120</td>
<td>1.107</td>
<td>1.094</td>
<td>1.080</td>
<td>1.067</td>
<td>1.053</td>
<td>1.040</td>
</tr>
<tr>
<td>n2</td>
<td>1.157</td>
<td>1.144</td>
<td>1.131</td>
<td>1.118</td>
<td>1.105</td>
<td>1.092</td>
<td>1.079</td>
<td>1.066</td>
<td>1.053</td>
<td>1.040</td>
</tr>
<tr>
<td>n3</td>
<td>1.172</td>
<td>1.169</td>
<td>1.165</td>
<td>1.159</td>
<td>1.153</td>
<td>1.144</td>
<td>1.135</td>
<td>1.124</td>
<td>1.112</td>
<td>1.099</td>
</tr>
<tr>
<td>n4</td>
<td>1.171</td>
<td>1.166</td>
<td>1.158</td>
<td>1.148</td>
<td>1.136</td>
<td>1.122</td>
<td>1.105</td>
<td>1.086</td>
<td>1.064</td>
<td>1.040</td>
</tr>
<tr>
<td>n5</td>
<td>1.172</td>
<td>1.171</td>
<td>1.157</td>
<td>1.144</td>
<td>1.130</td>
<td>1.117</td>
<td>1.104</td>
<td>1.090</td>
<td>1.077</td>
<td>1.063</td>
</tr>
<tr>
<td>%dn2</td>
<td>-0.31</td>
<td>-0.28</td>
<td>-0.25</td>
<td>-0.21</td>
<td>-0.18</td>
<td>-0.15</td>
<td>-0.11</td>
<td>-0.07</td>
<td>-0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>%dn3</td>
<td>1.01</td>
<td>1.93</td>
<td>2.75</td>
<td>3.48</td>
<td>4.11</td>
<td>4.64</td>
<td>5.05</td>
<td>5.36</td>
<td>5.55</td>
<td>5.63</td>
</tr>
<tr>
<td>%dn4</td>
<td>0.91</td>
<td>1.63</td>
<td>2.17</td>
<td>2.51</td>
<td>2.64</td>
<td>2.57</td>
<td>2.27</td>
<td>1.75</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>%dn5</td>
<td>1.01</td>
<td>2.04</td>
<td>2.06</td>
<td>2.09</td>
<td>2.11</td>
<td>2.14</td>
<td>2.17</td>
<td>2.19</td>
<td>2.22</td>
<td>2.25</td>
</tr>
</tbody>
</table>

The percent differences between values of n obtained using the different methods are relatively small (i.e. near 1.0 % when n is highest to nearly 6% when n is lowest).

However in a test to determine the relative impact of these differences on scattering, it was found that over the range of values expected for n, an increase or decrease of the magnitudes found in Table 7 could result in 30 to over 100 % increase or decrease in the scattering coefficient at 650 nm. The impact on $b_b$ was even greater ranging from 75 to greater than 200 % difference for high and low values of n respectively. Clearly, an accurate determination of bulk particle refractive index is necessary to understand the optical coefficients relative to bulk particle refractive index and TSM. The methods used to estimate scattering coefficients are described in Chapter IV.
Cruise Data Summary

Surface samples from all cruises were combined into one data set. Average, standard deviation, coefficient of variation (COV), minimum, and maximum values were computed (Table 8). Values of TSM were similar in magnitude to those reported in studies conducted in the same area (e.g. Redalje 1994; Trefry et al. 1994; D’sa et al. 2003; Corbett et al. 2004; Dagg et al. 2008). Optical scattering and absorption coefficients obtained with the ac-9 were also similar in magnitude to those reported in the same area (D’Sa et al. 2003; D’Sa et al. 2006; D’Sa et al. 2007). When multiplied by the constant 0.0513 to represent $T^*/f/Q$, average $Rrs$ is 0.013 which is within the range of reflectance values computed from MODIS band 1 for images of the study area by Miller and McKee (2004).

Coefficient of variation is greater than 0.5 for TSM and optical coefficients, indicating a high level of variability in the study area. The average single scattering albedo at 650 nm, i.e. the ratio of the scattering coefficient to the total beam attenuation coefficient $b/c650$, is 0.96 with scattering and absorption by water removed. The COV is 0.04 indicating that scattering is the dominant factor in controlling optical properties at 650 nm. This is also evident in the very similar statistics of the total scattering coefficient $b_t$ and the particle only scattering coefficient $b_p$. The very small difference between statistics of the total absorption coefficient $a_t$ and the particle only absorption coefficient $a_p$ indicates a small influence on absorption by CDOM at 650 nm. Because the scattering coefficients for water are much smaller than scattering coefficients for particles in the study area (Mobley 1994), scattering by water will not be included in the following analysis.
The average value of $b_{t\cdot 650}$ is 0.52 (m$^2$/g). This is very close to the average value of $b_{t\cdot 555} = 0.5$ (m$^2$/g) reported by Babin et al. (2003) for European coastal waters. Binding et al. (2005) reported an average $b_{t\cdot 665} = 0.4831$ (m$^2$/g) for PIM only in the Irish Sea. The average value of $b_{t\cdot 650}$ is 0.006 (m$^2$/g) and the average of $a_{t\cdot 650}$ is 0.02 (m$^2$/g). Because the remotely sensed signal represents the combined effects of scattering, backscattering and absorption by suspended particles, a mass specific coefficient, $Rrs_{\cdot 650}$, is also computed. The average value at 650 nm for the data in the study area was $Rrs_{\cdot 650} = 0.012$ (arbitrary units).

The scattering, backscattering and $Rrs$ coefficients are plotted with TSM (Figs. 8 – 10) to illustrate the range of the mass specific coefficients. There do not appear to be any dominant modes in any of these plots that would suggest there are particle assemblages in the study area that have distinctly different compositions. It should also be noted that the average values of the mass specific coefficients are not equal to the zero crossing regression slopes in the figures.

*Figure 8. $b_{t\cdot 650}$ vs. TSM for all data in the study area. Solid line is regression line passing through zero. The slope of this regression line would represent the ideal value of*
$b^*$. The large amount of variability in $b_{6650}$ vs. TSM indicates $b^*$ is variable throughout the study area.

Figure 9. $b_{6650}$ vs. TSM for all data in the study area. Solid line is regression line passing through zero.

Figure 10. $Rrs_{650}$ vs. TSM for all data in the study area. Solid line is regression line passing through zero.
The backscatter ratio is often used as an indicator of variability in particle composition. The average $b_b/b_{650}$ in all data is 0.011 and regression analysis reveals a backscattering to scattering relationship of $b_b = 0.0144 \, b - 0.0045$ ($r^2 = 0.94$, $n=70$). Average values of $b_b/b_{650}$ for water classes range from 0.015 to 0.01 from River Mouth to Shelf water (Table 9). Regression slopes for $b_b$ vs. $b$ in waters both within the bay and outside the mouth of Mobile Bay were reported as 0.01 and 0.013 respectively (Ladner et al. 2002). Loisel et al. (2007) reported $b_b(650) = 0.0137 \, b(650) + 0.00045$ for coastal waters around Europe but there was high variability attributed to up to two-fold differences in regional POC to TSM and Chl a ratios (their Figs. 4 and 8). Higher POC to TSM ratios were coincident with lower $b_b/b$ values in higher salinity waters (Loisel et al. 2007). All values of $b_b/b$ discussed here are lower than those derived from measurements of the volume scattering function (Petzold 1972) by Gould et al. (1999) who reported $b_b = 0.0189 \, b + 0.00006$.

**Water Classification Summary**

Surface data from each cruise was segregated by water classification as described above (Table 9). Parameter values in each class were averaged and differences in means between classes were tested for significance using the single factor ANOVA. As noted previously, only classes River Mouth, Ambient, Plume and Shelf were included in the ANOVA. The variability in all parameters was quite high as indicated by the parameter standard deviations (Table 9). However, with two exceptions, differences in the water class means of all parameters were significant ($p < 0.01$). The exceptions are the difference in class means of $b_b*650$ ($p < 0.031$), and differences in $Rrs*650$ means, which were significant only between Ambient and Shelf classes ($p < 0.01$).
Table 8

All Station Surface Data Summary

<table>
<thead>
<tr>
<th>All Stations</th>
<th>Mean</th>
<th>St. Dev.</th>
<th>COV</th>
<th>MIN</th>
<th>MAX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dist. from SWP (km)</td>
<td>25.65</td>
<td>21.62</td>
<td>0.84</td>
<td>1.59</td>
<td>76.97</td>
</tr>
<tr>
<td>Salinity</td>
<td>22.30</td>
<td>7.85</td>
<td>0.35</td>
<td>0.00</td>
<td>34.40</td>
</tr>
<tr>
<td>Chl a (ug/l)</td>
<td>5.13</td>
<td>8.17</td>
<td>1.59</td>
<td>0.02</td>
<td>46.20</td>
</tr>
<tr>
<td>TSM (mg/l)</td>
<td>6.53</td>
<td>7.10</td>
<td>1.09</td>
<td>0.37</td>
<td>41.15</td>
</tr>
<tr>
<td>%OM</td>
<td>47.33</td>
<td>27.61</td>
<td>0.58</td>
<td>13.27</td>
<td>100.00</td>
</tr>
<tr>
<td>a₆₅₀ (m⁻¹)</td>
<td>0.07</td>
<td>0.06</td>
<td>0.92</td>
<td>0.00</td>
<td>0.29</td>
</tr>
<tr>
<td>b₆₅₀ (m⁻¹)</td>
<td>2.50</td>
<td>2.85</td>
<td>1.14</td>
<td>0.01</td>
<td>15.15</td>
</tr>
<tr>
<td>b₆₅₀ (m⁻¹)</td>
<td>0.029</td>
<td>0.036</td>
<td>1.225</td>
<td>0.001</td>
<td>0.177</td>
</tr>
<tr>
<td>bₜ/b₆₅₀</td>
<td>0.011</td>
<td>0.003</td>
<td>0.287</td>
<td>0.004</td>
<td>0.018</td>
</tr>
<tr>
<td>bₗ₆₅₀</td>
<td>0.96</td>
<td>0.04</td>
<td>0.74</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Rrs₆₅₀</td>
<td>0.26</td>
<td>0.15</td>
<td>0.56</td>
<td>0.03</td>
<td>0.66</td>
</tr>
<tr>
<td>a₉₆₅₀ (m⁻¹)</td>
<td>0.06</td>
<td>0.07</td>
<td>1.16</td>
<td>0.00</td>
<td>0.28</td>
</tr>
<tr>
<td>b₉₆₅₀ (m⁻¹)</td>
<td>2.46</td>
<td>2.98</td>
<td>1.21</td>
<td>0.09</td>
<td>15.17</td>
</tr>
<tr>
<td>bₗ₉₆₅₀ (m²/g)</td>
<td>0.52</td>
<td>0.35</td>
<td>0.67</td>
<td>0.01</td>
<td>2.00</td>
</tr>
<tr>
<td>b₉ₚ₆₅₀ (m²/g)</td>
<td>0.54</td>
<td>0.35</td>
<td>0.65</td>
<td>0.05</td>
<td>2.00</td>
</tr>
<tr>
<td>bₗ₉₆₅₀ (m²/g)</td>
<td>0.006</td>
<td>0.004</td>
<td>0.759</td>
<td>0.000</td>
<td>0.028</td>
</tr>
<tr>
<td>a₉₉₆₅₀ (m²/g)</td>
<td>0.020</td>
<td>0.018</td>
<td>0.906</td>
<td>0.000</td>
<td>0.096</td>
</tr>
<tr>
<td>a₉ₚ₆₅₀ (m²/g)</td>
<td>0.016</td>
<td>0.020</td>
<td>1.223</td>
<td>0.000</td>
<td>0.093</td>
</tr>
<tr>
<td>r₁ (g/cm³)</td>
<td>1.92</td>
<td>0.44</td>
<td>0.23</td>
<td>1.08</td>
<td>2.65</td>
</tr>
<tr>
<td>r₂ (g/cm³)</td>
<td>1.98</td>
<td>0.43</td>
<td>0.22</td>
<td>1.14</td>
<td>2.65</td>
</tr>
<tr>
<td>n₁</td>
<td>1.11</td>
<td>0.04</td>
<td>0.03</td>
<td>1.04</td>
<td>1.16</td>
</tr>
<tr>
<td>n₃</td>
<td>1.14</td>
<td>0.03</td>
<td>0.03</td>
<td>1.07</td>
<td>1.17</td>
</tr>
<tr>
<td>Ngct</td>
<td>1.05</td>
<td>0.04</td>
<td>0.04</td>
<td>1.00</td>
<td>1.13</td>
</tr>
<tr>
<td>Ngcp</td>
<td>1.09</td>
<td>0.05</td>
<td>0.04</td>
<td>1.00</td>
<td>1.17</td>
</tr>
<tr>
<td>ζ₂</td>
<td>2.16</td>
<td>0.59</td>
<td>0.27</td>
<td>3.23</td>
<td>0.79</td>
</tr>
<tr>
<td>O₂</td>
<td>10.67</td>
<td>0.75</td>
<td>0.07</td>
<td>9.36</td>
<td>12.52</td>
</tr>
<tr>
<td>ζ₉₉ct</td>
<td>4.27</td>
<td>0.47</td>
<td>0.11</td>
<td>3.59</td>
<td>5.47</td>
</tr>
<tr>
<td>ζ₉₉cp</td>
<td>4.11</td>
<td>0.44</td>
<td>0.11</td>
<td>3.60</td>
<td>5.46</td>
</tr>
<tr>
<td>Rrs*₆₅₀</td>
<td>0.12</td>
<td>0.17</td>
<td>1.37</td>
<td>0.01</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Because the study area represents an unbounded estuary, the segregation of stations into classes representing different mixing regimes was expected to reveal conservative mixing trends between classes, similar to trends observed in an enclosed
estuary between the freshwater inflow and the saltwater mouth. This progression is represented in the defined classes as *River Mouth* (freshwater inflow), *Ambient* (intermediate zone), *Plume* (conservative mixing zone) and *Shelf* (saltwater mouth). Between class trends in mean salinity, TSM, %OM, \(b_t\), \(b_b\), \(b_t/b_b\), bulk index of refraction, and bulk density were consistent with each other. All were higher near the river mouth and lowest in shelf waters. The *Plume* class means were generally between those of *Ambient* and *Shelf*. Salinity and %OM followed the opposite trend, i.e. lower near the river mouth and highest in shelf waters.

Trends between classes in parameter COV’s were not as consistent between the parameters (Table 10). The COV of salinity was highest near the river mouth and lowest in shelf waters. The COV’s of TSM, \(b_t\) and \(b_b\) were lowest near the mouth and highest in shelf waters. The COV’s of derived parameters such as %OM, \(n\), \(r\), \(b_t/b_b\) Rrs, \(b^*\) and \(b_b^*\) did not share any particular spatial patterns. This high spatial variability in both the means and standard deviations was also observed in the study area in an analysis of spatial changes in the output of a flow-through chlorophyll fluorometer (Yuan, et al. 2005).

Overall, the means of parameters grouped by water class were significantly different, with noted exceptions. However, high standard deviation and high COV’s for most parameters indicated there was high variability and much overlap in data values between water classes. The lowest COV’s were for parameters associated with change in particle composition, i.e. %OM, bulk density and index of refraction, and the \(b_t/b\) ratio. These results indicate that while the differences between classes are significant, the presence of both mineral and organic particles in spatially varying proportions will make
Table 9

Water Class Parameters. (†-For classes Mouth, Plume, Ambient and Shelf, Differences in Mean are Significant ($p < 0.01$, Single Factor ANOVA)), (‡-p < 0.031), (§-Ambient and Shelf only [p<0.01])
it difficult to detect distinctly different values of mass specific optical coefficients for the water classes. Further partitioning of optical coefficients relative to numbers of mineral and organic particles may be helpful in identifying trends for mass specific optical coefficients in the classes.

Table 10

**Water class Coefficient of Variation**

<table>
<thead>
<tr>
<th></th>
<th>Mouth</th>
<th>Ambient</th>
<th>Plume</th>
<th>Shelf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity</td>
<td>0.626</td>
<td>0.234</td>
<td>0.291</td>
<td>0.175</td>
</tr>
<tr>
<td>TSM</td>
<td>0.754</td>
<td>0.770</td>
<td>0.843</td>
<td>1.428</td>
</tr>
<tr>
<td>%OM</td>
<td>0.332</td>
<td>0.665</td>
<td>0.513</td>
<td>0.366</td>
</tr>
<tr>
<td>$b_0$650</td>
<td>0.535</td>
<td>0.703</td>
<td>0.805</td>
<td>1.543</td>
</tr>
<tr>
<td>$b_0$650</td>
<td>0.606</td>
<td>0.803</td>
<td>0.940</td>
<td>1.842</td>
</tr>
<tr>
<td>$b_0/b_650$</td>
<td>0.121</td>
<td>0.317</td>
<td>0.300</td>
<td>0.226</td>
</tr>
<tr>
<td>$Rrs_{650}$</td>
<td>0.366</td>
<td>0.418</td>
<td>1.062</td>
<td>0.628</td>
</tr>
<tr>
<td>r1</td>
<td>0.050</td>
<td>0.161</td>
<td>0.231</td>
<td>0.270</td>
</tr>
<tr>
<td>r2</td>
<td>0.044</td>
<td>0.152</td>
<td>0.219</td>
<td>0.253</td>
</tr>
<tr>
<td>n1</td>
<td>0.009</td>
<td>0.026</td>
<td>0.033</td>
<td>0.031</td>
</tr>
<tr>
<td>n3</td>
<td>0.004</td>
<td>0.021</td>
<td>0.029</td>
<td>0.030</td>
</tr>
<tr>
<td>$\xi_2$</td>
<td>0.136</td>
<td>0.350</td>
<td>0.220</td>
<td>0.111</td>
</tr>
<tr>
<td>O2</td>
<td>0.049</td>
<td>0.058</td>
<td>0.046</td>
<td>0.071</td>
</tr>
<tr>
<td>ngct</td>
<td>0.021</td>
<td>0.048</td>
<td>0.041</td>
<td>0.036</td>
</tr>
<tr>
<td>ngcp</td>
<td>0.030</td>
<td>0.057</td>
<td>0.042</td>
<td>0.039</td>
</tr>
<tr>
<td>$\xi_{gct}$</td>
<td>0.049</td>
<td>0.123</td>
<td>0.107</td>
<td>0.120</td>
</tr>
<tr>
<td>$\xi_{gcp}$</td>
<td>0.053</td>
<td>0.136</td>
<td>0.113</td>
<td>0.112</td>
</tr>
<tr>
<td>$b_t*650$</td>
<td>0.534</td>
<td>0.627</td>
<td>0.445</td>
<td>0.675</td>
</tr>
<tr>
<td>$b_p*650$</td>
<td>0.552</td>
<td>0.673</td>
<td>0.408</td>
<td>0.629</td>
</tr>
<tr>
<td>$b_b*650$</td>
<td>0.597</td>
<td>0.643</td>
<td>0.473</td>
<td>0.536</td>
</tr>
<tr>
<td>$b_p650$</td>
<td>0.585</td>
<td>0.742</td>
<td>0.883</td>
<td>1.590</td>
</tr>
<tr>
<td>k2</td>
<td>0.841</td>
<td>2.744</td>
<td>0.942</td>
<td>2.714</td>
</tr>
<tr>
<td>$Rrs*650$</td>
<td>0.398</td>
<td>0.746</td>
<td>1.969</td>
<td>1.169</td>
</tr>
</tbody>
</table>
Mass Specific Optical Coefficients

The scattering, and backscattering coefficients were plotted with TSM to graphically demonstrate the regional differences and overlap in $b^*$ and $b_b^*$ (Figs. 11 and 12). The regression line slopes were not tested for statistical significance but they are similar in magnitude to the average values for each water class. While the slopes for each class are different, the scatter and overlap in the data is clear in the figures. Values of the regression coefficients in Figs. 11 and 12 increase as the influence of mineral particles on TSM decreases in the progression of water classes from Ambient to Plume to Shelf. As noted previously this trend is similar to observations in other coastal waters (e.g. Babin et al. 2003; Loisel et al. 2007). However the magnitudes of $b^{*650}$ reported here are all within the range of values reported for near shore waters by Babin et al. (2003) and do not reach the value of $b^* = 1.0$ observed in their Atlantic Ocean stations. The values of $b^{*650}$ and $b_b^{*650}$ in the River Mouth stations range dramatically in magnitude and exhibit no trend with TSM. This is probably a result of the difference in time and location between the collection of water samples and the measurement of optical coefficients.

It can also be seen in Figs. 11 and 12 that the ratio of the magnitudes of $b^*$ and $b_b^*$ in each class are very similar. This indicates that the backscatter to total scatter ratio does not vary much between water classes.
Figure 11. Regional differences in $b_{650}$ vs. TSM. Solid lines are zero crossing regression lines not tested for significance, (RM = River Mouth, Amb = Ambient, Sh = Shelf). Note that in Shelf stations where there are fewer mineral particles the regression slope is highest, whereas in Ambient water where mineral particles are more abundant the regression slope is lowest. This trend is similar to that reported by Babin et al. (2003).

Figure 12. Regional differences in $b_{650}$ vs. TSM. Solid lines are zero crossing regression lines not tested for significance (RM = River Mouth, Amb = Ambient, Sh = Shelf). Note the trend in values of the regression slope is similar to that found for $b_{650}$ vs. TSM above.
Percent difference between all data set values and regional values of $b^*$, $b_b^*$, $a^*$, and $Rrs^*$ were computed for comparison, e.g. the percent difference between $b^*_t$ of All stations and $b^*_t$ of Shore stations is $d_{Shore} = 100(b^*_t(\text{All}) - b^*_t(\text{Shore})/(b^*_t(\text{All}))$ (Table 11). There does not appear to be any consistent pattern in errors between variables. The percent error is highest for the Blue station. While TSM at this station was expected to be low, scattering and backscattering were higher than expected. The value for $b^*$ of 0.135 is much lower than other reported open ocean values (e.g. $b^* \sim 1.0$ in Atlantic stations reported by Babin et al. 2003). It is possible that either or both the TSM measurement and the optical measurements were not accurate due to the low (0.37 mg/l) TSM found at this station. There was no backscatter data for the MR station because the instrument was saturated in all channels.

Table 11

*Regional Differences in Mass Specific Optical Coefficients Between All Stations and Water Class Stations. Negative Numbers Indicate Class Values are Greater Than Average Values*

<table>
<thead>
<tr>
<th>Water Class</th>
<th>$b^*_t650$</th>
<th>$b_b^*_t650$</th>
<th>$a^*_t$</th>
<th>$Rrs^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore</td>
<td>0.508</td>
<td>0.006</td>
<td>0.012</td>
<td>0.032</td>
</tr>
<tr>
<td>Blue</td>
<td>0.135</td>
<td>0.002</td>
<td>0.047</td>
<td>0.129</td>
</tr>
<tr>
<td>Shelf</td>
<td>0.525</td>
<td>0.005</td>
<td>0.025</td>
<td>0.199</td>
</tr>
<tr>
<td>Plume</td>
<td>0.531</td>
<td>0.005</td>
<td>0.023</td>
<td>0.188</td>
</tr>
<tr>
<td>Ambient</td>
<td>0.375</td>
<td>0.005</td>
<td>0.010</td>
<td>0.053</td>
</tr>
<tr>
<td>River Mouth</td>
<td>0.648</td>
<td>0.010</td>
<td>0.011</td>
<td>0.052</td>
</tr>
<tr>
<td>MR</td>
<td>0.601</td>
<td></td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>All</td>
<td>0.520</td>
<td>0.006</td>
<td>0.020</td>
<td>0.125</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% Difference from All</th>
</tr>
</thead>
<tbody>
<tr>
<td>dShore</td>
</tr>
<tr>
<td>dBlue</td>
</tr>
<tr>
<td>dShelf</td>
</tr>
<tr>
<td>dPlume</td>
</tr>
<tr>
<td>dAmbient</td>
</tr>
<tr>
<td>dRiver Mouth</td>
</tr>
<tr>
<td>dMR</td>
</tr>
</tbody>
</table>
To estimate error in calculated TSM, $Rrs^{650}$ for All stations was used to compute the average TSM for each water class (Table 12). TSM is significantly underestimated in all water classes except Blue.

Table 12

<table>
<thead>
<tr>
<th>Water Class</th>
<th>TSM</th>
<th>$Rrs$</th>
<th>TSM (All $Rrs^*$)</th>
<th>%error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore</td>
<td>9.92</td>
<td>0.31</td>
<td>2.51</td>
<td>-74.73</td>
</tr>
<tr>
<td>Blue</td>
<td>0.37</td>
<td>0.05</td>
<td>0.38</td>
<td>3.25</td>
</tr>
<tr>
<td>Shelf</td>
<td>2.50</td>
<td>0.22</td>
<td>1.77</td>
<td>-29.37</td>
</tr>
<tr>
<td>Plume</td>
<td>4.49</td>
<td>0.34</td>
<td>2.69</td>
<td>-40.14</td>
</tr>
<tr>
<td>Ambient</td>
<td>8.82</td>
<td>0.32</td>
<td>2.56</td>
<td>-70.98</td>
</tr>
<tr>
<td>River Mouth</td>
<td>13.28</td>
<td>0.45</td>
<td>3.62</td>
<td>-72.74</td>
</tr>
<tr>
<td>MR</td>
<td>25.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All</td>
<td>6.53</td>
<td>0.26</td>
<td>2.11</td>
<td>-67.73</td>
</tr>
</tbody>
</table>

Cause of Variability in $b^*$, $b_b^*$, $a^*$ and $Rrs^*$

The estimates of bulk particle refractive index and density are based on several assumptions about the relationship between %OM and the relative numbers and volumes of organic vs. inorganic particles. Because these assumptions can not be validated with direct measurements regression analysis was used to compare both individual optical coefficients and mass specific optical coefficients to %OM, bulk index of refraction and bulk density. In regression analysis with all data combined, $b_{650}$, $b_b^{650}$, and $Rrs_{650}$ were significantly correlated with bulk index of refraction ($p < 0.01$) although correlation coefficients were low ($r^2 < 0.32$) (Figs. 13 - 15). The regression trend line indicated higher $b_{650}$, $b_b^{650}$, and $Rrs_{650}$ occurred with higher bulk index of refraction. Variability in optical coefficients is partially explained by the variability in bulk index of refraction computed using the weighting by %OM. Up to 25 % of the variability in $b_{650}$
can be explained by the variability in n1 (Fig. 13). Up to 30% of the variability in $b_{650}$ is explained by n1 (Fig. 14). These results indicate that %OM can be used to interpret bulk particle characteristics but there are clearly additional factors related to particle sizes and numbers that must be investigated.

As expected, no significant trends were found between $a_{650}$ and bulk index of refraction. This is due to the low particle absorption at 650 nm as seen in the nearly constant scattering to beam attenuation ratio ($b/c_{650}$) relative to %OM (Fig. 17). There is a slight significant ($p < 0.011$) trend of lower $b/c_{650}$ with increasing %OM (Fig. 17), however the high average $b/c_{650}$ (0.96) and low COV (0.04) indicates the influence of absorption on the total beam attenuation coefficient is very small at 650 nm. Because $a_{650}$ is not significantly correlated with n1, only 12% of the variability in $Rrs \propto b_{650}/(b_{650} + a)$ is explained by variability in n1 (Fig. 15).

![Figure 13](image_url)

Figure 13. $b_{650}$ vs. n1 and n3. Note the greatest scattering occurs with particles having the highest refractive index. While the data in the scatter plot appear to have a somewhat exponential relationship, regression analysis indicates a first order linear equation best describes the relationship.
Figure 14. \( b_{650} \) vs. n1 and n3.

Figure 15. \( Rrs_{650} \) vs. n1 and n3. Note there is a trend toward increasing \( Rrs_{650} \) with increasing refractive index however only 12% of the variability is accounted for in this relationship.
Figure 16. $b_\nu/b_{650}$ vs. n1. Variability in the $b_\nu/b$ ratio is often associated with variability in particle composition however in this data set variability in n1 only accounts for about 24% of the variability in $b_\nu/b$.

Figure 17. $b/c_{650}$ vs. %OM. The single scattering albedo remains relatively constant for the entire data set as %OM varies from about 10% to 100% suggesting that other factors such as the PSD or relative numbers of particles of different types may be affecting this relationship.

There was also an increase in the $b_\nu/b_{650}$ ratio with increase in bulk index of refraction (Fig. 16). Regression of log-log transformed data results in a significant
correlation between $b_b/b_{650}$ and $n_1$ using a power law function with coefficients $n = 1 + 1.994(b_b/b)^{0.662}$ (Fig. 18). These coefficients are very similar to those reported by Twardowski et al. (2001, their equation 16) as $n = 1 + 1.671(b_b/b)^{0.582}$. This regression demonstrates about 23% of the variability in $b_b/b_{650}$ is due to variability in $n_1$.

\[
\begin{align*}
n_{pb650} &= 1 + 1.671(b_b/b_{650})^{0.582} \\
n_1\text{regr} &= 1 + 1.994(b_b/b_{650})^{0.662}
\end{align*}
\]

**Figure 18.** $n_1$ vs. $b_b/b_{650}$. Triangles are $n_{pb650}$ (Twardowski et al. 2001), squares are regression coefficients between $n_1$ and $b_b/b_{650}$ and diamonds are $n_1$ computed from %OM.

The mass specific optical coefficients were compared to the bulk index of refraction using regression analysis. In regressions including all data there are no significant trends between $b_t^*650$ and $n_1$ or $n_3$ (Fig. 19). There was a trend of decreasing $b_t^*650$ with increasing $n_1$ in the Plume class data (Fig. 22, $r^2 = 0.30$, $p < 0.02$, $n = 15$).

However no significant trends were observed in other water classes. A similar trend was observed between $a_t^*650$ and $n_1$ in Ambient water (Fig. 23, $r^2 = 0.39$, $n = 13$, $p <0.013$).

No significant trends were observed in other water classes. There was no significant
trend between $b_t*650$ and n1 in all data (Fig. 20) or any water class (Fig. 24). There was a weak trend of decreasing $Rrs*650$ with increasing n1 in all data (Fig. 21, p<0.01) and in Ambient, Plume, and Shelf waters although not significant at p < 0.01 (Fig. 25). This trend is due to the influence of the trend between $a_t*650$ and n1.

Figure 19. n1 and n3 vs. $bt*650$. Solid line is non-significant trend line.

Figure 20. n1 and n3 vs. $b_t*650$. Solid lines are non-significant trend lines.
$y = -0.1241x + 1.1221$

$R^2 = 0.32, n=60, p<0.01$

$y_{Plume} = -3.7909x + 4.7198$

$R^2 = 0.30, n=15, p<0.02$

**Figure 21.** $Rrs*650$ vs. $n_1$ and $n_3$. Solid line is regression indicating that about 32% of the variability in $n_1$ is due to variability in $Rrs*650$.

**Figure 22.** $b_t*650$ vs. $n_1$. Solid line is regression line indicating about 30% of variability in $b_t*650$ is due to variability in $n_1$ in plume transect stations. No significant correlations were found in the other water class stations.
Figure 23. $a_t \cdot 650$ vs. $n_1$. Solid line is regression line indicating that about 39% of the variability in $a_t \cdot 650$ is due to variability in $n_1$ in Ambient water stations. No similar trends were found in Shelf and Plume stations.

Figure 24. $b_b \cdot 650$ vs. $n_1$. No significant correlations were found between $b_b \cdot 650$ and $n_1$ segregated by water class.
\( y_{\text{Amb}} = -0.7797x + 0.9336 \)  
\( R^2 = 0.37, n=13, p<0.016 \)

\( y_{\text{Plume}} = -5.5218x + 6.2897 \)  
\( R^2 = 0.25, n=15, p<0.033 \)

\( y_{\text{Shelf}} = -3.4927x + 3.9858 \)  
\( R^2 = 0.22, n=21, p<0.02 \)

Figure 25.  \( R_{rs*650} \) vs. \( n_1 \) segregated by water class.  Solid lines are weakly significant (i.e. p < 0.033) regression lines indicating that variability in \( R_{rs*650} \) is partially due to variability in \( n_1 \) when data is segregated by water class.

**Plume Transect Stations**

In the water class analysis above, the means of *Plume* class parameters fell between *Ambient* and *Shelf* water means.  Because plume transect stations represent the locations where fresh water and the associated high mineral particle load extend out from the river mouth, the particle and optical properties in this elongated mixing zone will be examined in detail.  Regression analysis demonstrated that variables measured in the plume transect stations had higher correlation coefficients when compared to distance from the mouth than when compared to salinity.  TSM was found to decrease rapidly with distance from the mouth (Fig. 27).  Regression analysis found the strongest relationship between TSM and distance from the mouth was \( \text{TSM} = 48.072x^{-0.9642} \) \( (r^2 = 0.82, n = 19, p < 0.01) \).  The relationship between %OM and distance was also best fit with a power function, \( \%\text{OM} = 11.327x^{0.4949} \) \( (\text{Fig. 28}, r^2 = 0.78, p<<0.01) \).
Optical coefficients also decreased with distance from the mouth. The relationship between $b_{650}$ and $b_{b650}$ vs. distance were best fit with power functions $b_{650} = 28.959x^{-1.028}$ (Fig. 29, $r^2 = 0.72$, $n=15$, $p<<0.01$) and $b_{b650} = 0.5278x^{-1.239}$ (Fig. 30, $r^2 = 0.85$, $n=15$, $p<<0.01$). The power law relationships between distance from the mouth and measured TSM and scattering are indicative of the deceleration and multidimensional expansion of the fresh water plume as it leaves the narrow (~750 m) channel at the mouth of Southwest Pass (Wright and Coleman 1971).

The absorption coefficient $a_{650}$ can also be fit with a power function but the correlation is much lower (Fig. 31, $r^2 = 0.27$, $p < 0.024$). This lack of correlation between $a_{650}$ and distance clearly has an impact on $Rrs_{650}$ (Fig. 32). There is a trend of higher values of $Rrs_{650}$ near the mouth, decreasing with distance but the trend is not statistically significant.

The power law exponents for $b_{650}$ (-1.028) and TSM (-0.9642) are very similar in magnitude indicating a strong correlation in plume data. The power law exponent of $b_{b650}$ (-1.239) indicates a greater decrease with distance than $b_{650}$. This difference is also observed in the approximately 50% decrease in the $b_{b}/b_{650}$ ratio along the plume (Fig. 33). The simultaneous increase in %OM and decrease in $b_{b650}$ and $b_{b}/b_{650}$ ($r^2 = 0.37$, $p<0.01$, linear regression, data not shown) also demonstrates the importance of particle composition on the backscattering coefficient. This also demonstrates the influence of the decrease in bulk index of refraction on the backscattering coefficient over the length of the plume (Fig. 34). It should be noted that change in the slope of the particle size distribution function could also be a significant contributor to this observation and will be investigated in subsequent chapters.
Optical properties were all significantly correlated with TSM and %OM in plume stations (p < 0.01, data not shown). However, as demonstrated above (Figs. 19 – 25), mass specific optical coefficients were not, with the exception of $R_{rs}*650$ vs. n1 (Fig. 21). Reasons for this are not readily apparent. One possibility is that the presence of mineral particles, even in small relative proportion, dominates both TSM and scattering coefficients. Comparison between density and TSM (Fig. 7) shows that as density increases from the lowest values (1.08 g/cm$^3$) to the highest values (2.65 g/cm$^3$), TSM only increases from near zero to less than 5 mg/l. For TSM between 5 and 40 mg/l, bulk densities are at the maximum value. Similarly, when $b_{\beta}650$ is compared to n1 in plume stations, $b_{\beta}650$ increases dramatically after n1 increases beyond mid-range (Fig. 35, $r^2 = 0.56$, n=15, p < 0.01). The same increase occurs with $b_{\beta}650$ (data not shown). The simultaneous increase in both scattering coefficients and TSM in the presence of mineral particles could reduce the variability in the mass specific coefficients.
Figure 26. Salinity vs. Distance from Southwest Pass in plume transect stations. Note that the non-linear regression equation indicates the multi-dimensional dispersal of the plume waters in the un-bounded shelf water.

\[ y = 8.5647x^{0.3114} \]

\[ r^2 = 0.57, n=18, p<<0.01 \]
**Figure 27.** TSM vs. Distance from Southwest Pass in plume transect stations. Trend line indicates $1/distance$ decrease in TSM. This trend holds for plume transect data in each of the three cruises conducted at different times and flow conditions.

**Figure 28.** %OM vs. Distance from Southwest Pass in plume transect stations. Solid regression line is similar to regression between Salinity and Distance above.
Figure 29. $b_{650}$ vs. Distance from Southwest Pass in plume transect stations. Note the solid regression line is similar to the TSM vs. Distance regression line above.

Figure 30. $b_{b,650}$ vs. Distance from Southwest Pass in plume transect stations. Note the solid regression line is similar to both the TSM and $b_{650}$ regression lines above.
Figure 31. $a_{650}$ vs. Distance from Southwest Pass in plume transect stations. Note the solid regression line indicates that variability in $a_{650}$ is not as closely coupled to distance as is $b_{650}$ and $b_{b_{650}}$.

Figure 32. $R_{rs650}$ vs. Distance from Southwest Pass in plume transect stations. Solid line is non-significant trend line which shows that the low correlation between $a_{650}$ and distance (Fig. 31 above) has a significant impact on $R_{rs650}$ vs. distance even when TSM, $b_{650}$, and $b_{b_{650}}$ are strongly correlated with distance.
Figure 33. $b/b_{650}$ vs. Distance from Southwest Pass in plume transect stations.

Figure 34. $n_1$ vs. Distance from Southwest Pass in plume transect stations. The solid regression line indicates the change in particle composition from mostly mineral near the river mouth to mostly organic particles in shelf waters.
Figure 35. $b_{650}$ vs. $n_1$ in plume transect stations. The solid regression line indicate the greater amount of backscatter by particles with high refractive indices.

Discussion and Conclusions

The large amount of variability in this data set makes it difficult to draw any widespread conclusions in this study area. However, the results above clearly demonstrate significant correlations between optical properties, TSM, and bulk particle density and index of refraction derived from %OM. The weak but significant correlations between parameters suggest that the variability in the data is possibly due mostly to the methodologies used in this study. The uncertainty in the %OM computations where the organic fraction is high appears to be largely affected by the low mass of suspended particles, the uncertainty in the salt mass retention and the ashing step in the loss on ignition technique. Uncertainty in %OM where there is a high mineral fraction is possibly due to the unaccounted for loss of structural water from the clay minerals during the ashing process.
Scatter between optical coefficients and TSM values is also due in part to the difference in time and location between water sampling and optical measurements. This time difference is usually at least 20 minutes. During cruises NE2 and NE3 the ship often drifted at a rate of between 1.0 and 2.0 knots while on station. While the uncertainty due to sample time and location is not quantified, there is a potential for samples to have been collected in very different waters from where optical properties were measured, especially at stations near the plume or ambient waters.

The hypothesis of this work was that the mass specific scattering and absorption coefficients vary as a function of change in bulk particle density and bulk particle index of refraction as determined by %OM. When stations were grouped by water class, differences in mean parameter values were significant. Trends between water classes indicated particle composition changed from low percentage of organic matter near the river input, to higher percentage of organic matter as river water mixed with shelf waters. These trends were also observed in plume transect stations. Both TSM and optical coefficients decreased in magnitude coincident with the change in composition. However, while the $b_t/b$ ratio decreased in samples away from the river mouth, the $b_t/b$ ratio did not vary as much as the change in composition or the change in TSM. As noted previously these observations do not consider the possible impact on optical coefficients due to changes in the particle size distribution function.

When all data were combined there were no significant correlations between $b_t*650$, $b_p*650$ and bulk index of refraction (Figs. 19 and 20). There was a weak but significant correlation between $Rrs*650$ and $n1$ (Fig. 21), suggesting that even though $a_t650$ is small relative to $b_t650$, it is nearly equal in magnitude to $b_p650$ and therefore has
a significant impact on the remote sensing signal, i.e. $Rrs \propto b_r/(a+b_b)$. The $b_r/b_{650}$ ratio was also weakly but significantly correlated with n1 as expected (Fig. 17).

When all data were considered, there were weak but significant linear correlations between optical coefficients $b_r650$, $b_{b650}$, $Rrs650$, and n1 (Figs. 13 – 15). These correlations were higher in plume stations and were best represented by power law functions. As noted previously, in Figs. 13 – 15, and Fig. 35, the magnitude of optical coefficients increased significantly as n1 increased from low values representing organic particles to higher values representing mineral particles. Similar results were obtained in the relationship between density and TSM (Fig. 7). It appears that the rates of change in density and refractive index result in simultaneous changes in scattering and TSM such that there is only a small variation in the scattering to TSM ratio. Because the $b_r/b$ ratio is also relatively constant there is a similarly small variation in the backscattering to TSM ratio.

To gain additional insight into the similar behavior in the relationship between n1 and $b_r650$ and the relationship between r1 and TSM, Figs. 14 and 7 were re-visited. In each case the response in both $b_r650$ and TSM to increases in n1 and r1 respectively was relatively small until n1 and r1 reached the mid point in their respective ranges. Above that point the response in both $b_r650$ and TSM was much more dramatic.

To investigate further the data were sorted and separated at the point where %OM was about 50%. Regression analysis for data with OM > 50 % showed that neither n1 and $b_r650$ or r1 and TSM were significantly correlated (Figs. 36 and 37). For data with OM < 50 %, correlations were significant and relationships between n1 and $b_r650$ and between r1 and TSM were best described by power law functions.
The $b_{b650}$ to TSM ratios were also different for data above and below the 50 % OM point (Fig. 38). The regression slope between $b_{b650}$ and TSM for data with OM < 50 % was 0.0048 (Fig. 38). The regression slope between $b_{b650}$ and TSM for data with OM > 50 % was 0.0087. Correlations in both cases were significant ($p < 0.01$). It is interesting to note however that $b_{b*650}$ was not significantly correlated with n1 in either case (Fig. 39). As was the case in the water class groupings described above, the average values of $b_{b*650}$ were not significantly different in the high and low OM groupings.

These results suggest that rather than a continuous change over the range of %OM, the relationships discussed above have more of a binary state with a switching point at OM = 50 %. These results suggest that relationships associated with mostly organic particles are overshadowed by relationships associated with mineral particles (Figs. 36 and 37). Because the average OM in Shelf waters in only about 67 %, the remaining mineral particles continue to dominate the variability in both TSM and the optical coefficients. This could explain the apparent lack of correlation between $b*$ and n1, i.e. there are few stations within the study area where mineral particles are not present.

Further investigation is needed to address the issues of uncertainty in the methodology noted above. Additional data further from the influence of plume waters could provide a greater range in data values thus adding contrast to the existing data set. The next section will investigate the particle size distribution function as a contributing factor in explaining the variability in $b*$ in the study area.
Figure 36. $b_{650}$ vs. $n_1$ for data segregated into high and low OM groups. $n_1L$ are values of $n_1$ with OM < 50%. $n_1H$ are values of $n_1$ with OM > 50%.

$$y = 0.8304x^{3.3394} \quad R^2 = 0.4157, \ n=46, \ p<0.01$$

$$y = 0.7377x + 0.8421 \quad R^2 = 0.0936$$

Figure 37. TSM vs. $r_1$ for data segregated into high and low OM groups. $r_1L$ are values of $r_1$ with OM < 50%. $r_1H$ are values of $r_1$ with OM > 50%.

$$y = 0.8304x^{3.3394} \quad R^2 = 0.4157, \ n=46, \ p<0.01$$

$$y = 0.7377x + 0.8421 \quad R^2 = 0.0936$$
Figure 38. $b_{b650}$ vs. TSM for data segregated into high and low OM groups. OML are values with OM < 50%. OMH are values with OM > 50%.

Figure 39. $b_{b*650}$ vs. n1 for data segregated into high and low OM groups. OML are values with OM < 50%. OMH are values with OM > 50%.
CHAPTER III
OPTICAL PROPERTIES AND SIZE DISTRIBUTIONS OF PARTICLE SUSPENSIONS IN THE NORTHERN GULF OF MEXICO

Abstract

The objective of this chapter was to determine if changes in the mass specific optical scattering coefficient $b*_{650}$ described in Chapter II, can be attributed to changes in the scaling factor $k$ and the slope parameter $\xi$ of the power law particle size distribution function of the particles suspended in the marine waters of the Louisiana continental shelf where mixing with Mississippi River water occurs. To accomplish this objective the PSD was measured using a particle size analyzer, the LISST-100b (Sequoia Scientific). The scaling factor $k$ and slope parameter $\xi$ were obtained by first converting the volumetric output of the LISST-100b to the number concentration $N(D)$ in each diameter $D$, of the output size bins of the LISST-100b, assuming all particles were homogeneous spheres. A least squares regression analysis was used to obtain the slope and offset of a first order polynomial regression equation for the log transformed values of $N(D)$ and $D$ of the LISST-100b data. The slope of this equation is $\xi$ and the offset determines the scaling factor as $k = 10^{\text{offset}}$. A second method was used to obtain $\xi$ using the spectral beam attenuation $c_p(\lambda)$ (Boss et al. 2001b). The values of $\xi$ obtained from the two methods were used with $k$ and density as inputs to the PSD to calculate $t_{sm}$ for comparison with measured TSM. Bulk particle density was obtained from the methods for $r_1$ described in Chapter II and by inverting the bulk particle index of refraction obtained using %OM and the backscattering to total scattering ratio at 650 nm $b_{b}/b_{650}$ (Twardowski et al. 2001). Results from the LISST-100b data produced an
average value of $\xi_2 = 2.16$. Results from the spectral beam attenuation method produced an average value of $\xi_{gcp} = 4.11$. When used as inputs to the PSD function $\xi_2$ over-estimated $\text{tsm}$ relative to TSM and $\xi_{gcp}$ underestimated $\text{tsm}$. When $\xi_{gcp}$ and $\xi_2$ were adjusted independently to obtain a match between $\text{tsm}$ and TSM, each was adjusted to a value near 3.0. Also, in each case the correlation between $\text{tsm}$ and TSM increased due to the adjusted values of $\xi_{gcp}$ and $\xi_2$. Regression analysis resulted in no significant correlation between $b^*_{650}$ and $\xi_{gcp}$ and $\xi_2$ or between $b^*_{650}$ and the bulk refractive index $n_1$ computed using %OM in Chapter II or bulk refractive index computed using $b_\nu/b_{650}$. These regression results applied to the entire data set as well as to the data grouped by region as described in Chapter II.

Introduction

Light scattering and absorption by particles suspended in marine waters is dependent on the bulk particle index of refraction and the numbers and size ranges of particles in suspension. The total dry mass or total suspended matter (TSM) of the particle assemblage is dependent on the bulk particle density and the numbers and sizes of particles. In Chapter II, the relationship between optical scattering, TSM, and bulk particle density and index of refraction were investigated. In this chapter variability in the relationship between optical scattering and TSM due to variability in the particle size distribution will be investigated.

Particle size distributions measured in marine waters are often characterized using the power law function $N(D) = kD^{\xi}$, where $N$ is the number of spherical particles of diameter $D$, in a volume of water, $\xi$ is the slope parameter of $N(D)$ vs. $D$ with log transformed data, and $k$ is a scaling factor (e.g. Bader 1970; Mobley 1994; Stramski et al.
The exponent $\xi$ is expected to be in the range of 2.5 to 5 for particles in the size range from ca. 0.01 µm to 250 µm (e.g. Mobley 1994; Stramski 2001; Boss et al. 2001b). The slope parameter $\xi$, and the scaling factor $k$ were the parameters of interest for this study. Because the PSD function $N(D) = kD^{-\xi}$ only accounts for the number of particles present, the particle density must be included to determine the total mass of the particle assemblage. The bulk particle density will be obtained from %OM as described in Chapter II.

It has been shown via Mie theory modeling (Ulloa 1994) that the ratio of backscattering (i.e. scattering at angles 90 to 180) to total scattering (i.e. angles from 0 to 180) varies in proportion to refractive index in the presence of small particles ($0.01 < D < 10$ µm). A model based on Mie theory for homogeneous spheres has been developed for obtaining bulk particle index of refraction using $\xi$ and the backscattering to total scattering ratio $b_b/b$ (Twardowski et al. 2001). This model was used here to provide a comparison with the bulk particle refractive index $n_1$ derived from %OM as described in Chapter II. The bulk particle refractive index computed with $b_b/b$ was inverted to obtain %OM using the weighting function and particle specific refractive indices described in Chapter II. Inverting this refractive index to %OM allowed for the estimation of bulk particle density from %OM as described previously in Chapter II.

It is understood that the assumptions with respect to using %OM to partition the bulk particle properties, i.e., refractive index and density, may not accurately represent the true proportions of the numbers of mineral and organic particles. In this chapter the power law PSD is assumed to represent the size characteristics of the total particle assemblage. If it is assumed that the particle assemblage could be partitioned into
separate organic and mineral assemblages, each having the same slope parameter, range of sizes and spherical shapes, the PSD for the combined assemblage could be partitioned into numbers of particles of each type using the measured TSM, %OM and particle specific densities described in Chapter II. Preliminary analysis using this approach showed that this was a feasible approach to partitioning the particle assemblage by numbers of particles of each type. The results clearly demonstrated that partitioning the particle assemblage by %OM alone to estimate bulk refractive index and density was not equivalent to partitioning by numbers of particles. However, because the relationships were algebraically derived from %OM the relationships that are the objective of this study are still valid. Partitioning of the particle assemblage by numbers of mineral and organic particles represents an approach for further research.

The methods of Twardowski et al. (2001) and Boss et al. (2001b) have been used to determine the bulk particle refractive index and the power law slope parameter in a range of coastal locations. In a study of suspended particle characteristics at nine locations in near-shore (depth < 30 m) U. S. coastal waters of the Atlantic and Pacific Oceans and Gulf of Mexico, Sullivan et al. (2005) found five somewhat distinct combinations of variable $b_p/b$ ratio, bulk particle index of refraction, and $\xi$, thus demonstrating need to consider particle characteristics on a regional basis. Using the model of Twardowski et al. (2001) to determine the relationships between $b_p/b$, bulk particle index of refraction and $\xi$, Sullivan et al. (2005) found the majority of particles had $\xi < 4.0$, $b_p/b$ was between 0.005 and 0.03, and bulk particle refractive index ranged from 1.02 to greater than 1.2 (their Fig. 2). Samples from the coasts of Florida and Texas, which Sullivan et al. (2005) characterized as Blue water or clear ocean water, had
the smallest range of $\xi$, with the majority of samples having $\xi$ between 3.7 and 4.0. The $b_r/b$ ratio ranged between 0.005 and 0.015, and the bulk particle index of refraction ranged between 1.04 and 1.08. In contrast, stations from Monterrey Bay, CA had $\xi$ ranging from 2.5 to about 3.7 and the majority of samples had $b_r/b$ between 0.005 and about 0.01 and bulk particle refractive index ranging from 1.08 to 1.14. The much lower values of $\xi$ in Monterrey Bay were attributed to high concentrations of large phytoplankton, many of which were diatoms having hard siliceous shells. There was much scatter in all the data sets with samples from each location having values found in all ranges of $\xi$, $b_r/b$, and bulk particle refractive index. In results obtained in the Gulf of California (Twardowski et al. 2001), $\xi$ ranged between about 3.5 and 4.0, bulk particle refractive index was between 1.04 and 1.18 and $b_r/b$ ranged between 0.005 and 0.025.

Using the same model on data from European coastal waters Loisel et al. (2007) found that samples containing mostly phytoplankton had lower variability in the $b_r/b$ ratio (~0.003 to 0.013) and bulk particle index of refraction (~1.02 to 1.12) but variability in $\xi$ was greater with $\xi$ ranging from about 3.0 to 4.5. In samples containing a greater percentage of inorganic and non-phytoplankton organic detritus, $b_r/b$ (~0.01 to 0.035) and bulk particle index of refraction (~1.04 to $>1.2$) had the greatest range and variability while $\xi$ ranged only from about 3.5 to 4.0 (Loisel et al. 2007). These two sample sets are similar to those reported for Monterey Bay and the Florida and Texas coastes respectively (Sullivan et al. 2005).

The average $b_r/b$ ratio reported in Chapter II of this study was 0.011 and ranged between 0.004 and 0.018, similar to data reported for the Texas and Florida coasts and
Monterey Bay (Sullivan et al. 2005). Similar values were found in Mobile Bay data 
\((b_/b_\sim 0.013, \text{ Ladner et al. 2002}).\)

The average value of bulk particle refractive index reported in Chapter II of this study was 1.11. Considering the average \(b_/b\) ratio also reported in Chapter II was 0.011, the model of Twardowski et al. (2001) would put the average for \(\xi\) for this study near about 3.4.

The scaling factor \(k\) has not been specifically addressed in the studies cited above. Babin et al. (2003) used Mie theory for homogeneous spheres, published particle densities and refractive indices, and an estimate of the volume concentration of particles obtained from \(b^*\) measured in European coastal waters, to demonstrate the possible values of \(\xi\) relative to \(b^*\) and particle density. The average value of \(b^*\) reported in Chapter II of this study was 0.54 \(\pm\) 0.35 \(m^2/g\), the average density was 1.92 \(g/cm^3\) and the average bulk refractive index was 1.11. Using the results of Babin et al. (2003) (their Fig. 10), this combination of values best matches a value of \(\xi \approx 4.0\) for data in this study.

The studies noted above demonstrate that there are a range of possible combinations of the power law size distribution parameters and the \(b_/b\) ratio that could be representative of a particular suspension of particles. The values of \(n\) and \(\xi\) obtained using the optical methods of Twardowski et al. (2001) and Boss et al. (2001b) do not provide an indication of the value of \(k\) or indicate the relative numbers of mineral and organic particles. Therefore those methods can not be readily validated without having more information about the particle composition or the size distribution.
The hypothesis of this chapter is that the variability in the scattering to TSM ratio can be attributed to variability in $\xi$, the scaling factor $k$, and bulk particle density, and that these relationships will hold when data is grouped by water class as defined in Chapter II.

The objective for this work was to examine the variability in the particle size distribution in the study area relative to the variability in the scattering to TSM ratio. The particle size distribution parameters $k$ and $\xi$ were determined using an *in situ* particle size analyzer, the LISST-100b (Sequoia Scientific). For comparison, $\xi$ was estimated from the spectral beam attenuation (Boss et al. 2001b) and the bulk particle refractive index was estimated from $b_\alpha/b$ and $\xi$ using the model of Twardowski et al. (2001).

Because the methods of Twardowski et al. (2001), Boss et al. (2001b), and the LISST-100b to determine the PSD parameters are based on different optical principles the results obtained here for $n$, $k$, and $\xi$ from the different methods were used as inputs to the PSD function to calculate the TSM. These results were used to provide insight into how the differences between these methods impacted $b^*$. Variability in derived values of $n$, $k$, and $\xi$, and calculated values of TSM were compared with variability in the measured scattering to TSM ratio for the study area and for the water classes defined in Chapter II.

**Methods**

**Cruises**

As described in Chapter II, data were collected during four cruises over the Louisiana shelf during fall, spring and summer in the period from October 2002 to May 2004 (Chapter II, Tables 1 and 4). Two cruises NE2 and NE3 were conducted south of the Louisiana Bight and west of the Mississippi River Birdfoot Delta and Southwest Pass when prevailing winds were driving the river plume mostly west across the shelf. Two
cruises, A3 and A4, were conducted in the plume mostly south of Southwest Pass and within 20 km of the mouth when winds were driving the river plume mostly south or east of the Birdfoot Delta.

Water samples from discrete depths were collected on separate casts from those for optical measurements. On cruises NE2 and NE3, water was acquired from 20 l Niskin bottles on the ship’s CTD rosette. Samples were collected at the surface, near the bottom and within a high chlorophyll or high turbidity region usually near a strong salinity gradient in the lower part of the mixed layer. On cruises A3 and A4, a single Niskin was deployed after the optical cast for a surface and near bottom sample. Time between CTD and optics casts was nominally 20 minutes to as much as an hour. Ship drift speed while on-station was often 1.0 – 2.0 knots so distance between sample locations could be as much as 3 km. Depths and salinities recorded for sample collections were used to match optical measurements for analysis.

On cruises A3, A4, NE2 and NE3 two optical casts were made at most stations. The first cast had no filter on the in-take tubes of the ac-9. The second cast was made with a 0.2 um filter on the in-take feeding both the absorption and attenuation tubes.

Optical Measurements

Optical measurements and coefficients used in this chapter were described in Chapter II. As was done in Chapter II, only absorption, scattering and backscattering coefficients at 650 nm will be used for analysis in this chapter.

Particle Size Distribution

Particle size distributions were measured using the Laser In situ, Scattering and Transmissometry, or LISST-100 B-type (Sequoia Scientific, Redmond, WA). The
LISST-100B is a laser diffraction, small forward scattering angle (near zero to 20 deg) particle size analyzer that can be used in situ in a profiling mode. This model uses a red LED laser as a source. The B version outputs a volumetric (μl/l) particle size distribution in 32 logarithmically spaced size bins between 1.25 and 250 μm (Agrawal and Pottsmith 2000, 2004). Because it is based on diffraction in the forward scattering angles, the measurement is assumed to be largely independent of the particle refractive index and internal structure. Particles are assumed to be spherical in shape and homogeneous in structure. Issues with respect to particle shape, orientation, and internal structure are assumed to be averaged out due to the random orientation and large number of independently oriented particles per sample volume present in marine waters.

Output units of μl/l are converted to number of particles per size bin assuming spherical particles. The new data is log transformed and a first order polynomial is fit to the data using least squares regression. The slope of the regression represents the exponent of the power law particle size distribution. This slope will be referred to as PSD slope $\xi_1$. The offset of the regression $O_1$, represents the scaling factor. The offset is converted to the power law scaling factor $k_1$ by inverting the log transformation, i.e. $k_1 = 10^{O_1}$.

When the data from the LISST-100b are converted to units of ul/l, there are occasionally values of zero in the smallest size bins. Other LISST 100 users have reported similar results (Reynolds 2008; Deric Grey, personal communication). In the regression analysis described above, values of zero are removed from the processing so they do not influence the regression coefficients. Because the presence of zero values did not appear to follow any consistent patterns relative to particle characteristics or TSM
values it was decided that a more consistent approach to obtain the regression coefficients was to remove the output for the smallest size bins from all the LISST-100b samples. A second regression was obtained using only data from bins in sizes 3 – 250 μm. This slope will be referred to as PSD slope \( \xi_2 \). The scaling factor will be referred to as \( k_2 \). Differences in \( \xi_1 \) and \( \xi_2 \) over all samples included in this study were small and did not produce differences in observed trends or other relationships.

**PSD Slopes \( \xi \) From the Beam Attenuation Spectrum**

It has been demonstrated using Mie theory that for non-absorbing particles \((n(im) = 0)\), with constant refractive index \( n \), distributed in size by a power law size distribution function, the shape of the particle beam attenuation spectrum can be described by the equation \( c_p(\lambda) = A\lambda^{-\gamma} \) over the wavelength range \( 420 \leq \lambda \leq 650 \) nm, where \( c_p(\lambda) \) is the spectral beam attenuation coefficient due to particles (Boss et al. 2001b). \( A \) and \( \gamma \) are the coefficients to be determined. Further, the slope parameter of the PSD function is related to \( c_p(\lambda) \) by the equation \( \xi = 3 + \gamma \) (Diehl and Haardt 1979; Kitchen et al. 1982; Boss et al. 2001b). For particles ranging in size from 0 to infinity, \( \xi \) varies between 3 and 5 (Boss et al. 2001b). However, when the size range \( D, n(re), n(im) \), and wavelength are limited to the ranges of \( 0.01 \leq D \leq 300 \) um, \( 1.02 \leq n(re) \leq 1.2 \), \( 0 \leq n(im) \leq 0.01 \), and \( 420 \leq \lambda \leq 650 \) nm, \( \xi \) becomes \( \xi = \gamma + 3 - 0.5e^{-6\gamma} \), over the range \( 2.5 \leq \xi \leq 5 \) (Boss et al. 2001b).

The values for \( A \) and \( \gamma \) were obtained by fitting the values of \( c_p(\lambda) \) in the equation \( c_p(\lambda) = A\lambda^{-\gamma} \) using the non-linear curve fitting algorithm, *nlinfit*, available in the statistics toolbox in Matlab. This method is based on an optimized Levenberg-Marquardt technique. The calculations were performed on binned profiles. Results for this study were extracted from the binned profiles using the same method as the other optical
parameters. Coefficients from all ac-9 wavelengths except 715 nm were used for curve fitting. Values of γ ≤ 0.6 were included only when r^2 > 0.8. Values of γ > 3 were excluded. In these two extreme cases c_p(λ) was very irregularly shaped.

Casts with both filtered and unfiltered ac-9 data were not available at all stations. To evaluate the impact on γ, both c_t(λ) and c_p(λ) were used to obtain values for γ. Values for ξ were then obtained from ξ = γ + 3 – 0.5e^{-6γ} (Boss et al. 2001b). The two sets of results are designated by ξ_gct and ξ_gcp. Because absorption by CDOM at 412 nm is significantly higher than particle absorption at 412 nm, a subsequent fit to c_t(λ) was done without c_t(412) to determine the impact on γ. No significant difference was found (p<0.01).

Optical Bulk Particle Index of Refraction

The bulk index of refraction was derived from %OM in Chapter II based on the expected mineral and organic refractive indices of the suspended particles present in the study area. An alternate method using the backscatter ratio b/b and γ has been developed using Mie theory for homogeneous spheres (Twardowski et al. 2001). The purpose of using this alternate method is two-fold. The first is to provide common terms for comparison with other published results. The second is to provide an alternate method for obtaining the bulk particle density. This process will be discussed below. Twardowski et al. (2001) used Mie theory to calculate b/b over the ranges of ζ, b/b, and n(re) expected in natural waters. Using these results they developed the relationship

n_p(b/b,γ) = 1 + 1.671(b/b)^{0.5377+0.4847(γ)^2}[1.4676 + 2.295(γ)^2 + 2.3113(γ)^4].

This relationship is valid over the ranges 0 ≤ b/b ≤ 0.03, and 2.5 ≤ ζ ≤ 4.5 (Twardowski et al. 2001).
Bulk particle index of refraction was calculated using the spectral $b_f/b$ and $\gamma$ derived from the methods described above using the three wavelengths of the ECOVSF3, i.e. 440, 532, 650 nm. Only $b_f/b$ at 650 nm is used in this work. Notation for bulk particle index of refraction calculated using the method of Twardowski et al. (2001) is $ng_{ct}$ or $ng_{cp}$ depending on whether $\gamma$ was obtained from $c_t$ or $c_p$ respectively.

**TSM Calculations From Power Law Size Distribution Function**

Several different methods were employed in this chapter to obtain the parameters $n$, $\rho$, $k$, and $\xi$ in the power law size distribution function. In order to interpret and compare the results obtained from the various methods, total suspended matter was calculated using the power law function with different combinations of derived parameters.

Mass per unit volume is obtained from the power law distribution function by multiplying the number of particles in each size bin by the density and sphere volume for each size bin. Total mass is obtained by summing the mass from each size bin over the size range of the distribution using the following equation,

$$mass_{total} = \sum_i mass(D_i) = \sum_i kD_i^{-\xi}\frac{4}{3}\pi\left(\frac{D_i}{2}\right)^3 (\rho_M (1 - OM) + \rho_{OM} OM)$$

(2)

In this equation $D_i$ is the particle diameter in the $i^{th}$ size bin, $k$ is the scaling factor, OM is $%OM/100$, $\rho_M$ is the average density of mineral particles found in the study area and $\rho_{OM}$ is the average density of organic particles found in the study area (see Chapter II for details on density calculations using $%OM$ as a weighting function).

Size bins and size limits were adapted from those used for the LISST-100b. The LISST-100b output is produced in 32 logarithmically spaced size bins covering the
diameter range $1.0 \leq D_i \leq 250 \, \mu m$ where $1 \leq i \leq 32$. An exponential curve was fit to the LISST-100b bins which were then extended to 62 bins covering the range $0.01 \leq D_i \leq 250 \, \mu m$ with $1 \leq i \leq 62$. The calculations for total $N$ and mass per unit volume ($tsm$) using different particle size ranges can then be compared. The notation $tsm$ is used to differentiate between $tsm$ calculated using the equation above and the TSM measured in situ.

The lower limit of the size range used for calculating $tsm$ and IOP’s is designated as $d_{min}$. Five values for $d_{min}$ are used in this analysis including 0.01, 0.1, 0.2, 0.7 and 1.0 $\mu m$. $D_{min} = 1.0 \, \mu m$ is used to represent output from the LISST-100. $D_{min} = 0.2$ and 0.7 $\mu m$ represent the minimum particle size captured on commonly used polycarbonate and glass fiber filters (Whatman, GF/F) respectively. $D_{min} = 0.01 \, \mu m$ represents a lower bound for comparison and $d_{min} = 0.1 \, \mu m$ represents the lower range of sizes that contribute significantly to scattering. In an analysis by Stramski et al. (2005), modeling results indicated that scattering by colloidal particles, i.e. those sizes between dissolved and smaller than about 0.1 $\mu m$, is on the same order as that of water molecules. The instruments used in this study are calibrated to remove scattering and absorption by water and so it is assumed for this study that measured scattering is due to particles larger than 0.1 $\mu m$. To obtain particle only absorption and scattering coefficients using the WETLabs ac-9, a filter is attached to the input port blocking particles larger than 0.2 $\mu m$. To obtain a relationship between particle density and index of refraction, the measured $\%OM$ is used along with estimated density and refractive indices for particles expected in the study area (Chapter II, Tables 2 and 3). In the case of bulk refractive index obtained from the model of Twardowski et al. (2001), $\%OM$ is obtained by inverting the equation.
for \( n_1 \) developed in Chapter II as follows, \( n = n_{\text{min}}(1 - \text{OM}) + n_{\text{OM}}\text{OM} \). Therefore, rearranging \( \%\text{OM} = 100(n - n_{\text{min}})/(n_{\text{OM}} - n_{\text{min}}) \).

Particle density is obtained from the equation for \( r_1 \) developed in Chapter II, \( r_1 = \rho_{\text{min}}(1 - \text{OM}) + \rho_{\text{OM}}\text{OM} \). The values for \( n_{\text{min}}, n_{\text{OM}}, \rho_{\text{min}} \), and \( \rho_{\text{OM}} \) can be found in Chapter II, Table 2.

The objective of this comparison is to determine whether \( \xi, k, \) and \( \rho \) found from either of the two methods described above can be used to reliably predict TSM. Because \( \xi, k, \) and \( \rho \) can vary independently of each other in the study area, some simple cases were tested to illustrate the impact of variability in TSM due to variability in \( \xi, k, \) and density(OM, ngcx). Initially, one parameter was varied while the others were held constant. In subsequent tests, parameters were varied simultaneously to represent the various combinations observed in the study area. Ranges of values for \( \xi, k, \) and \( \%\text{OM} \) were established based on measured values from the study area (Chapter II, Table 8). Results are shown below.

**Results**

*LISST-100b S2 and k2*

The output data from the LISST-100b was converted from units of ul/l to \( N/m^3 \) using the assumption that all particles are homogeneous spheres and \( N \) is the number of particles. Least squares linear regression was used to obtain the slope and offset of \( \log(N(D)) \) vs. \( \log(D) \) from the LISST-100b data for each sample. The values of \( N(D) \) for each size bin were averaged for the entire data set and plotted with the values of \( N \) reconstructed from the average values of \( \xi_2 \) and \( k_2 \) (Fig. 40). The minimum and
maximum values of \( \log(N(D)) \) are plotted along with the data set average \( \log(N(D)) \) to provide a sense of the variability in the data.

![Graph showing LISST-100b output \( \log(N(D)) \) vs. \( \log(D) \). Triangles are the linear regression line with slope \( \xi_2 \) and offset \( k_2 \). Diamonds are the average in each size bin for the entire data set. \( N(D)_{min} \) and \( N(D)_{max} \) are the minimum and maximum values from each size bin of the entire data set.]

*Figure 40.* LISST-100b output \( \log(N(D)) \) vs. \( \log(D) \). Triangles are the linear regression line with slope \( \xi_2 \) and offset \( k_2 \). Diamonds are the average in each size bin for the entire data set. \( N(D)_{min} \) and \( N(D)_{max} \) are the minimum and maximum values from each size bin of the entire data set.

**Optically Derived Bulk Index of Refraction and \( \xi \)**

There were two objectives for using alternate methods for computing bulk index of refraction and \( \xi \). The first is to provide a comparison for the method of computing \( n_1 \) using \%OM as a weighting function as described in Chapter II. The second is to provide a comparison for using the LISST-100b data to estimate \( \xi_2 \). In order to make this comparison the values of \( n_{gcp} \), \( n_{gct} \), \( \xi_{gcp} \) and \( \xi_{gct} \) were computed. To calculate the bulk index of refraction using the method of Twardowski et al. (2001), both the backscatter ratio \( b_n/b \) and \( \xi \) must be determined.
The backscatter ratio for this study was obtained from the ratio of the backscatter coefficient measured by the ECOVSF3 and the total scattering coefficient measured by the ac-9, both at wavelengths of 650 nm (Fig. 41). The $b_b/b_{650}$ ratio is very consistent in this data set ($r^2 = 0.94$), unlike the ratio reported by Loisel et al. (2007) which had two distinct lobes in the scatter plot representing two distinctly different types of particles. The slope of the regression line between $b_b650$ and $b_{650}$ is 0.0144 (Fig. 41) but the average value of $b_b/b_{650}$ for the data set is 0.011. Separation of $b_b/b_{650}$ values by water type indicates slightly higher values of $b_b/b_{650}$ in River Mouth and Ambient stations while lower values are found in Plume and Shelf stations (Fig. 42 and Table 9) though the difference is not as large as reported by Loisel et al. (2007).

\[
b_b = 0.0144b - 0.0045
\]

\[
R^2 = 0.944
\]

*Figure 41. $b_b/b_{650}$ ratio for all data in study area.*
Figure 42. $b_b/b_{650}$ for each water class. Solid lines are regression defined by equations in the figure. Note that $RM$ and Ambient slopes are close to each other as are Plume and Shelf slopes.

The values of $\xi_{gcp}$ and $\xi_{gct}$ were computed from $c_t(\lambda)$ and $c_p(\lambda)$ (Boss et al. 2001b). For values less than about 4.5 $\xi_{gcp}$ and $\xi_{gct}$ are nearly equal (Fig. 43). Above 4.5 they begin to diverge. This is probably due to higher absorption by CDOM in shorter wavelengths causing an increase in $\gamma$ and therefore $\xi_{gct}$. Values of $\xi_{gcp}$ and $\xi_{gct}$ were plotted with $\xi_2$ for comparison (Fig. 44). There is no significant correlation between $\xi_2$ and either $\xi_{gcp}$ or $\xi_{gct}$.
**Figure 43.** $\xi_{gcp}$ vs. $\xi_{gct}$. Solid line is 1:1. Note the divergence from the 1:1 line for $\xi > 4.5$. This is possibly due to the greater influence on the spectral beam attenuation due to CDOM absorption in particle assemblages having greater numbers of small organic particles.

**Figure 44.** $\xi_2$ vs. $\xi_{gcp}$ and $\xi_{gct}$. $\xi_{gcp}$ and $\xi_{gct}$ were not significantly correlated with $\xi_2$. 
The model for bulk particle index of refraction (Twardowski et al. 2001) includes both \( b_b/b \) and \( \gamma \) as input parameters. Because \( \gamma \) was computed from both \( c_t(\lambda) \) and \( c_p(\lambda) \), each was used in the computation of \( n_{gcx} \). Both methods, i.e. \( n_{gc} \) and \( n_{ct} \) were weakly correlated with \( n_1 \) (Fig. 45, \( p < 0.01 \)).

![Figure 45. \( n_1 \) vs. \( n_{gc} \) and \( n_{cp} \). Trend lines between \( n_1 \) vs. \( n_{gc} \) and \( n_{cp} \) were weakly but significantly correlated (\( p < 0.01 \)).](image)

Numerically, the various computed average values of \( n(re) \) are within the expected range, \( 1.02 \leq n(re) \leq 1.2 \). However, there were differences in the average values, i.e. \( n_1 = 1.11 \pm 0.04 \), \( n_{gc} = 1.05 \pm 0.04 \) and \( n_{cp} = 1.09 \pm 0.05 \). Results of ANOVA indicate the means of \( n_1 \), \( n_{gc} \) and \( n_{cp} \) were significantly different from each other (\( p < 0.01 \)).

**Cruise Summary**

Average parameter values from all cruise data reveal differences between methods used to obtain both \( \zeta \) and bulk index of refraction (Chapter II, Table 8). The
average value of $\xi_2$ obtained from the LISST-100b data is 2.16 with a standard deviation of 0.59 and a range of 0.79 to 3.23. The average values of $\xi_{gct}$ and $\xi_{gcp}$ were 4.27 and 4.11, and standard deviations were 0.47 and 0.44 respectively. The ranges were between 3.6 and 5.47 for both $\xi_{gct}$ and $\xi_{gcp}$. Results of ANOVA indicate the means of $\xi_2$, $\xi_{gct}$, and $\xi_{gcp}$ were significantly different from each other ($p << 0.01$). The differences between $\xi_2$, $\xi_{gct}$, and $\xi_{gcp}$ will be evaluated below.

*Water Classification Summary*

Results for PSD slope parameter and bulk refractive index were segregated by water class as described in Chapter II. Several parameters from Chapter II, Table 9 were repeated for comparison here (Table 13).

The water class averages of PSD slope $\xi_2$ are significantly different from each other but the scaling factor averages $k_2$, are not ($p < 0.01$). The water class averages of $\xi_{gcp}$ are not significantly different from each other. Only *River Mouth* and *Shelf* water class averages of $\xi_{gct}$ are different from each other (Fig. 46). There was no significant correlation found between any combinations of $\xi$.

The water class averages of $n_1$ are significantly different from each other ($p < 0.01$). However $n_{gcp}$ averages are not. Only averages of $n_{gct}$ in water classes *River Mouth* and *Shelf* are significantly different from each other (Fig. 47). There were no significant correlations between $n_1$ and either $n_{gcp}$ or $n_{gct}$ within water class data sets.
<table>
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<th>MR</th>
<th>Mouth ((n=10))</th>
<th>Ambient ((n=21))</th>
<th>Plume ((n=18))</th>
<th>Shelf ((n=25))</th>
<th>Blue ((n=1))</th>
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<td>stddev</td>
<td>mean</td>
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<td>8.82</td>
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<td>1.13</td>
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<tr>
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<td>0.06</td>
<td>1.09</td>
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<td>4.18</td>
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Figure 46. Water class averages of $\xi$ (data from Table 13). There appears to be a trend of greater influence of smaller particles offshore relative to those nearest the river mouth.

Figure 47. Water class averages of bulk index of refraction (data from Table 13). There is a trend of lower refractive indices offshore indicating less influence of river supplied mineral particles.
Regression analysis was used to test the relative impact of variability in bulk refractive index on variability in \( b_{t*650} \). No significant correlations were found between \( b_{t*650} \) and any combination of water class data or the total data set. Similar results were obtained in testing the relationship between \( b_{t*650} \) and bulk refractive index. No significant correlations were found in data segregated by water class but when all data were taken together there was a weak but significant correlation between \( b_{t*650} \) and \( n_{gct} \) \((r^2 = 0.09, n = 59, p<0.01)\).

In Chapter II the backscatter ratio was found to be different in each water class. Because the backscatter ratio was used to obtain the bulk index of refraction, the three methods used to obtain bulk refractive index reported in Table 13 were regressed against \( b_{t/b650} \). When all data were included there were weak but significant correlations between \( b_{t/b650} \) and \( n_1, n_{gct}, \) and \( n_{gcp} \). The trend of increasing backscatter ratio with increasing bulk refractive index was observed in each regression. The slopes and offsets of the regression equations were all similar in magnitude to each other (Fig. 48). The weak correlation coefficients suggest there are other factors affecting these relationships. Further partitioning of the particle assemblage by numbers of particles of each type may provide additional insight.

Trends between \( \xi \) and \( b_{t/b} \) were also examined. Weak trends were observed between \( b_{t/b650} \) and \( \xi_{gcp} \) \((r^2 = 0.15, p<0.011)\) and \( \xi_{gct} \) \((r^2 = 0.09, p < 0.011)\). Correlation between \( b_{t/b650} \) and \( n_1 \) was not significant. Values of \( \xi \) all decreased slightly with increasing \( b_{t/b650} \).
Results from all the methods used here to obtain \( b_6/650 \), bulk index of refraction and \( \xi \) were plotted together for comparison (Fig. 49). Contours are modeled refractive index from the model of Twardowski et al. (2001). The points representing \( n_{gct} \) and \( \xi_{gct} \) (open circles) are in the same general plot location as points representing \( n_{gcp} \) and \( \xi_{gcp} \) (*). The points representing \( n_{gcp} \) and \( \xi_{gcp} \) are spread more widely along the \( \xi \) axis and many of the higher \( \xi_{gcp} \) points are below the \( n = 1.02 \) contour. This suggests that using the total beam attenuation spectrum \( c_r(\lambda) \), to obtain gamma overestimates \( \xi \) which in turn causes an underestimation of the modeled value of \( n \). This is due to the higher beam attenuation due to absorption in the shorter wavelengths, leading to larger values of \( \gamma \).

The points representing \( n_{gcp} \) and \( \xi_{gcp} \) fall mostly within the ranges of \( 1.02 \leq n_{gcp} \leq 1.13 \) and \( 3.5 \leq \xi_{gcp} \leq 4.5 \) and don’t exhibit any trends on either the \( b_6/b \) axis or the \( \xi \) axis.

In contrast, the points representing \( n_1 \) and \( \xi_2 \) all fall on a separate region of the plot with \( 1.02 \leq n_1 \leq 1.16 \) and \( 2.0 \leq \xi_2 \leq 3 \). Values of \( \xi_2 \) less than 2.0 are not plotted but

\[ \text{Figure 48. } b_6/650 \text{ vs. } n_1, n_{gct}, n_{gcp}. \text{ Solid lines are regression lines and all correlations are significant (} p < 0.01 \text{) although } r \text{ values were low.} \]
would have been outside the valid range of modeled bulk refractive index. These differences will be further investigated below.

In comparison with results obtained from the Gulf of California (Twardowski et al. 2001), Monterey Bay and the Gulf of Mexico (Sullivan et al. 2005) and European coastal waters (Loisel et al. 2007), the points in Fig. 49 corresponding to $n_{cgp}$, $\xi_{gcp}$, $n_{cgt}$, and $\xi_{gct}$ are similar in the range of $b_n/b$ reported for other regions while they have slightly higher average values of $\xi$. In contrast, the points corresponding to $n_1$ and $\xi_2$ are in a much lower range of values of $\xi$.

The average value of $b_t * 650$ for this study is $0.52 \pm 0.35$ (m$^2$/g) corresponds with a PSD slope near 4.0 for high density particles in the study of Babin et al. (2003). These results appear to be consistent with the average values of $\xi_{gcp}$ and $\xi_{gct}$ (4.11 and 4.27 respectively). However, the lower average value of $\xi_2$ (2.16 in this study) does not fall within the ranges predicted by Babin et al. (2003). This will be investigated further below.
Figure 49. $b_b/b_{650}$ and $\xi$ with contours of bulk refractive index from the model of Twardowski et al. (2001). Symbols are $n_1$ and $\xi_2$ (+), $n_{gcp}$ and $\xi_{gcp}$ (*), $n_{gct}$ and $\xi_{gct}$ (o). This plot illustrates the difference in results obtained from the LISST-100b (+) vs. those obtained using the optical models of Boss et al. (2001b) and Twardowski et al. (2001) (*,o).

**Plume Transect Data**

Plume transect data were examined to determine if there were any significant trends related to the PSD slope and bulk refractive index. As was described in Chapter II, for plume transect stations TSM, %OM and scattering coefficients were better correlated with distance from the river mouth at Southwest Pass than with salinity. Although variability in both $\xi$ and bulk refractive index was high relative to salinity, trends indicated conservative mixing in plume data. All three variables for bulk index of refraction decreased significantly with distance from the mouth (Fig. 50).
Figure 50. $n$ vs. distance from Southwest Pass in plume transect stations. Bulk refractive index decreases as the numbers of mineral particles decreases.

As plume water flows from the channel into open water, fresh water spreads laterally and decreases in velocity allowing larger particles to settle out of the plume (e.g. Wright and Coleman 1971; Libes 1992). The loss of larger particles from surface waters is expected to cause $\xi$ to increase as the relative number of smaller particles increases in the assemblage. When comparing plume transect station values of $\xi^2$, $\xi_{gct}$, and $\xi_{gcp}$ with distance from the mouth no significant correlations were found (Fig. 51).

Although not significant, trend lines did indicate a slight increase in the slope parameters as distance from the mouth increased, similar to trends found in data segregated by water class. There were no significant trends in $b_r*650$ or $b_b*650$ relative to either bulk index of refraction or PSD slopes. Recall in Chapter II, scattering coefficients and TSM were all significantly correlated with distance from Southwest Pass in plume transect stations.
Figure 51. $\xi$ vs. Distance from Southwest Pass. Trend lines are not significant.

The plots of $b/b$, $n_1$, $ngcp$, and $ngct$, and $\xi_2$, $\xi_{gct}$, and $\xi_{gcp}$ for plume transect stations appear to vary more along the $\xi$ axis (Fig. 52). The points representing $ngcp$ and $\xi_{gcp}$ (diamonds), and $ngct$ and $\xi_{gct}$ (*) appear to follow a weak trend of lower values of $\xi$ with higher values of $n$, progressing to higher values of $\xi$ with lower values of $n$. Because some points for $\xi_2$ are outside the range of this plot, differences in the apparent trends between $\xi$ and $n$ are difficult explain. The models of Twardowski et al. (2001) and Boss et al. (2001b) have not been validated outside the range of these plots. Because data derived from these models and data derived from the LISST-100b fall outside these bounds additional factors not considered here may be affecting these results.
In this section the effect on particle mass due to change in k, ξ and density was examined. The lower case \( tsm \) indicates particle mass calculated using the PSD function while uppercase TSM represents field measurements. Density was calculated using %OM in the method for r1 described in Chapter II. In the figures presented below, %OM is plotted rather than r1. It should be noted also that the values of \( tsm \) reported here are all within reasonable ranges expected in the study area.

To test the response of \( tsm \) to change in k while \( \rho(\%OM) \) and ξ were held constant, k was varied over the range of 1E12 to 5E12 for ξ = 2 and ξ = 5. The response
in calculated $tsm$ with $d_{\text{min}} = 0.1 \, \mu\text{m}$ is linear with change in $k$ but the range and average value of $tsm$ at $\xi = 2$ is about 5 times that of $\xi = 5$ (Fig. 53).

As $\rho(\%\text{OM})$ was varied and $k$ was held constant at the average for this data set, $tsm$ varied linearly. As with the previous test the range and average values of $tsm$ were quite different when $\xi$ changed from 3 to 5 (Fig. 54).

To test the variability in $tsm$ for different values of $\xi$, $k$ and $\%\text{OM}$ were held constant while $\xi$ was varied over the range of 0.0 to 5.0. Because the minimum size range of included particles differs, this test was repeated for the values of $d_{\text{min}} = 0.01$, 0.1, 0.2, 0.7 and 1.0 $\mu\text{m}$ (Fig. 55). For values of $\xi$ between 0.0 and about 3.0, the minimum particle size included has very little impact on $tsm$. However, for $\xi$ between 3.0 and 5.0, the minimum included particle size becomes very important. The choice of minimum particle size produces dramatically different values for $tsm$. This difference can be an order of magnitude for higher values of $\xi$ (Fig. 55).

These results demonstrate very clearly that $k$, $\xi$, density and particle size range included can all have a significant impact on $tsm$. Because these parameters can vary independently it is clear that there can exist combinations that result in equivalent values of $tsm$. 
Figure 53. \( tsm \) vs. \( k \). %OM and \( \xi \) are constant.

Figure 54. \( tsm \) vs. %OM. \( k \) and \( \xi \) are constant.
**LISST-100 mass calculations**

To evaluate the PSD parameters obtained from the LISST-100b data, $\xi_2$ and $k_2$, combined with density calculated using the method for $r_1$ described in Chapter II were used with the power law function to calculate $tsm$. Calculations of total mass were made using LISST-100b derived values of $\xi_2$ and $k_2$ using the 32 size bins of the LISST-100b (i.e. over the size range of 1.0 to 250 µm). Average density for each sample was computed from $\rho = \rho_{\text{MIN}}(1-\%OM) + \rho_{\text{OM}}*\%OM$, where $\rho_{\text{MIN}} = 2.65$ g/cm$^3$ and $\rho_{\text{OM}} = 1.08$ g/cm$^3$ as described for $r_1$ in Chapter II. The first calculation used the actual number of particles per size bin $N(D)$, reported by the LISST-100b, summed over all bins to get total mass. In cases where $N(D)$ was reported as zero by the LISST-100b, $N(D)$ was computed from the regression equation with slope $\xi_2$ and offset $O_2$.

To compare the values of $tsm$ and TSM, least squares linear regression was used where the desired result was a first order polynomial with slope = 1.0, offset = 0.0, and a correlation coefficient of 1.0. In the equation for calculating $tsm$ from the power law
function coupled with the particle volume and density, the variables k2 and density are constant factors, each having a linear affect on the final $tsm$ result (Figs. 53 and 54 above). The variable $\xi_2$ produces a non-linear response over its range of expected values (Fig. 55). Variability in either k2 or density would affect the slope and offset coefficients but not the correlation coefficient. Variability in $\xi_2$ could affect the slope and offset as well as the regression coefficient.

An initial comparison between $tsm$ and TSM simply compared only the average of the sample values of $tsm$ and TSM for the entire data set. The average of the sample values provided an initial indication of magnitude of the difference between $tsm$ and TSM. The data set average $tsm$ calculated using $N(D)$ derived directly from each size bin of the LISST-100b was 403 mg/l. The average value of measured TSM was 6.2 mg/l. When $tsm$ was calculated using $\xi_2$ and k2 to compute $N(D)$, the average calculated $tsm$ was 295 mg/l. When the $tsm$ values obtained from each of the two methods were compared to measured TSM using regression analysis, there were no significant correlations found for either method and the regression slopes and offsets where much different from 1.0 and 0.0 respectively. These results demonstrate that the LISST-100b derived data overestimated $tsm$ by a factor of 67 when actual $N(D)$ values are used. When $\xi_2$ and k2 were used to calculate $N(D)$ the LISST-100b derived data overestimated $tsm$ by a factor of about 48. This magnitude of difference between $tsm$ and TSM is potentially due to the use of %OM to directly partition the organic and mineral fractions of the particle assemblage. If there were information about the relative numbers of particles of each type it is likely that this method would have resulted in $tsm$ values much closer to TSM.
Three variables affect the value of $tsm$ in the PSD function, $r_1$, $k_2$ and $\xi_2$. The variables $r_1$ and $k_2$ are directly proportional to $tsm$ (Figs. 53 and 54). Either one can be varied to change the estimated $tsm$. The value of $r_1$ has a very limited range relative to $k_2$. It was only varied between 1.08 and 2.65, effectively limiting its influence on $tsm$ to a maximum factor of about 2.5. This is clearly insufficient to correct a factor of 48 in overestimated $tsm$. The value of $k_2$ is limited on the lower bound by 0 but can increase to any value. To test the possible effect on $tsm$ assuming the derived value of $k_2$ was incorrect, the variable $k_2$ was adjusted by decreasing its value in each sample by a factor of 48. This resulted in an average value of $tsm$ equal to the measured average value of TSM. However, when $tsm$ was compared with TSM in regression analysis, the two were uncorrelated ($r^2 << 0.01$). A comparison of the individual data values showed that the greatest variability between $tsm$ and TSM occurred for values of $\xi_2$ less than 2.0. The values of $tsm$ calculated with $\xi_2 < 2.0$ were up to 3 orders of magnitude greater than the measured values. This suggests that $\xi_2$ may be too low. Because tsm varies non-linearly with change in $\xi_2$ a constant value was added to all $\xi_2$ samples to test the impact on the correlation coefficient between $tsm$ and TSM. The data set average value of $\xi_2$ was increased via trial and error until the average $tsm$ matched the average TSM. The variables $r_1$ and $k_2$ remained at their original values. A match between average $tsm$ and average TSM was achieved when a constant value of 0.8865 was added to $\xi_2$. This resulted in reduction in the largest values of $tsm$ predicted by the LISST-100b, and an increase in correlation between $tsm$ and TSM ($r^2 = 0.20$, $n = 50$, $p << 0.01$).

To examine the impact of including smaller sizes in the estimate of $tsm$, the number of size bins of the LISST-100b were extended to include diameters of 0.7, 0.2,
and 0.1 μm. The un-adjusted values of r1, k2 and ξ2 were used to calculate $t_{sm}$. The values of average $t_{sm}$ for size ranges with minimum included sizes of 0.1, 0.2, 0.7 and 1.0 μm were 298.7, 296.0, 295.8 and 294.8 mg/l respectively. There is a maximum increase in average $t_{sm}$ of 1.3 % when particles between 1.0 and 0.1 μm are included. Because measurements of TSM were done using filters with a nominal pore size of 0.7 μm, ξ2 was again adjusted via trial and error until the average $t_{sm}$ with minimum included size of 0.7 μm was equal to the average value of TSM, i.e. 6.2 mg/l. A constant of 0.9485 was added to ξ2 resulting in a nearly 1:1 ratio and a correlation of $r^2 = 0.37$ between $t_{sm}$ and TSM (Fig. 56, n = 50, p << 0.01).

The average value of ξ2 for this data set was 2.12. Adding 0.9485 brought the average of ξ2 to 3.07 and increased the correlation between $t_{sm}$ and TSM from $r^2 < 0.01$ to $r^2 = 0.37$. Although correlation between $t_{sm}$ and TSM is low, it does appear reasonable to assume that the conversion of LISST-100b data to the power law PSD slope and offset parameters ξ2 and k2 results in an under estimate of ξ2 by a constant of 0.9485. It is clear that the calculated value of $t_{sm}$ is very sensitive to ξ2, especially in the prediction of $t_{sm}$ greater than about 5 mg/l (Fig. 56). The similarity in magnitude of $t_{sm}$ calculated for different minimum size ranges using the un-adjusted ξ2 also supports the assumption that ξ2 is too low. In Chapter II it was noted that partitioning mineral and organic particles by relative numbers of each type of particle could provide a better estimate of bulk density based on %OM. In preliminary analysis using this alternate method, $t_{sm}$ was still higher than TSM indicating estimates of ξ2 still appear to be too low. However the over-estimate was only by a factor of about 3, much less than the factor of 48 reported above. In addition, without adjusting any parameters the correlation
coefficient between \( tsm \) and TSM was much higher \( (r^2 > 0.5) \) than values reported above. These preliminary results clearly indicate further investigation is warranted.

![Graph showing TSM vs. tsm predicted by data derived from the LISST-100b with 0.9485 added to slope parameter \( \xi_2 \). Note the regression slope is nearly 1:1.](image)

**Figure 56.** TSM vs. \( tsm \) predicted by data derived from the LISST-100b with 0.9485 added to slope parameter \( \xi_2 \). Note the regression slope is nearly 1:1.

**Beam Attenuation Slope Mass Calculations**

The PSD parameters \( \xi_{gcp} \) and \( \xi_{gct} \) were used along with \( k_2 \) derived from LISST-100b output to estimate \( tsm \) using the power law size distribution function. The values of \( ng_{gcp} \) and \( ng_{gct} \) were inverted to \%OM to estimate particle density. The average values of \( \xi_{gcp} \) and \( \xi_{gct} \) were 4.05 and 4.23 and the average densities obtained from \( ng_{gcp} \) and \( ng_{gct} \) were 1.62 and 1.29 g/cm\(^3\) respectively. Recall the average values of \( \xi_2 \) and \( r_1 \) were 2.12 and 1.88 g/cm\(^3\) respectively. The parameter \( k_2 \) derived from the LISST-100b data was used since there is no equivalent estimate of \( k \) from the methods for obtaining \( \xi_{gcp}, \xi_{gct},\) \( ng_{gcp}, \) and \( ng_{gct} \). Values for the constant \( A \), obtained from the non-linear fit to \( c(\lambda) = A\lambda^{-\gamma} \) provided no reasonable results when used for \( k \).
The size range used for this analysis included minimum particle diameters of 0.7 μm. In each case, the combined parameter sets ξgcp, density(ngcp), k2, and ξgct, density(ngct), k2, underestimated \( tsm \) by factors of about 7.4 and 3.5 respectively. There were no significant correlations between \( tsm \) and TSM in either case. In separate tests, constants were added to density and k2 to obtain matches between average \( tsm \) and average TSM. These tests did not result in improved correlations between \( tsm \) and TSM. Because \( tsm \) was underestimated, the values of ξgcp, ξgct were decreased to obtain matches between average \( tsm \) and average TSM. In each case, after decreasing ξ, weak correlations between \( tsm \) and TSM became significant (\( r^2 < 0.15, p<0.01 \)) and regression slopes were near 0.92. ξgcp was reduced by 1.08 resulting in an average ξgcp = 2.97. ξgct was reduced by 0.979 resulting in an average ξgct = 3.25. The process of adding a constant to each density to bring the average up to match \( r_1 \) was repeated. The values of ξgcp and ξgct were re-adjusted to match average \( tsm \) and TSM, resulting in average values of ξgcp = 3.02 and ξgct = 3.35.

Recall that the average value of ξ2 became 3.07 after adjusting to obtain a match between average tsm and average TSM. After adjusting density(ngcp) to match the average value of \( r_1 = 1.88 \text{ g/cm}^3 \), ξgcp was adjusted to obtain the average value of ξgcp = 3.02. These two average PSD slopes ξgcp = 3.02 and ξ2 = 3.07 are remarkably similar considering they were obtained using very different methods. Revisiting Fig. 49, above, \( b_\theta/b650 \) and adjusted values of ξ2 and ξgcp were re-plotted (Figs. 57 and 58). The values of ξ2 now fall mostly in the range between 2.5 and 3.5 with some extreme points between 2 and 4 (Fig. 57). Values of ξgcp now fall mostly between 2.5 and 3.5 with a few points between 3.5 and 4.0 (Fig. 58).
Figure 57. $b_b/b_{650}$ vs. $\xi_2$ adjusted to make average $tsm$ equal average TSM. Note that the greatest variability is along the $\xi_2$ axis and that the range of $\xi_2$ now overlaps the range obtained using the spectral beam attenuation methods (cf. Figs. 49 and 52).
Note the range of $\xi_{gcp}$ is now similar to that of the adjusted values of $\xi_2$ (cf. Fig. 57).

**Scattering coefficients vs. TSM**

When scattering and backscattering coefficients were compared to calculated $t_{sm}$ using the un-adjusted PSD slopes, no correlations were found. When PSD slopes $\xi_2$, $\xi_{gcp}$, and $\xi_{gct}$ were adjusted as described above, correlations between adjusted $t_{sm}$ and $b_{t,650}$ and $b_{b,650}$ became significant ($p < 0.01$). Regression slopes were similar to those obtained for TSM vs. $b_{t,650}$ and $b_{b,650}$. These results indicate that mass specific scattering coefficients are dependent on the values of $\xi$, $k$, density, and minimum included particle size.

When compared individually to parameters $\xi$, $k$, and bulk refractive index there were no significant correlations between mass specific coefficients $b_{t}*650$ and $b_{b}*650$. 

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**Figure 58.** $b_{b}/b_{650}$ vs. $\xi_{gcp}$ adjusted to make average $t_{sm}$ equal to average TSM. Note the range of $\xi_{gcp}$ is now similar to that of the adjusted values of $\xi_2$ (cf. Fig. 57).
However, $Rrs_{*650}$ as described in Chapter II was significantly correlated with $\xi_2$ and $\xi_{gct}$ (Fig. 59).

The scattering coefficients $b_{s650}$ and $b_{b650}$ along with $Rrs_{650}$ were weakly correlated in different combinations with both modeled bulk refractive index and $\xi_2$ and $\xi_{gct}$ (See Figs. 60 – 64 for specific relationships).

Figure 59. $Rrs_{*650}$ vs. $\xi_{gcp}$, and $\xi_{gct}$. Solid lines are regression lines.
Figure 60. \( Rrs650 \) vs. ngcp and ngct. Solid lines are regression lines. Only regression between \( Rrs650 \) and ngct (diamonds) is significant.

Figure 61. \( b,650 \) vs. n1, ngct, and ngcp. Solid lines are regression lines. Correlations with ngct and n1 are significant.
$y_{ct} = -0.0783x + 4.4803$
$r^2 = 0.32, n=61, p<<0.01$

**Figure 62.** $b_{t650}$ vs. $\xi_2$, $\xi_{gcp}$, and $\xi_{gct}$. Solid lines are regression lines.

$y_{ct} = 0.7501x + 1.0267$
$r^2 = 0.42, n=65, p<<0.01$

$y_{cp} = 0.4271x + 1.0764$
$r^2 = 0.1, n=65, p<0.01$

$y_{n1} = 0.567x + 1.0886$
$r^2 = 0.31, n=59, p<0.01$

**Figure 63.** $b_{b650}$ vs. $n_1$, $ngct$, and $ngcp$. Solid lines are regression lines. All correlations are significant.
Results of regression analysis between scattering coefficients, mass specific coefficients and PSD parameters were similar to results obtained in Chapter II for bulk particle index of refraction. Scattering coefficients and $Rrs_{650}$ exhibited weak but significant correlations with $\xi$, but mass specific coefficients did not. As in Chapter II the exception was $Rrs*_{650}$. In Figures 63 and 64 above about 42% of the variability in $b_{b_{650}}$ is attributable to variability in ngct and about 28% of the variability is attributable to variability in $\xi_{gct}$. These results suggest that the scattering coefficients at 650 nm may be useful for characterizing the particle composition and size distribution but not the total mass.

Revisiting the results of Babin et al. 2003 (their Fig. 10), relating $b*_{555}$ with density, bulk index of refraction and PSD slope, the average values found in this study of $b_{t*650} = 0.52$, $n_1 = 1.0$, density = 1.88 g/cm$^3$ do not match their combination of values associated with adjusted values of $\xi$ near 3.07. Reasons for this are not clear. Babin et al.
(2003) noted the importance of minimum included particle size, density, and correct identification of ξ in their results. They also noted a significant difference in the contribution to total scattering due to differences in the density of particles in the smallest size ranges. These results could indicate that the assumed uniformity of particle density in all size bins is incorrect. Also as noted previously, it is likely that results may be better matched to the work of Babin et al. (2003) if the numbers of particles of each type (i.e. mineral and organic) can be derived from the measured %OM. Further investigation is needed to address these issues.

Conclusions

The hypothesis of this study was that variability in the mass specific scattering coefficients would be dependent on variability in the parameters ξ and k of the power law size distribution function. Results presented here do not appear to support this hypothesis when considering the parameters individually. Only $R_{rs}*{650}$ was significantly correlated with $\xi_{gct}$. However when PSD parameters were adjusted to match average $tsm$ with average TSM, scattering to $tsm$ ratios became similar to those obtained with TSM. This suggests that interpretation of mass specific scattering coefficients must consider the simultaneous variability in the PSD parameters. In addition, as noted previously partitioning the organic and mineral particles by relative numbers of each may provide a better indication of how the PSD parameters of each assemblage affect $b^*$ individually.

The main reason for lack of significant correlation between mass specific coefficients and ξ is that there was very little difference in average values throughout the study area. While there was a wide range in values the standard deviations were low and the COV’s of all forms of ξ were among the lowest of all parameters.
There is also very little difference in average bulk refractive index throughout the study area. When inverted to %OM and reconverted to density a similarly low range of densities is obtained. This indicates the average density of particles is relatively uniform throughout the study area. The relatively minor influence of density on the \( tsm \) calculation would also make trends between scattering and TSM difficult to detect.

The difference in results from this study relative to those of Babin et al. (2003) with respect to the combination of mass specific scattering, bulk index of refraction, bulk density and \( \xi \) suggest that the particle composition and size distribution parameters may not be represented by the assumptions made here. Further investigation is needed to provide additional insight into these issues.
CHAPTER IV

MODELING THE INFLUENCE OF POWER LAW PARTICLE SIZE DISTRIBUTION PARAMETERS AND % ORGANIC MATTER ON THE RELATIONSHIP BETWEEN TOTAL SUSPENDED MATTER AND OPTICAL PROPERTIES IN MARINE WATERS IMPACTED BY THE MISSISSIPPI RIVER

Abstract

The Mie theory for homogeneous spheres was used to investigate the relationships between scattering and absorption coefficients and TSM. It was also used to reconcile differences in the measurement of parameters k and ξ in the power law particle sized distribution equation \( N(D) = kD^{-\xi} \) obtained from the LISST-100b and the spectral beam attenuation \( c_p(\lambda) \) methods of Boss et al. (2001b). To illuminate the possible affects on modeled \( tsm \) and optical coefficients due to the differences in measured k and ξ, parameters obtained from both methods were adjusted independently to obtain a nearly 1:1 relationship between modeled \( tsm \) and TSM measured in situ.

Results from this closure process also produced a value of \( b*650 = 0.31 \) which was very close to the measured value of 0.35. In addition a value of \( b_{\text{b}}/b_{650} = 0.018 \) was obtained which was close to the measured value of 0.0144, and an average value of \( \xi = 3.21 \) was obtained from all data in the study area.

Mie theory modeling also demonstrated the very complex relationships between \( b* \), the percent organic matter of TSM, and the PSD parameters k and ξ. These results indicate that generalized use of values of \( b* \) to characterize suspended particle composition should not be made without verification of actual particle assemblage characteristics. These results also demonstrated the significance of the minimum
included particle size and ξ on the value of $b^*$. This result calls out the need for better methods for determining TSM from filtration.

**Introduction**

In the previous two chapters the relationship between observed scattering and backscattering coefficients relative to TSM was examined. Optical scattering, backscattering, and absorption coefficients at 650 nm were significantly correlated to TSM but these relationships were not constant throughout the study area. The remote sensing reflectance using the form $Rrs \propto b_0/(a+b_0)$, was not significantly correlated to TSM at 650 nm. Mass specific optical coefficients were compared to bulk particle density and index of refraction, and the slope parameter ξ, of the assumed power law particle size distribution function. No significant correlations were found using mass specific coefficients. However, optical coefficients $b_{650}$ and $b_b650$ were weakly but significantly correlated with bulk refractive index and ξ. Although these relationships were significant, correlation coefficients were low and variability in the data was high. In addition, different methods were used to obtain bulk particle refractive index and the PSD slope parameter ξ, but the different methods produced somewhat different results. Theoretical modeling was used to further investigate these differences.

In this chapter the Mie theory for homogeneous spheres (Van de Hulst 1957; Bohren and Huffman 1983) was used to model the scattering and absorption coefficients from the power law PSD function and the PSD parameters k, ξ, and the bulk refractive index of the particle assemblage. The Mie theory has been used routinely to explain light scattering by particles suspended in marine waters (Mobley 1994) and the methods used here to obtain bulk refractive index and ξ are based on the Mie theory (Boss et al. 2001b;
Twardowski et al. (2001). Other researchers routinely use the Mie theory for analysis of results obtained in similar research (e.g. Babin et al. 2003; Sullivan et al. 2005; Loisel et al. 2007). Further modeling is warranted in this case to help explain the relationships between measured optical coefficients and TSM because of the high variability in the measured data and because different methods produced different results for the value of $\zeta$.

The purpose of this effort is two-fold. The first is to examine the theoretical relationship between the optical coefficients and TSM with respect to variability in $k$, $\zeta$, bulk particle refractive index, bulk particle density and the minimum included particle size. The second is to use the theoretical relationships determined here, to explain the observed variations between optical coefficients and TSM in the study area. A final objective is to utilize these results to determine the impact of the variability in particle characteristics on the remote sensing signal at 650 nm. As in the previous chapters, calculations are done using only the wavelength of 650 nm due to the availability of simultaneous measurements of absorption, scattering and backscattering at this wavelength.

Methods

Data Collection and Processing

Data collection and processing for this study has been described in Chapters II and III. Briefly, the LISST-100b (Sequoia Scientific) was used to collect volumetric particle size distributions in the range 1.0 to 250 µm in 32 size bins. These data were converted to number of particles per size bin using the assumption of homogenous spheres. The least-squares linear regression analysis was used to obtain a first order
regression equation for the log transformed LISST-100b output data. The slope of the
regression equation is the power law size distribution parameter $\xi_2$ and the scaling factor
$k_2$ is $10^{O_2}$ where $O_2$ is the regression equation constant (see Chapter III).

Beam attenuation $c_t(\lambda)$, and absorption $a_t(\lambda)$, coefficients were measured using the
WETLabs ac-9. The backscattering coefficients were measured using the WETLabs
ECOVSF-3. At most stations the ac-9 was deployed twice to obtain total absorption $a_t(\lambda)$
and beam attenuation $c_t(\lambda)$, with unfiltered sampling, and CDOM absorption $a_{CDOM}(\lambda)$,
and beam attenuation $c_{CDOM}(\lambda)$, with filtered sampling. Subtraction of the filtered
coefficients from the unfiltered coefficients provides the particle specific coefficients, i.e.
$c_p(\lambda) = c_t(\lambda) - c_{CDOM}(\lambda)$, $a_p(\lambda) = a_t(\lambda) - a_{CDOM}(\lambda)$. Scattering coefficients are obtained
from $b_t(\lambda) = c_t(\lambda) - a_t(\lambda)$ or $b_p(\lambda) = c_p(\lambda) - a_p(\lambda)$. Unfiltered coefficients include the
subscript t as $a_t$, $b_t$, and $c_t$ and particle specific coefficients include the subscript p as $a_p$,
$b_p$ and $c_p$. As noted in the previous chapters, only measurements at 650 nm were used in
this analysis.

Total suspended matter (TSM), particulate inorganic matter (PIM), particulate
organic matter (POM) and percent organic matter (%OM) were obtained via filtering and
loss-on-ignition processing as described in Chapter II. POM was obtained by subtracting
PIM from TSM. Percent organic matter was obtained from the ratio POM/TSM.

The PSD function and bulk density were used to calculate total mass
concentration. These results were given the lower case designation $tsm$ to differentiate
them from TSM measured in situ.

Methods for calculating bulk index of refraction $n_1$, and bulk particle density $r_1$,
using %OM as a weighting function are described in Chapter II. In the theoretical
analysis that follows, results are sometimes plotted using %OM or just OM in lieu of
density or refractive index to reduce the complexity of the graphical presentation. This is
done when comparing modeled scattering and tsm results because modeled tsm varies
with r1 and modeled scattering varies with n1 and the change in both n1 and r1 are
linearly proportional to change in %OM as described in Chapters II and III.

Bulk particle index of refraction obtained from the model of Twardowski et al.
(2001) was inverted to OM which was subsequently used to estimate density (Chapter
III). The PSD slopes $\xi_{gcp}$ and $\xi_{get}$ obtained from the model of Boss et al. (2001b)
(Chapter III) are used with bulk density in the PSD function to calculate tsm, and with
bulk refractive index in the Mie theory model to calculate optical coefficients. The
LISST-100b derived PSD parameters $\xi_2$ and scaling factor $k_2$ are also used for
comparison. The scaling factor $k_2$ is used in all modeling calculations.

Size ranges used in this study were selected based on several factors. The
measurement range of the LISST-100b is $1.0 \leq D \leq 250 \ \mu m$. The nominal pore size of
the filters used for TSM analysis is 0.7 $\mu m$ (Whatman GF/F). The assumed minimum
particle size important for light scattering at 650 nm is 0.1 $\mu m$ (see Chapters II and III for
detailed explanation).

**Mie Theory Code**

Mie theory for homogeneous spheres shows that light scattering by particles
varies as a function of particle refractive index and particle size relative to wavelength:

$$b(\lambda) = \int \int \sigma_b(D; m_r; \lambda) N(D) dD dm_r$$

where $\sigma_b(D; m_r; \lambda) \equiv Q_b A_s = Q_b \pi \frac{D^2}{4}$ is the
scattering cross section, $Q_b$ is scattering efficiency, $D$ is particle diameter, $N$ is the

number of particles of a given diameter and \( m_r = n(re) + in(im) \) is particle index of refraction relative to a seawater medium (Mobley 1994). The total scattering cross section \( \sigma_p \) is obtained by integration over all scattering angles. As noted previously the particle size distribution function \( N(D) = kD^\xi \) is used to define the particle sizes used in the scattering equation above.

The FORTRAN model of Mie theory scattering (Bohren and Huffman 1984) translated to Matlab code by Emmanuel Boss is a numerical implementation of the equation described above. For this study the model was used to calculate the volume scattering function (VSF), total scattering, absorption, and backscattering coefficients (\( b, a, \) and \( b_b \) respectively) over the ranges of \( n, D, k, \) and \( \xi \) of particle assemblages in the study area. Scattering calculations were done only at 650 nm because simultaneous measurements of absorption, scattering and backscattering coefficients are only available at 650 nm.

**Modeling**

In Chapter III, the PSD and bulk particle density were used to calculate \( tsm \) using selected ranges of \( k, \xi, D, \) and \( \rho \). The parameters were varied separately to demonstrate their individual impacts on \( tsm \). In Chapter II the \( %OM \) was the common factor between bulk particle density and bulk particle index of refraction. The same process was used here to investigate the impact of the PSD and bulk particle index of refraction on the optical coefficients. As noted in Chapters II and III the method to obtain bulk particle density and bulk particle index of refraction using \( %OM \) does not account for relative numbers of organic and inorganic particles, which would could be used in the modeling processes as a relative weighting of \( k \) for each particle type. In this analysis \( m_r \) includes
$n(\text{im})$ obtained from Chapter II, Table 2. The proportion was determined with %OM using the same method as was used for $n(\text{re})$. Note however that at 650 nm the same value of $n(\text{im})$ is used for both mineral and organic particles.

Parameter values and ranges were set based on observed data in the previous chapters. The values and ranges for k were based on the average value of k2 obtained from the LISST-100b data where kavg = 4.68E10. To create a range of values for k, kavg was multiplied by a set of constant multipliers kfac, where $0.1 \leq \text{kfac}(i) \leq 2.0$, and i is the index for each factor. This range of k covered the range of the standard deviation of k2 in the study area.

The range of %OM used in the modeling was 0 to 100 %. The range for $\xi$ was usually limited to $3.0 \leq \xi \leq 5.0$ but the lower bound was extended to zero in some cases for illustration of specific points.

Once the optical coefficients were calculated they were compared with the values of $\text{tsm}$ which were calculated using the same values for k, $\xi$, and %OM. Because %OM was the common link between bulk particle density and bulk particle index of refraction, %OM is used as a proxy to represent the variation in those two parameters (i.e. r1 and n1) in the scatter plots used below comparing $\text{tsm}$ and optical coefficients. The regression equations displayed in some of the scatter plots below were used to provide an indication of the complex relationships between variables. The correlation coefficients were presented to remind us that these are not exact relationships.
Results and Analysis

*Optical coefficients vs. k, S, %OM*

The methods used in Chapter III to measure $k$, $\xi$, and bulk particle density each produced different results. Adjustments were made to $\xi$ and density to force values of $t_{sm}$ calculated using the PSD function to match those of measured TSM. Results of these adjustments demonstrated that the final values of $\xi$ and density produced using the different methods, converged to similar values. Because these same parameters determine the optical scattering characteristics of the particle assemblage, they will be used with the Mie theory model to calculate optical coefficients. In order to determine whether the adjustments made in Chapter III represent reasonable results, the calculated optical coefficients will be compared with coefficients measured *in situ*.

To assess their impact on $b$, $b_{650}$, $a$, and $R_{rs}$, the variables $k$, $\xi$, %OM and minimum included particle size ($d_{min}$) were varied independently using the same values and ranges as those in Chapter III. Recall that %OM is used to calculate $m_r$ as described in Chapter II for input to the Mie code. Unless otherwise specified, optical coefficients are reported for minimum included particle diameter, $d_{min} = 0.1 \ \mu m$, and $t_{sm}$ is reported for $d_{min} = 0.7 \ \mu m$ to represent the values measured *in situ*.

To evaluate the optical response due to change in $k$, %OM was held constant at %OM = 40 %. Calculations were repeated using different values of constant $\xi = 3.0$, 4.0, and 5.0. Results indicate $b_{650}$, $b_{b650}$ and $a_{650}$ (not shown) vary linearly with change in $k$ (Figs. 65, 66). The ratio of $b_{b650}$ to $k$ increases as $\xi$ increases from 3 to 5. However, there is only a small difference in the $b_{650}$ to $k$ ratio when $\xi$ changes between 3 and 4. The ratio of $b_{650}$ to $k$ is actually greater when $\xi = 3$ than when $\xi = 4$. The difference in
the change in the $b_{\xi,650}$ to k ratio relative to the $b_{650}$ to k ratio as $\xi$ increases from 3 to 5 results in a significant change in the $b_{\xi}$/$b$ ratio for different values of $\xi$ (cf. Fig. 68 below).

Using the equation $Rrs \propto b_{\xi}/(a+b_{\xi})$, as a proxy for remote sensing reflectance (see Chapter II), $Rrs_{650}$ does not change at all with change in k since the relationships between $k$ and both $b_{\xi,650}$ and $a_{650}$ are linear with zero offset (Fig. 67). This can be further explained by substituting the regression equations of $b_{\xi,650}$ (Fig. 66) and a similar equation for $a_{650}$ (data not shown) in the equation for $Rrs$. Because the regression equations are first order polynomials with zero offset, $k$ can be factored out of both the numerator and denominator thus cancelling the variable $k$ from the equation. This leaves only the constant slope coefficients of the regression equations in the remote sensing equation, demonstrating that for a fixed value of %OM and $\xi$, the remote sensing signal is constant and independent of $k$ as is seen in Fig. 67. Different values of $\xi$ do produce different values of $Rrs_{650}$ although all are constant with $k$. Note there is a small difference in $Rrs_{650}$ for $\xi = 4$ and 5, but there is a large difference when $\xi = 3$ (Fig. 67).
Figure 65. $b_{650}$ vs. $k$. Each set of symbols represents a different value of $\xi$. In this plot $kavg = 2.734 \times 10^{11}$ and $0.1 \leq kfac \leq 2.0$, %OM is proxy for $n$. Note the range of $b_{650}$ is much more realistic for $\xi = 3$ or 4 than for $\xi = 5$.

Figure 66. $b_{650}$ vs. $k$. Each set of symbols represents a different value of $\xi$. In this plot $kavg = 2.734 \times 10^{11}$ and $0.1 \leq kfac \leq 2.0$, %OM is proxy for $n$. 
Recall the bulk refractive index is calculated using %OM to weight the relative contributions by mineral and organic particles (Chapter II). To test the response to change in bulk refractive index n1, optical coefficients are calculated for different values of n1 as %OM is varied over the range of 0 ≤ %OM ≤ 100, with ξ = 3 and k = kavg held constant (Figs. 68, 69). Optical coefficients $b_{650}$ and $b_{b650}$ (Fig. 68), and $a_{650}$ (Fig. 69) exhibit a nearly linear response to change in n1 as %OM varies from 0 to 100 %. The $b_{b}/b$ ratio (Fig. 69) also varies greatly, increasing from 0.005 to about 0.33 as the influence of mineral particles increases. Note that, as %OM is varied over its range none of the optical coefficients are 100 % linear (i.e. $r^2 \neq 1$). The greatest impact is observed in the $Rrs_{650}$ response which also increases greatly from about 0.4 to 0.9 as mineral particles become the dominant particle type. Note that this increase has a strong second order regression component (Fig. 68).
**Figure 68.** $b_{650}$, $b_{bb650}$, $Rrs_{650}$ vs. %OM. %OM is proxy for $n$. In this plot $kavg = 2.734E11$.

**Figure 69.** $b_{bb}/b_{650}$, $a_{650}$ vs. %OM. %OM is proxy for $n$. In this plot $\xi = 3$, $kavg = 2.734E11$.

To evaluate the impact on optical coefficients when $\xi$ is varied from 3 to 5, %OM and $k$ are held constant at $k = kavg$ and %OM = 40 % (Fig. 70). Variation in all optical coefficients due to change in $\xi$ are non-linear while $k$ and %OM are held constant.
Coefficients $a_{650}$, $b_{650}$ and $Rrs_{650}$ are best approximated by 2\textsuperscript{nd} order polynomial regressions and $b_b_{650}$ is best approximated with an exponential function as $\xi$ varies from 3 to 5 (Fig. 70). Note that the values of $Rrs_{650}$, $a_{650}$ and $b_{650}$ are not unique and are similar in magnitude as $\xi$ changes from 3 to 4. The small difference in $b_{650}$, and the large difference in $b_b_{650}$ when $\xi$ increases from 3 to 4, results in a large change in $b_b/b_{650}$ (data not shown). When $\xi = 3$, $b_b/b_{650} = 0.022$ but when $\xi = 4$, $b_b/b_{650} = 0.076$. The value $b_b/b_{650} = 0.076$ is a much higher than is usually reported in marine waters.

\[
y_{bb} = 0.0009e^{1.4946x}
\]
\[
R^2 = 0.9875
\]
\[
ya = 0.0584x^2 - 0.4084x + 0.7231
\]
\[
R^2 = 0.985
\]
\[
y_{rrs} = -0.0501x^2 + 0.4468x - 0.0622
\]
\[
R^2 = 0.9577
\]
\[
y_{b} = 2.7689x^2 - 19.702x + 38.528
\]
\[
R^2 = 0.9917
\]

Figure 70. $b_{650}$, $b_b_{650}$, $a_{650}$, $Rrs_{650}$ vs. $\xi$. %OM is proxy for n. In this plot $kavg = 2.734E11$.

**Modeled Optical Coefficients vs. Modeled \textit{tsm}**

To evaluate the relationship between optical coefficients and \textit{tsm}, \textit{tsm} is calculated with the same values of \textit{k}, $\xi$, and %OM that were used to calculate the optical coefficients described above. Recall the bulk particle density $r_1$, is calculated using %OM to weight the relative contributions by mineral and organic particles (Chapter II).

In Fig. 71 below, %OM or just OM is the variable for constant values of $k = kavg$ and $\xi = \ldots$
3. The variation in OM represents the simultaneous variation in n1 and r1. Calculations were done for two values of the minimum included particle size, dmin = 0.2 and 0.7 µm. Note the large range of $Rrs650$ vs. the relatively small range of $tsm$ due only to change in %OM.

The $tsm$ to $Rrs650$ ratio differs somewhat over the range of %OM for different values of $\xi$, especially for OM > 50 %, however for different values of $\xi$ $Rrs650$ changes by orders of magnitude (Fig. 72). The non-linear relationship between $tsm$ and $Rrs650$ when $\xi$ is constant is due to the non-linear relationship between $Rrs$ and n1 (Fig. 68 above), but the $tsm$ to $Rrs650$ relationship changes with different values of $\xi$ (Fig. 72). The average $Rrs*650$ for all stations was 0.12 which similar to the modeled value $Rrs*650$ when $\xi$ is 3.0 (Fig. 72).

![Graph](https://via.placeholder.com/150)

$yt02 = 27.843x^2 - 23.353x + 10.128$
$R^2 = 0.9821$

$yt07 = 23.31x^2 - 19.551x + 8.4796$
$R^2 = 0.9821$

$Rrs650 \ (\xi=3, \ 0<OM<1, \ Kavg)$

dmin=0.2

dmin=0.7

Figure 71. $tsm$ vs. $Rrs650$. Two values of dmin were used, dmin = 0.2 µm and dmin = 0.7 µm. %OM is proxy for n and $\rho$. In this plot kavg = 2.734E11.
Comparing change in $tsm$ to change in $b_{650}$ over the range of %OM as described above results in a nearly linear relationship between $tsm$ and $b_{650}$ (Fig. 73). The value of $b*650$ changes significantly over the range of %OM and both the range and direction of change are affected by the value of $\xi$ (Fig. 74). For values of $\xi$ greater than 3.0, $b*650$ is greater than 1.0. Values of $b*650$ are between 0.1 and 1 for $\xi = 3$. The average value of $b*650$ for the study area is 0.54, suggesting that the average value of $\xi$ in the study area is near 3.0.

The change in $tsm$ relative to change in $b_b*650$ is nearly constant when mineral particles are greater than about 50 % of the mass concentration (Figs. 75 and 76). When organic particles become more dominant $b_b*650$ begins to decrease at a greater rate until OM reaches 100% (Fig. 76). Once again the range of $b_b*650$ is nearest the modeled value when $\xi$ is near 3.0.
Figure 73. \( tsm \) vs. \( b_{650} \). Two values of \( d_{\text{min}} \) were used, \( d_{\text{min}} = 0.2 \) µm and \( d_{\text{min}} = 0.7 \) µm. \%OM is proxy for \( n \) and \( p \). In this plot \( k_{\text{avg}} = 2.734 \times 10^{11} \).

Figure 74. \( b_{\times 650} \) vs. \%OM. \( k = k_{\text{avg}} \), \( \xi \) is constant. Note the change in the \( b_{\times 650} \) to \%OM relationship when \( \xi \) changes from 2 to 3.
Figure 75. $tsm$ vs. $b_{b650}$. Two values of $d_{min}$ were used, $d_{min} = 0.2 \, \mu m$ and $d_{min} = 0.7 \, \mu m$. $\%OM$ is proxy for $n$ and $\rho$. In this plot $k_{avg} = 2.734E11$.

$y_{d02} = 20.067x^{0.317}$  
$R^2 = 0.9974$

$y_{d07} = 16.8x^{0.317}$  
$R^2 = 0.9974$

$d_{min}=0.2$

$d_{min}=0.7$

Figure 76. $b_{b*650}$ vs. $\%OM$. $k = k_{avg}$, $\xi$ is constant.

When $\xi$ and $\%OM$ are held constant and $k$ varies, $tsm$ varies linearly with change in both $b_{650}$ and $b_{b650}$ (Figs. 77 and 79). These linear relationships result in constant values for both $b_{b*650}$ and $b_{b*650}$ over the range of $k$ (Fig. 78). When $\%OM$ is 40 $\%$, $d_{min} = 0.7$ and $\xi = 3$, $b_{b*650} = 0.011$, and when $\xi = 4$, $b_{b*650} = 0.154$ (Fig. 78). The average value of $b_{b*650}$ in the study area was about 0.006. Once again these results suggest the average value of $\xi$ is near 3.0 in the study area.
The regression slopes between $tsm$ and $b_{650}$ for $d_{\text{min}} = 0.2$ and $0.7 \, \mu\text{m}$, are very similar when $\xi = 3$ (Fig. 79). On cruises NE2 and NE3, a separate research group measured TSM using $0.2 \, \mu\text{m}$ filters (Dr. Brent McKee, unpublished). When TSM values measured with $0.2$ and $0.7 \, \mu\text{m}$ filters are compared to each other, the slope of the regression line between them is about $1.11$ (Fig. 80). This is very close to the slope of $1.19$ between calculated values of $tsm$ at $d_{\text{min}} = 0.2$ and $d_{\text{min}} = 0.7 \, \mu\text{m}$ when $\xi = 3$ (Fig. 79).

**Figure 77.** $tsm$ vs. $b_{650}$. K varies as %OM and $\xi$ are held constant. $b_{b}^{*}(\xi = 3) = 0.011$, $b_{b}^{*}(\xi = 4) = 0.154$. $D_{\text{min}} = 0.7 \, \mu\text{m}$ %OM is proxy for n and p. In this plot $k_{avg} = 2.734\text{E}11$. 
Figure 78. $b_b*650$ vs. k. OM = 40%, 3 values of constant $\xi$. Note the variability in $b_b*650$ is primarily due to change in $\xi$.

Figure 79. $tsm$ vs. $b_{650}$. K varies while %OM and $\xi$ are held constant. Note the difference in slope between results for $d_{min}=0.2$ and $d_{min}=0.7$ µm at different values of $\xi$. $b^*(\xi = 3, d_{min} = 0.2) = 0.45$, $b^*(\xi = 3, d_{min} = 0.7) = 0.54$, $b^*(\xi = 4, d_{min} = 0.7) = 2.02$. %OM is proxy for $n$ and $\rho$. In this plot $k_{avg} = 2.734E11$. Note the small difference in slope between $d_{min} = 0.2$ and $d_{min}=0.7$µm at $\xi = 3$. 
Figure 80. TSM measured with 0.2 µm filters vs. TSM measured with 0.7 µm filters. Squares are tsm values predicted using $\xi = 3$. The slightly higher values obtained with the 0.2 um filters indicates that the PSD slope $\xi$, must be between 2 and 4 (cf. Fig. 79). (0.2 µm data provided by Dr. Brent McKee).

The above results provide a number of clues that help in the interpretation of relationships between optical scattering and bulk particle composition and size distributions in this study. The greatest variation in mass specific coefficients appears to be caused by changes in $\xi$. All coefficients, $b*650$, $b_b*650$, and $Rrs*650$ change by an order of magnitude when $\xi$ changes incrementally between 3.0, 4.0 and 5.0 (Figs. 72, 74, 76). Change in $b*650$, $b_b*650$, and $Rrs*650$ is usually less than a factor of 10 when n1 and r1 both change as %OM varies from 0 to 100 % (Figs. 72, 74, 76). When only the scaling factor k, is changed there is no change in the mass specific coefficients (Fig. 78).

The final modeling exercise allows k, $\xi$, and %OM to vary simultaneously. The variability is based on the assumed changes that occur in the particle assemblage between the river mouth and shelf water (cf. Chapter III, Table 13). The greatest values of TSM and k, and the lowest values of $\xi$ and %OM are found near the river mouth. The lowest values of TSM and k, and the highest values of $\xi$ and %OM are found in shelf waters. To
simulate the changes between river mouth and shelf waters all parameters were varied linearly in ten steps across their respective ranges. Optical coefficients and tsm were calculated at each step. The endpoints represent the extreme conditions. The intermediate steps do not necessarily represent actual combinations of expected values, however they are not un-realistic. These results are recorded below in Figs. 81 – 85. Note that the value of kavg was changed from 2.734E11 to 4.6E10 and the range of kfac was changed from 0.1 ≤ kfac ≤ 2.0, to 0.1 ≤ kfac ≤ 5.6. Recall that kfac is simply a multiplier to expand the range of k around kavg. These changes were made to account for differences in average values due a reduction in the number of stations available for conducting this analysis.

Change in tsm and b650 are plotted vs. change in %OM, while k is plotted as well to remind us that it is changing inversely with %OM for the minimum included particle diameter of dmin = 0.7 µm (Fig. 81). Both tsm and b650 are slightly non-linear with simultaneous change in %OM and k, with ξ = 3. The values of b*650 for ξ = 2.5, 3.0, 3.5 and 4.0 demonstrate the impact on magnitude and range of b*650 as k, ξ and %OM vary simultaneously (Fig. 82). When ξ = 2.5 and 3.0, b*650 is relatively constant over the entire range of k and %OM. The magnitude of b*650 is about 0.43 when mineral particles are dominant, decreasing to near 0.3 when organic particles are dominant. However when ξ = 3.5, b*650 decreases from about 1.1 to less than 0.5. This trend appears to conflict with trends predicted by Babin et al. (2003). This warrants further investigation however, these results do not represent a direct comparison of either the methods or modeled parameters used here vs. those of Babin et al. (2003). In particular,
Babin et al. (2003) made no attempt to mix particle types in their modeling efforts either by the method used here (i.e. %OM) or by numbers of particles of each type.

The magnitude of $b*650$ when $d_{\text{min}} = 0.7$ um is much greater than when $d_{\text{min}} = 0.2$ um, although the trends remain similar (data not shown). This difference is expected and further serves to emphasize the sensitivity in $b*650$ to values of $\xi > 3.0$. The same differences are observed for $b_\nu*650$ and $Rrs*650$ (data not shown).

The decrease in $Rrs650$ relative to %OM at $\xi = 3.0$ is identical to results obtained when %OM was varied and $k$ was held constant (Fig. 83, note $tsm$ moved to secondary axis, cf. Fig. 68.) This indicates $Rrs650$ is independent of change in $k$. However, $Rrs*650$ increases as %OM increases but the increase in $Rrs*650$ due to increase in $\xi$ appears to be constant over the same range (Fig. 84).

The value of $b_\nu/b650$ is plotted using the same parameters as above and like $Rrs650$ it decreases as %OM increases. Values of $b_\nu/b650$ presented here are identical to values obtained when $k$ was held constant (Fig. 85, cf. Fig. 69). The values of $b_\nu/b650$ reported here appear to be two times greater than what was measured in the study area. The average $b_\nu/b650$ was the highest at about 0.015 in the River Mouth water class, where the average %OM was about 22 %. In the Shelf water class, average $b_\nu/b650$ was the lowest at about 0.010 where the average %OM was about 68 %. The modeled values of $b_\nu/b650$ reported here are higher overall at 0.0267 when OM is 20 % and 0.0135 when OM is 70 % OM. The modeled numbers get even larger when $\xi$ is increased. Although the modeled values of $b_\nu/b650$ are higher than those measured, the trend relative to %OM is consistent.
Figure 81. $b_{650}$ vs. %OM and k. $\xi = 3$, solid line with stars is kfac shown for comparison with %OM scale. OM is increasing while k is decreasing. Note that $b_{650}$ and tsm decrease at different rates.

Figure 82. $b*_{650}$ vs. %OM and k. Solid line with stars is kfac shown for comparison with %OM scale. OM is increasing while k is decreasing. Note the variability in $b*_{650}$ over the range of OM is most affected by the value of $\xi$. 
Figure 83. $Rrs_{650}$ vs. %OM and k. $\xi = 3$, and solid line with stars is kfac shown for comparison with %OM scale. OM is increasing while k is decreasing. Note the very different changes in $Rrs_{650}$ and tsm relative to change in OM and k.

Figure 84. $Rrs^{*650}$ vs. %OM, k, solid line with stars is kfac shown for comparison with %OM scale. OM is increasing while k is decreasing. Note log scale for $Rrs^{*650}$. $\xi$ is clearly the dominant influence on $Rrs^{*650}$. 

$y = -0.5699x^2 + 0.0797x + 0.8867$

$R^2 = 0.9969$

$0 < \%OM < 100$, $k_{avg}^{*}k_{fac} (5.6 > k_{fac} > 0.1)$, $d_{min}=0.7\mu m$, $\xi = 3$
Figure 85. Rrs650 vs. %OM and k. ξ = 3 and solid line with stars is kfac shown for comparison with %OM scale. OM is increasing while k is decreasing. bb/b650 and tsm change at a similar rate.

$tsm$ vs. Optical Coefficients Modeled with $k_2$, $ξ$, and Density From the Study Area

Two methods were used to determine the power law PSD scaling and slope parameters $k$, and $ξ$. Each method produced very different results (Chapter III). To reconcile these differences in Chapter III, the values of $k_2$, $ξ_2$, $ξ_{gct}$, $ξ_{gcp}$, $n_1$, $ng_{ct}$ and $ng_{cp}$ were used as inputs to the power law PSD function to calculate $tsm$. Recall that data derived from the LISST-100b, i.e. $k_2$ and $ξ_2$, overestimated $tsm$ while $ξ_{gct}$, $ξ_{gcp}$, $ng_{ct}$ and $ng_{cp}$ underestimated $tsm$ using the method of determining bulk $n_1$ and $r_1$ from %OM. It should be noted that preliminary results using %OM to partition the relative numbers or organic and inorganic particles resulted in much better estimates of $tsm$ using $k_2$ and $ξ_2$ derived from the LISST-100b (data not reported here). The average values of $k$, $ξ$, and density were adjusted until the average value of $tsm$ matched the average value of measured TSM for the entire data set (Chapter III). A significant observation made during that process was that the adjustment of $ξ$ was the only one that resulted in a change in the correlation coefficient between $tsm$ and TSM. With all three methods for
obtaining \( \xi \), i.e. \( \xi_2 \), \( \xi_{gct} \), and \( \xi_{gcp} \), the correlation coefficient between \( tsm \) and TSM increased while adjusting \( \xi \) until \( \xi \) approached a value of 3.0.

In this chapter, the values of \( k_2 \), \( \xi_2 \), \( \xi_{gct} \), \( \xi_{gcp} \), \( n_1 \), \( n_{gct} \) and \( n_{gcp} \) were used as inputs to the Mie code to calculate the optical coefficients. These modeled coefficients, \( b_m650 \), \( b_{tm650} \), \( a_m650 \), \( b_t/b_m650 \), \( Rrsm650 \), and \( tsm \), were then compared to the measured coefficients to determine the affects of adjusting the input parameters \( k \) and \( \xi \) on the optical coefficients and \( tsm \). Observations from the modeling efforts above were used to guide the further adjustment of \( k \) and \( \xi \) until the best match was obtained for both optical coefficients and \( tsm \).

The Mie code was executed using three sets of the values of \( k \), \( \xi \), and \( \%OM(n1,r1) \), representing the unadjusted results of the different methods used to obtain them, i.e. the LISST-100b, \( c_i(\lambda) \) and \( c_p(\lambda) \) (Table 13). A value for \( b_m650 \), \( b_{tm650} \), \( a_m650 \), \( b_t/b_m650 \), \( Rrsm650 \), and \( tsm \) was calculated for each data sample for five values of the minimum particle diameter \( d_{min} = 1.0, 0.7, 0.2, 0.1, 0.01 \) µm. The largest included particle diameter was 250 µm. A second model run used adjusted values of \( \xi \) from Chapter III. Recall that adjustments to \( k \), \( \xi \) consist only of adding a constant to the measured value, resulting in an increase or decrease to the average value (Table 14). Modeled optical coefficients were then compared to measured coefficients. After the first model run the \( b_m/b_t650 \) ratio was less than 1 (see \( b_m/b_t \) in Table 14). In the modeling effort above it was found that when \( \xi \) decreased from 4.0 to 3.0 \( b650 \) increased only by 2.9 % (Fig. 70). Because adjusted values of \( \xi \) were near 3.0, further adjustment would not affect \( b_m650 \). The average value of \( k \) was increased by the inverse of \( b_m/b_t \). After \( tsm \) was calculated using the new average value of \( k \), \( \xi \) was adjusted again to obtain a
match between \textit{tsm} and TSM. These new values of \(k\) and \(\zeta\) were input to the Mie code and optical coefficients and \textit{tsm} were re-calculated. These final values resulted in a \(b_m/b_t\) ratio much closer to 1:1 (Table 14). The closest match between \(b_m,650\) and \(b_t,650\), \(b^*_{m,650}\) and \(b^*_{t,650}\), as well as a match between \(b_t/b_m,650\) and \(b_t/b_t,650\) was obtained for the data obtained using \(c_p(\lambda)\) to get \(\zeta_{gcp}\). The ratio between \(b_m,650\) and \(b_t,650\) was 1.05 (Fig. 86). The \(b^*_{m,650} = 0.31\) was very close to the measured value of \(b^*_{650} = 0.35\) (Fig. 88) and \(b_t/b_m,650 = 0.018\) was very close to the measured value of \(b_t/b_t,650 = 0.0144\) (Fig. 87, cf. Chapter III, Fig. 41).
Table 14

*Original and Adjusted Values of Average \( \bar{\zeta} \), O2, and Comparison Between Modeled \( b_m \) and Measured \( b_t \) and the New \( b/b_t \). The First 3 Rows Represent Original Data, the Next 3 Rows Represent Adjustments to \( \bar{\zeta} \) Made in Chapter III and the Final 2 Rows Represent the Final Adjustments in Chapter IV That Best Matched Measured Data*

<table>
<thead>
<tr>
<th></th>
<th>( b*_\text{mie} )</th>
<th>( b/b_m\text{mie} )</th>
<th>( b_m/b_t )</th>
<th>( \bar{\zeta} )</th>
<th>O2</th>
<th>density</th>
<th>n(re)</th>
<th>%OM</th>
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<td>0.025</td>
<td>2.04</td>
<td>2.08</td>
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<td>1.11</td>
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<td>0.34</td>
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<td>1.37</td>
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<td>48.6</td>
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<tr>
<td>ct</td>
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<td>0.37</td>
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<td>10.92</td>
<td>1.37</td>
<td>1.09</td>
<td>48.6</td>
</tr>
</tbody>
</table>

*Figure 86. \( b_m650\text{cp} \) vs. \( b_650 \) using the adjusted values of \( \bar{\zeta} \) and k. Note the nearly 1:1 regression line between \( b_m650\text{cp} \) and \( b_650 \).*
$y = 0.0177x - 0.0046$

$R^2 = 0.9717$

Figure 87. $b_m$ vs. $b_m650cp$ using the adjusted values of $\xi$ and $k$. Note the regression line between $b_m$, $650cp$ and $b_m650cp$ is similar to the measured $b_m$ regression equation (cf. Fig. 41, Chapter II).

The modeled $b_m*650$ data are much closer to the trend line than the measured $b_t*650$ data (Fig. 88). This result suggests that the variability in the measured $b_t*650$ data is not due to differences in $k$, $\xi$ and %OM but may be due to methods used for collecting and processing samples as described in Chapter II.

$y = 0.3057tsm$

$R^2 = 0.9223$

$y = 0.3344TSM$

$R^2 = 0.1013$

Figure 88. $b_m650cp$ vs. $tsm$ and $b_p650$ vs. TSM. Measured data is much more scattered (squares). $R^2$ are displayed for qualitative comparison only.
The results above demonstrate that adjustments made to both the LISST-100b data $k_2$, $\xi_2$, and the data obtained using the methods of Boss et al. (2001b) and Twardowski et al. (2001), i.e., $\xi_{gct}$, $\xi_{gcp}$, ngct and ngcp, can produce results very similar to those obtained from measured data. While this effort to obtain “closure” between methods does not prove the adjusted values are “correct”, the un-adjusted values were significantly different from both measured and modeled results. One important possible reason for the significant difference is not accounting for the relative numbers of particles of each type when using %OM to determine bulk particle density and refractive index.

$b^*650$, $b_b^*650$, and $Rrs^*650$ vs. $k$, $\xi$ and %OM

The hypothesis of this dissertation was that variability in the mass specific optical coefficients, i.e. $b^*$, $b_b^*$, $Rrs^*$ could be attributed to variability in $k$, $\xi$, and %OM. In Chapters II and III, $b650$, $b_b650$, and $Rrs650$ were significantly correlated with TSM but no significant correlations were found for $b^*650$ or $b_b^*650$. $Rrs^*650$ was significantly correlated with $\xi_{gct}$ and $\xi_2$ but $r^2$ was < 0.31 and < 0.1 respectively (Chapter III, Fig. 59).

The modeling analysis above demonstrates that $b^*$, $b_b^*$, $Rrs^*$ are not dependent on $k$. This is not unexpected since both $tsm$ and $b_b650$ increase linearly with increases in $k$ when $\xi$ and %OM were held constant.

The modeling analysis above demonstrates that $b^*650$, $b_b^*650$ and $Rrs^*650$ do change with change in %OM and $\xi$ (Figs. 74, 76, 78, 80, 82 and 84). The observed trends are also dependent on the minimum included particle diameter $d_{min}$. An important point to notice in the figures above is the relatively narrow range over which $b^*650$, $b_b^*650$ and $Rrs^*650$ vary relative to %OM. For cases where $\xi$ may not be constant, variability in optical coefficients due to change in %OM may not be detected. In the cases where $\xi$
does not change significantly changes due to small variations in %OM may be detectable in the optical coefficients.

The data shown above is re-plotted here to emphasize the dependence of $b^{*650}$ and $Rrs^{*650}$ on $\xi$ and $dmin$ (Figs. 89 – 92, cf. Chapter III, Fig. 59). For both $b^{*650}$ and $Rrs^{*650}$, the relationship with $\xi$ is very different depending on the value of $dmin$ (Figs. 89 - 92). The range of $b^{*650}$ decreases by an order of magnitude and the range of $Rrs^{*650}$ decreases by a factor of four when $dmin$ changes from 0.7 to 0.2 $\mu$m. When $dmin = 0.7$ $\mu$m, change in the smallest values of both $b^{*650}$ and $Rrs^{*650}$ are dominated by change in $\xi$ while change in the largest values are dominated by change in %OM (Figs. 89 and 91). There is a similar effect when $dmin = 0.2$ $\mu$m, however changes in $b^{*650}$ and $Rrs^{*650}$ are not unique as $\xi$ varies above and below a value of about 3.0 depending on the simultaneous value of %OM (Figs. 90 and 92).

It is very clear from these modeled relationships that changes in $b^{*650}$ and $Rrs^{*650}$ are dependent on $\xi$, %OM, and $dmin$. It is also clear that these relationships do not always produce unique results. Because each of these variables can change independently and because relationships are not all unique, a simple least squares regression analysis cannot be expected to detect any patterns except in the case where one or more of the variables may be relatively constant. It is also clear that the choice of filter type and effective pore size can produce dramatically different results based on TSM measurements.
Figure 89. \( \xi \) vs. \( b*_{650} \). \( k \) is constant while \( \xi \) and %OM are varied. Note the range in magnitude of \( b*_{650} \) for different combinations of \( \xi \) and %OM.

Figure 90. \( \xi \) vs. \( b*_{650} \) for \( d_{min} = 0.2 \mu m \). \( K \) is constant while \( \xi \) and %OM change simultaneously. \( b*_{650} \) is clearly not unique over the ranges of \( \xi \), \( k \), and %OM. Note the range in magnitude of \( b*_{650} \) for different combinations of \( \xi \) and %OM.
Figure 91. $\xi$ vs. $Rrs*650$ for $d_{min} = 0.7 \, \mu m$. $K$ is constant while $\xi$ and %OM change simultaneously. Note the overlap in values of $Rrs*650$ for the ranges of $\xi$, $k$, and %OM.

Figure 92. $\xi$ vs. $Rrs*650$ for $d_{min} = 0.2 \, \mu m$. $K$ is constant while $\xi$ and %OM change simultaneously. Note the magnitude of $Rrs*650$ for $d_{min} = 0.2 \, \mu m$ (cf. Fig. 71).

Remote Sensing Reflectance

Throughout this work the remote sensing reflectance using the equation $Rrs \propto \frac{b\ell}{(a+b\ell)}$ has been included in the analysis. The individual optical coefficients $a_{650}$, $b_{650}$, and $b_{650}$ vary linearly with change in either $k$ or %OM. However $Rrs_{650}$ does not. When %OM and $\xi$ are constant, $Rrs_{650}$ is independent of change in $k$. When $k$ and $\xi$ are
constant, $Rrs_{650}$ decreases as %OM increases and is best represented by a 2$^{nd}$ order polynomial (Fig. 68). When k and %OM are held constant $Rrs_{650}$ increases as $\xi$ increases over the range of 3 to 5 (Fig. 70). When k, %OM and $\xi$ vary simultaneously $Rrs_{650}$ produces non-unique results. As $\xi$ increases from 2.5 to 4.0 the magnitude of $Rrs_{650}$ increases but the range decreases (Fig. 83). The impact of these uncertainties is evident in the value of $Rrs_{650}$ obtained from measured $a_{650}$ and $b_{650}$ in plume transect stations from Chapter II, Fig. 32. Only a weak trend is detected with distance from the river mouth while all other optical coefficients and TSM are significantly correlated with distance from the mouth. Furthermore the other parameters are well described with power law functions as they decrease with distance from the river mouth.

These results indicate that for the data in this study $Rrs_{650}$ is a poor predictor of TSM. Modeling results indicate that change in $Rrs_{650}$ is dependent on change in %OM and change in $\xi$ but not k. The relationship between $Rrs_{650}$ and $tsm$ is non-linear with change in either %OM or $\xi$, further confounding the interpretation of the $Rrs_{650}$ signal. Further modeling using relative numbers of particles, particle specific $n(im)$ and different wavelengths may provide more insight into the relationship between TSM and the remotely sensed signal.
Figure 93. $R_{rs650}$ as $\xi$, %OM, and $k$ vary simultaneously. Note that $R_{rs650}$ is not unique for the combinations of $\xi$, $k$ and %OM presented here.

Conclusions

The objectives of this study were to use the Mie theory code to model optical coefficients using both prescribed values and data from this study for input parameters. These results were used to compare data obtained from in situ measurements with theoretical results. A second purpose was to reconcile inconsistent output data from two separate methodologies. These results were then used to revisit the original hypothesis of this dissertation.

Theoretical modeling using the Mie theory with input parameters representing magnitudes and ranges of data expected in the study area, produced output values similar in range and magnitude to measured values. The relationship between $k$ and optical coefficients $b_{650}$, $b_{b650}$, and $a_{650}$ were linear when %OM and $\xi$ were constants. When $k$ and $\xi$ were constant the relationship between $b$, $b_{b}$, and $a$, and %OM were approximately linear but $r^2$ was 0.998. When $\xi$ was varied all relationships were best approximated with 2nd order polynomials. None of the combinations of input parameters
resulted in linear relationships with $R_{rs650}$ due to the differences in rates of change in $b_650$ and $a_{650}$ relative to $k$, $\xi$, and $%OM$.

The results of the reconciliation of measurements of $k$, $\xi$, and $%OM$ using the LISST-100b and the methods of Boss et al. (2001b) and Twardowski et al. (2001) indicated that each produced results inconsistent with measured TSM and optical coefficients. The final results of this attempt at closure obtained by simple addition of a common constant to all samples of $k$ and $\xi$, produced surprisingly consistent results from both methods. The addition of the constant produced little change in the range and standard deviations for the data set average. The final average values for the data set were $\xi = 3.21 \pm 0.49$, $k_2 = 10^{10.91}$, $n(\text{re}) = 1.09 \pm 0.04$ and density $= 1.37 \pm 0.44$ g/cm$^3$. Modeled scattering and $tsm$ also produced much more consistent relationships for $b^*$ and $b_6/b$ than were obtained with measured scattering and TSM. This suggests that the high variability in the measured data could be due to the methods for sampling and data collection rather than presumed variability in composition and the PSD of the suspended particle assemblage. This would also indicate that even though the Mississippi River is injecting large quantities of particles into the region and there is a wide range in the mass concentration, the particle suspensions outside the direct influence of the plume retain a level of homogeneity in composition and PSD. It was also observed in Chapter II that when high density mineral particles are present they have a much greater influence on TSM than the organic matter.

The evaluation of the original hypothesis that trends in mass specific optical coefficients could be observed in trends of $\xi$, $k$, and $%OM$, resulted in unanticipated conclusions. In Chapters II and III regression analysis between $b^*650$, $b_6^*650$, $Rrs^*650$
and $\xi$, $k$, and $\%OM$ produced either non-significant or very weak correlations.

Theoretical modeling demonstrated that all coefficients, $b_{650}$, $b_b$, $R_{rs_{650}}$, had complex (i.e. non-linear) relationships with change in $\xi$, $k$, and $\%OM$ when they were varied individually. When $\xi$, $k$, and $\%OM$ were varied simultaneously, relationships with $b_{650}$, $b_b$, $R_{rs_{650}}$ became very complex with many non-unique combinations.

These results made it clear that no simple regression equations could be used to identify patterns because all variables can change independently.

Another result of the modeling effort was demonstration of the impact of the choice of $d_{\text{min}}$ used to determine the mass specific coefficients. When $d_{\text{min}} = 0.7 \, \mu m$ was used, mass specific coefficients increased by a factor of 10 from their value when $d_{\text{min}} = 0.2 \, \mu m$ was used. This impact increased when $\xi$ increased. These results illustrate the need for greater attention to the process of collecting TSM using filtration methods. Issues such as effective pore size vs. specified or nominal pore size should be investigated. Multiple filters with progressive effective pore sizes could provide indications of the average values of $\xi$. Issues of salt retention and loss of clay structural water also need further investigation. All of the works cited used various inconsistent techniques for collecting as well as processing sample filters.

Modeling results for $R_{rs}$ at 650 nm demonstrated an independence from change in $k$. These results also demonstrated that $R_{rs_{650}}$ varied non-linearly with change in $\%OM$ and $\xi$. Because $tsm$ varies linearly with change in $k$ these results indicate that remote sensing observations at 650 nm are primarily indications of particle assemblage composition. At wavelengths where absorption is much greater than for inorganic particles or for organic detritus, the value of $R_{rs}$ provides an indication of the
concentration of organic particles but not necessarily TSM if there are high
concentrations of mineral particles present. There is clearly a need for further
investigation here.
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