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Bio-optical variability of surface waters in the Northeastern Gulf of Mexico

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Bio-Optical Variability of Surface Waters in
the Northeastern Gulf of Mexico

by

Bisman Nababan

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Marine Science
College of Marine Science
University of South Florida

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SeaWiFS, cyclonic and anticyclonic eddies, packaging effect, pigment composition

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Note To Reader

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Bio-Optical Variability of Surface Waters in the Northeastern Gulf of Mexico

Bisman Nababan

ABSTRACT

Bio-optical variability of surface waters in Northeastern Gulf of Mexico (NEGOM) was examined using satellite and in situ data. Relatively high chlorophyll-\(a\) concentration (\(\text{chl} \geq 1 \text{ mg m}^{-3}\)) and high colored dissolved organic mater (\(a_{g443} \geq 0.1 \text{ m}^{-1}\)) were generally observed inshore, near major river mouths, and in plumes of Mississippi River water that extended offshore during the three consecutive summer seasons (1998, 1999, and 2000). River discharge dominated chlorophyll-\(a\) concentration variability inshore, particularly near major river mouths. Strong interannual variability in chlorophyll-\(a\) concentration was observed inshore from Escambia to Tampa Bay region during the winter to spring transition, which was different in 1998 compared to the winter to spring transition in 1999 and 2000. This was related to higher fresh water discharge during the 1997-1998 El Niño-Southern Oscillation event as well as strong upwelling in spring 1998. The Mississippi plume extended >500 km southeast of the Mississippi delta and up to the Florida Keys was observed for the periods extending over 14 weeks between May and September every year of the study.

In general, \(a_{g443}\) covaried linearly and inversely with salinity inshore during spring and fall, indicating conservative mixing. The NEGOM salinity-\(a_{g443}\) relationship of fall
1998, i.e., Salinity=36.59-29.86\(a_{\text{g443}}\) (n=8771, \(r^2=0.86\); \(0.01\leq a_{\text{g443}}\leq0.52\), \(16\leq S\leq36\), served as the best predictor of NEGOM salinity based on \textit{in situ} \(a_{\text{g443}}\) observations for spring and fall seasons from all years (<3% mean percentage errors; corresponding to <1.03 psu). This may help estimate salinity from satellite ocean color data, but further testing using data from multiple years is needed to improve such relationship. While river discharge was an important source of colored dissolved organic matter (CDOM), phytoplankton blooms also contributed to CDOM formation in the NEGOM.

Using a pigment index of phytoplankton taxonomic groups, the variability in biomass proportion of microphytoplankton explained up to 76% of the variability of the average of normalized phytoplankton absorption coefficients (545, 625, and 673 nm). The chlorophyll-specific absorption coefficient, \(a_{\text{ph}}^*(440)\), varied by a factor of 7 (0.02-0.15 m\(^2\) mg\(^{-1}\)). Particle size and pigment composition played important roles in determining \(a_{\text{ph}}^*(440)\) variability. This must be accounted for in chlorophyll-\(a\) concentration algorithms based on \(a_{\text{ph}}\).
INTRODUCTION

The Northeastern Gulf of Mexico (NEGOM), defined as the region north of 27°N between the Mississippi River Delta and the Florida coast, is one of great national importance because of its oil, gas, fisheries, and recreational resources. This area includes pristine water quality and important shelf, and coastal ecosystems resources such as wetlands and coastal ocean bottoms. These areas have great economic importance for tourism and fisheries industries.

The NEGOM region receives more fresh water and riverine sediments than any other North American shelf from the Mississippi, Mobile, Apalachicola and Suwannee Rivers. This leads to strong seasonal buoyancy variation on the shelf, and to high nutrient, chlorophyll, and high dissolved organic carbon concentrations (Guo et al., 1995; Gilbes et al., 1996; Turner and Rabalais, 1999; Pennock et al., 1999; Del Castillo et al., 2000). This region also experiences an intense upwelling (Gilbes et al., 1996; Muller-Karger, et al., 1991; Muller-Karger, 2000; Weisberg et al., 2000; He and Weisberg, 2002, 2003,), and sometimes is affected by the Loop Current or by cold and warm rings shed by the large western Boundary Current (Vukovich et al., 1979; Huh et al., 1981; Vukovich and Hamilton, 1989; Muller-Karger, et al., 2001; He and Weisberg, 2003; Weisberg and He, 2003).

The diversity of oceanographic processes in the NEGOM region leads to variability in the distribution of chlorophyll-a, colored dissolved organic carbon, salinity, and bio-
optical properties. Previous studies indicated that the NEOM ecosystem varies from eutrophic in coastal water to oligotrophic in the deeper ocean (Livingston et al., 1975; McPherson et al., 1990; Muller-Karger et al., 1991; Gilbes et al., 1996, 2002; Lohrenz et al., 1990, 1999; Muller-Karger, 2000). However, occasional high levels of chlorophyll concentration (plume) in the deeper ocean (offshore) specifically during late spring and summer had also been documented (Huh et al., 1981; Ortner et al., 1995; Gilbert et al., 1996; Gilbes et al., 1996, 2002; Wiseman and Sturges, 1999; Jochens et al., 1999, 2002; Muller-Karger, 2000; Muller-Karger et al., 2001; Belabbassi, 2001; Biggs and Ressler, 2001; Del Castillo et al., 2001; He and Weisberg, 2002, 2003; Weisberg and He, 2003; Morey et al., 2003; Hu et al., 2003; Qian et al., 2003). High levels of chlorophyll concentration in the coastal region and offshore have been attributed to the input of new nutrients from the river discharge and upwelling processes (Riley, 1937; Thomas and Simmons, 1960; Sklar and Turner, 1981; Muller-Karger et al., 1991; Walsh et al, 1989; Ortner et al., 1995; Gilbert et al., 1996; Gilbes et al, 1996, 2002; Wiseman and Sturges, 1999; Jochens et al., 1999, 2002; Pennock et al., 1999; Muller-Karger et al., 2000; Muller-Karger, 2000; Belabbassi, 2001; Biggs and Ressler, 2001; Del Castillo et al., 2001; Salisbury et al, 2001, 2004; He and Weisberg, 2002; Weisberg and He, 2003; Morey et al., 2003; Hu et al., 2003; Qian et al., 2003). However, synoptic patterns of variability of chlorophyll-α and the variability in factors that drive this are still unclear.

Knowledge of the spatial and temporal distribution of colored dissolved organic matter (CDOM) is very important since CDOM strongly absorbs light in the biologically damaging ultraviolet (UV) and blue spectral regions. This can cause inaccuracies in satellite-derived chlorophyll concentrations, can help in understanding biogeochemical
processes, and can be used to trace transport and mixing processes in estuaries and coastal regions. Several studies often found an inverse linear relationship between CDOM and surface salinity indicating conservative mixing near river mouths (Vodacek et al., 1997; Ferrari and Dowel, 1998; Carder et al., 1989, 1993; Del Castillo et al., 2000, 2001; Hu et al., 2003). However, a non-linear relationship was also observed indicating non-conservative mixing arising from *in situ* production or loss of CDOM (Carder et al., 1993; Blough et al., 1993; Nelson and Guarda, 1995; Vodacek et al., 1997; Klinkhammer et al., 2000; Benner and Opsahl, 2001; Blough and Del Vecchio, 2002). Previous studies have also proposed use of CDOM to estimate surface salinity from high-resolution ocean color sensors (Carder et al., 1993; D’Sa et al., 2002; Hu et al., 2003). To achieve this goal, one requirement is that there exists a predictable relationship between CDOM and salinity (Carder et al., 1993; D’Sa et al., 2002; Hu et al., 2003). Several studies on CDOM characteristics and distribution in the NEGOM region have been conducted (Carder et al., 1989, 1993; Del Castillo et al., 2000, 2001; Stoval-Leonard, 2003). However, these studies mostly focused on single cruises and not on understanding the spatial and temporal distribution of CDOM, or on factors affecting this distribution. Further, little information has been available in the literature regarding the relationship between CDOM and salinity and factors affecting the relationship for this region.

Light absorption by particulate matters affects satellite-derived pigment biomass, primary production and mixed-layer heating (Yentsch and Phinney, 1989; Bricaud and Stramski, 1990; Nelson et al., 1993; Carder et al., 1995; Cleveland, 1995; Sosik and Mitchell, 1995; Lee et al., 1996; Suzuki et al., 1998). For these reasons and to improve remote-sensing capabilities, information on the magnitude, range and sources of
variability in the absorption coefficient of particulate matters is very important. Given the
traditional difficulty of estimating phytoplankton pigment concentration in coastal waters,
information from these areas may be of particular interest for the refinement of Case-II
algorithms.

In general, the operational ocean-color algorithms have provided a single
phytoplankton pigment index (chlorophyll-a) as a general indicator of algal biomass.
However, it is also well known that accessory pigments strongly absorb light in the blue
and blue-green region, and hence influence spectral variations of ocean reflectance.
Some of these pigments are considered as taxonomic markers (e.g., fucoxanthin for
diatoms, phycoerythrin and zeaxanthin for cyanobacteria, divinyl-chl-a for
prochlorophytes, etc.), and therefore provide information on the presence and abundance
of these groups (Gieskes and Kraay, 1983; Guillard et al., 1985; Wright and Jeffrey,
1987; Kimor et al., 1987; Gieskes et al., 1988; Chilsom et al., 1988; Hooks et al., 1988;

The chlorophyll-specific absorption coefficients (the absorption coefficient of
phytoplankton at a particular wavelength normalized to its chlorophyll-a concentration)
can vary as a consequence of differences in the composition and concentration of
pigments as well as pigment packaging, and cell size structure of phytoplankton
populations (Duysens, 1956; Bricaud et al., 1983; Carder et al., 1986, 1991, 1999, 2004;
Morel and Bricaud, 1986; Sathyendranath et al., 1987; Hoepffner and Sathyendranath,
1991, 1992, 1993; Bissett et al., 1997; Nelson et al., 1993). Previous studies conducted
on the West Florida Shelf documented that chlorophyll-specific absorption coefficients at
440 nm vary directly with the submicron chlorophyll fraction, which itself varies
inversely with total chlorophyll concentration or phytoplankton size (Carder et al., 1986). In the same region, Bisset et al. (1997) and Lohrenz et al. (2003) reported that pigment packaging and pigment composition affected variations in chlorophyll-specific absorption coefficients. These studies, however, only dealt with a small region of the NEGOM with single cruise and not on the understanding of the spatial and temporal distribution of particulate matter and chlorophyll-specific absorption coefficients, or on factors affecting this distribution. Further, little information is available in the literature regarding spatial and temporal variations in particulate matter and chlorophyll-specific absorption coefficients in the NEGOM region.

Earth-observing satellites (SeaWiFS, AVHRR, and TOPEX/POSEIDON) can provide valuable information on the distribution of river water and sediments on the continental shelf as well as on the circulation affecting the interaction of river plumes with oceanic water. Using satellite data and extensive in situ hydrographic, biological, and optical data collected in collaboration with Texas A&M University NEGOM-Chemical Oceanography and Hydrography study supported by the Minerals Management Service (MMS) of the U. S. Department of the Interior, the variability of bio-optical properties of surface water in the Northeastern Gulf of Mexico was examined, with two major goals:

To determine the temporal and spatial variability of bio-optical properties;

To evaluate forcing factor mechanisms for such variations.

Specifically, my overall objectives are:

(1) To examine the spatial and temporal variability of chlorophyll-α concentrations and to determine the inter-annual variability;
(2) To examine the spatial and temporal variability of CDOM and to further determine whether surface salinity in the NEGOM can be estimated from CDOM;

(3) To examine the spatial and temporal variability of particulate matter and chlorophyll-specific absorption coefficients, and to determine whether the phytoplankton species or groups can be estimated from phytoplankton absorption coefficients \( a_{ph}(\lambda) \);

(4) To examine the effect of river discharge on the variability of chlorophyll-\(a \) concentrations and colored dissolved organic matter (CDOM) absorption coefficients of surface waters in the inshore regions near the river mouths of the NEGOM region.

The dissertation is developed into two separate chapters and a summary of the dissertation. Chapters are entitled as follows:

Chapter I: “The impact of rivers and oceanic processes on chlorophyll-\(a \) and CDOM variability of surface water of the Northeastern Gulf of Mexico”.

Chapter II: “Variability in the particulate absorption coefficients of the Northeastern Gulf of Mexico surface waters”.

A list of the cited literature then follow to conclude this dissertation.
CHAPTER I:

THE IMPACT OF RIVERS AND OCEANIC PROCESSES ON
CHLOROPHYLL-A AND COLORED DISSOLVED ORGANIC MATTER
VARIABILITY IN THE SURFACE WATERS OF THE NORTHEASTERN
GULF OF MEXICO
Abstract

In situ data revealed that relatively high chlorophyll-\(a\) concentrations (\(\geq 1\) mg m\(^{-3}\)) and high CDOM absorption coefficients (\(a_{g443} \geq 0.1\) m\(^{-1}\)) were generally observed inshore particularly near the major river mouths, and in spatially coherent Mississippi plume extending offshore and to the southeast during summer seasons of 1998, 1999, and 2000. The Mississippi plume extended over 500 km from the river delta and to Florida Keys for periods between May and September. River discharge appeared to be the major factor influencing chlorophyll-\(a\) variability at the surface for the inshore regions particularly near the river mouths regions. Strong interannual variability (by factor 4) in chlorophyll-\(a\) concentrations was observed during winter to spring transition in 1998 compared with winter to spring transition in 1999 and 2000 off Escambia, Choctawhatchee, Apalachicola, Suwannee and Tampa Bay regions. This was related to high fresh water discharge during the 1997-1998 El Nino event and to strong upwelling along the coast in spring 1998. In general, \(a_{g443}\) covaried linearly and inversely with salinity in the inshore regions during spring and fall seasons, indicating a fairly conservative mixing. During summer seasons, however, non-conservative mixing behaviors were observed. The NEGOM salinity-\(a_{g443}\) relationship of fall 1998, i.e., Salinity=36.59-29.86*\(a_{g443}\) (\(n=8771\), \(r^2=0.86\); 0.01\(\leq a_{g443} \leq 0.52\), 16\(\leq S \leq 36\)), served as the best predictor of NEGOM salinity based on in situ \(a_{g443}\) observations for spring and fall seasons from all years (<3% mean percentage errors; corresponding to <1.03 psu). This may serve to estimate salinity from satellite ocean color data, but further testing using data from multiple years is needed to improve such relationship. Phytoplankton blooms during spring, summer, and fall seasons were significant sources for CDOM formation in the NEGOM region.
1.1. INTRODUCTION

The Northeastern Gulf of Mexico (NEGOM) is an area that experiences significant variability due to a variety of oceanographic processes acting on shelf and coastal waters. Particularly, upwelling, cold- and warm-core rings, river discharge, and winds, force significant biogeochemical variability within the NEGOM. Several studies have focused on the effect of river outflow on chemistry and biology of estuarine zones within the NEGOM (Livingstone et al., 1975; Lohrenz et al., 1990; McPherson et al., 1990). However, synoptic patterns of variability of chlorophyll-a and colored dissolved organic matter (CDOM) and the factors that drive their variability were still unclear.

The Gulf of Mexico is frequently considered to be an oligotrophic system (Ortner et al., 1984; Biggs, 1992). However, satellite data and in situ observations (Huh et al., 1981; Ortner et al., 1995; Gilbert et al., 1996; Gilbes et al., 1996, 2002; Wiseman and Sturges, 1999; Jochens et al., 1999, 2002; Muller-Karger et al., 1991; Muller-Karger, 2000; Belabbassi, 2001; Biggs and Ressler, 2001; Del Castillo et al., 2001; He and Weisberg, 2002, 2003; Weisberg and He, 2003; Morey et al., 2003; Hu et al., 2003; Qian et al., 2003) have shown that the Gulf of Mexico does experience intermediate to high phytoplankton concentrations both over the shelf and in certain offshore areas, and that some of these patterns are seasonal. Some changes in the inshore areas are related to wind-driven coastal upwelling (Murray, 1972; Chuang et al., 1982; Schroeder et al., 1987; Li and Weisberg, 1999a, 1999b; Yang and Weisberg, 1999; Yang et al., 1999;
Muller–Karger, 2000, Weisberg et al., 2000) and river plumes (Walker, 1996; Pennock et al., 1999). Over the shelf, variation in chlorophyll-$a$ is affected by seasonal convective mixing, upwelling associated with eddies (Biggs and Muller-Karger, 1994; Wiseman and Sturges, 1999), and the offshore dispersal of riverine outflow.

Using Coastal Zone Color Scanner (CZCS) images, Muller-Karger et al. (1991) found that to first order variability in pigment concentration seaward of the shelf was synchronous throughout the Gulf, with the highest values from December to February and the lowest from May to July. Using CZCS images, Gilbes et al. (1996) observed that an episodic plume with high pigment concentration occurs along the West Florida Shelf each the spring and persists 1-6 weeks in a pattern that extends >250 km southward over the middle shelf. During the summer, low pigment concentrations were generally observed along the outer shelf and continental slope of the West Florida Shelf (Gilbes et al., 1996).

The Northeastern Gulf of Mexico (NEGOM, Figure 1.1) receives significant fresh water input from the Mississippi, Mobile, Escambia, Choctawhatchee, Apalachicola, and Suwannee Rivers. River discharge varies seasonally, with a maximum typically during spring and a minimum during summer (Gilbes et al., 1996). The discharge and the increase in insolation lead to strong seasonal buoyancy variation on the shelf, and to high nutrient, chlorophyll, and dissolved organic carbon concentrations in inshore (Turner and Rabalais, 1991; Guo et al., 1995; Gilbes et al., 1996; Pennock et al., 1999; Del Castillo et al., 2000). The Mississippi River provides more than half of all of the fresh water input into the Gulf of Mexico (Deegan et al., 1986) and is the dominant source of terrestrial nutrient input (Twilley et al., 1999). Indeed, Walsh et al. (1989) suggested that the
Mississippi plume area is the most productive within the Gulf of Mexico. Walsh (1983) also mentioned that secondary production due to sinking herbivores and ungrazed prey, specifically from menhaden fishery activities, was an important factor in increasing productivity in the Gulf of Mexico. Chlorophyll-a concentrations in the Mississippi River plume are highly variable in space and time, ranging between 1.1 and 14.4 mg/m³ in the outer plume during four cruises in 1990-1992 (Redalje et al., 1994), but as high as 40-80 mg/m³ in near-coastal waters during the late spring in 1993 (Nelson and Dortch, 1996). Del Castillo et al. (2000) concludes that the CDOM on the West Florida Shelf is directly related to river input, and that high phytoplankton concentrations did not automatically result in the production of significant amounts of CDOM. Carder et al. (1989, 1993), however, showed evidence of CDOM derived from primary production for the Gulf of Mexico and elsewhere.

While buoyancy and wind forcing largely control the circulation of shelf waters (Weisberg et al., 1996, 2000; Li and Weisberg, 1999a, 1999b; Yang et al., 1999; Yang and Weisberg, 1999; Hsueh and Golubev, 2002; He and Weisberg, 2002, 2003; Weisberg and He, 2003), it is also affected by northward intrusions of the Loop Current and associated eddies (Huh et al., 1981; Vukovich, 1988; Muller-Karger, 2000; Nowlin et al., 2000, Muller-Karger et al., 2001; Jochens et al., 2002; He and Weisberg, 2002, 2003; Weisberg and He, 2003). The Loop Current rarely penetrates north of 28°N in the eastern Gulf of Mexico (Vukovich et al., 1979); therefore, its direct influence in the NEGOM region is considered occasional (Muller-Karger et al., 2001). However, impingement of the Loop Current on the shelf break in the southeastern Gulf of Mexico
can lead to strong shelf circulation effects in the NEGOM (Hetland et al., 1999; He and Weisberg, 2003; Weisberg and He, 2003).

Knowledge of the spatial distribution and temporal changes of CDOM is important since CDOM strongly absorbs light in the biologically damaging ultraviolet (UV) and blue spectral regions, hence protecting phytoplankton and other biota but reducing light available for phytoplankton photo-synthesis (Blough and Green, 1995; Arrigo and Brown, 1996). It can also artificially enhancement of satellite-derived chlorophyll concentration estimates (Morel and Prieur, 1977; Carder et al., 1989; Hochman et al., 1994, 1995; Vodacek et al., 1994), and can be used to trace effects of transport and mixing processes in estuaries and coastal regions. Also, photolysis of CDOM is a pathway of carbon cycling in the ocean (Moran and Zepp, 1997).

Colored dissolved organic matter (CDOM) originates from the degradation of organic material in terrestrial and aquatic ecosystems (Kirk, 1994). Near rivers, most CDOM typically derives from land drainage. Away from continental margins the effect of rivers declines, and CDOM is presumably related to primary productivity as a by-product of algal cell degradation (Fogg and Boalch, 1958; Yentsch and Reichert, 1962; Carder et al., 1989, 1991, 1993; Siegel and Michaels, 1996) and zooplankton grazing (Momzikoff et al., 1994). In upwelling areas, an increase in nutrient availability may lead to an increase in chlorophyll concentration exceeding two orders of magnitude. While historical observations have suggested that there may be little change in CDOM concentration in these areas affected by upwelling (Bricaud et al., 1981) there is evidence that, in some regions at least, upwelling source water itself may be colored by higher
background CDOM concentrations (Carder et al., 1991; Coble et al., 1998; Siegel et al., 2002).

Since CDOM and pollutants transported in river plumes are often diluted in a manner consistent with that of salinity, CDOM has been proposed as a proxy to estimate surface salinity from high-resolution (~<1km) ocean color sensors (e.g., Carder et al., 1993; D’Sa et al., 2002; Hu et al., 2003). Surface salinity is a conservative property (assuming balanced precipitation/evaporation), and therefore it can be used to trace transport and mixing processes in estuaries and coastal areas. Salinity is also frequently used as an index of the health of coastal habitats (e.g., Montague and Ley, 1993). It would be of great utility to establish a methodology to assess synoptic salinity distribution rapidly and repeatedly. Unfortunately, planned space-based microwave sensors provide only coarse spatial resolution (~80 km) and limited accuracies for instantaneous salinity estimates (~0.4-0.6 psu; Lagerloef et al., 1995). It would be ideal to complement such capabilities with higher-resolution information. The potential use of CDOM as a salinity proxy is based on the assumptions that 1) CDOM can be estimated accurately from satellites and 2) there exists a predictable relationship between CDOM and salinity.

Several studies have documented the relationship between CDOM and surface salinity in coastal regions (Carder et al., 1993; Vodacek et al., 1997; Ferrari and Dowell, 1998; Klinkhammer et al., 2000; Benner and Opsahl, 2001; Hu et al., 2003). Although an inverse linear relationship is often found because of conservative mixing (Hu et al., 2003; Ferrari and Dowell, 1998; Carder et al., 1999), non-conservative relationships have also been reported (Blough et al., 1993; Carder et al., 1993; Benner and Opsahl, 2001).
Studies on CDOM characteristics and distribution in the NEGOM region have also been conducted (Carder et al., 1989; Del Castillo et al., 2000, 2001). Yet, these focused on single cruises and not on the understanding of the spatial and temporal distribution of CDOM, or on factors regulating the distribution and variability. Further, little information has been available in the literature regarding the relationship between CDOM and salinity, and factors affecting the relationship in this region. Presumably, each river plume in the region will have a different mixing curve depending on the CDOM concentration in the source waters.

Using field observations of hydrographic and biological data from nine cruises within the NEGOM region conducted between 1997 and 2000 and satellite data from Sea-viewing Wide-Field-of-View Sensor (SeaWiFS), and TOPEX/POSEIDON, I examined the spatial and temporal variability of chlorophyll-α and CDOM in the NEGOM region and assessed factors regulating their distribution and variability. The specific objectives of this section of the dissertation are: (1) to determine the spatial and temporal variability of chlorophyll-α and CDOM, and to identify the factors affecting the variability; (2) to determine the extent, duration and forcing factors of offshore river plumes in the NEGOM during the three consecutive years of 1998, 1999, and 2000; (3) to examine the relationship between surface salinity and CDOM and determine whether surface salinity in the NEGOM can be estimated from CDOM, specifically because this is relevant to the possibility of using ocean color to assess the distribution of salinity in areas affected by rivers; (4) to evaluate several bio-optical algorithms for estimation of chlorophyll-α concentration and CDOM.
1.2. METHODOLOGY

1.2.1. Study Area

The study was conducted in the region extending from the Mississippi River Delta to the West Florida Shelf off Tampa Bay. For this study the NEGOM is bounded inshore by the 10-m isobath and offshore by the 1000-m isobath. Six major river-impacted regions, namely the Mississippi (R1), Mobile (R2), Escambia (R3), Choctawhatchee (R4), Apalachicola (R5), and Suwannee (R6), plus one coastal region near Tampa Bay (R7), and three offshore regions (R8A, R8B, and R8C) were chosen to characterize the NEGOM (Figure 1.1).

1.2.2. In situ Data Collection, Processing and Analysis

Nine two-week cruises were conducted in three different seasons between 1997 and 2000 onboard the Texas A&M University (TAMU) R/V Gyre (Table 1.1). Each of the cruises surveyed eleven cross-margin transects from the 10-m to the 1000-m isobath (Figure 1.1).

About 100 stations were occupied for conductivity-temperature-depth (CTD) casts on each cruise. During a CTD cast, water samples from twelve 10-liter niskin bottles were collected and analyzed by TAMU for oxygen, salinity, nutrients, DOC, and pigment analysis. Salinity was analyzed using an Autosal Laboratory Salinometer as described in Fofonoff and Millard, Jr. (1983). Nitrate and Nitrite were analyzed using an
Figure 1.1. Study area: the NEGOM region, encompassing the area between 27.3 - 30.7° N and 82.6 - 89.6°W. The map shows the 10, 20, 100, 200, 500, and 1000 m bathymetric contours. The line connecting closed triangles shows a typical cruise track and stations, with cross-shelf transect lines numbered L1-L11. Numbered open squares show regions at which time series of chlorophyll-a concentration, CDOM and salinity were analyzed. Inset: the Gulf of Mexico the area of the study.

Table 1.1. Cruise identifiers, dates, and seasons.

<table>
<thead>
<tr>
<th>Cruise no.</th>
<th>Start date</th>
<th>End date</th>
<th>Cruise ID</th>
<th>Cruise season</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16 November 1997</td>
<td>26 November 1997</td>
<td>Fa-97</td>
<td>fall-1997</td>
</tr>
<tr>
<td>8</td>
<td>15 April 2000</td>
<td>26 April 2000</td>
<td>Sp-00</td>
<td>spring-2000</td>
</tr>
<tr>
<td>9</td>
<td>28 July 2000</td>
<td>8 August 2000</td>
<td>Su-00</td>
<td>summer-2000</td>
</tr>
</tbody>
</table>
AutoAnalyzer technique as described in Atlas et al. (1971). Both salinity and nutrients were analyzed by TAMU aboard ship.

In addition to the discrete stations, continuous (along track) surface data were collected by TAMU every 2 minutes using a flow-through system for chlorophyll-\(a\) fluorescence, temperature (SST), and salinity (SSS). Flow-through data were collected using a stream pumped at a rate of 10 liters/minute from a hull depth of 3-m into the main laboratory through a debubbler and mixing chamber of 10-liter volume. The residence time of water in the mixing chamber was about one minute. Using garden hoses connected by adjustable ball valves to a “Y” splitter valve leading off the debubbler, the flow of the water was reduced from 10 liters/minute to 1 liter/minute. The 1 liter/minute flow was directed to conductivity and temperature sensor (Sea-Bird\(^{\text{TM}}\)) and to a Turner Designs\(^{\text{TM}}\) model-10 Fluorometers for chlorophyll-\(a\) and CDOM fluorescences. Chlorophyll-\(a\) fluorescence was measured with 440 nm (blue) excitation and 683 (red) nm emission filters. CDOM fluorescence was measured with 330 nm (ultraviolet) excitation and 450 nm (blue) emission filters. CDOM fluorescence data were recorded by USF.

Water samples from the fluorometer out-flow hose were collected by TAMU at about 100 locations to calibrate the fluorescence data with concurrent chlorophyll-\(a\) concentration. Glass fiber filters (GF/F) were used to filter water samples and pigments were extracted using acetone. Samples were extracted in 90% acetone immediately after water collection and then analyzed at sea using a calibrated Fluorometer.

At selected stations, water samples from the flow-through outflow were filtered using 0.2 \(\mu\)m Millipore filters into amber-colored glass bottles precombusted at 500\(^\circ\)C for
24 h. Samples were stored in a freezer for later analysis of the CDOM (Gelbstoff) absorption coefficient \( a_g \). The water absorption spectra were analyzed using a Hitachi U-3000 Double Beam Spectrophotometer (10-cm pathlength). Absorption coefficients were determined using the equation: 
\[
 a_g(\lambda) = \frac{A(\lambda) \times 2.303}{L}
\]
where, \( A(\lambda) \) is the absorbance spectra and \( L \) is the cuvette length (m). The \( a_g \) spectra were also smoothed to eliminate instrument noise and corrected for residual scattering by subtracting residual absorption at 700 nm from the entire spectra.

The flow-through CDOM fluorescence data were converted to \( a_{g443} \) (i.e., \( a_g \) at 443 nm) using 30 discrete samples collected during each cruise following the method of Hu et al., (2003). This ensured coverage of various water types and a broad dynamic range. Linear regression coefficients \( (r^2) \) between these variables for each cruise ranged from 0.80 to 0.96, and only \( a_{g443} \) is reported in the dissertation.

Continuous subsurface (10-14 m-deep) currents were measured using a shipboard 153 kHz Acoustic Doppler Current Profiler (ADCP). To produce circulation maps, the ADCP data were gridded by TAMU graduate student Ou Wang, employing 40 km as the smoothing radius (Daley, 1991). Features with scales less than 40 km are therefore likely smoothed out, but this allowed filtering out noise features and keeping the basic large-scale patterns. Details of these measurements and data processing can be found in Jochens et al. (2002) and Wang et al. (2002). To see the pattern of subsurface currents, the ADCP gridded currents were overlaid with the sea surface height (SSH) field rendered at the middle date of each of the nine cruises (see Section 1.2.4).
1.2.3. Wind Field and River Discharge

Hourly wind speed and direction were obtained from NDBC buoys (http://www.ndbc.noaa.gov) of BURL1 (28.90°N, 89.40°W) for the Mississippi region, DPIA1 (30.25°N, 88.07°W) for Mobile, Escambia, and Choctawhatchee regions, CSBF1 (29.67°N, 85.36°W) for Apalachicola region, and CDRF1 (29.14°N, 83.03°W) for Suwannee region. Hourly wind speed and direction were averaged to produce daily and weekly mean wind speed and direction employing a true vector average. In this scheme, the magnitude of the vector was represented by the wind speed observation and the direction observations were used for the orientation. The vectors were then broken down into their u and v components. All u and v components are then averaged separately. The resulting average speed and direction were calculated from the Pythagorean Theorem and “arctan(u/v)”, respectively.

Surface wind field data for NEGOM region of each of nine cruises were obtained from Texas A&M University. The product was produced by gridded averaging of surface wind field data from several NDBC buoys station in the NEGOM region for the same cruises period of time.

River discharge data were compiled from six major rivers entering into NEGOM region i.e., The Mississippi, Mobile, Escambia, Choctawhatchee, Apalachicola and Suwanne Rivers for the period of October 1997 to December 2000. The data were obtained from the U.S. Geological Survey Water Data Report. The Mississippi, Escambia, Choctawhatchee, Apalachicola, and Suwannee discharge was recorded respectively at Tarbert Landing (30.96°N, 91.66°W), near Century (30.96°N, 87.23°W), near Bruce (30.45°N, 85.89°W), Sumatra (29.95°N, 85.02°W), and Branford (29.96°N,
82.93°W). The Alabama River discharge recorded at Claiborne (31.54°N, 87.51°W) and Tombigbee River at Coffeeville (31.75°N, 88.12°W) were used to estimate Mobile River discharge. Both Alabama and Tombigbee Rivers join to form the Mobile River. Weekly mean time series were built from these rivers discharge data.

1.2.4. Satellite Data Collection, Processing and Analysis

The satellite data used in this study are chlorophyll-\(a\) concentration from SeaWiFS ocean color measurements, and sea surface height from TOPEX/ERS observations. The SeaWiFS data were collected using a high resolution picture transmitter (HRPT) antenna located at University of South Florida (USF), St. Petersburg, Florida, USA.

SeaWiFS data were processed using the atmospheric correction algorithms described by Gordon and Wang (1994), and Chlorophyll-\(a\) concentration fields were derived using the OC4v4 bio-optical algorithm described by O'Reilly et al. (2000). I am aware that there are unresolved issues that lead to severe errors in estimates of chlorophyll-\(a\) using SeaWiFS data in coastal zones, particularly in Case II waters (Morel and Prieur, 1977) where suspended sediments and CDOM significantly affect the ocean color signal.

An algorithm (Carder et al., 1999) used for MODIS was also used to estimate both the chlorophyll-\(a\) concentration and CDOM absorption from the remote sensing reflectance spectra. This algorithm uses the 412 nm band to distinguish CDOM from chlorophyll-\(a\) pigment because of the strong absorption of CDOM at 412 nm. For validation purposes, I compared \textit{in situ} chlorophyll-\(a\) concentration to chlorophyll-\(a\) concentration derived from satellite data using the OC4v4 and Carder et al. (1999)
algorithms. I also compared the in situ absorption coefficient of CDOM at 440 nm ($\alpha_{e}(440)$) to $\alpha_{e}(440)$ derived from satellite using Carder et al. (1999) algorithm.

For time series and statistical analyses, SeaWiFS (October 1997 - December 2000) images were averaged (arithmetic average) into a time series of weekly means.

Sea surface height (SSH) fields were obtained from the University of Colorado (courtesy of Dr. Robert Leben). This was a blended product of TOPEX/POSEIDON and ERS-2 satellite altimeter data. SSH fields were produced by temporal and spatial smoothing using decorrelation scales of 12 days and 100 km. Therefore, features may appear weaker than they actually were, and smaller-scale features may not be represented. To estimate the total dynamic topography, the residual mean in the SSH was removed before adding a model mean to produce the synthetic height estimate. The resulting time series of SSH fields were interpolated to obtain one SSH field per day. More details about data processing and analysis can be found in Lillibridge et al. (1997) and Leben et al. (2002). For comparison with ADCP gridded currents, the SSH field at the middle date of each of the seven cruises was selected. For weekly time series, each middle date of a week range (e.g., a week range of 1-7, middle date of the week is 4) for sea surface height was overlaid over the weekly mean composite of SeaWiFS.

To determine the difference between data collected in situ and data estimated by satellite, the mean relative error (MRE) was estimated. MRE is defined as follows:

$$\text{MRE} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{\text{satellite}_i - \text{in situ}_i}{\text{in situ}_i} \right)$$

(1.1)

where $i$ is the index for all valid data points and $N$ is total number of valid points. In order to avoid misinterpretation, data were grouped into two categories i.e., satellite, $< \text{in situ}$
\( \textit{situ}_i \) (MRE1) and \( \geq \textit{situ}_i \) (MRE2). Otherwise large positive errors could be neutralized by any large negative errors, producing small, inaccurate mean errors.

1.2.5. Statistical Analyses

Programs based on Interactive Data Language (IDL) software by Research System, Inc. were developed to process and analyze data as well as for descriptive statistical analysis. A one-way analysis of variance (ANOVA) using Statistix8 Software by Analytical Software was used to test for significance of differences in chlorophyll-\( \alpha \) concentration, \( a_{g443} \) concentration, salinity and aquatic optical properties among regions and seasons. Statistix8 Software was also used for multivariate regression analyses to test the significant impact of salinity and chlorophyll-\( \alpha \) concentration variability on CDOM absorption variability.
1.3. RESULT AND DISCUSSION

1.3.1. Spatial and Temporal Distribution of In Situ Chlorophyll-α and CDOM

The spatial and temporal near-surface distribution of in situ chlorophyll-α concentration and CDOM absorption coefficients at 443-nm ($a_{g443}$) for the different sampling periods are shown in Figures 1.2 and 1.3, respectively. Relatively high chlorophyll-α concentrations ($\geq 1$ mg m$^{-3}$) and $a_{g443} (\geq 0.1$ m$^{-1}$) were generally found only inshore, particularly near the major river mouths, or offshore in the Mississippi River plume during summer sampling periods (Su-98, Su-99, and Su-00).

The spatial and temporal distribution of near-surface salinity (Figure 1.4) generally followed those of chlorophyll-α concentration and $a_{g443}$. Low salinity ($\leq 34$) was generally observed inshore, particularly near the major river mouths, but it was also found in offshore waters during summer cruises (Su-98, Su-99, and Su-00).

The results clearly show an influence of freshwater discharge on the distribution of chlorophyll-α concentration, CDOM, and salinity and the importance of the Mississippi plume as a source of nutrients and terrigenous CDOM to offshore waters of the Gulf of Mexico. To facilitate understanding of the transport of the high chlorophyll-α concentration, high CDOM, and low salinity Mississippi River water to the southeast along the West Florida Shelf during summers, I examined the ship-mounted ADCP data and the SSH field product. Satellite altimeter data are usually considered of limited value over continental shelves because of reflectance of radar diffractive side-lobes from
Figure 1.2. Spatial and temporal distributions of near-surface chlorophyll-α concentration in the NEGOM region based on in situ data. Thin white lines show the cruise track where continuous chlorophyll fluorescence observations were collected. See Table 1.1 for cruise identification.
Figure 1.3. Near-surface $a_{g443}$ (m$^{-1}$) distributions in the NEGOM. Thin white lines show the cruise track where continuous CDOM fluorescence observations were collected. Note: There are no CDOM data for fall 1997 and spring 1998 cruises. See Table 1.1 for cruise identification.
Figure 1.4. Near-surface salinity distributions in the NEGOM. Thin white lines show the cruise track where continuous salinity observations were collected. See Table 1.1 for cruise identification.
adjacent land areas, a poor knowledge of the geoid, and because of short time and space scales that may not be resolved by the sampling frequency of present-day altimeters.

Figure 1.5 suggested the presence of two distinct surface circulation regimes in the NEGOM, namely one to the west and one to the east of 85°W (Cape San Blas). To the west of 85°W, there was a significant difference in SSH fields from season to season. To the east of 85°W, a region of low (negative) sea surface height was almost always found near the coast. Golubev and Hsueh (submitted) also found that the currents on the shelf to the west and to the east of 85°W of the NEGOM had different origins. From drifter path data, they concluded that the monthly mean surface currents on the shelf east of 85°W were well correlated with sea surface height anomalies in Florida Strait, reflecting an offshore pressure forcing that drives a barotropic flow on the west Florida shelf on a nearly annual basis. Based on the field observations (e.g., Niiler, 1976; Koblinsky and Niiler, 1980; Mitchum and Sturges, 1982; Cragg et al., 1983; Marmorino, 1983; Mitchum and Clark, 1986; Weisberg et al., 1996), the West Florida Shelf circulation and sea level variations along the coast were highly correlated with wind stress. Meanwhile, based on field observations and numerical model circulations (e.g., Li and Weisberg, 1999a, b; Yang and Weisberg, 1999; He and Weisberg, 2002, 2003; Weisberg and He, 2003), the West Florida Shelf circulation were also correlated to both the local effects of winds and surface heat flux and the remote effects of the deep-ocean Loop Current. Monthly mean surface currents on the shelf west of 85°W were also correlated with the zonal wind component, indicating that alongshore winds drive alongshore shelf currents (see also Muller-Karger, 2000). Schroeder et al. (1987) and Chuang et al. (1982) also
Figure 1.5  Sea surface height (SSH) dynamic and ADCP-generated (10-14 m-deep) currents in the NEGOM. Note: There are no ADCP data from cruise of fall 1998 east of 87°W because of mechanical damage to ADCP equipment. See Table 1.1 for cruise identification.
reported that the inshore circulation off eastern Mississippi and Mobile was strongly wind dependent, in spite of the potential for westward geostrophic flow generated by coastal fresh water input.

The SSH field maps constructed for each summer cruise indicated that either small or large anticyclonic (warm) eddies were present near the slope off the Mississippi delta. SSH ranged from +11 cm for a mesoscale (~100 km diameter) eddy in summer 2000 (Su-00) to +35 cm for a large offshore eddy (centered around 88.5°W and 26.5°N) in summer 1999 (Su-99; eddy largely outside the area shown in Figure 1.5). These anticyclonic eddies entrained and transported low salinity with high nutrients, and high CDOM surface water from the delta area offshore (see also Qian et al., 2003; Jochens et al., 2002; Belabbassi, 2001). The ADCP currents at 10-14 m depth documented northeastward and eastward (Su-00), or eastward and southeastward (Su-98, Su-99) flows along the northern edge of the anticyclonic eddies, with speeds of up to 0.6 m s⁻¹. These vectors help explain the chlorophyll-α concentration, a_{443} and salinity patterns observed.

Based on a numerical circulation model and long time series of in situ observations at several locations, He and Weisberg (2002) and Weisberg and He (2003) also found a strong southeastward current at mid-shelf of NEGOM by the baroclinic response to combined wind and buoyancy forcing that leads to annually occurring cold and low salinity tongues. Eastward dispersal of the Mississippi plume was also recorded during summer of 1993 (Walker et al., 1994), summer of 1997 (Biggs et al., 2000), and in many other instances (see Del Castillo et al., 2000 and 2001; Gilbes et al., 1996 and 2002; Muller-Karger, 2000; Muller-Karger et al., 1991, Dowgiallo, 1994; Ortner et al., 1995).
Some cyclonic features appeared along the coast west of 85° W during summer (Figure 1.5). It is unclear whether these features are mesoscale cyclonic eddies or whether they are simply local areas of lower than average sea surface height or artifacts in the altimeter data.

In fall 1997 and 1998 (Fa-97, Fa-98), SSHs of +8 cm and +13 cm were seen off the Mississippi Delta (Figure 1.5). Although sub-surface currents indicated eastward flow, there was no indication of eastward dispersal of the Mississippi River water. This evidence can be seen from the relatively low chlorophyll-\(a\) concentration, high salinity and low CDOM near the slope off the Mississippi delta (Figure 1.2, 1.3, 1.4). Relatively high westward (easterly) wind speed components during fall season (at speeds up to \(\sim 10.5 \text{ m s}^{-1}\)) may have helped keep the Mississippi water inshore and to the west of the delta (Figure 1.6, Jochens et al. 2002).

Figure 1.7 shows the \textit{in situ} mean values and standard deviation of chlorophyll-\(a\) concentration, salinity, and \(a_{g443}\) for each region (as defined in Figure 1.1) and for each season (cruise). In general, there is no consistent seasonal pattern of chlorophyll-\(a\) concentration off Mississippi, Mobile, Escambia, Choctawhatchee, Apalachicola, and Suwannee regions (Figure 1.7, top panel). Based on weekly river discharge and SeaWiFS chlorophyll-\(a\) concentration, positive correlation between fresh water discharge and chlorophyll-\(a\) concentration was found in the above regions as further discussed in Section 1.3.3, indicating that the variability of chlorophyll-\(a\) concentration seemed to relate to the variability of fresh water discharge of each major rivers. While the fresh water discharge of Mobile and Escambia Rivers was relatively low during summer 1999 compared to spring 1999 (Figure 1.8), the higher chlorophyll-\(a\) concentration observed
Figure 1.6. Average surface wind field in the NEGOM during the 9 cruise period (data obtained from Texas A&M University). Diamonds and their identification indicate stations where wind speed and direction were collected. Several offshore NDBC stations used to generate wind gridded average were not shown in the picture because they were located south of 27°N.
Figure 1.7. Mean and standard deviation of near-surface chlorophyll-α concentration (top panel), salinity (middle panel) and a_{443} (m^{-3}) (bottom panel) values for each subregion and for different time periods sampled. Note: There were no a_{443} data for fall 1997 and spring 1998. See Table 1.1 for cruise identification.
Figure 1.8. Fresh water discharge of six major rivers in the NEGOM region during the period of nine cruise observations. Y-axis is daily average of river discharge \( \times 10^8 \) (m³/d).
during summer 1999 than during spring 1999 along the Mobile and Escambia regions (Figure 1.7) may be attributed to the eastward dispersal of Mississippi River water that contains high nutrients (see Figure 1.2) and due to eastward (westerly) upwelling-favorable winds.

For the Apalachicola region, the chlorophyll-\(a\) concentrations during fall seasons were higher than those of spring and summer (Figure 1.7, R5, top panel). However, the discharge of the Apalachicola River during fall was less than in spring (Figure 1.8). If the river discharge was considered as the only nutrient source for this region, the opposite pattern for chlorophyll-\(a\) concentration should be observed i.e., higher chlorophyll-\(a\) concentration during spring than that of fall. Therefore, there must be other sources of nutrients for this fall bloom. Strong upwelling-favorable wind observed several weeks prior to fall cruises provided nutrients from deeper water (Walsh et al. 2003, Weisberg and He, 2003). He and Weisberg (2003) found that Loop Current in fall 1998 reinforced the mid-shelf currents and increased the across-shelf transports in the bottom Ekman layers, therefore accentuating the shoreward transport of cold, nutrient rich water of deep-ocean origin. Cold frontal systems and stronger winds during fall and winter may also increase the vertical mixing of the photic layer, bringing nutrients from the deeper water.

For the central offshore NEGOM region (R8A, R8B, and R8C), a seasonal pattern of chlorophyll-\(a\) concentration was observed with maxima occurring during summer seasons and minima during spring seasons (Figure 1.7, top panel). The opposite pattern for salinity was consistently observed in these regions during summer seasons (Figure 1.8, middle panel). Using salinity as an independent variable, variability in chlorophyll-\(a\) concentration can be explained up to 93% (R8C), indicating fresh water with high
nutrients from the Mississippi River play a major role for the phytoplankton bloom in these regions during the three consecutive summer seasons.

Mean \( a_{443} \) ranged from 0.011±0.001 in the offshore NEGOM (R8C) during spring 2000 (Sp-00) to 0.201±0.065 off the Mississippi (R1) during summer 2000 (Su-00) (Figure 1.7, lower panel). While specific locations showed seasonality in \( a_{443} \) within the NEGOM, there was no consistent (synchronized) seasonal pattern for the entire NEGOM. Seasonality was strongest off Mobile (R2), Tampa Bay (R7), and in the central offshore NEGOM (R8). Off Mobile (R2), the maxima were found during spring (Sp-99, Sp-00) and the minima during summer and fall (Fa-98, Su-99). Off Tampa Bay (R7), maxima occurred in fall and minima during spring. In offshore NEGOM (R8A, R8B, R8C), maxima occurred in summer and minima during spring. If all locations are considered, a one-way analysis of variance (ANOVA) showed that there are significant differences in the mean of chlorophyll-\( a \) concentration and \( a_{443} \) values among seasons for each location (P<0.01). The mean chlorophyll-\( a \) concentration and \( a_{443} \) values are also different (P<0.01) among locations within each season (cruise). \( a_{443} \) had a positive relationship with chlorophyll-\( a \) concentration and a negative relationship with salinity (Figure 1.7). More detail of the relationship between \( a_{443} \) and salinity and chlorophyll-\( a \) will be discussed in section 1.3.4 and 1.3.5.

1.3.2. Comparison between in situ and SeaWiFS chlorophyll-\( a \) concentration

To improve the spatial coverage and reduce noise, SeaWiFS images were averaged over the time period of each of the nine cruises. Chlorophyll-\( a \) concentrations estimated from these SeaWiFS images were compared with in situ chlorophyll-\( a \) concentration.
Figure 1.9 shows the \textit{in vivo} chlorophyll-\textit{a} concentration and $a_{g443}$ estimated from the \textit{in situ} flow-through measurements compared with the SeaWiFS (OC4v4) retrievals along the ship tracks of all nine NEGOM cruises. The correlation between \textit{in situ} and satellite chlorophyll-\textit{a} measurements, and the mean relative errors (MRE, see section 1.25 for the formula) are shown in the Figure 1.9.

Figure 1.9 shows that positive MRE range from 84.24\% (Fa-99) to 283.40\% (Su-98) and most SeaWiFS data points (\textasciitilde 75\%) overestimated \textit{in situ} chlorophyll-\textit{a} concentration (Figure 1.10). This indicates that the SeaWiFS estimates (OC4v4 algorithm) generally overestimates \textit{in situ} measurements by up to 300\%. This result is consistent with the finding of Hu \textit{et al.} (2003). The higher positive MRE values were found where \textit{in situ} chlorophyll-\textit{a} concentration and CDOM were also high, specifically during summer seasons where relatively high CDOM values were observed offshore. High SeaWiFS data points were also found along the coast and offshore during summer seasons, indicating suspended particulate materials, bottom reflectance, and CDOM may interfere with chlorophyll-\textit{a} retrieval from SeaWiFS data. Meanwhile, negative MRE values ranged from just -8.46\% (Sp-00) to -38.60\% (Sp-99) and these values were generally within the SeaWiFS Project Office objective of accuracy to within \textpm 35\% over the range of 0.05-50.0 mg m$^{-3}$ (Hooker \textit{et al.}, 1992).

To see the performance of the SeaWiFS estimates (OC4v4 algorithm) for low chlorophyll-\textit{a} concentrations (case-I waters) and to understand errors due to suspended materials, CDOM and bottom reflectance, SeaWiFS chlorophyll-\textit{a} concentration data between 0.01 mg m$^{-3}$ and 1.0 mg m$^{-3}$ were considered for comparison with \textit{in situ} data. The correlation between \textit{in situ} and satellite measurements, and the mean relative errors
Figure 1.9. Comparison between in situ and SeaWiFS estimates (OC4v4) of chlorophyll-a concentration (0.0<[SeaWiFS chlorophyll-a]≤50 mg m⁻³) along ship track lines for nine NEGOM cruises. In situ a₉₄₄ values were also plotted for the comparison. MRE1 is negative MRE and MRE2 is positive MRE for chlorophyll-a concentration comparison (see section 1.2.4 for the formula).
Figure 1.10. Relationship between in situ and SeaWiFS estimates (OC4v4) of chlorophyll-α concentration (0.0<[SeaWiFS chlorophyll-α]≤50 mg m⁻³) along ship track lines for nine NEGOM cruises. Solid blue line is one-to-one line.
(MRE) are shown in the Figure 1.11. The satellite estimates generally agreed well with the correlation between in situ and satellite measurements, and the mean relative errors the in situ data for fall (Fa-97, Fa-98, Fa-99), when the Mississippi plume influence was minimal. The MREs for these three cruises were generally within ±35% (Hooker et al., 1992). Meanwhile, for spring and summer, SeaWiFS overestimated in situ chlorophyll-a concentration even for the lower-chlorophyll-a concentration range. The positive MRE for spring and summer cruises ranged from 60.07% (Sp-00) to 146.80% (Sp-98) (Figure 1.11).

Some factors that may lead to a divergence between satellite and in situ measurements are (Hu et al. 2003) the time difference between satellite and in situ measurements, which is further masked by averaging SeaWiFS data over the cruise period. Further, the atmospheric correction used over turbid coastal water may have led to additional errors in estimating chlorophyll-a concentration (Hu et al., 2000). The SeaWiFS Project only collected data within 6 hours of a satellite overpass. It is clear, however, that the SeaWiFS chlorophyll algorithm was affected by colored dissolved organic matter (CDOM) absorption of light. It seemed that the higher CDOM concentrations resulted in higher errors between in situ and satellite derived chlorophyll-a concentration. These evidences were observed during summer 1998, 1999, 2000 and spring 1999 and 2000. The largest error (MRE=146.80%) between in situ and satellite derived chlorophyll-a concentrations for the lower-chlorophyll-a concentration range was observed during summer 1998 where the largest CDOM concentrations and distribution in offshore NEGOM were observed (see also Figure 1.3).
Figure 1.11: Similar to Figure 1.9 but for SeaWiFS derived chlorophyll-α concentration ≤1.0 mg m⁻³.
The MODIS algorithm proposed by Carder et al. (1999) to estimate chlorophyll-a concentration as well as CDOM absorption from satellite data was also used and results were compared with in situ data (Figure 1.12, 1.13, 1.14). Even though the positive MRE is still above ±35%, there was better agreement between in situ and MODIS chlorophyll estimates vs. OC4v4 chlorophyll estimates, particularly for spring and summer cruises. For SeaWiFS derived chlorophyll-a concentration ranged from >0.0 mg m^{-3} to ≤50 mg m^{-3}, the positive MRE values ranged from 48.58% (Sp-00) to 121.30% (Su-98) (Figure 1.12). These errors were reduced up to almost three times from the errors produced by OC4v4 algorithm.

For the lower range of SeaWiFS derived chlorophyll-a concentration (≤1.0 mg m^{-3}), significant improvements were observed. The positive MRE values using MODIS algorithm during fall seasons were generally within ±35%, which agreed with the SeaWiFS mission specification. Meanwhile, during summer and spring the positive MRE values ranged from 41.82% (Sp-00) to 99.44% (Su-98) (Figure 1.14). These values were still above 35%, however, significant improvement compared to OC4v4 results was found. Similar to the OC4v4 algorithm problem, the MODIS algorithm also produced relatively larger errors when relatively high CDOM was found. Clearly, more research is needed to properly separate effects such of those from CDOM in the algorithms.
Figure 1.12. Comparison between *in situ* and SeaWiFS estimates using MODIS algorithm (Carder *et al.*, 1999) of chlorophyll-*a* concentration (0.0≤[SeaWiFS chlorophyll-*a*]≤50 mg m⁻³) along ship track lines for nine NEGOM cruises. *In situ* a₄₄₃ values were also plotted for the comparison. MRE1 is negative MRE and MRE2 is positive MRE for chlorophyll-*a* concentration comparison (see section 1.2.4 for the formula).
Figure 1.13. Relationship between in situ and SeaWiFS estimates using MODIS algorithm (Carder et al., 1999) of chlorophyll-\(a\) concentration (0.0<\(\text{SeaWiFS}\) chlorophyll-\(a\)<50 mg m\(^{-3}\)) along ship track lines for nine NEGOM cruises. Solid blue line is one-to-one line.
Figure 1.14. Similar to Figure 1.11 but for SeaWiFS estimates using MODIS algorithm of chlorophyll-\(a\) concentration \(\leq 1.0\) mg m\(^{-3}\).
1.3.3. Spatial and Temporal Distribution of Satellite Retrieved Chlorophyll-α

SeaWiFS satellite data revealed relatively high chlorophyll-α concentration (≥1 mg m⁻³) inshore, particularly near the major river mouths, or offshore in the Mississippi River plume during summer cruises (Su-98, Su-99, Su-00) (Figure 1.15). Based on error analysis between in situ and satellite-retrieved chlorophyll-α concentration, as discussed in previous section, the SeaWiFS estimates (OC4v4 algorithm) produce errors up to about 300% in coastal regions or in region with high CDOM concentration. Employing the MODIS algorithm (Carder et al., 1999) these errors were significantly reduced to about 120%. Therefore, for monthly and weekly time series analysis, satellite-retrieved chlorophyll-α employing the MODIS algorithm was used. It is also important to note that in the region of high CDOM absorption (a₉₄₄³<0.25 m⁻¹), the MODIS algorithm tends to “mask out” low and inconsistent satellite radiance (valid SeaWiFS data become zero or invalid). Therefore, to study the extent and duration of offshore dispersal of the Mississippi plume in the NEOM region, weekly mean SeaWiFS images employing the OC4v4 algorithm were generated and superimposed with sea surface height field.

Based on weekly mean SeaWiFS images, a plume of elevated chlorophyll-α concentration was seen extending east-southeastward (ESE) from the Mississippi River delta each summer in 1998, 1999, and 2000, respectively. The plume normally formed toward the end of May and lasted until about the first week of September. In 1998, a spatially coherent plume, with highest concentrations up-plume and lowest concentrations down-plume, up to 330 km to the ESE, was first observed toward the end week of June extending from the Mississippi Delta. Apparent chlorophyll-α concentration toward the distal end of the plume was about 1 mg m⁻³. The plume reached
Figure 1.15. Spatial and temporal distribution of near-surface chlorophyll-α concentration in the NEGOM region based on SeaWiFS data during the nine separate NEGOM cruise periods. White and purple contours are positive and negative total sea surface height, respectively.
a maximum eastward extent of more than 550 km to the ESE of the Mississippi Delta in late July (Figure 1.16). The plume became smaller afterward and was effectively absent by mid August.

In 1999, a spatially coherent plume of \(~280\) km was observed in the offshore NEGOM region the last week of May, extending ESE from the Mississippi Delta. The plume reached its maximum extent in late July (\(~550\) km ESE; Figure 1.16). This plume lasted about 14 weeks, through the first week of September.

In 2000, the Mississippi plume was first observed in early July, extending some 220 km ESE off the Mississippi Delta. The plume reached its maximum extent in late July and early August (about 530 km ESE from the Mississippi Delta; Figure 1.16). The plume lasted about 9 weeks and disappeared during the first week of September.

The offshore dispersal plume observed in summers of three consecutive years (1998, 1999, 2000) appears to be related to wind direction and speed, surface heat flux, the Mississippi River discharge, the sea surface dynamic height off the Mississippi delta, and the specifics of where the Loop Current impacts the shelf slope. Weekly average wind data measured south and east of the Mississippi delta (BURL1, 28.9°N, 89.4°W, and NDBC 42040, 29.2°N, 88.2°W) recorded eastward (westerly) wind from the end of April to the end of September, with average speeds of 0.5 to 6.10 m s\(^{-1}\). It seemed that a spatially coherent plume (south or southeastward Mississippi plume) developed when the advent of eastward (westerly) winds concomitant with the migration of a warm core ring (anticyclonic, high sea surface height) into the vicinity of the Mississippi delta (Table 1.2, see also Figure 1.16). The SSH field maps indicated that either small or large anticyclonic (warm) eddies were present near the slope off the Mississippi delta during
Figure 1.16. Initial and maximum position of the Mississippi River plume during summer of 1998, 1999, and 2000. White and purple contour lines indicate positive and negative sea surface height. White arrow indicates the extent of the plume.
each summer season. SSH ranged from +7 cm for a mesoscale (~100 km diameter) eddy in summer 2000 (Jul 7-13, 2000) concomitant with the initiation of the plume, to +20 cm for a large offshore eddy in summer 1998 (Jul 22-28, 1998) with the maximum offshore dispersal plume (Figure 1.16).

Table 1.2. Starting and ending period (in week number of 52) of eastward wind component measured at south of Mississippi delta (BURL1) and east of Mississippi delta (42040) in relation to sea surface height and the Mississippi plume period. Sea surface height (SSH) was extracted from the location of 87.5°W and 28.2°N.

<table>
<thead>
<tr>
<th>Year</th>
<th>wk # of 52</th>
<th>SSH (cm)</th>
<th>BURL1 start</th>
<th>BURL1 end</th>
<th>42040 start</th>
<th>42040 end</th>
<th>Initiation and maximum extent of the Mississippi plume</th>
</tr>
</thead>
<tbody>
<tr>
<td>1998</td>
<td>18</td>
<td>-10</td>
<td>18</td>
<td>30</td>
<td>26</td>
<td>30</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+20</td>
<td></td>
<td></td>
<td>+8</td>
<td>+20</td>
<td>+16</td>
</tr>
<tr>
<td>1999</td>
<td>20</td>
<td>-12</td>
<td>20</td>
<td>34</td>
<td>22</td>
<td>29</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+4</td>
<td></td>
<td></td>
<td>-10</td>
<td>+10</td>
<td>-10</td>
</tr>
<tr>
<td>2000</td>
<td>21</td>
<td>-7</td>
<td>21</td>
<td>34</td>
<td>28</td>
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<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+5</td>
<td></td>
<td></td>
<td>+4</td>
<td>+6</td>
<td>+6</td>
</tr>
</tbody>
</table>
1.3.4. Driving Forces Affecting Chlorophyll-a Concentration Variability

Figure 1.17 shows the monthly mean values of chlorophyll-a concentration derived from SeaWiFS data employing the MODIS algorithm (Carder et al., 1999) for each region (as defined in Figure 1.1) and for each season (cruise). Based on SeaWiFS data, mean chlorophyll-a concentration ranged from 0.1±0.0 mg m⁻³ in the central NEGO (R8C) in June 2000 to 23.2±11.2 mg m⁻³ off the Mississippi (R1) in April 1999. While specific regions showed seasonality in chlorophyll-a concentration, there was no consistent (synchronized) seasonal pattern for the entire NEGO.

Figure 1.17 also shows strong interannual variability of chlorophyll-a concentration in most regions, particularly during winter and spring. The year 1998 was different from 1999 and 2000 and showed much higher chlorophyll-a concentrations higher by a factor of 4 off Escambia (R3), Choctawhatchee (R4), Apalachicola (R5), Suwannee (R6) and Tampa Bay (R7) regions, particularly between January and May. The anomalous chlorophyll-a concentration during winter and spring of 1998 appeared to be related to the 1997-1998 El Nino event with anomalously high river discharge. The discharges of Mobile, Escambia, Choctawhatchee, Apalachicola, and Suwannee Rivers during spring 1998 were up to 5 times the discharge of spring 1999 or 2000 (see also Figure 1.8).

Indeed, Schmidt et al. (2000) reported that Florida experienced excessive rain in winter and spring 1998 due to the 1997-1998 El Nino event. In late spring and summer 1998, significant upwelling was also observed in these regions (Muller-Karger, 2000; He and Weisberg, 2002; Weisberg, and He, 2003), which may also result in enhanced phytoplankton production.
Figure 1.17. Time series of near-surface monthly mean chlorophyll-\(a\) concentration based on satellite SeaWiFS data employing the MODIS algorithm (Carder et al., 1999) for ten selected regions.
Considering only non-El Nino years (i.e., 1999 and 2000), a seasonal pattern in chlorophyll-\(a\) concentration was found off the Mississippi (R1), Central NEGOM (R8), Apalachicola (R5), Suwannee (R6) and Tampa Bay (R7) regions. Off the Mississippi and central NEGOM regions, the maxima occurred in summer and minima in fall. Off Apalachicola, the maximum occurred at the end of fall and early winter (December, December, January) and minima in spring (March, May). Off the Suwannee (R6) region, the maxima occurred during summer months (August, September) and the minima in winter months (December, February). Off Tampa Bay (R7) region, the maxima occurred in fall (October) and the minima in spring (March, May) (Figure 1.17). These patterns were also consistent with \textit{in situ} observations of chlorophyll-\(a\) concentration (see Figure 1.7).

To study the effect of river discharge on chlorophyll-\(a\) concentration in the NEGOM region, cross-correlation analyses of weekly satellite chlorophyll-\(a\) concentration \textit{vs.} river discharge were conducted for the period of October 1997 to December 2000. River discharge has a strong influence on chlorophyll-\(a\) concentration variability off Mississippi, Mobile, Escambia, Choctawhatchee, Apalachicola, and Suwannee regions. This evidence can be seen from cross-correlation coefficients i.e., Mississippi (\(r=0.50\), lag=5 weeks), Mobile (\(r=0.70\), lag=1 week), Escambia (\(r=0.50\), lag=1 week), Choctawhatchee (\(r=0.55\), lag=9 week), Apalachicola (\(r=0.55\), lag=0 week), and Suwannee (\(r=0.65\), lag=1 week) (Figure 1.18). These results demonstrated that changes in the river discharge preceded changes in chlorophyll-\(a\) concentration by a few days to several weeks for the above regions. The relatively low cross-correlation coefficient \((r)\) values and sometimes multiple correlation peaks suggest that unmeasured
Figure 1.18. Lagged cross-correlation analyses for weekly mean river discharge vs. chlorophyll-\(a\) concentration, with lags measured in weeks. Satellite chlorophyll-\(a\) concentration was derived from SeaWiFS data employing the MODIS algorithm (Carder et al., 1999).
sources of fresh water from local runoff and interference from other river sources may have played a role in nutrient delivery as well. Jolliff (2004) discussed upwelling interactions with river plumes in affecting primary productivity in this region for spring 1998.

Off Mobile, Escambia, and the Choctawhatchee regions, upwelling-favorable winds were observed intermittently between early spring and late summer. Muller-Karger (2000) reported strong intermittent upwelling in May-June 1998 in the inshore areas, generally within 15 km of the coast along the Florida Panhandle. Upwelling-favorable winds also occur occasionally during winter. SeaWiFS-derived chlorophyll-\(a\) concentrations appeared to be elevated during these periods of upwelling-favorable winds. However, variability in the freshwater discharge appears to have a stronger influence on the variability of chlorophyll-\(a\) concentration than the upwelling process. The strength of the upwelling signal was also probably masked in part by the large size of the sampling boxes along the coast (Figure 1.1), since west of Cape San Blas, upwelling was largely confined to a narrow strip along the coast.

Off the Apalachicola, chlorophyll-\(a\) concentrations rose during fall seasons. The variability in the freshwater discharge seemed to have an influence on the variability of chlorophyll-\(a\) concentration (\(r=0.55\), lag=0 week) (Figure 1.16). However, upwelling and strong vertical mixing due to stronger wind may also play roles in the variability of chlorophyll-\(a\) concentration. As discussed in previous sections, \textit{in situ} chlorophyll-\(a\) concentrations during fall seasons were relatively higher than during spring and summer, even though the Apalachicola River discharge during fall was relatively lower than during spring. Therefore, the phytoplankton blooms observed during fall seasons were
apparently related to upwelling and strong vertical mixing due to stronger winds during fall. Satellite-derived chlorophyll-\(a\) concentrations also supported the \textit{in situ} observation in which higher chlorophyll-\(a\) concentrations were higher in fall than during spring and summer in 1999 and 2000 (see Figure 1.17, R5). He and Weisberg (2003) explained that Loop Current played a role to reinforce the mid-shelf currents and to increase the across-shelf transports in bottom Ekman layer, hence accentuating the shoreward transport of cold, nutrient rich water of deep-ocean origin during fall season off the Apalachicola region.

A chlorophyll plume that extends from Cape San Blas to the south parallel to the shelf break and as far south as the Florida Keys has been observed in this region for many years, each lasting 1-6 weeks during spring (Dowgiallo, 1994; Ortner \textit{et al.}, 1995; Gilbes \textit{et al.}, 1996). Our observations confirmed its regular occurrence. Gilbes \textit{et al.} (1996) speculated that the plume might be associated with one or a combination of the following processes: (1) discharge from small, local rivers along the northwest Florida coast; (2) seasonal changes in steric height differences between the shelf and deep gulf of Mexico waters; (3) circulation of water associated with the Loop Current and upwelling in the DeSoto Canyon; and (4) discharge from the Mississippi and Mobile Rivers. Gilbes \textit{et al.} (2002) have confirmed that the Apalachicola River has a major role in the formation of offshore blooms. A cold tongue of water has been detected in AVHRR images in the same area as this chlorophyll plume during spring 1998. This is independent of the Loop Current position and is a result of circulation driven by buoyancy and heat-flux forcing, plus the remote influence of the Loop Current (Weisberg and He, 2003; He and Weisberg, 2002).
Off the Suwannee river, a significant increase in chlorophyll concentration was observed in the region. From a purely statistical point of view, variability in the Suwannee discharge had stronger influence on the variability of chlorophyll-α concentration ($r=0.65$, lag=1 week) than the wind-driven upwelling processes.

In the central NEGOM (R8A, R8B, R8C) region, the relatively high chlorophyll-α concentrations observed in summer of three consecutive years (1998, 1999, 2000) appeared to be related to wind direction and speed, to the Mississippi River discharge, and to sea surface height. As discussed in previous sections, a spatially coherent Mississippi plume was observed when eastward (westerly) wind was concomitant with the presence of an anticyclonic eddy off the Mississippi delta.

1.3.5. CDOM versus Salinity

Figures 1.19, 1.20, and 1.21 show salinity-$a_{g443}$ scatter plots within each of the selected sampling regions organized by summer, spring and fall cruises. Statistics are provided in Table 1.3. In general, $a_{g443}$ covaried linearly and inversely with salinity. Using ANOVA, there were also significant differences among slopes of salinity-$a_{g443}$ regressions, both among regions within each season, and among seasons within each region ($P<0.01$), indicating strong regional and seasonal differences in CDOM sources and composition. For the inshore regions, mostly in spring and fall seasons, high coefficients of determination ($r^2 \geq 0.70$ to $r^2=0.98$) were found, indicating fairly conservative mixing behavior (Figure 1.20, 1.21). Some low ($r^2<0.70$) to non-significant ($r^2=0.00$) coefficients of determination were also found, but mostly during summer. One
Figure 1.19. Scatter plots of salinity vs \( a_g 443 \) for each region for summer seasons (cruises). See Table 1 for cruise identification. Blue line is the global NEGOM regression line for fall 1998 (Fa-98), yielding the lowest error of observed vs. predicted salinities for spring and fall seasons within 8 selected regions and global NEGOM region. Note: the x and y axes are in different scales.
Figure 1.20. Scatter plots of salinity vs $a_{0443}$ for each region for spring seasons (cruises). See Table 1 for cruise identification. Blue line is the global NEGOM regression line for fall 1998 (Fa-98), yielding the lowest error of observed vs. predicted salinities for spring and fall seasons within 8 selected regions and global NEGOM region. Note: the x and y axes are in different scales.
Figure 1.21. Scatter plots of salinity vs $a_{943}$ for each region for fall seasons (cruises). See Table 1 for cruise identification. Blue line is the global NEGOM regression line for fall 1998 (Fa-98), yielding the lowest error of observed vs. predicted salinities for spring and fall seasons within 8 selected regions and global NEGOM region. Note: the x and y axes are in different scales.
Table 1.3. Regression coefficient of determination ($r^2$), intercept, and slope, with respective standard error (se), between salinity and $a_{g443}$ (S=a +b*$a_{g443}$), and mean percentage error (MPE) for salinity prediction based on $a_{g443}$ data within 95% prediction interval of each region in different cruises (seasons).

<table>
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<th>Region</th>
<th>cid</th>
<th>n</th>
<th>intercept(se)</th>
<th>slope(se)</th>
<th>$r^2$</th>
<th>MPE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Mississippi River region</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>-31.16(0.76)</td>
<td>0.90</td>
<td>4.75</td>
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<tr>
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<td>-34.60(0.39)</td>
<td>0.98</td>
<td>5.71</td>
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</tr>
<tr>
<td>Sp-99</td>
<td>176</td>
<td>36.99(0.09)</td>
<td>-33.81(1.06)</td>
<td>0.84</td>
<td>8.17</td>
<td></td>
</tr>
<tr>
<td>Su-99</td>
<td>240</td>
<td>30.98(0.21)</td>
<td>-17.42(1.44)</td>
<td>0.38</td>
<td>7.67</td>
<td></td>
</tr>
<tr>
<td>Fa-99</td>
<td>496</td>
<td>36.49(0.03)</td>
<td>-25.87(0.41)</td>
<td>0.88</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>Sp-00</td>
<td>272</td>
<td>36.36(0.03)</td>
<td>-36.19(0.57)</td>
<td>0.94</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td>Su-00</td>
<td>283</td>
<td>35.66(0.22)</td>
<td>-23.30(0.95)</td>
<td>0.69</td>
<td>7.22</td>
<td></td>
</tr>
<tr>
<td>Escambia River region</td>
<td></td>
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</tr>
<tr>
<td>Su-98</td>
<td>140</td>
<td>36.36(0.14)</td>
<td>-38.84(2.07)</td>
<td>0.72</td>
<td>3.55</td>
<td></td>
</tr>
<tr>
<td>Fa-98</td>
<td>170</td>
<td>36.65(0.05)</td>
<td>-27.44(0.53)</td>
<td>0.94</td>
<td>1.68</td>
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<tr>
<td>SP-99</td>
<td>152</td>
<td>36.37(0.16)</td>
<td>-36.01(1.23)</td>
<td>0.85</td>
<td>3.43</td>
<td></td>
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<tr>
<td>Su-99</td>
<td>139</td>
<td>35.44(0.25)</td>
<td>-20.34(3.87)</td>
<td>0.17</td>
<td>5.81</td>
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<tr>
<td>Fa-99</td>
<td>135</td>
<td>36.84(0.07)</td>
<td>-21.40(1.76)</td>
<td>0.86</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td>Sp-00</td>
<td>135</td>
<td>36.66(0.13)</td>
<td>-34.03(1.32)</td>
<td>0.83</td>
<td>2.01</td>
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</tr>
<tr>
<td>Su-00</td>
<td>139</td>
<td>35.07(0.12)</td>
<td>-2.61(2.24)</td>
<td>0.01</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>Apalachicola River region</td>
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<tr>
<td>Su-98</td>
<td>158</td>
<td>36.37(0.16)</td>
<td>-30.14(3.83)</td>
<td>0.28</td>
<td>2.44</td>
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<tr>
<td>Fa-98</td>
<td>138</td>
<td>35.92(0.04)</td>
<td>-11.74(0.29)</td>
<td>0.92</td>
<td>1.01</td>
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<tr>
<td>Sp-99</td>
<td>140</td>
<td>36.51(0.02)</td>
<td>-35.75(0.67)</td>
<td>0.96</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>Su-99</td>
<td>132</td>
<td>34.41(0.46)</td>
<td>7.31(9.47)</td>
<td>0.01</td>
<td>3.17</td>
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<tr>
<td>Fa-99</td>
<td>126</td>
<td>36.59(0.04)</td>
<td>-20.16(0.53)</td>
<td>0.92</td>
<td>0.78</td>
<td></td>
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<tr>
<td>Sp-00</td>
<td>218</td>
<td>37.16(0.03)</td>
<td>-32.71(0.62)</td>
<td>0.92</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>Su-00</td>
<td>290</td>
<td>36.56(0.04)</td>
<td>-13.63(0.69)</td>
<td>0.58</td>
<td>1.13</td>
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</tr>
<tr>
<td>Tampa Bay region</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Su-98</td>
<td>175</td>
<td>33.70(0.06)</td>
<td>7.00(2.03)</td>
<td>0.06</td>
<td>1.27</td>
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<tr>
<td>Fa-98</td>
<td>183</td>
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<td>-13.91(0.35)</td>
<td>0.90</td>
<td>0.84</td>
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<tr>
<td>Sp-99</td>
<td>173</td>
<td>36.27(0.01)</td>
<td>-10.81(0.34)</td>
<td>0.84</td>
<td>0.44</td>
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<tr>
<td>Su-99</td>
<td>160</td>
<td>36.21(0.02)</td>
<td>-3.08(0.45)</td>
<td>0.23</td>
<td>0.53</td>
<td></td>
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<tr>
<td>Fa-99</td>
<td>87</td>
<td>36.81(0.05)</td>
<td>-12.13(0.86)</td>
<td>0.70</td>
<td>1.10</td>
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<tr>
<td>Sp-00</td>
<td>69</td>
<td>36.33(0.01)</td>
<td>2.70(0.17)</td>
<td>0.79</td>
<td>0.09</td>
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<tr>
<td>Su-00</td>
<td>343</td>
<td>36.69(0.03)</td>
<td>0.04(0.56)</td>
<td>0.00</td>
<td>0.63</td>
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<td>Central of the NEGOM region B (R8B)</td>
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<tr>
<td>Su-98</td>
<td>1058</td>
<td>33.99(0.04)</td>
<td>-38.52(0.33)</td>
<td>0.93</td>
<td>3.57</td>
<td></td>
</tr>
<tr>
<td>Fa-98</td>
<td>1159</td>
<td>36.12(0.03)</td>
<td>-2.45(1.84)</td>
<td>0.00</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>Sp-99</td>
<td>1057</td>
<td>37.24(0.01)</td>
<td>-89.93(0.78)</td>
<td>0.93</td>
<td>0.63</td>
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<tr>
<td>Su-99</td>
<td>1149</td>
<td>36.46(0.05)</td>
<td>-72.59(0.64)</td>
<td>0.92</td>
<td>5.40</td>
<td></td>
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<tr>
<td>Fa-99</td>
<td>752</td>
<td>36.87(0.02)</td>
<td>-39.39(1.02)</td>
<td>0.67</td>
<td>0.66</td>
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</tr>
<tr>
<td>Sp-00</td>
<td>1007</td>
<td>36.44(0.00)</td>
<td>0.62(0.14)</td>
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<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Su-00</td>
<td>1520</td>
<td>35.82(0.03)</td>
<td>-29.41(0.28)</td>
<td>0.87</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>Central of the NEGOM region C (R8C)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Su-98</td>
<td>792</td>
<td>33.03(0.05)</td>
<td>-36.45(0.62)</td>
<td>0.81</td>
<td>2.11</td>
<td></td>
</tr>
<tr>
<td>Fa-98</td>
<td>802</td>
<td>36.17(0.05)</td>
<td>-0.97(3.21)</td>
<td>0.00</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Sp-99</td>
<td>766</td>
<td>36.99(0.01)</td>
<td>-72.82(1.04)</td>
<td>0.87</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>Su-99</td>
<td>718</td>
<td>32.53(0.11)</td>
<td>-13.96(0.85)</td>
<td>0.27</td>
<td>4.74</td>
<td></td>
</tr>
<tr>
<td>Fa-99</td>
<td>556</td>
<td>35.99(0.01)</td>
<td>-3.67(0.56)</td>
<td>0.07</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Sp-00</td>
<td>623</td>
<td>36.44(0.00)</td>
<td>2.08(0.24)</td>
<td>0.10</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Su-00</td>
<td>1407</td>
<td>36.25(0.01)</td>
<td>-38.15(0.42)</td>
<td>0.85</td>
<td>1.30</td>
<td></td>
</tr>
</tbody>
</table>

Note: cid=cruise identification (see Table 1.1), n=number of observations
example is in the Mississippi river region (R1) during summer 1999 (Su-99) when effectively no high-salinity waters were found within this sample region.

The most non-conservative CDOM mixing curves (non-linear plots) were found during most of the summertime cruises in the inshore (low salinity) regions, suggesting that destructive (removal) processes (e.g. CDOM photo-degradation, consumption) and in situ formation (addition) processes (e.g. phytoplankton degradation, CDOM released by phytoplankton during active growth, excretion by organisms, and microbial remineralization) may play a role. Nelson et al. (1998) indicated that the microbial community may be the source of the “new” summertime CDOM in sub-surface waters in the Sargasso Sea. The removal processes were apparent as convex (upward) salinity-\(a_{g443}\) curves during summer 1998 and 1999 in Mississippi region (Figure 1.19). Strong thermal and salinity stratification during summertime may also enhance rates of CDOM photolytic decay in near-surface waters (Vodacek et al., 1997). Jolliff et al. (2003) also reported that photochemical losses of CDOM on the West Florida Shelf were significant during summer 1998. A non-conservative behavior with net removal of dissolved organic carbon in the Mississippi River plume was also observed during summer by Benner et al. (1992). Meanwhile, the in situ CDOM formation (addition) processes were also observed as concave (upward) salinity-\(a_{g443}\) curves especially during summer in most of the NEGOM regions (Figure 1.19). I speculate that this in situ CDOM formation was due to the phytoplankton degradation, zooplankton excretion, or microbial remineralization. Examination of CDOM in relation to phytoplankton (chlorophyll-\(a\) concentration) is discussed in the next section.
In the two central NEGOM regions (R8B and R8C), low \( (r^2<0.7) \) to no correlations \( (r^2=0.0) \) between salinity and \( a_{g443} \) were observed fall 1998, 1999 and late spring 2000 (Table 1.3), indicating low influence of freshwater. Low correlations between salinity and \( a_{g443} \) were also observed during summer 1999 in central NEGOM regions A and B (R8A and R8B). In central NEGOM region A (DeSoto Canyon region), however, high negative correlation coefficients between salinity and \( a_{g443} \) were recorded in most seasons, except during summer and fall 1999, indicating that this region was affected by fresh water discharge most of the year. For summer and early spring seasons, high negative correlations and steep negative slopes were observed in all three central NEGOM regions (R8A, R8B, and R8C) (Table 1.3, Figure 1.19, and 1.20). The high correlation was due to the east and southeastward transport of the Mississippi River plume during summer and late spring periods (Hu et al., 2003; Del Castillo et al., 2001; Nowlin et al., 2000; Muller-Karger, 2000, and others).

1.3.6. CDOM versus Chlorophyll

River plumes and upwelling are the two significant sources of new nutrients to the NEGOM. In upwelling areas, chlorophyll concentration and CDOM often covary or chlorophyll is the dominant bio-optical constituent, indicating a classical Case I water type (Morel and Prieur, 1977). Carder et al. (1989) found that \( a_{g}(440) \) covaried with primary production for upwelling sites off Peru and North West Africa, where there are no riverine sources. Kowalczuk (1999) also reported a significant correlation between CDOM absorption and chlorophyll concentration in offshore waters, suggesting that in situ formation of CDOM from phytoplankton was also playing an important role. In
contrast, in river plumes (Case II water) there are frequently conditions where CDOM and chlorophyll are not correlated (Klinkhammer et al., 2000; Hu et al., in press).

*In situ* CDOM formation processes include release or excretion by organisms, lysis of cells by viruses (Nelson and Siegel, 2002), phytoplankton release during active growth (Vernet and Whitehead, 1996; Whitehead and Vernet, 2000), microbial remineralization, (Nelson, *et al.*, 1998; Nelson and Siegel, 2002), phytoplankton degradation (Fogg and Boalch, 1958; Yentsch and Reichert, 1962; Harvey *et al.*, 1983, Zweifel *et al.*, 1995), the release of CDOM from sediments (Skoog, *et al.*, 1996), and vertical transport from “deep” CDOM (Nelson and Siegel, 2002). In this study, I examined the contribution of phytoplankton to *in situ* CDOM formation by analyzing the relationship of $a_{g443}$ as a function of salinity, and $a_{g443}$ as a function of salinity and chlorophyll-$a$ concentration using multivariate regression.

Table 1.4 shows the adjusted coefficient of determination (adj-$R^2$) both for $a_{g443}$-salinity and $a_{g443}$-salinity and *in situ* chlorophyll-$a$ concentration relationships. Adjusted $R^2$ was used in order avoid the bias of $R^2$ due to an additional variable to a regression. For each additional variable added to a regression equation, $R^2$ increases even when the new variable has no real predictive capability. Instead, when variables are added to a regression equation, the adjusted $R^2$ does not increase unless the new variables have additional predictive capability (Chatterjee and Price, 1991; Weisberg, 1985). Results show that there was no significant increase in adjusted $R^2$ values between $a_{g443}$ *vs.* salinity and $a_{g443}$ *vs.* salinity and chlorophyll-$a$ concentration during fall seasons for most inshore regions, except in the Suwannee and Tampa Bay regions in fall 1999 (Table 1.4). This suggests that in most coastal regions there were no significant increases in CDOM
Table 1.4. Adjusted coefficient of determination of $a_{g443}$ as function of salinity (adj $R^2_{sal}$) and $a_{g443}$ as function salinity and in situ chlorophyll-$a$ concentration (adj $R^2_{sal+chl}$).

<table>
<thead>
<tr>
<th>Cruise Id.</th>
<th>Mississippi region (R1)</th>
<th>Mobile region (R2)</th>
<th>Escambia region (R3)</th>
<th>Choctawhatchee region (R4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>adj $R^2_{sal}$</td>
<td>adj $R^2_{sal+chl}$</td>
<td>adj $R^2_{sal}$</td>
<td>adj $R^2_{sal+chl}$</td>
</tr>
<tr>
<td>Su-98</td>
<td>0.90</td>
<td>0.91</td>
<td>0.01</td>
<td>0.45**</td>
</tr>
<tr>
<td>Fa-98</td>
<td>0.97</td>
<td>0.97</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>Sp-99</td>
<td>0.85</td>
<td>0.85</td>
<td>0.78</td>
<td>0.87*</td>
</tr>
<tr>
<td>Su-99</td>
<td>0.39</td>
<td>0.80**</td>
<td>0.15</td>
<td>0.29**</td>
</tr>
<tr>
<td>Fa-99</td>
<td>0.89</td>
<td>0.89</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>Sp-00</td>
<td>0.88</td>
<td>0.88</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>Su-00</td>
<td>0.69</td>
<td>0.77**</td>
<td>0.46</td>
<td>0.51*</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Cruise Id.</th>
<th>Apalachicola region (R5)</th>
<th>Suwannee region (R6)</th>
<th>Tampa Bay region (R7)</th>
<th>Central Negom A (R8A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>adj $R^2_{sal}$</td>
<td>adj $R^2_{sal+chl}$</td>
<td>adj $R^2_{sal}$</td>
<td>adj $R^2_{sal+chl}$</td>
</tr>
<tr>
<td>Su-98</td>
<td>0.28</td>
<td>0.46**</td>
<td>0.92</td>
<td>0.96</td>
</tr>
<tr>
<td>Fa-98</td>
<td>0.92</td>
<td>0.92</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>Sp-99</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
<td>0.96</td>
</tr>
<tr>
<td>Su-99</td>
<td>0.00</td>
<td>0.60**</td>
<td>0.79</td>
<td>0.89**</td>
</tr>
<tr>
<td>Fa-99</td>
<td>0.92</td>
<td>0.94</td>
<td>0.02</td>
<td>0.38**</td>
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<tr>
<td>Sp-00</td>
<td>0.93</td>
<td>0.96</td>
<td>0.95</td>
<td>0.95</td>
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<tr>
<td>Su-00</td>
<td>0.57</td>
<td>0.89**</td>
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<table>
<thead>
<tr>
<th>Cruise Id.</th>
<th>Central Negom B (R8B)</th>
<th>Central Negom C (R8C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>adj $R^2_{sal}$</td>
<td>adj $R^2_{sal+chl}$</td>
</tr>
<tr>
<td>Su-98</td>
<td>0.93</td>
<td>0.94</td>
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<td>Fa-98</td>
<td>0.00</td>
<td>0.47**</td>
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<tr>
<td>Sp-99</td>
<td>0.67</td>
<td>0.82**</td>
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<tr>
<td>Su-99</td>
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<td>0.92</td>
</tr>
<tr>
<td>Fa-99</td>
<td>0.67</td>
<td>0.82**</td>
</tr>
<tr>
<td>Sp-00</td>
<td>0.02</td>
<td>0.13**</td>
</tr>
<tr>
<td>Su-00</td>
<td>0.88</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Note: *) Indicates $\geq5\%$ increase after adding chlorophyll-$a$ concentration to the equation. 
**) Indicates $\geq10\%$ increase after adding chlorophyll-$a$ concentration to the equation.
associated with increases in chlorophyll. These results also indicate that the main source of CDOM during fall and winter seasons was river inflow. Del Castillo et al. (2000) reported a similar result, finding that there was no increase in CDOM abundance associated with increases in chlorophyll concentration and primary productivity on West Florida Shelf during March 1995. Jolliff (2004), however, found that autochthonous CDOM production was required in spring 1998 in order to explain ocean color signals.

In spring and summer seasons, there were significant increases in adjusted R² values when adding a chlorophyll-α concentration component to the multivariate equation \( \text{adj R}_{\text{sal+chl}}^2 \) in most NEGOM regions (Table 1.4). The increase in adjusted R² after adding the chlorophyll-α concentration component to the equation \( \text{adj R}_{\text{sal+chl}}^2 \) ranged from 5% (R2, Su-00) to 78% (R7, Su-00) (Table 1.4). This indicates that phytoplankton blooms during spring and summer played a significant role in enhancing the CDOM pool. Carder et al. (1989, 1993) reported that phytoplankton degradation was likely a significant source of CDOM on the West Florida Shelf. In general, the increase in adjusted R² values \( \text{adj R}_{\text{sal+chl}}^2 \) were larger in summer relative to the previous spring season. Higher increase in adjusted R² values \( \text{adj R}_{\text{sal+chl}}^2 \) during summer may be related to slower growth of phytoplankton as growth diminishes in summer as nutrients become limiting. In the central NEGOM regions (R8B and R8C), there were significant additions of CDOM associated with the increase of chlorophyll-α concentration (up to 47%) during fall (Table 1.4). High salinity (>36) was observed in these regions during fall, indicating limited or no freshwater influence. The increase in CDOM was therefore most likely produced by phytoplankton or its degradation.
1.3.7. Estimating Salinity from CDOM

Can surface salinity be estimated from CDOM observations? CDOM has been proposed as a proxy to estimate surface salinity from satellite ocean color sensors previously (Carder et al., 1993; D'Sa et al., 2002; Hu et al., 2003). However, this will depend on whether CDOM can be estimated accurately from satellite (Carder et al., 1999; Hu et al., 2003) and whether or not there is a robust relationship between CDOM and salinity.

To answer this question I analyzed the errors for salinities estimated from \( a_{g443} \) data, using empirical relationships between these variables (Table 1.3). I first estimated salinities at the 95% confidence interval (also called the predicted interval). I then calculated the mean percentage error (MPE), i.e. the average of the absolute value of the difference between the estimated salinities at the 95% confidence interval and the estimated salinities at the regression line, divided by the estimated salinity at the regression line multiplied by 100% (graphical example presented in Figure 1.22).

The MPE of \( a_{g443} \)-derived salinity varied regionally and seasonally, ranging between 0.09% (R7, Sp-00, correspond to \( \pm 0.03 \) psu) and 8.17% (R1, Sp-99, correspond to \( \pm 2.29 \) psu). These results indicate that using CDOM data to estimate salinity of river plumes results in MPE of less than 9%. In average for all seasons for each region, the lower MPEs were found off the Suwannee River (0.51%-0.83%, corresponding to \( \pm 0.18 \) to \( \pm 0.29 \) psu), and the higher MPEs off the Mississippi River (1.41%-8.17%, corresponding to \( \pm 0.43-2.29 \) psu) (Table 1.3). The higher MPE found in the Mississippi River region may result from variation in the CDOM content from the various tributaries, marshlands, and primary production. Note the multiple adjacent lines in Figures 1.19 and
1.20 for the same year and seasons. Lower MPE variability was found during fall and higher during summer seasons. It is clear that phytoplankton blooms contribute to distortion of the $a_g$-salinity relationship as described in the previous section, but also widespread patchiness, greater influence from adjacent rivers, primary production, and photo-bleaching may all contribute to variation in the salinity-$a_g$ relationship.

To assess whether a single universal relationship between CDOM and salinity is applicable within each of eight selected regions and within the whole NEGOM area, I derived a salinity-$a_g$443 regression (applying all NEGOM combined salinity-$a_g$443 data) for each season of each year, and attempted to predict salinity in other seasons and in each of eight selected regions. First, I performed a “global” (whole NEGOM area) error analysis on observed vs. predicted salinity. For example, the salinity-$a_g$443 regression for fall 1998 (Fa-98) was used to predict salinities based on $a_g$443 data of spring 1999 (Sp-99). The results showed that mean percentage error of observed vs. predicted salinity for the global analysis ranged from 0.67% to 10.33% (corresponding to $\pm$0.24 to $\pm$3.28 psu; Table 1.5; Figure 1.23). Relatively high global mean percentage errors (up to 10.33%) were found when fall or spring regression formulas were applied to predict salinities for summer cruises and vice-versa. This may be due to the local production by phytoplankton as well as to photobleaching during summer seasons as discussed in the previous section.

Meanwhile, relatively low global mean percentage errors were obtained when applying global relationships based only on fall and spring data to other seasons in other years (Table 1.5). The fall 1998 (Fa-98) relationship i.e., Salinity (S)=36.59-29.86*$a_g$443 (n=8771, $r^2=0.86$, $0.01 \leq a_g443 \leq 0.52$, $16 \leq S \leq 36$) produced the lowest mean percentage errors for fall and spring seasons (0.82%-2.92%; corresponding to $\pm$0.29-1.01 psu; Table
Table 1.5. Mean percentage error of observed vs. predicted salinity employing seasonal global NEGOM salinity-$a_{g443}$ relationships to predict salinities in other seasons.

<table>
<thead>
<tr>
<th>Cruise Id</th>
<th>Number of obs.</th>
<th>Mean percentage error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RSu-98</td>
<td>RFa-98</td>
</tr>
<tr>
<td>Su-98</td>
<td>8899</td>
<td>3.46</td>
</tr>
<tr>
<td>Fa-98</td>
<td>8771</td>
<td>6.72</td>
</tr>
<tr>
<td>Sp-99</td>
<td>9057</td>
<td>5.06</td>
</tr>
<tr>
<td>Su-99</td>
<td>8733</td>
<td>4.92</td>
</tr>
<tr>
<td>Fa-99</td>
<td>7483</td>
<td>6.32</td>
</tr>
<tr>
<td>Sp-00</td>
<td>7865</td>
<td>6.51</td>
</tr>
<tr>
<td>Su-00</td>
<td>11817</td>
<td>6.85</td>
</tr>
</tbody>
</table>

Note: RSu-98, RFa-98, RSp-99, RSu-99, RFa-99, RSp-00 and RSu-00 refer to regression formula derived from global NEGOM salinity-$a_{g443}$ relationship during Su-98, Fa-98, Sp-99, Su-99, Fa-99, Sp-00 and Su-00, respectively used to predict salinities in others seasons (cruises).
Figure 1.22. Example of the error analysis of salinity predictions based on $a_{g443}$ data. Mean percentage error (MPE) equals to average of absolute values of 95% predicted interval values minus regression line values divided by regression line value multiplied by 100%. MPE for (A)=0.86% and (B)=8.17% (see also Table2). Note axis scales are different for better display purpose.

Figure 1.23. Two examples of observed and predicted global NEGOM salinity employing global NEGOM salinity-$a_{g443}$ relationship of other season. MPE equals to average of absolute values of estimate salinity minus observed salinity divided by observed salinity multiplied by 100%. These two cases represent the best and the worst scenarios.
1.5). Employing the global fall 1998 (Fa-98) relationship to predict salinities in fall and spring seasons both globally and regionally produced the lowest mean percentage errors. Therefore, this relationship may be useful to estimate salinity from satellite ocean color data for non-summer data. However, further testing using data from multiple years is required to improve the relationship between salinity and CDOM absorption coefficient in NEGOM region.

Applying global NEGOM cruise-by-cruise relationships, in most cases, it consistently yielded lowest MPE for spring and fall seasons. Meanwhile, applying global NEGOM cruise-by-cruise relationships for summer seasons, it yielded relatively low MPE (MPE<5%, see diagonal elements of the matrix at Table 1.5). Relatively low MPE during summer seasons indicated that the summertime global NEGOM CDOM-salinity relationships was not too bad, even though the global NEGOM CDOM-salinity of fall-1998 does not do a good job in predicting summertime salinity from summertime CDOM.
1.4. Conclusions

Analyses of in situ surface CDOM and chlorophyll-$a$ concentrations collected within nine of two-weeks cruises from fall 1997 to summer 2000 showed relatively high chlorophyll-$a$ concentrations ($\geq 1$ mg m$^{-3}$) and CDOM absorption ($a_{443}\geq 0.1$ m$^{-1}$) inshore particularly near the major river mouths and offshore in the Mississippi plume during summers of 1998, 1999, and 2000. These patterns were also observed from SeaWiFS images. The transport of Mississippi River water offshore created a spatially coherent high chlorophyll-$a$ concentration, low salinity, and high CDOM absorption cross-margin plume. The spatially coherent high chlorophyll-$a$ concentration plume was observed in SeaWiFS imagery as early as late May and usually lasted until the first week of September. The plume usually extended $>500$ km southeast of the Mississippi delta and up to the Florida Keys in August 1998.

The variability of river discharge appeared to be the dominant forcing factor in the variability of chlorophyll-$a$ concentration off Mississippi, Mobile, Escambia, Choctawhatchee, Apalachicola and Suwannee regions.

A strong interannual variability of chlorophyll-$a$ concentration during winter and spring 1998 compared to winter and spring of 1999 and 2000 was observed off Escambia (R3), Choctawhatchee (R4), Apalachicola (R5), Suwannee (R6) and Tampa Bay (R7). Mean chlorophyll-$a$ concentrations during winter and spring 1998 were anomalously higher by a factor of four than during winter and spring of 1999 and 2000. The high
concentrations related to anomalously high fall/winter river discharge in connection with 1997-1998 El Nino Southern Oscillation event and the spring 1998 upwelling events observed throughout the region.

In general, a_g443 covaried linearly and inversely with salinity, particularly below salinities of ~36 psu. For all near-shore regions, relatively high linear coefficients of determination (r^2~0.70 to r^2~0.98) between salinity and a_g443 were observed during spring and fall seasons, indicating a fairly conservative mixing behavior. In contrast, during summer seasons low (r^2<0.70) to non-significant (r^2=0.0) coefficients of determination were observed between salinity and a_g443, indicating non-conservative mixing behavior. In contrast to near-shore regions, outer-shelf regions showed high inverse correlations during summer seasons because of the presence of the Mississippi plume on the outer shelf.

There was no significant increase of the CDOM pool associated with the increase of chlorophyll-a concentration in most coastal regions during fall seasons, indicating river discharge was the main source of CDOM. However, a significant increase of the CDOM pool associated with the increase of chlorophyll-a concentration in coastal and offshore regions was observed during spring and summer seasons, indicating phytoplankton blooms play important roles in the *in situ* CDOM formation during spring and summer seasons. The increase of *in situ* CDOM formation associated with phytoplankton blooms ranged from 10% to 100%. In central NEGOM, it seemed that phytoplankton was also a significant source for CDOM formation during fall seasons.

The high inverse correlation between a_g443 and surface salinity during fall and spring seasons in near-shore regions suggested that it might be possible to derive salinity from
satellite ocean color sensors, provided that $a_{g443}$ is estimated consistently from ocean color, and the relationship between $a_{g443}$ and salinity is obtained empirically from field measurements. The global NEGOM salinity-$a_{g443}$ relationship of fall 1998 (Fa-98), i.e., Salinity=36.59-29.86*$a_{g443}$ (n=8771, $r^2=0.86$; $0.01\leq a_{g443}\leq 0.52$, $16\leq S\leq 36$) produced the lowest mean percentage error of observed vs. predicted salinity for all other fall and spring seasons ($<3\%$ errors; corresponding to $<1.03$ psu); therefore, this relationship may be useful to estimate salinity from satellite ocean color data. However, there was no robust global relationship that helped explain summer values. This may be affected by the influence of phytoplankton to significantly increase CDOM production during summer seasons. Further testing using data from multiple years is required in order to get better relationship between salinity and CDOM absorption coefficient.

For chlorophyll-$a$ concentrations ranging from $>0.0$ mg m$^{-3}$ to $\leq 50$ mg m$^{-3}$, comparison between in situ and SeaWiFS retrieved chlorophyll-$a$ concentration employing OC4v4 indicated that satellite estimates generally overestimate in situ data up to about 300%. For the same range of chlorophyll-$a$ concentration, MODIS algorithm (Carder et al., 1999) improved significantly estimates of chlorophyll-$a$ concentration by as much as 2.5 times compared to the OC4v4 estimates specifically within the regions of relatively high CDOM concentration. For chlorophyll-$a$ concentration $\leq 1.0$ mg m$^{-3}$, both OC4v4 and MODIS algorithms produced errors falling within the SeaWiFS mission specification ($\pm 35\%$) during fall seasons. However, during spring and summer seasons, when high CDOM concentrations were observed, MODIS algorithm improved results significantly compared to the OC4v4 algorithm in estimating chlorophyll-$a$ concentration. The OC4v4 algorithm used the blue band (443 nm channel) to estimate
chlorophyll-$a$ concentration which is subject to the effects of $a_{g443}$ being interpreted as pigments. The MODIS algorithm partially corrects chlorophyll retrievals for CDOM effects.
CHAPTER II:

VARIABILITY IN THE PARTICULATE ABSORPTION COEFFICIENTS OF
THE NORTHEASTERN GULF OF MEXICO SURFACE WATERS
Abstract

Variability in the light absorption coefficient of particulate materials in near-surface waters of the Northeastern Gulf of Mexico (NEGOM) was examined during 7 seasonal cruises in 1998-2000. Generally, the absorption coefficient of phytoplankton at 440 nm [$a_{ph}(440)$] followed a power law relationship ($r^2=0.87-0.98$) with chlorophyll-$a$ concentration. For the range of chlorophyll-$a$ concentration of 0.06-12.25 mg m$^{-3}$, the chlorophyll-specific absorption coefficient, $a_{ph}^*(440)$, varied by a factor of 7 (0.02-0.15 m$^2$ mg$^{-1}$). In general, lower values of $a_{ph}^*(440)$ (<0.06 m$^2$ mg$^{-1}$) were observed in the inshore particularly in the major river mouths. During summer, lower values of $a_{ph}^*(440)$ were also observed offshore associated with low-salinity waters of the Mississippi River plume. Higher values of $a_{ph}^*(440)$ (>0.1 m$^2$ mg$^{-1}$) were otherwise observed outside the river plumes in the outer shelf and slope, where lower chlorophyll-$a$ concentration occurred. Using pigments to derive taxonomic phytoplankton groups, variability in biomass proportion of microphytoplankton ($BP_{micro}$) can explain up to 76% of the variability in the average of $a_{ph}(545)/a_{ph}(440)$, $a_{ph}(625)/a_{ph}(440)$, and $a_{ph}(673)/a_{ph}(440)$. The average value of $a_{ph}^*(440)$, corresponding to major $BP_{micro}$, was also significantly lower than that of nanophytoplankton and picophytoplankton groups, suggesting that an increase in cell optical size (pigment packaging) resulted in decreasing $a_{ph}^*(440)$ values. The relationship between $a_{ph}^*(440)$ and chlorophyll-$a$ concentration was also not linear, indicating pigment composition played an important role in determining $a_{ph}^*(440)$ variability.
2.1. INTRODUCTION

Light absorption by phytoplankton and particulate material (detritus) play a significant role in determining the variability of optical properties of oceanic and coastal waters (Allali, et al., 1997). This optical variability also affects primary production, remote sensing of pigment biomass and mixed layer heating (Yentsch and Phinney, 1989; Bricaud and Stramski, 1990; Nelson et al., 1993; Carder et al., 1995; Cleveland, 1995; Sosik and Mitchell, 1995; Lee et al., 1996; Suzuki et al., 1998). For these reasons, and a requirement to improve remote sensing capabilities, information on the magnitude, range and sources of variability in the absorption coefficient of phytoplankton and other particulate matter is very important. Given the traditional difficulty of estimating phytoplankton pigment concentration in coastal waters, information from these areas may be of particular interest for the refinement of Case-II algorithms.

The phytoplankton absorption coefficient per unit of chlorophyll concentration (chlorophyll-specific absorption coefficient, $a_{ph}^*(\lambda)$) is a key factor when modeling light propagation within the ocean and ocean color (e.g., Carder et al., 1986; Gordon et al., 1988; Morel, 1988), carbon fixation by phytoplankton (Kiefer and Mitchell, 1983), the contribution of phytoplankton to the total absorption coefficient of seawater, as well as for modeling marine primary production (Morel and Andre, 1991; Carder et al., 1995; Sakshaug et al., 1997; Ishizaka, 1998).
In many studies, the spectrum and average value of $a^*_{ph} (\lambda)$ has been considered to be relatively constant (Bannister, 1974; Kiefer and Mitchel, 1983; Berthon and Morel, 1992). However, the variability in $a^*_{ph} (\lambda)$ has been extensively documented for both laboratory cultures (e.g., Bricaud et al., 1983, 1988; Mitchell and Kiefer, 1988a; Berner et al., 1989; Bidigare et al., 1990; Stramski and Morel, 1990; Ahn et al., 1992; Fujiki and Taguchi, 2002) and natural populations (e.g., Carder et al., 1986, 1991, 1999, 2004; Mitchell and Kiefer, 1988b; Yentsch and Phinney, 1989; Bricaud and Stramski, 1990; Hoepffner and Sathyendranath, 1991, 1992; Babin et al., 1993; Nelson et al., 1993; Bricaud et al., 1995; Cleveland, 1995; Sosik and Mitchell, 1995; Allali et al., 1997; Suzuki et al., 1998; Lohrenz et al., 2003). For instance, using a data set that included 815 spectra from different regions of the world ocean and covering chlorophyll concentrations ranging from 0.02 to 25 mg m$^{-3}$, $a^*_{ph} (440)$ values were observed to increase from eutrophic to oligotrophic waters over more than one order of magnitude (0.01 to 0.18 m$^2$ mg$^{-1}$, respectively) (Bricaud et al., 1995).

Variability in the magnitude and spectral shape of $a^*_{ph} (\lambda)$ can be attributed to three factors: (1) packaging effect i.e., pigments packed into stacks of shelf-shaded chloroplasts are less efficient in absorbing light per unit pigment mass than an optically thin solution (Kirk, 1994), (2) pigment composition and (3) cell size. An increase in pigment packaging can occur either as cell size increases or the internal concentration of pigments increases (Morel and Bricaud, 1981; Kirk, 1994; Lohrenz et al., 2003). Differences in phytoplankton species, as well as variation within a species grown under different environmental conditions (e.g., growth irradiance), also causes variability in $a^*_{ph} (\lambda)$ due
to pigmentation and packaging effects (Dubinsky et al., 1986; Morel and Bricaud, 1986; Bricaud et al., 1988; Mitchell and Kiefer, 1988a; Berner et al., 1989, Stramski and Morel 1990; Fujiki and Taguchi, 2002).

Several investigators have reported an increase in $a^*_{ph} (\lambda)$ with a decrease in chlorophyll concentration (Carder et al., 1986, 1991; Bricaud and Stramski, 1990; Cleveland, 1995; Bricaud et al., 1998, 1995). They interpreted this result mainly due to packaging effect or a general trend of decreasing cell size with decreasing chlorophyll concentration. However, the above trend can instead be attributed solely to the increasing contribution of accessory pigments in waters with low chlorophyll concentration, with no consideration of packaging effect (Wozniak and Ostrowska, 1990; Bricaud et al., 1995; Sakshaug et al., 1997; Ciotti et al., 1999). Carder et al. (1991) also suggested that chlorophyll dependency of $a^*_{ph} (\lambda)$ could differ between regions such as subtropical and temperate regions due to the typical differences in cell size, light, and nutrient regimes. In contrast, Hoepffner and Sathyendranath (1992) reported that there was no dependency of $a^*_{ph} (440)$ on chlorophyll concentration in the Gulf of Maine and Georges Bank regions within the range of 0.05-2.5 mg m$^{-3}$ chlorophyll, although that could all be considered part of the same region.

The Northeastern Gulf of Mexico (NEGOM) encompasses a wide variety of ecosystems which are influenced by a combination of nutrient-rich input from rivers and estuaries, coastal upwelling, vertical mixing (Muller-Karger, 2000; Pennock et al., 1999; Gilbes et al., 1986), and the Loop Current (Vukovich, 1988; Huh et al., 1981; Muller-Karger et al., 2001; Weisberg and He, 2003). These processes exert strong influences on
the phytoplankton abundance and distribution in the NEGOM. To date, $a^*_p(\lambda)$ variability has not been studied in the NEGOM region.

This study uses field observations from seven two-week cruises in the NEGOM region (1998 through 2000), to examine the relationships among variability in $a^*_p(\lambda)$, riverine influence (salinity), nutrient supply, and pigment concentration. The specific objectives of this dissertation chapter are to: (1) determine the seasonal and spatial variation of the chlorophyll-specific absorption coefficient of phytoplankton in the NEGOM, (2) determine the percentage contribution of phytoplankton and detritus to the total particulate absorption coefficient, (3) determine whether phytoplankton species or groups can be estimated from phytoplankton absorption coefficients ($a_{ph}(\lambda)$), and (4) understand the relationship between community structure and pigment composition of surface waters.
2.2. METHODOLOGY

2.2.1. Sample Collection

Near-surface (about 3 m-deep) water samples were collected from the Northeastern Gulf of Mexico (NEGOM; Figure 1.1, Chapter I) during seven two-week cruises aboard the Texas A&M University R/V Gyre. Cruises were conducted in spring (April or May; Sp-99, Sp-00), summer (July/August; Su-98, Su-99, Su-00), and fall (November; Fa-98, Fa-99) of 1998, 1999, and 2000 (Table 1.1). Each cruise surveyed eleven cross-margin transects from the 10-m to the 100-m isobath.

Water samples for determining the total particulate, phytoplankton, and detritus absorption coefficients were collected from the outflow of a flow-through system that pumped at a rate of 10 liters/minute from a hull depth of about 3-m, which passed water via a 10-liter debubbler and mixing chamber. Seawater samples (0.5-5.0 L) were collected and filtered immediately aboard ship through Whatman GF/F filters (25 mm diameter) under low vacuum pressure (<0.5 atm). The volume of water filtered varied between ~0.05 and 5.0 liters depending on the concentration of pigmented particles in the sample. Filtering was discontinued once the filter displayed sufficient color to the naked eye. Each filter pad was folded and placed into a 2.0 ml sterile Nalgene cryogenic vial, and stored in liquid N₂ for analysis. After arrival from the field, samples were stored in a deep-freezer.
Water samples for pigment analyses were collected from one of twelve 10-L Niskin bottles operated with a Sea-Bird SBE 911 profiling system used to collect conductivity-temperature-depth (CTD) profiles. Pigment sampling and analyses, including the calibration of a fluorometer on the flow-through system, were conducted by Texas A&M University. Detailed description of data collection and analysis methods can be found in Qian et al. (2003).

2.2.2. Absorption Measurements

The quantitative filter technique (Yentsch, 1962; Kiefer and SooHoo, 1982) was used to determine absorption spectra due to total particulates (phytoplankton and detritus, \(a_p(\lambda)\)) and detritus (\(a_d(\lambda)\)). Prior to analysis, sample and reference filter pads were allowed to thaw slowly at room temperature for about 5-10 minutes prior to being placed in a dark petri dish and moistened with a drop of Milli-Q water. The moist sample and reference filter pads were placed on individual glass plates (diameter=2.4cm) in a custom-made diffuse transmissometer box. Prior to each scan, the filters were slid one at a time over a tungsten-halogen light source that shone through a blue long-pass/cut-off filter and a quartz glass diffuser. Using a custom made, 512-channel spectroradiometer (~350-850nm), the transmittances of the sample filter (\(T_{\text{sample}}(\lambda)\)) and the reference filter (\(T_{\text{reference}}(\lambda)\)) were measured three times. These measurements were averaged and used to obtain the optical densities of total particulate matter (\(OD_p(\lambda)\)) as shown below.

The sample filter was then soaked with ~40-50ml of hot 100% methanol for 10-15 minutes in the dark to extract phytoplankton pigments (Kishino et al., 1985; Roesler et al., 1989; Bissett et al., 1997). Transmittances of the extracted filter (\(T_{\text{detritus}}(\lambda)\)) and the
reference filter were once again measured three times, and the optical density of detritus 
(OD_d(λ)) calculated.

Optical densities were calculated as follows:

\[
OD_p(λ) = \log_{10} \left( \frac{T_{\text{reference}}(λ)}{T_{\text{sample}}(λ)} \right) \tag{2.1a}
\]

\[
OD_d(λ) = \log_{10} \left( \frac{T_{\text{reference}}(λ)}{T_{\text{detritus}}(λ)} \right) \tag{2.1b}
\]

The absorption coefficients of particulate matter (a_p(λ)) and detritus (a_d(λ)), were 
calculated as follows:

\[
a_p(λ) = \frac{\ln 10 \times OD_p(λ) \times β}{l} \tag{2.2a}
\]

\[
a_d(λ) = \frac{\ln 10 \times OD_d(λ) \times β}{l} \tag{2.2b}
\]

where “l” is the geometric pathlength equal to the volume of seawater filtered divided by 
the effective filtration area of the filter (Πr^2, r=0.0215/2 m), and β is the pathlength 
amplification or “β factor” (Butler, 1962). The β factor is an empirical formulation 
defined as the ratio of optical to geometric pathlength that corrects for multiple scattering 
inside the filter. In this study, an average of two published β factor formulations (Bricaud 
and Stramski, 1990; Nelson et al., 1993) was used as follows:

\[
β = 1.0 + 0.6 \times OD_p(λ)^{-0.5} \tag{2.3}
\]

Spectra with OD_p(675) less than 0.04 were omitted from this study (Bissett et al., 1997) 
to minimize artifacts due to uncertainty in the β factor (Mitchell and Kiefer, 1988a;
Bricula and Stramski, 1990; Cleveland and Weidemann, 1993; Nelson et al., 1993; Moore et al., 1995; Lohrenz, 2000). All other spectra were set to zero at 750 nm to correct for residual scattering caused by non-uniformity in wetness between the sample and reference filters or for stray light.

Using Eqs. 2a and 2b, the absorption spectra due to phytoplankton pigments, \( a_{ph}(\lambda) \), were calculated as follows:

\[
a_{ph}(\lambda) = a_p(\lambda) - a_d(\lambda)
\]  

(2.4)

Fluorometric chlorophyll and phaeopigment concentrations were determined on the filtrate of phytoplankton pigments extracted from the sample filter with hot 100% methanol using a Turner 10-AU-005 fluorometer according to the methods of Holm-Hansen and Riemann (1978). Finally \( a_{ph}(\lambda) \) was converted to chlorophyll-\( a \) specific absorption coefficient (\( a_{ph}^*(\lambda) \)) dividing by chlorophyll-\( a \) concentration.

The local maxima of the total particulate absorption coefficient spectra near 440, 545, and 673 nm were usually observed in the range of 440±5, 545±5, and 673±5 nm, respectively. Therefore, the magnitude of phytoplankton, detritus, total particulate and chlorophyll-specific absorption coefficients at these wavelengths (440, 545 and 673 nm) was obtained by averaging spectra from the above range of wavelengths.
2.3. RESULTS AND DISCUSSION

2.3.1. Total Particulate, Detritus and Phytoplankton Absorption Coefficients

The near-surface absorption coefficients for total particulate \( a_p(\lambda) \), detritus \( a_d(\lambda) \), and phytoplankton \( a_{ph}(\lambda) \) in the NEGOM from 1998 to 2000 are presented in Figures 2.1, 2.2 and 2.3. Higher total particulate absorption coefficients at 440 nm were observed near the coast and particularly near the Mississippi river mouth (as high as 0.85 m\(^{-1}\), with salinity of 28.22). Lower values were observed offshore (as low as 0.01 m\(^{-1}\), with salinity of 36.24 psu) (Figure 2.1). Detritus and phytoplankton absorption coefficients at 440 nm also showed higher values in the coastal region relative to offshore (range of 0.01 m\(^{-1}\) in offshore region to 0.51 m\(^{-1}\) in coastal region for detritus and 0.01 m\(^{-1}\) in offshore region to 0.61 m\(^{-1}\) in coastal region for phytoplankton; Figure 2.2 and 2.3). A similar pattern was observed for all absorption coefficients at 673 nm.

In coastal waters, particularly near river mouths, chlorophyll concentrations were relatively high, but absorption by detritus in the blue \( a_d(440) \) exceeded that of phytoplankton absorption \( a_{ph}(440) \). In other words, detritus contributed on average between 52\% and 66\% at that wavelength to the total particulate absorption in coastal areas near the river mouths. In contrast, in offshore waters where chlorophyll concentration was relatively low, absorption by phytoplankton generally exceeded that by detritus (phytoplankton contributed on average between 68\% and 77\% to the total particulate absorption). This result is contrary to many previous studies that have reported
that the proportion of detritus absorption increases offshore (especially in oligotrophic areas) relative to the inshore, upwelling regions (Gordon, 1989; Morel, 1988; Smith and Baker, 1978).

The mean absorption coefficient at 440 nm for total particulate, detritus, and phytoplankton varied seasonally, with maxima observed during summer cruises (i.e., $a_p(440)=0.0875 \text{ m}^{-1}$, $a_d(440)=0.0277 \text{ m}^{-1}$ and $a_{ph}(440)=0.0605 \text{ m}^{-1}$, respectively) and minima during spring cruises (i.e., $a_p(440)=0.0206 \text{ m}^{-1}$, $a_d(440)=0.0076 \text{ m}^{-1}$ and $a_{ph}(440)=0.0130 \text{ m}^{-1}$, respectively).

There was no clear relationship between the detritus absorption coefficient at 440 nm normalized to phytoplankton absorption coefficient at 440 nm and chlorophyll-$a$ concentration in individual samples (Figure 2.4). At low chlorophyll-$a$ concentrations (<1 mg m$^{-3}$), $a_d/a_p$ seems to vary significantly. However, the average absorption coefficients ($a_g$, $a_{ph}$, and $a_d$) for each cruise for water salinity >34.5 (limit for oceanic water not affected by fresh water) showed a tendency to covary with average chlorophyll concentration (Figure 2.5, top panel). These results indicate that both detritus and chlorophyll-$a$ played a major role in determining total particulate absorption coefficient in the NEGOM region where there is no recent fresh-water influence. At higher chlorophyll concentrations (>1 mg m$^{-3}$) and where there is fresh water influence (salinity ≤34.5), there was no clear relationship between average absorption coefficients ($a_g$, $a_{ph}$, and $a_d$) and chlorophyll concentration (Figure 2.5, lower panel). In both salinity ranges, however, $a_g(440)$ exceeded $a_{ph}(440)$ with average values for $a_g(440)/a_{ph}(440)$ of 3.09±0.88 (for salinity range ≤34.5) and 1.81±0.58 (for salinity range >34.5).
Figure 2.1. Near-surface total particulate absorption spectra in the NEGOM between 1998 and 2000. See Table 1.1 for cruise identification. Note different scales on y-axis.
Figure 2.2. Near-surface detritus absorption spectra in the NEGOM between 1998 and 2000. See Table 1.1 for cruise identification. Note different scales on y-axis.
Figure 2.3. Near-surface phytoplankton absorption spectra in the NEGOM between 1998 and 2000. See Table 1.1 for cruise identification. Note different scales on y-axis.
Figure 2.4. Proportion of detrital to total particulate absorption coefficient at 440 nm versus chlorophyll-α concentration for each cruise. See Table 1.1 for cruise identification.
Figure 2.5. Time series of mean $a_g(440)$, $a_d(440)$, $a_{ph}(440)$ and chlorophyll-$a$ concentration of each cruise. Region with salinity $>34.5$ (Top Panel) and region with salinity $\leq 34.5$ (Lower Panel). Right y-axis is for chlorophyll-$a$ concentration (mg m$^{-3}$). See Table 1.1 for detail cruise identification.
2.3.2. Variation in Spectral Shape of the Phytoplankton Absorption Coefficient

Most phytoplankton absorption spectra collected in NEGOM (Figure 2.3) show peaks at approximately 440 and 673 nm, typical of absorption by chlorophyll-\textit{a} (e.g., Cleveland, 1995). The spectral shape of the absorption coefficient associated with phytoplankton pigments was examined by normalizing each of the spectra to its value at 440 nm and averaging normalized spectra for spring, summer, and fall as presented in Figure 2.6. There was considerable variation around the mean for each season, which is attributed to spatial variation along the cruise track.

A secondary absorption peak was observed around 545 nm in inner shelf samples (water depth ≤50 m), except during summer cruises when this also occurred in the river plume extending over the outer shelf (water depth 50-400 m) and slope (water depth ≥400 m).

The 545 nm peak may be due to the presence of fucoxanthin and/or phycoerythrobilin pigments. Anderson and Barrett (1986) reported that the fucoxanthin-chlorophyll\textit{a/c}-protein complex enhances absorption near 542 nm. Phycoerythrobilin, found in cyanobacteria, also has an absorption band around 545 nm (Moore \textit{et al.}, 1995; Morel \textit{et al.}, 1993, Hoepffner and Sathyendranath, 1991). Indeed, fucoxanthin concentrations (a biomarker for diatoms) were generally high in the inner shelf of the NEGOM and offshore areas affected by fresh water discharge (Figure 2.7). On the other hand, zeaxanthin concentrations (a biomarker for cyanobacteria) were observed in patches over the NEGOM during spring and summer seasons (Figure 2.8) mostly in oligotrophic areas (see Figure 1.2). These results are similar to those Qian \textit{et al.} (2003), derived based on the same data.
Figure 2.6. Phytoplankton absorption spectra normalized to 440 nm from seven NEGOM cruises. Individual normalized spectra are shown in black and the average normalized spectra in blue. Panel H shows the average normalized spectra for spring, summer and fall seasons. See Table 1.1 for cruise identification.
Figure 2.7. Near-surface distribution of fucoxanthin concentration normalized with chlorophyll-\(a\) concentration in the NEGOM. White dots show location of water sample collections. See Table 1.1 for cruise identification.
Figure 2.8. Near-surface distribution of zeaxanthin concentration normalized with chlorophyll-α concentration in the NEGOM. White dots show location of water sample collections. See Table 1.1 for cruise identification.
There was no significant difference between the phytoplankton absorption spectra of spring (Sp-99, Sp-00) and fall (Fa-98, Fa-99). However, a one-way analysis of variance (ANOVA) showed that there were significant differences in the mean values of normalized phytoplankton absorption coefficient at 545 nm and 673 nm between those of summers (Su-98, Su-99, Su-00) and those of spring and fall (P>0.05). There were no significant differences between spring and fall. For example, the mean values of normalized phytoplankton absorption coefficient for 545 nm was higher during summer (0.209) than during spring (0.122) and fall (0.124) seasons (Figure 2.6, plot H).

Higher mean normalized phytoplankton absorption coefficients at 545 during summer may be attributed to the offshore dispersal of the Mississippi River plume in the NEGOM which provides nutrients for growth and development of large-celled diatoms. Diatoms containing fucoxanthin pigment enhances absorption around 542 nm (Anderson and Barrett, 1986). Patches of cyanobacteria found during summer may also contribute to higher normalized \( a_{ph}(545) \) versus spring and fall seasons. Relatively high mean chlorophyll-\( a \) concentrations during summer versus spring and fall lead to higher normalized \( a_{ph}(673) \) in summer than that in spring and fall.

Seasonal and spatial distributions of \( a_{ph,545}/a_{ph,440} \), \( a_{ph,673}/a_{ph,440} \) and the average of \( a_{ph,545}/a_{ph,440} \), \( a_{ph,673}/a_{ph,440} \) and \( a_{ph,673}/a_{ph,440} \) are presented in Figures 2.9, 2.10 and 2.11. Relatively high values of these normalized phytoplankton absorption coefficients were observed in the inner shelf, especially near the major river mouths, and relatively low values observed offshore, except during summer season where high values were also observed offshore associated with the Mississippi river plume. The spatial distribution of \( a_{ph,545}/a_{ph,440} \) and \( a_{ph,673}/a_{ph,440} \) also seems to correlate with spatial distributions of
Figure 2.9. Near-surface distribution of the $a_{ph,545}/a_{ph,440}$ in the NEGOM. White dots show location of water sample collections. See Table 1.1 for cruise identification.
Figure 2.10. Near-surface distribution of the $a_{ph \lambda 673/440}$ in the NEGOM. White dots show location of water sample collections. See Table 1.1 for cruise identification.
Figure 2.11. Near-surface distribution of the of mean $a_{ph}545/440+a_{ph}625/440+a_{ph}673/440$ in the NEGOM. White dots show location of water sample collections. See Table 1.1 for cruise identification.
chlorophyll-α (see also Figure 1.2). The correlation between these normalized phytoplankton absorption coefficients seem to be better when $a_{ph,545}/a_{ph,440}$, $a_{ph,625}/a_{ph,440}$ and $a_{ph,673}/a_{ph,440}$ were averaged (Figure 2.11).

To study the use of normalized phytoplankton absorption coefficients on taxonomic classification of phytoplankton groups in the NEGOM, an index was computed based on pigment composition as per Vidussi et al., (2001). They used pigments to derive cell-size class markers of phototroph groups, such as picophytoplankton (<2 μm), nanophytoplankton (2-20 μm), and microphytoplankton (>20 μm).

Pigment markers for picophytoplankton (<2 μm) used were Zeaxanthin (biomarker for cyanobacteria and prochlorophytes e.g., Guillard et al., 1985; Chisholm et al., 1988; Gieskes et al., 1988), Divinyl-chlorophyll a (biomarker for prochlorophytes e.g., Gieskes and Kraay, 1983; Chisholm et al., 1988; Goericke and Repeta, 1992), and Chlorophyll b+Divinyl-chlorophyll b (biomarkers for green flagellates and prochlorophytes e.g., Jeffrey, 1976; Partensky et al., 1993; Simon et al., 1994; Moore et al., 1995).

Pigment markers for nanophytoplankton used were 19’hexanoyloxyfucoxanthin, 19’butanoyloxy-fucoxanthin (biomarker for cryptophytes nanoflagellates e.g., Arpin et al., 1976; Jeffrey and Vesk, 1977; Wright and Jeffrey, 1987; Hooks et al., 1988; Bjornland et al., 1989; Bjornland and Liaaen-Jensen, 1989; Andersen et al., 1993) and Alloxanthin (a biomarker for cryptophytes e.g., Jeffrey and Vesk, 1977; Gieskes and Kraay, 1983).

Pigment markers for microphytoplankton used were Fucoxanthin (a biomarker for diatoms e.g., Kimor et al., 1987; Wright and Jeffrey, 1987; Hooks et al., 1988;
Bjornland and Liaeen-Jensen, 1989) and Peridinin (a biomarker for
dinoflagellates e.g., Johansen et al., 1974; Jeffrey et al., 1975; Kimor et al.,
1987).

The formula to derive cell size class marker is as follows:

\[
\text{DP (Diagnostic Pigments)} = \text{Zea} + \text{chl}_b + \text{Allo} + 19^\prime \cdot \text{HF} + 19^\prime \cdot \text{BF} + \text{Fuco} + \text{Peri} \tag{2.5}
\]

\[
\text{BP}_{\text{pico}} = \frac{(\text{Zea} + \text{chl}_b)}{\text{DP}} \tag{2.6}
\]

\[
\text{BP}_{\text{nano}} = \frac{(\text{Allo} + 19^\prime \cdot \text{HF} + 19^\prime \cdot \text{BF})}{\text{DP}} \tag{2.7}
\]

\[
\text{BP}_{\text{micro}} = \frac{(\text{Fuco} + \text{Peri})}{\text{DP}} \tag{2.8}
\]

where \( \text{BP}_{\text{pico}} = \) Biomass Proportion of picophytoplankton, \( \text{BP}_{\text{nano}} = \) Biomass Proportion of nanophytoplankton, \( \text{BP}_{\text{micro}} = \) Biomass Proportion of microphytoplankton, Zea= [zeaxanthin], chl\_b=[chlorophyll\_b], Allo=[alloxanthin], 19^\prime \cdot \text{HF}=[19^\prime \text{hexanoyloxyfucoxanthin}], 19^\prime \cdot \text{BF}=[19^\prime \text{butanoyloxyfucoxanthin}], Fuco=[fucoxanthin], Peri=[peridinin].

Distribution of biomass proportion for microphytoplankton, nanophytoplankton and picophytoplankton are presented in Figures 2.12, 2.13, and 2.14. Relatively high biomass proportions of microphytoplankton (diatoms and dinoflagellates) were observed in the inshore particularly near the major river mouths with relatively low values found offshore. During summer cruises, relatively high biomass proportions of microphytoplankton were also observed in the offshore region (Figure 2.12) along the Mississippi River plume. It seems that relatively high biomass proportions of microphytoplankton were associated with low salinity. This trend is consistent with those shown in Qian et al. (2003) in which they applied different methods to quantify the abundance and distribution of diatoms in the same region. It appears that the distribution pattern of
Figure 2.12. Spatial distribution of biomass proportion of cell size marker for microphytoplankton. See Table 1.1 for cruise identification.
Figure 2.13. Spatial distribution of biomass proportion of cell size marker for nanophytoplankton. See Table 1.1 for cruise identification.
Figure 2.14. Spatial distribution of biomass proportion of cell size marker for picophytoplankton. See Table 1.1 for cruise identification.
microphytoplankton biomass proportion is best related to the distribution of $a_{ph545/440}$ and $a_{ph673/440}$ (see Figure 2.9 and 2.10).

Relatively high values of biomass proportion for nanphytoplankton (chromophytes nanoflagellates and cryptophytes) were observed particularly offshore, and were relatively low inshore. Relatively high biomass proportion for nanphytoplankton were associated with low chlorophyll-$a$ concentrations. During summer, it appeared that relatively low nanphytoplankton biomass proportions extended offshore following the Mississippi River plume (Figure 2.13).

The abundance of the picophytoplankton group (cyanobacteria, prochlorophytes and green flagellates) was mixed along the NEGOM but relatively high biomass proportions were only observed in late spring (Sp-99) and summer (Su-98, Su-99, Su-00) over the outer shelf and slope (Figure 2.14) in mostly oligotrophic waters since this group is a nitrogen fixer phytoplankton. This pattern was also consistent with the observation conducted by Qian et al. (2003).

To examine whether algal groups can be estimated from normalized phytoplankton absorption coefficients, I examined several relationships between the combinations of several bands of normalized phytoplankton absorption coefficients and taxonomic phytoplankton groups ($BP_{pico}$, $BP_{nano}$, and $BP_{micro}$). From several combinations and trials, the average of $a_{ph545/440}$, $a_{ph625/440}$, $a_{ph673/440}$ produced better relationships with taxonomic phytoplankton groups. Results also showed that only the biomass proportion for microphytoplankton ($BP_{micro}$) has a significant relationship with the average of $a_{ph545/440}$, $a_{ph625/440}$, $a_{ph673/440}$. Positive relationships between the average of $a_{ph545/440}$, $a_{ph625/440}$, $a_{ph673/440}$ and $BP_{micro}$ were found with coefficient of
determination ($r^2$) from 0.21 (Su-99) to 0.76 (Sp-99) (Figure 2.15). In general, the relationships between the average of $a_{ph,545/440}$, $a_{ph,625/440}$, $a_{ph,673/440}$ and $BP_{micro}$ were lower during summer than during fall and spring seasons (Figure 2.15). The lower relationships during summer may be due to the relatively high biomass proportion of picophytoplankton ($BP_{pico}$). Picophytoplankton (cyanobacteria) contains phycoerythrobilin pigment producing a peak absorption at around 545 nm (Hoeppfner and Sathyendranath, 1991; Morel et al., 1993; Moore et al., 1995). Microphytoplankontn (diatoms) containing fucoxanthin pigment also enhanced absorption near 542 nm (Anderson and Barnet (1986). Therefore, high biomass proportion of these two phytoplankton groups in summer and late spring could confound the relationship between the normalized phytoplankton absorption coefficients and taxonomic phytoplankton groups. Since the phycoerythrobilin pigment is water soluble, it may be possible to reduce the influence of this pigment to phytoplankton absorption at 545 nm. If the influence of phycoerythrobilin pigment on phytoplankton absorption at 545 nm can be eliminated, then the relationship between the average of $a_{ph,545/440}$, $a_{ph,625/440}$, $a_{ph,673/440}$ and $BP_{micro}$ may improve, and therefore normalize phytoplankton absorption coefficient may be used to estimate biomass proportion of microphytoplankton.

### 2.3.3. Phytoplankton Absorption Coefficient vs. Chlorophyll-$a$ Concentration

I examined the relationship between phytoplankton absorption coefficient ($a_{ph}(\lambda)$) at 440 and 673 nm and chlorophyll-$a$ concentration (Figure 2.16 and 2.17). The general trend of $a_{ph}(440)$ was to increase with increasing chlorophyll-$a$ concentration. This trend was similar to observations conducted by Carder et al, (1986, 1991, 1999, 2004), Yentch
Figure 2.15. Relationship between the average of $a_{ph}545/440 + a_{ph}625/440 + a_{ph}673/440$ and microphytoplankton biomass proportion ($BP_{micro}$) for each cruise. See Table 1.1 for detail of cruise identification.
Figure 2.16. Relationship between phytoplankton absorption coefficient at 440 nm ($a_{ph}(440)$) and chlorophyll-$a$ concentration for each cruise. See Table 1.1 for detail of cruise identification.
Figure 2.17. Relationship between phytoplankton absorption coefficient at 673 nm ($a_{ph}(673)$) and chlorophyll-α concentration for each cruise. See Table 1.1 for detail of cruise identification.
and Phinney (1989), and Bricaud et al. (1995). The relationship between \( a_{\text{ph}}(440) \) and chlorophyll-\( a \) concentration, exhibited a power law relationship with coefficient of determination \( (r^2) \) range from 0.87 to 0.98 (Figure 2.16).

The general trend of \( a_{\text{ph}}(673) \) values was also to increase with increasing chlorophyll-\( a \) concentration. However, stronger power law relationship between \( a_{\text{ph}}(673) \) and chlorophyll-\( a \) concentration were generally observed during all seasons \( (r^2=0.97-0.99, \text{ Figure 2.17}). Using linear regression, the relationships between \( a_{\text{ph}}(673) \) and chlorophyll-\( a \) concentration were also strong \( (r^2=0.94-0.99) \). The results also documented that the exponent values of the power law relationships were very close to one, indicating the relationship between \( a_{\text{ph}}(673) \) and chlorophyll-\( a \) concentration can be considered linear. The slopes of the regressions also spanned a small range \( (0.013-0.017) \). Strong relationships between \( a_{\text{ph}}(673) \) and chlorophyll-\( a \) concentration for all cruises indicated that variability in chlorophyll-specific absorption coefficient at 673 nm was small. By combining all data from seven cruises, the relationship between \( a_{\text{ph}}(673) \) and chlorophyll-\( a \) concentration employing linear and power law equations are as follows:

\[
a_{\text{ph}}(673) = 0.0153 \times \text{chl}a \quad (r^2=0.96, \text{ n=436})
\]

\[
a_{\text{ph}}(673) = 0.0167 \times \text{chl}a^{0.972} \quad (r^2=0.96, \text{ n=436})
\]

In linear scale, for chlorophyll-\( a \) concentrations < 1.0 mg m\(^{-3}\), it clearly showed that the slopes of both \( a_{\text{ph}}(440) \) and \( a_{\text{ph}}(673) \) versus chlorophyll-\( a \) concentration were steeper than at chlorophyll-\( a \) concentrations > 1.0 mg m\(^{-3}\). I believe that the non-linearity of these relationships was largely due to the differences in pigment packaging of
phytoplankton species (Bricaud et al., 1983, 1995; Yenstch and Phinney, 1989; Sathyendranath et al., 1999).

2.3.4. Variation in Chlorophyll-Specific Absorption Coefficient

The chlorophyll-specific absorption coefficient at 440 nm was found to be highly variable in the NEGOM region for all cruises (Figure 2.18). $a_{ph}^*$ (440) varied by about a factor of 7 ranging from 0.02 to 0.15 m$^2$ mg$^{-1}$ for the chlorophyll-a range of 0.06-12.25 mg m$^{-3}$ over the study period (Figure 2.18). Variability of $a_{ph}^*$ (673) was less pronounced and only varied by a factor 2. For chlorophyll-a range of 0.06-12.25 mg m$^{-3}$ over the study period, $a_{ph}^*$ (673) ranged from 0.0100 to 0.0248 m$^2$ (mg chl)$^{-1}$ with the average value of 0.0175 m$^2$ (mg chl)$^{-1}$.

Near-surface spatial and temporal variability of $a_{ph}^*$ (440) for seven cruises is presented in Figure 2.19. There was a general trend of increasing $a_{ph}^*$ (440) with distance from shore where chlorophyll-a concentration also decreased. During summer cruises, relatively low $a_{ph}^*$ (440) was also observed in the outer shelf and slope of the western NEGOM (Figure 2.19) and higher $a_{ph}^*$ (440) values (~0.15 m$^2$ mg$^{-1}$) were observed only in the middle shelf off Florida. Relatively low $a_{ph}^*$ (440) were observed along the inner shelf and specifically near river mouths including the Mississippi, Mobile, Apalachicola and Suwannee river outflow regions.

The general spatial pattern of $a_{ph}^*$ (440) seemed to relate to general spatial pattern of zeaxanthin (a biomarker for cyanobacteria) (see Figure 2.8) and biomass proportion of
Figure 2.18. Near-surface chlorophyll-specific absorption spectra measured on the NEGOM region during summer, spring and fall seasons between 1998 and 2000. See Table 1.1 for cruises identification. Note the different scales on y-axis.
Figure 2.19. Near-surface distribution of the chlorophyll-specific absorption coefficient at 440 nm in the NEGOM. White dots show location of water sample collections. See Table 1.1 for cruise identification.
nanophytoplankton (Figure 2.13), indicating increase in $a''_{ph}(440)$ values associated with increase small-celled phytoplankton. Meanwhile, the opposite pattern was observed between $a''_{ph}(440)$ and biomass proportion of microphytoplankton (see Figure 2.12), indicating decrease in $a''_{ph}(440)$ values associated with increase large-celled phytoplankton. The $a''_{ph}(440)$ values were also higher in areas of lower chlorophyll-a concentration and vice versa. The positive relationship between $a''_{ph}(440)$ and small-celled phytoplankton and the negative relationship between $a''_{ph}(440)$ and large-celled phytoplankton and chlorophyll-a concentration suggesting that particle size (packaging effect) played a role in determining $a''_{ph}(440)$ variability. Because the relationship between $a''_{ph}(440)$ and chlorophyll-a concentration was not linear, pigment composition also likely played a role in determining $a''_{ph}(440)$ variability (Morel and Bricaud, 1981; Carder et al., 1986, 1999; Dubinsky et al., 1986; Morel and Bricaud, 1986; Bricaud et al., 1988; Mitchell and Kiefer, 1988a; Berner et al., 1989; Stramski and Morel 1990; Kirk, 1994; Fujiki and Taguchi, 2002; Lohrenz et al., 2003). The spatial distribution of $a''_{ph}(440)$ also followed salinity patterns. Low salinity, with a higher nutrient content, may have played a role in selecting for species with low $a''_{ph}(440)$. However, there was no statistical relationship between surface nutrient concentrations ($\text{NO}_2+\text{NO}_3+\text{NH}_4+\text{Urea}$) and $a''_{ph}(440)$, likely because nutrients are consumed as fast as they are supplied.
To examine the effect of taxonomic groups on $a_{ph}^* (440)$ in the NEGOM, an index was computed based on pigment composition as per Vidussi et al., (2001) as discussed in Section 2.3.2. For each major Biomass Proportion (BP≥0.5), the $a_{ph}^* (440)$ values were grouped into the three corresponding cell size markers. Scatter plots of $a_{ph}^* (440)$ and Biomass Proportion of cell size markers are presented in Figure 2.20. Although scatter is high, it seems that biomass proportion of nanophytoplankton and picophytoplankton have a positive correlation with $a_{ph}^* (440)$. While, microphytoplankton showed negative correlation suggesting higher abundance of microphytoplankton lowered the value of $a_{ph}^* (440)$ (Figure 2.20). The average value of $a_{ph}^* (440)$ corresponding to the major biomass proportion of microphytoplankton was also significantly lower than that of nanophytoplankton and picophytoplankton groups (Table 2.1). These results strongly suggest that an increase in cell size resulted in decrease $a_{ph}^* (440)$ values or increase in pigment packaging.

Table 2.1. Mean values of $a_{ph}^* (440)$ for all seven NEGOM cruises data corresponding with the three major size cell markers of phytoplankton (BP≥0.5).

<table>
<thead>
<tr>
<th>ID</th>
<th>Cell size markers</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
<th>Different From ID*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>nanophytoplankton</td>
<td>136</td>
<td>0.0875</td>
<td>0.0020</td>
<td>C</td>
</tr>
<tr>
<td>B</td>
<td>picophytoplankton</td>
<td>64</td>
<td>0.0815</td>
<td>0.0029</td>
<td>C</td>
</tr>
<tr>
<td>C</td>
<td>microphytoplankton</td>
<td>29</td>
<td>0.0484</td>
<td>0.0044</td>
<td>A,B</td>
</tr>
</tbody>
</table>

*Average values were compared for the differences among cell size markers using the Least Significant Difference (LSD) Method*
Figure 2.20. Scatter plots of $a_{ph}(440)$ and biomass proportion per algal group for all seven NEGOM cruises.
2.4. Conclusions

In the coastal NEGOM near river outflows where chlorophyll concentration was relatively high, light absorption in the blue band (440 nm) by detritus normally exceeded that of phytoplankton absorption ($a_d$ was 54% to 66% of the total particulate absorption or $a_p$). In contrast, in offshore waters, absorption by phytoplankton contributed more than that of detritus ($a_{ph}$ was 68% to 77% of $a_p$). There was no clear relationship between detritus absorption coefficient and chlorophyll-$a$ concentration. For water salinity $>34.5$, chlorophyll-$a$ and detritus seemed to play major role in determining total particulate absorption coefficient. Meanwhile, for water salinity $\leq 34.5$, there was no clear correlation between chlorophyll-$a$ concentration and total particulate absorption coefficient. In both salinity ranges, however, $a_g(440)$ exceeded $a_{ph}(440)$ with average values for $a_g(440)/a_{ph}(440)$ of $3.09 \pm 0.88$ (for salinity $\leq 34.5$) and $1.81 \pm 0.58$ (for salinity $>34.5$)

The spatial distributions of $a_{ph}(545)/a_{ph}(440)$ and $a_{ph}(673)/a_{ph}(440)$ seem to correlate with spatial distribution of chlorophyll-$a$ concentration and fucoxanthin pigment (biomarker for diatoms), indicating that information from normalized phytoplankton absorption coefficients may be used to estimate taxonomic phytoplankton groups. Up to 76% variability of biomass proportion of microphytoplankton (B$P_{micro}$) specifically during spring and fall seasons can be explained by the variability of the average values of $a_{ph}545/440$, $a_{ph}625/440$, $a_{ph}673/440$. During summer, however, the relationships between
BP_{micro} and the average of a_{ph,545/440}, a_{ph,625/440}, a_{ph,673/440} were relatively less coherent than during spring and fall. This may be due to the simultaneous presence of different taxonomic phytoplankton groups i.e. diatoms (microphytoplankton, containing fucoxanthin pigment) and cyanobacteria (picophytoplankton, containing phycoerythrobilin pigment) during summer and late spring in NEGOM.

In general, relationship between a_{ph,440} and chlorophyll-\textit{a} concentration, exhibited a power law relationship with coefficient of determination (r^2) range from 0.87 to 0.98. Meanwhile, a_{ph,673} covaried linearly with chlorophyll-\textit{a} concentration in all seasons (r^2=0.94-0.99).

Variability of $a_{ph}^*(440)$ was more pronounced within a cruise than among the seasons. It varied by about a factor of 7, i.e. $a_{ph}^*(440)$ ranged from 0.02 to 0.15 m^2 mg^{-1} for the range of 0.06-12.25 mg m^{-3} chlorophyll-\textit{a} concentration. In general, lower values of $a_{ph}^*(440)$ were observed inshore particularly in the major rivers mouth regions. Higher $a_{ph}^*(440)$ were observed offshore, associated with high salinity, and lower chlorophyll-\textit{a}, except during summer when lower $a_{ph}^*(440)$ were also observed offshore to the west of about 85\degree W in the low salinity Mississippi plume. Mean values of $a_{ph}^*(440)$ in waters dominated by microphytoplankton (diatoms) were significantly lower than in waters with nanophytoplankton and picophytoplankton communities, indicating particle size (packaging effect) play a role in determining $a_{ph}^*(440)$ variability. The relationship between $a_{ph}^*(440)$ and chlorophyll-\textit{a} concentration was also not linear, indicating pigment composition also play a role in determining $a_{ph}^*(440)$ variability.
Variability of $a_{ph}^*(673)$ was less pronounced and only varied by a factor 2, i.e. $a_{ph}^*(673)$ ranged from 0.0100 to 0.0248 m$^2$ (mg chl)$^{-1}$ with average value of 0.0175 m$^2$ (mg chl)$^{-1}$ for the range of 0.06-12.25 mg m$^{-3}$ chlorophyll-$a$ concentration.
SUMMARY

The influence of nutrient inputs through riverine discharge and offshore river plume dispersal on the surface waters of the northeastern Gulf of Mexico (NEGOM) was studied by examining weekly winds, river discharge, satellite data (ocean color and altimetry) and in situ observations including chlorophyll-a concentration, absorption coefficients of colored dissolved organic matter (CDOM) and particulate materials from October 1997 to December 2000. Six major river-impacted regions, namely the Mississippi (R1), Mobile (R2), Escambia (R3), Choctawhatchee (R4), Apalachicola (R5), Suwannee (R6), plus one coastal region near Tampa Bay (R7), and three offshore regions (R8A, R8B, and R8C) were used to characterize the NEGOM. Nine two-week cruises were conducted in three different seasons between 1997 and 2000 onboard the Texas A&M University R/V Gyre: spring (April or May), summer (July and August), and fall (November).

Relatively high in situ chlorophyll-a concentrations (≥1 mg m⁻³) and CDOM absorptions (a₆₄₃≥0.1 m⁻¹, as high as a₆₄₃=0.38 m⁻¹ with salinity=25.77) were observed inshore, particularly near the major river mouths, and in spatially coherent Mississippi plumes that extended offshore and to the east-south-east (ESE) of NEGOM during the three consecutive summer seasons (1998, 1999, and 2000). The patterns of in situ chlorophyll-a concentration were also confirmed by the SeaWiFS images. The extended plume was observed as early as late May and lasted until the first week of September and
exhibit lengths >500 km southeast of the Mississippi delta and up to Florida Keys in August 1998. Offshore movement and transport of the Mississippi River water to the southeast was observed during late spring and summer every year of the study (1998, 1999, 2000).

River discharge appeared to be the dominant forcing factor in determining chlorophyll-\(a\) concentration variability off Mississippi, Mobile, Escambia, Choctawhatchee, Apalachicola and Suwannee regions. Surface chlorophyll-\(a\) concentration showed highly significant inverse relationship with salinity. Chlorophyll-\(a\) concentration peaks were largely tied to peaks in discharge of regional rivers. In some years, such as in 1998, there was clear evidence of wind-driven upwelling in a narrow strip the coast during late spring and summer in the Mobile, Escambia, and Choctawhatchee regions.

A strong interannual variability (up to a factor of four) in \textit{in situ} chlorophyll-\(a\) concentration was observed during winter to spring in 1998 compared to winter and spring in 1999 and 2000 off Escambia, Choctawhatchee, Apalachicola, Suwannee and Tampa Bay regions. Anomalously high (up to a factor of four) of chlorophyll-\(a\) concentration in winter and spring 1998 relative to the year of 1999 and 2000 in these regions was related to higher fresh water discharge during winter/fall of the 1997-1998 El Niño-Southern Oscillation event and anomalous coastal upwelling in spring 1998.

The comparison between \textit{in situ} and satellite derived chlorophyll-\(a\) concentrations showed that the SeaWiFS algorithm OC4v4 overestimated \textit{in situ} measurements up to about 300\% during summer cruises when relatively high CDOM absorptions were found offshore. Using MODIS algorithm (Carder \textit{et al.}, 1999), however, errors can be reduced
up to about 120% (about three times better than OC4v4). For chlorophyll-\(a\) concentration \(\leq 1.0 \text{ mg m}^{-3}\), both OC4v4 and the MODIS algorithm agreed well within the SeaWiFS project mission (\(\pm 35\%\) errors) during fall cruises. During spring and summer seasons when CDOM absorption was relatively high offshore, MODIS algorithm performed significantly better than the OC4v4. However, the errors produced by MODIS algorithm during spring and summer seasons are still higher than the SeaWiFS project mission (\(\pm 35\%\) errors) indicating CDOM plays a major role in resulting errors of satellite measurement, and therefore, more research is needed to properly separate effects such of those from CDOM in the algorithms.

The evidence supports earlier studies that suggest that crude estimates of salinity are possible from ocean color observations through the linear salinity-CDOM absorption coefficient relationship. Strong inverse correlations between the CDOM absorption coefficient at 443 nm (\(a_{g,443}\)) and CDOM fluorescence (330 nm excitation and 450 nm emission filters) were consistently observed (\(r^2>0.86\)). In general, \(a_{g,443}\) covaried linearly and inversely with salinity in the inshore areas during spring and fall cruises, indicating conservative mixing. Using all NEGOM data of fall 1998, the salinity-\(a_{g,443}\) relationship i.e., Salinity (S)=36.59-29.86*\(a_{g,443}\) (\(n=8771\), \(r^2=0.86\), 0.01\(\leq a_{g,443}\leq 0.52\), 16\(\leq S\leq 36\)) produced the lowest mean percentage errors of observed vs. predicted salinities (<3% errors, corresponding to <1.04 psu) for all other spring and fall seasons, therefore, this relationship may be useful to estimate salinity from satellite ocean color data. However, estimates with this relationship led to unacceptable errors in the summer (>10% errors in salinity estimates), due to less of a coherent relationship between \(a_g\) and salinity over the range of salinities observed, and the significant influence of phytoplankton in CDOM
production during summer seasons. Only within the river plumes in outer shelf and slope regions was the correlation somewhat more robust and similar to that seen in the inshore regions. Further testing using data from multiple years is needed to improve relationship between salinity and CDOM absorption coefficient in NEGOM region.

In most regions of inshore in NEGOM, there was no indication that a local increase of chlorophyll-\(a\) concentration led to increase CDOM during fall seasons. However, during spring and summer seasons, significant increases in CDOM pool associated with the increase of chlorophyll-\(a\) concentration were observed in coastal and offshore regions, indicating phytoplankton blooms were a significant source of CDOM pool. In the central NEGOM, it seemed that phytoplankton was also a significant source for CDOM formation during fall seasons. The increase of \textit{in situ} CDOM formation related to phytoplankton blooms ranged from 10\% to 100\%.

Chlorophyll-\(a\) concentration variability seemed to have a major influence on the variability of total particulate absorption coefficients where there was low or no fresh water impacted a region (salinity>34.5). Meanwhile, no clear correlation between chlorophyll-\(a\) concentration and total particulate absorption coefficients was seen where fresh water influence was significant (salinity\(\leq\)34.5). In general, however, CDOM absorption was higher than phytoplankton absorption by a factor of 3.

This study provided, for the first time, a first-order estimate of the spatial distribution of major phytoplankton groups in NEGOM. The spatial distributions of chlorophyll-\(a\) concentration and fucoxanthin pigment (biomarker for diatoms) seemed to correlate with spatial distributions of normalized phytoplankton absorption coefficients at 545 and 673 nm. Using microphytoplankton biomass proportion (BP\textsubscript{micro}) as an
independent variable, we were able to explain as much as 76% of the variance in the average normalized phytoplankton absorption coefficient of 545, 625, and 673 nm specifically during spring and fall seasons, indicating normalized phytoplankton absorption coefficient can be used to estimate biomass proportion of microphytoplankton (diatoms). Lower correlation, however, was observed during summer seasons due possibly to the high abundance of cyanobacteria (containing phycoerythro-bilin pigments) and diatoms (containing fucoxanthin pigment). Both these pigments enhance absorption at around 545 nm.

The absorption coefficient of phytoplankton at 440 nm [$a_{ph}(440)$] followed a power law relationship ($r^2=0.87-0.98$) with chlorophyll-$a$ concentration. Meanwhile, $a_{ph}(673)$ covaried linearly with chlorophyll-$a$ concentration ($r^2=0.94-0.99$). The variability of $a_{ph}^*(673)$ was very small (0.0100-0.0248 m$^2$ (mg chl)$^{-1}$ with average value of 0.0175 m$^2$ (mg chl)$^{-1}$ for the range of 0.06-12.25 mg m$^{-3}$ chlorophyll-$a$ concentration). The chlorophyll-specific absorption coefficient at 440 nm, $a_{ph}^*(440)$, varied by a factor of 7 (0.02-0.15 m$^2$ mg$^{-1}$ with chlorophyll-$a$ concentration range of 0.06-12.25 mg m$^{-3}$). This variability must be accounted for in algorithms determining chlorophyll-$a$ concentrations from $a_{ph}$ values derived from satellite data in order that chlorophyll retrievals be accurate. Lower values of $a_{ph}^*(440)$ (<0.06 m$^2$ mg$^{-1}$) were observed inshore particularly near the major rivers outflow. During summer, lower values of $a_{ph}^*(440)$ were also observed in the outer shelf and slope in the western NEGOM (west of 85°W) in low salinity waters of the Mississippi River plume. Higher values of $a_{ph}^*(440)$ (>0.1 m$^2$ mg$^{-1}$) were otherwise observed outside the river plumes in the outer shelf and slope, where lower chlorophyll-$a$
concentration occurred. There were no differences in the mean spectral phytoplankton absorption coefficients between spring and fall seasons, but these were different from those observed in the summer. The average value of $a_{ph}^*(440)$ in waters dominated by microphytoplankton (diatom) was significantly lower than in waters dominated by nanophytoplankton and picophytoplankton communities, suggesting particle size (packaging effect) plays a role in determining $a_{ph}^*(440)$ variability. The relationships between $a_{ph}^*(440)$ and chlorophyll-a concentration were non-linear, indicating pigment composition also plays a role in determining $a_{ph}^*(440)$ variability.
REFERENCES


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Golubev, Y., and Y. Hsueh, Low-frequency variability of surface currents on the northeastern Gulf of Mexico (NEGOM) shelf, submitted.


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Bisman Nababan received a Bachelor’s Degree in Agrometeorology from Bogor Agricultural University, Bogor, Indonesia in 1989. Starting in Fall 1989, he worked as a teaching assistant for Marine Meteorology and Introduction to Oceanography Laboratories at the Department of Fisheries and Marine Science, Bogor Agricultural University, Bogor, Indonesia. In 1990, he started as junior lecturer (tenure) at the University. He also involved in the development of Higher Education in Marine Science Project in Indonesia (ADB loans) from 1989 to 1993. In April 1994, he started his Master Program majoring in Coastal Zone Management at Nova Southeastern University, Dania, Florida and graduated with M.Sc. in 1998. During his masteral program, he also served as a teaching assistant for undergraduate program at the University. While finishing his masteral program, he started his Ph.D. program at the College of Marine Science, University of South Florida, St. Petersburg in Fall 1997.