Phytoplankton and Carbon Dynamics in the Estuarine-Coastal Waters of the Northern Gulf of Mexico from Field Data and Ocean Color Remote Sensing

Bingqing Liu

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PHYTOPLANKTON AND CARBON DYNAMICS IN THE ESTUARINE-COASTAL WATERS OF THE NORTHERN GULF OF MEXICO FROM FIELD DATA AND OCEAN COLOR REMOTE SENSING

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agriculture and Mechanical College in partial fulfilment of the requirements for the degree of Doctor of Philosophy in The Department of Oceanography and Coastal Sciences

by

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May 2020
ACKNOWLEDGEMENTS

For the past five years, I felt like it was the fastest time with longest nights of my life. I gained great knowledge in the study of oceanography and made amazing friends across the globe in science. I would acknowledge everyone who encourages and criticizes me to make me move forward.

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**ABSTRACT**

In this study, phytoplankton community and carbon dynamics were examined in the optically complex estuarine-coastal regions of the northern Gulf of Mexico (nGOM) from field and satellite ocean color observations. As part of this study, bio-optical ocean color algorithms for i) dissolved organic carbon (DOC), ii) phytoplankton pigment composition, iii) adaptive estimation of Chl a and iv) phytoplankton size fractions were developed to facilitate the study of biogeochemical cycling in the nGOM.

The phytoplankton based algorithms were applied to Sentinel 3A/B-OLCI ocean color data to assess phytoplankton community dynamics to extreme river discharge conditions as well as hurricanes in the nGOM. This study revealed that the effects of hurricanes on phytoplankton community dynamics were dependent on background nutrient conditions, as well as the intensity, track and translational speed of storms: 1) Strong flooding associated with Hurricane Harvey (2017) shifted the dominance of phytoplankton community in Galveston Bay from cyanobacteria and dinoflagellate to diatom and chlorophyte; 2) high levels of organic matter delivered from estuaries to shelf waters after Hurricane Michael (2018) fueled a red tide mixed with coccolithophore bloom in the nGoM; 3) the physical and chemical environment after hurricanes are favorable for the growth and dominance of coccolithophores in shelf waters. Further, microphytoplankton mainly controlled by freshwater inflows showed dominance in estuaries of the nGoM, with highest/lowest values observed in spring/fall. In comparison, phytoplankton size fraction (PSF) dynamics in the midshelf and offshore waters of the nGoM are strongly influenced by Loop Current (LC) expansion, and eddy shedding with highest picophytoplankton fraction observed in the warm waters of LC.

DOC dynamics was studied using an empirical algorithm that was developed and applied to multiple satellite sensors (Landsat 5 TM and MODIS-Aqua) to assess multi-decadal (1985-2012) DOC trends in Barataria Basin. The linkages between DOC and environmental variations were investigated. The relationships between satellite-derived DOC and land cover variations (1985–2011) derived from Landsat-5 TM supervised classification indicate soil loss in the salt marsh to be an important DOC source in the wetland-estuary system, and overall strong land use/land loss impact on the long-term DOC trends in the Barataria Basin.
CHAPTER 1. INTRODUCTION

Estuaries are transitional zones between the land and the sea, where the mixing of freshwater from rivers and streams with saline oceanic waters result in strong biogeochemical gradients (e.g., salinity, particulate and dissolved materials) along the freshwater-marine end member continuum (Bianchi et al., 2007; Mannino and Harvey, 2004). Estuarine-coastal ecosystems are some of most biogeochemically active zones (Figure 1.1), where are stressed by both natural processes and human activities. The bio-geochemical responses and linkages to environmental variabilities in estuarine-coastal waters are thus far more complex compared to open ocean. For example, coastal zones receive large mounts of freshwater from river discharge and ground water, that frequently fuels eutrophication, algae blooms and hypoxia events. Also, the frequent storms and hurricanes that impact the estuarine-coastal regions cause extreme flooding, storm surges or coastline erosion that often adversely affect their ecosystems. More importantly, climate change which has been argued will increase the frequency and intensity of hurricanes, have potential for longer term impacts on the coastal systems. These scenarios are largely applicable to the U.S. Gulf of Mexico (GoM), a semi-enclosed marginal sea of the Atlantic Ocean, largely surrounded by the U.S. continent with a coastline stretching approximately 2624 km (EPA-843-R-10-005D). The GoM provides a valuable case study to investigate the interconnected natural-human interactions on estuarine-coastal ecosystem diversity and functions. The landscape variations along the U.S. GoM coastline has been characterized by changes due to broad-scale, long-term climatic processes (e.g., coastline erosion, and coastal subsidence) as well as short-term meteorological events (e.g., hurricanes). Coastal development and restorations from human activities (e.g., levees and canals, oil and gas exploration and river diversions) exert increased stresses on the U.S. GoM ecosystem, which is further strengthened by climatic factors (e.g., sea level rise and intensifying hurricanes).

Figure 1.1. A modified diagram from Lu et al., (2018) illustrates the complex effects of the interconnected natural-human-climate interactions on estuarine-coastal ecosystem functions.

1.1. The U.S. Gulf Coast

The GoM is bounded on the Gulf Coast to the north by the coastal states of Texas, Louisiana, Mississippi, Alabama, and Florida (Figure 1.2). The western part of the Gulf Coast (west of 94° longitude) refers to the Texas coastline (purple line; Figure 1.2). The central part
of the Gulf Coast (between 94° to 89° longitude) comprises predominantly the Louisiana coast and west part of Mississippi Coast (green line; Figure 1.2). The eastern part of the Gulf Coast, (~89° to 83° longitude) consists of the eastern Mississippi, Alabama, and Florida coastlines (orange line; Figure 1.2). In this study, the northern U.S. Gulf of Mexico (nGoM) is defined as the region between Galveston Bay, Texas, to the Suwannee River mouth, Florida (Board et al., 2018). The coastline along the nGoM encompasses a variety of coastal landforms, including barrier islands and peninsulas, marshlands, cheniers, estuaries and bays, all of which respond distinctly to the natural, climatic and anthropogenic stressors. Many well-known estuarine systems (e.g., Galveston Bay, Mobile Bay, Apalachicola Bay, and Tampa Bay) along the U.S. Gulf Coast (EPA, 1999) are drowned river valleys, some of which are still connected to rivers that empty into the Gulf.

Figure 1.2. Geography-definition of U.S. Gulf Coast refered to Board (2018), with purple, green and orange representing western, central and eastern Gulf Coast, respectively.

1.1.1. Physical Processes in the Gulf of Mexico (GoM)

Physical processes in the GoM are influenced by a complex combination of factors originating in the ocean, atmosphere, and land. The circulation system in the pelagic zone of the GoM is dominated by the Loop Current (LC), which are the warm waters flowing from the Caribbean Sea that transport heat and moisture northward to the Gulf Coast. The LC, commonly observed to bulge out in the nGoM, episodically sheds warm core eddies that travel slowly (~3.5 km/day) west-southwestward towards Texas or Mexico), often colliding with the continental shelf slope (Zeng et al., 2015). The large warm core eddies along with the simultaneous extension and retraction of the LC, significantly influences the GoM hydrodynamics and biogeochemistry (Oey et al., 2005). Circulation on the Louisiana and Texas Shelf (LATEX), in contrast, is mainly affected by the regional wind regime and freshwater discharge, and less by the slope eddy field (Walker, 2011). The area adjacent to the mouth of the Mississippi River (e.g., Southwest Pass), which injects freshwater into the deep shelf region generally shows strong stratification with several meters of freshwater overlying saline waters (Kolker et al., 2014). Subtropical to tropical climate dominates the Gulf, with generally warm temperatures, and frequent thunderstorms, especially in summer (Kumpf et al., 1999). Further, tropical storms and hurricanes are prevalent starting from late summer to fall at an average rate of 3-4 hurricanes per decade (Doyle, 2009). Loop Current eddies (LCEs) also tend to intensify hurricanes crossing their paths in the GoM by providing a vast reservoir of heat energy, which
can significantly influence the physical-biogeochemical processes in the GoM (Trenberth and and Fasullo 2007; Miner et al., 2009). In late fall, winter and early spring seasons (November-March), the nGoM is frequently exposed to cold front events, which strongly influence local processes (e.g., resuspension and transport) from estuaries to coastal oceans (Roberts et al., 1989; Allison et al., 2000).

1.1.2. Episodic Flooding from Meteorological Events

The episodic riverine flood events along with normal discharge from rivers contribute ~860 km$^3$ freshwater per year (Board, 2018). The Mississippi River is the primary source of low-salinity waters to the Gulf, which has an annual mean discharge of over 534 km$^3$, almost double the neighboring Atchafalaya River (~238 km$^3$) (Dunn, 1996). The remaining freshwater sources are the Mobile (~60 km$^3$), and Apalachicola (~20.5 km$^3$) Rivers (Allison et al., 2012). Hurricane landfall is another significant contributor to the riverine flooding events due to the strong precipitation and storm surges. For example, a total of 8 out of 10 most severe U.S. hurricanes have made landfall along the Gulf Coast (Table 1.1).

<table>
<thead>
<tr>
<th>Rank</th>
<th>Tropical Cyclone</th>
<th>Category</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Katrina (southeast Florida, Louisiana, Mississippi)</td>
<td>3</td>
<td>2005</td>
</tr>
<tr>
<td>1</td>
<td>Harvey (Texas, Louisiana)</td>
<td>4</td>
<td>2017</td>
</tr>
<tr>
<td>3</td>
<td>Maria (Puerto Rico, U.S. Virgin Islands)</td>
<td>4</td>
<td>2017</td>
</tr>
<tr>
<td>4</td>
<td>Sandy (Mid-Atlantic &amp; northeast United States)</td>
<td>1</td>
<td>2012</td>
</tr>
<tr>
<td>5</td>
<td>Irma (Florida)</td>
<td>4</td>
<td>2017</td>
</tr>
<tr>
<td>6</td>
<td>Ike (Texas, Louisiana)</td>
<td>2</td>
<td>2008</td>
</tr>
<tr>
<td>7</td>
<td>Andrew (southeast Florida, Louisiana)</td>
<td>5</td>
<td>1992</td>
</tr>
<tr>
<td>8</td>
<td>Ivan (Alabama, northwest Florida)</td>
<td>3</td>
<td>2004</td>
</tr>
<tr>
<td>9</td>
<td>Wilma (south Florida)</td>
<td>3</td>
<td>2005</td>
</tr>
<tr>
<td>10</td>
<td>Rita (southwest Louisiana, north Texas)</td>
<td>3</td>
<td>2005</td>
</tr>
</tbody>
</table>

Hurricane Katrina (2005) which made landfall along the Louisiana coast, was one of the largest and most destructive storms in the United States that significantly altered the coastline of Louisiana and Mississippi (Day et al., 2011). For example, the region adjacent to the Barataria Basin lost 1.03×10$^8$ m$^2$ within a day, more than what was lost during the entire previous decade (Grenzeback and Lukmann, 2007). In 2004, Hurricane Ivan made landfall near Gulf Shores leading to large storm surges, beach erosions, and overwashing of roadways from the Florida panhandle westward to Mobile Bay, Alabama (Park et al., 2007). Flooding in inland areas is generally determined by the strength of storm surge and freshwater drainage caused by hurricanes. For example, Hurricane Harvey (2017) which made landfall twice on the Texas coast, also caused large scale inundation in some coastal areas due to storm surge; however, the extensive flooding in the Houston metropolitan area was largely due to unprecendented precipitation (~ 1500 mm) within a four-day period following the hurricane landfall.

1.1.3. Coastal Development and Climatic Processes

The Gulf Coast has undergone dramatic changes in its hydrology and landscape due to human intervention (Jackson et al., 2002). For example, the construction of levees along the Mississippi River has decreased the Mississippi River sediment-rich freshwater input to Barataria Basin; this has induced a severe imbalance between sediment deposition and subsidence leading to significant wetland loss. Construction of navigation channels and oil and gas exploration, has also contributed to rapid degradation of healthy wetlands and increased
salt water intrusion (Penland et al., 2000). Furthermore, fragmentation of natural forests and wetlands due to farmlands and urban areas (Liu et al., 2019a) has also increased anthropogenic-derived inputs including pollutants and nutrient loading to coastal waters. This can lead to algal blooms, hypoxia and other losses of marine life in coastal waters (Cloern, 2001). With the Gulf Coast on the front line of climate change, altered precipitation, river discharge patterns and sea level change could significantly impact the salinity of coastal waters, with a cascading effect on structuring the marine food web (Mouw et al., 2016) that could alter the magnitude of carbon fixation and export into ocean’s interior. Further, changes in coastal acidification can impede the growth of calcifying coccolithophores and bleach coral reefs (Lemasson et al., 2017), which are abundant in the coastal zones along the Gulf Coast. Increased frequency of extreme weather events in coastal areas could may also potentially alter the coastal ecosystems dynamics (Chen et al., 2017). Coupled with increases in sea level rise and insufficient sedimentation, there is increased risk of marshes succumbing to sea level rise in many areas along the Gulf Coast (Weston, 2014).

1.2. Characterizing Coastal Biogeochemistry from Optical Properties

Light is important for the ecology and biogeochemical cycling in the euphotic zone because that many chemical compounds are produced and decomposed via photochemical reactions. The optical properties are determined by the amount and type of optically-active constituents present in the water. Optically important constituents include colored dissolved organic matter (CDOM), phytoplankton and sediments (Werdell et al., 2018), which are also linked to biogeochemical properties of the ocean. There is an increasing interest in quantifying the size structure and composition of biogeochemical stocks (e.g., sediment and phytoplankton) from optical measurements (Oubelkheir et al., 2005). Characterizing spatiotemporal variations of light field in the ocean influenced by physical processes is fundamental to understand many optical-biogeochemical responses in the aquatic environment and vice versa (Dickey and Falkowski, 2002). Particularly in estuarine-coastal zones, the natural and anthropogenic processes together modulate the terrestrial input of dissolved and particulate matter, creating optically-complex waters which are highly variable in space and time with important ecological implications. For example, the backscattering properties can provide information on particle size distribution and composition (Zhang and Gray, 2015); the absorption properties have been used to derive information on phytoplankton taxonomy (Moisan et al., 2017) and size fractions (Ciotti et al., 2002). Thus, optical properties provide informative as well as specific perspective to understand carbon cycling, phytoplankton community dynamics, biological pump and also the aquatic food web structure.

1.2.1. Concepts in Optical Oceanography

The optical oceanography explores how the optically active constituents (e.g., CDOM and different phytoplankton groups) impact the light field in the water, and in turn, how the field optics and remote sensing techniques can facilitate the study of oceanography. The optical properties of the water include inherent optical properties (IOPs) and apparent optical properties (AOPs). IOPs are determined only by the water constituents themselves and the wavelength of light, which refer to the absorption (a) and scattering (b) properties of water. Variations in light absorption and scattering can be mainly attributed to four substances: pure seawater (w), phytoplankton (phy), non-algal particles (NAP), and CDOM. Therefore, The total backscattering coefficient \( b_{\text{bt}} \) is comprised of water \( b_{\text{bw}} \) and particles including both organic and inorganic particles \( b_{\text{bp}} \), while the total absorption coefficients \( a_{\text{total}} \) can be further separated into four sub-constituents (Roesler and Perry, 1995) as indicated by:

\[
b_{\text{b}} = b_{\text{bw}} + b_{\text{bp}}; \quad a_{\text{total}} = a_{\text{w}} + a_{\text{phy}} + a_{\text{CDOM}} + a_{\text{NAP}}
\]  (1.1)
Absorption from pure sea water (blue line; Figure 1.3) is much stronger in the red-NIR wavelength compared to the short wavelength in the blue-green range and co-varies with temperature and salinity (Röttgers, 2016). The absorption spectra of NAP (pink line) and CDOM (yellow) show a similar pattern in negative exponential shape; the slope of spectra can be estimated by non-linear regression:

\[
a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(440) \times \exp^{-S_{\text{CDOM}} \times (\lambda - 440)}
\]

\[
a_{\text{NAP}}(\lambda) = a_{\text{NAP}}(440) \times \exp^{-S_{\text{NAP}} \times (\lambda - 440)}
\]

where \( S_{\text{CDOM}} \) and \( S_{\text{NAP}} \) are the exponential slope for NAP and CDOM. Roesler et al., (1989) reported that \( S_{\text{CDOM}} \) ranges from 0.006 to 0.013 nm \(^{-1}\), which is statistically flatter than the \( S_{\text{CDOM}} \). Phytoplankton absorption \( a_{\text{phy}} \) (green line; Figure 1.3) typically have two absorption peaks, which are in blue (~440 nm) and red (~674 nm) wavelengths, respectively. However, phytoplankton can display different colors in the bloom waters (e.g., red tide, and brown tide; Figure 1.3c) because the pigment composition and concentration in different phytoplankton groups are distinct. Phytoplankton pigment can be classified in 3 clusters, namely, chlorophylls, carotenoids and phytobilipigments and each pigment has its unique spectrum. Chlorophylls dominate phytoplankton absorption spectra via those two apparent absorption peaks in the blue and red wavelength. Carotenoids generally show single-peaked absorption spectra in the range of ~ 475-525 nm for photosynthetic carotenoids and ~450-510 nm for photoprotective pigments. Phycobilipigments include phycocyanin and phycoerythrin, which typically show strongest absorption in the yellow to orange range and display single absorption peak at ~550 and 620 nm, respectively. Some of pigments are taxa-specific and have been considered as bio-marker pigments: e.g., fucoxanthin for diatoms, peridinin for certain dinoflagellates, alloxaanthin for cryptophytes, zeaxanthin for prokaryotes (e.g. cyanobacteria), and the degradation products of Chl a, namely, divinyl Chl a and divinyl-Chl b for prochlorophyte (Jeffrey and Vest, 1997). The unique absorption spectra of pigments contribute to a wide range of colors to phytoplankton (Figure 1.3c) and diverse spectral shapes to the respective absorption coefficients (Figure 1.3b).

Apparent optical properties (AOPs), such as radiance and irradiance are determined by both IOPs and the geometry of the ambient light field. It was more difficult to directly measure IOPs due to instrument limitations compared to radiometric variables in earlier optical oceanography, which led to the use of the easily measured AOPs to derive the IOPs in the water. Radiance, \( L(\theta, \phi, \lambda) \), one of the most fundamental AOPs, is defined as the radiant flux
at a point with a given direction (described as per solid angle, sr$^{-1}$) in per unit area perpendicular to the light propagating direction ($\mu W \text{ cm}^{-2} \text{ sr}^{-1} \text{ nm}^{-1}$) (Dickey et al., 2006). Downwelling irradiance $E_d(\lambda)$, which is another important AOP, refers to the downwelling radiant light flux per unit area impinging on the top of the surface area ($\mu W \text{ cm}^{-2} \text{ nm}^{-1}$) (Kirk, 1994). Conversely, upwelling irradiance, $E_u(\lambda)$, is the irradiance of an upwelling light measured on the bottom interface of the sea surface. The most practically-used AOPs are irradiance reflectance, $R(\lambda) = E_u(\lambda)/E_d(\lambda)$, which explains the amount of radiance traveling downward into the water column that can be reflected upward into any direction, and the directional component, radiance reflectance, $r_{rs}(\lambda) = L_u(\lambda)/E_d(\lambda)$ (sr$^{-1}$; Mobley et al., 2005). More recently, remote sensing reflectance $R_{rs}(\lambda) = L_w(\lambda)/E_d(\lambda)$, has been considered as the AOP of choice for ocean color remote sensing (O’Reilly et al., 1998). The upwelling radiance $L_u(\lambda)$ is the sum of water leaving radiance $L_w(\lambda)$ and the downward radiance and skylight that is reflected upward by the sea surface, $L_r(\lambda)$. In addition, the $L_w(\lambda)$ can not be measured directly and is generally obtained from (Mobley et al., 2010):

$$L_w(\lambda) = L_u(\lambda) - L_r(\lambda)$$

(1.4)

The IOPs and AOPs can be connected through the numerical solution of radiative transfer equation (RTE) (Gordon et al., 1975). A fundamental relationship that links $r_{rs}$ and IOPs was expressed using a quadratic function developed as (Gordon et al., 1988):

$$r_{rs} = g_1 * u(\lambda) + g_2 * u(\lambda)^2; \quad u(\lambda) = \frac{b_b}{a_{total}+b_b}$$

(1.5)

where, the parameters $g_1$ and $g_2$ are diverse coefficients determined for estuarine, coastal and open ocean waters (Joshi and D’Sa, 2018; Lee et al., 2002). This relationship promoted the development of inversion models that derive IOPs from either in-situ or remotely-sensed reflectance (Morel, 1988; Garver and Siegel, 1997; Barnard et al., 1999; Loisel et al., 2001; Morel and Maritorena, 2001; Lee et al., 2002; Roesler and Boss, 2003). Once the IOPs are retrieved, the types and concentration of the water constituents can be related to the spectral IOPs by using other relationships linking IOPs to the biogeochemical variables (Sosik, 2008; D’Sa et al., 2018).

1.2.2. Measurements of Optical Properties

A number of advanced optical sensors and oceanographic platforms (moorings, autonomous vehicles and earth-orbiting satellites) have been utilized to obtain diverse optical parameters at high spatiotemporal resolutions. Measurements of IOPs can be either done in situ or in the laboratory. Over the past decade, one of the most commonly used instruments for field IOPs measurements is the spectral absorption-attenuation meter (e.g., AC-9), which enables the profiles of absorption ($a$) and attenuation coefficients ($c$) to be obtained for both particulate and dissolved (using filters) material in the water column (Moore et al., 1992). The AC meter has two tubes that includes an attenuation coefficient tube (c tube) and an absorption coefficient tube (a tube). The scattering coefficient (b) can be estimated from the AC meter data by simply subtracting a from c. Further, $a_{phy}$, $a_{CDOM}$, and $a_{NAP}$ can be decomposed from the ac-meter measured spectra (Bricaud and Stramski, 1990; Roesler and Boss, 2003). Hyperspectral measurements of the absorption coefficient for optically-active constituents can be also obtained from in-situ collected water samples and filters via laboratory spectroscopic analysis using a spectrophotometer. Water samples for CDOM are required to be filtered immediately through 0.2 µm pore size membrane filters under low vacuum. The filtered samples are then transferred to a cuvettes (1 or 10 cm depending on the CDOM concentration in the samples) and then spectrophotometrically scanned onboard or in the laboratory in a spectrophotometer.
(generally in UV-VIS range) to obtain the Absorbance of CDOM ($A_{\text{CDOM}}$). Then the absorption coefficients of CDOM ($a_{\text{CDOM}}$) is calculated using the following equation:

$$a_{\text{CDOM}}(\lambda) = 2.303 \times \frac{A_{\text{CDOM}}(\lambda)}{L}$$  \hspace{1cm} (1.6)

where $L$ is the path length in meters. The absorption of particulate matter can also be spectrophotometrically measured by filter pads. The Quantitative Filter Technique (QFT), with 0.7-µm glass fiber filters (Whatman GF/F) is usually used to measure the absorbance of particles ($A_{\text{total}}$) and non-algal particles ($A_{\text{NAP}}$). The absorption coefficients of particles ($a_{\text{total}}$), $a_{\text{NAP}}(\lambda)$ and $a_{\text{phy}}(\lambda)$ are calculated using the following equations:

$$a_X(\lambda) = 2.303 \times \frac{A_X(\lambda)}{V_{\text{filtered}}/S_{\text{filter}}}$$  \hspace{1cm} (1.7)

$$a_{\text{phy}}(\lambda) = a_{\text{total}} - a_{\text{NAP}}$$  \hspace{1cm} (1.8)

where $X$ can be either total or NAP, $V_{\text{filtered}}$ is the filtered volume of sample, $S_{\text{filter}}$ is the area of filter pads, and the path length correction for filter pad are different depending on the modes selected, including Transmittance Mode (T-Mode; Roesler et al., 2018), Transmittance and Reflectance Mode (T-R Mode; Cleveland and Weidemann, 1993) and Inside an Integrating Sphere (IS Mode; Stramski et al., 2015).

The above-water radiometric measurements of AOPs can be obtained from shipboard, aircraft, or satellite platforms by measuring the radiance entering the aperture of an optical sensor via diverse scanning mechanisms (Yoder et al., 2001). Satellite remote sensing with its synoptic coverage over broad regions has provided efficient means to assess optical measurements on regional and global scales. For these radiometric measurements, significant contamination from surface sunglint due to specular reflection, bubbles in the air-sea interface, and atmosphere scattering must be accounted for in order to extract accurate water leaving radiance $L_{\text{w}}(\lambda)$ at the sea surface. In addition, downwelling irradiance $E_d(\lambda)$ at the sea surface is also required to be measured to generate remote sensing reflectance $R_{\text{rs}}(\lambda)$, which is one of the most quantitatively meaningful proxy associated with the concentrations of biogeochemical quantities and their dynamics.

1.2.3. Remote Sensing of Biogeochemical Variables

The Coastal Zone Color Scanner (CZCS) was the first satellite sensor to provide ocean color data from 1978 to 1986. Based on the potential of the CZCS, an international effort was made to increase the number of ocean color satellites (Table 1.2; International Ocean Color Coordinating Group (IOCCG)). Ocean color sensors together with some multispectral sensors primarily designed for land applications (high spatial resolution) have been widely used for monitoring a number of biogeochemical variables in oceanic and coastal waters (D'Sa et al., 2018; D'Sa et al., 2019; Doxaran et al., 2006; Kutser et al., 2005; Miller and McKee, 2004; Olmanson et al., 2008; Liu et al., 2019b; Tehrani et al., 2013; Brezonik et al., 2015).

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Country</th>
<th>Swath (km)</th>
<th>Spatial-Resolution (m)</th>
<th>Number of Bands</th>
<th>Spectral coverage (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOCI- COMS</td>
<td>Korea</td>
<td>2500</td>
<td>500</td>
<td>8</td>
<td>400-865</td>
</tr>
<tr>
<td>MODIS-Aqua</td>
<td>USA</td>
<td>2330</td>
<td>250/500/1000</td>
<td>36</td>
<td>405-14385</td>
</tr>
<tr>
<td>MODIS-Terra</td>
<td>USA</td>
<td>2330</td>
<td>250/500/1000</td>
<td>36</td>
<td>405-14385</td>
</tr>
<tr>
<td>MSI-Sentinel 2 A/B</td>
<td>ESA</td>
<td>290</td>
<td>10/20/60</td>
<td>13</td>
<td>442-2186</td>
</tr>
<tr>
<td>OCM-2 Oceansat 2</td>
<td>India</td>
<td>1420</td>
<td>360/4000</td>
<td>8</td>
<td>400-900</td>
</tr>
<tr>
<td>OLCI Sentinel 3-A/B</td>
<td>ESA</td>
<td>1270</td>
<td>300/1200</td>
<td>21</td>
<td>400-1020</td>
</tr>
<tr>
<td>SGLI-GCOM-C</td>
<td>Japan</td>
<td>1150-1400</td>
<td>250/1000</td>
<td>19</td>
<td>375-12500</td>
</tr>
</tbody>
</table>
A prerequisite for accurately mapping biogeochemical properties counts on the performance and improvement of the algorithms utilized to invert the ocean color signals from satellite sensors. The satellite algorithms can be divided into two classes: i) Derive the concentrations of water constituents from IOPs, based on diverse empirical relationships (e.g., $a_{\text{CDOM}}(412)-\text{DOC}$, $b_{\text{bp}}-\text{SPM}$, and $a_{\text{phy}}(440)-\text{Chl} \ a$) as reported in previous research (D’Sa et al., 2003; 2006; Liu et al., 2019b; Lutz et al., 1996; Vadosek et al., 1997; Babin et al., 2003); the IOPs in turn can be inferred from AOP inversion (Morel, 1988; Garver and Siegel, 1997; Barnard et al., 1999; Loisel et al., 2001; Morel and Maritorena, 2001; Lee et al., 2002; Roesler and Boss, 2003). Additional information, such as phytoplankton functional types (PFTs) and size fractions can also be retrieved from $a_{\text{phy}}$ by spectral decomposition (Bricaud et al., 2004; Ciotti et al., 2002). ii) Studies have also been documented algorithms to retrieve constituent quantities and characteristics directly from radiometric observations of AOPs including diverse phytoplankton pigments (Pan et al., 2011), algal blooms (Carvalho et al., 2011), suspended particulate matter concentrations (D’Sa et al., 2007), dissolved organic carbon dynamics (Liu et al., 2019b), and primary production (Uitz et al., 2010).

### 1.3. Motivations and Objectives

In Case I clear oceanic waters, ocean color remote sensing algorithms for optical-biogeochemical properties generally show reliable and robust performance (Mobley et al., 2004), however, most of these algorithms are not suitable for optically-complex waters. Thus, regional tuning and algorithm improvements are essential for estuarine-coastal waters such as the nGoM, where the waters display extremely complex nature with high turbidity, CDOM and frequent algal blooms. For example, the standard Chl a algorithm based on blue/green band ratio (e.g., OC4E) and Neural-Network (NN) generally fail and tend to significantly overestimate/underestimate Chl a concentrations in some estuaries due to the strong influences from riverine input of sediments as well as terrestrial input of CDOM. (Liu et al., 2019b). Thus, our ability to monitor the estuarine-coastal dynamics from space has remained limited, which is mainly attributed to the difficulty in applying the standard ocean color algorithms in this turbid aquatic environment for characterizing biogeochemical constituents; especially challenging, is extracting information associated with phytoplankton community structure because the absorption of phytoplankton photosynthetic pigments show less imprints on the $L_w(\lambda)$ relative to suspended sediments and CDOM. To overcome these difficulties and to better understand the optical-biogeochemical properties of waters in the nGoM, this study utilizes novel satellite algorithms in combination with field data obtained pre- and post-meteorologic/hydrographic conditions within the nGoM. These field and in-situ datasets matched up with satellite data can be further used for the validation of the bio-optical remote sensing algorithms to facilitate the establishment of more practical and accurate monitoring of the optical-biogeochemical parameters in the nGoM.

The objectives of this dissertation are (1) the development and validation of ocean color remote sensing algorithms for the optically-complex estuarine-coastal waters in the nGoM; (2) the estimation of optical- biogeochemical constituents from satellite-derived optical properties; (3) evaluating the performance of ocean remote sensing measurements and the long-term trends of derived biogeochemical parameters; (4) interpreting the satellite products of surface layer biogeochemical constituent generated from Landsat 5 TM, aqua-MODIS, and sentinel 3-OLCI observations to understand the biogeochemical responses and linkages to coupled natural-anthropogenic processes in the nGoM.
1.4. Outline

This dissertation is organized as follows: Chapter 2 focuses on the analysis of historical Landsat 5-TM and aqua-MODIS satellite data, and development of bio-optical algorithms to generate dissolved organic carbon (DOC) distributions and to evaluate the long-term trend of DOC in response to physical processes (landscape variations, hurricanes and riverine flooding) in Barataria Basin. Chapter 3 proposes a non-negative least square (NNLS) bio-optical algorithm for mapping phytoplankton pigments from Sentinel-3A OLCI ocean color observations; results are further used to explore the floodwater impact on Galveston Bay (GB) phytoplankton taxonomy, pigment composition and photo-physiological state following Hurricane Harvey. Chapter 4 presents the successful application of NNLS bio-optical algorithm originally developed for GB to detect dominant species of a large-scale phytoplankton bloom in shelf waters adjacent to Apalachicola Bay after Hurricane Michael. Chapter 5 proposes an adaptive Chl a algorithm and further another bio-optical algorithm for phytoplankton size fractions (PSFs) to investage the coupling between physical processes and phytoplankton community dynamics in time scales of days to years in the nGoM. The research areas along with the methods of field- and laboratory-based sample analysis for the development of bio-optical algorithms for ocean color satellite are introduced in each of the chapters. Chapter 6 summarizes the major contribution and findings of this dissertation research with a discussion on significance and future improvements in monitoring optical-biogeochemical parameters in the nGoM from ocean color remote sensing.
CHAPTER 2. MULTI-DECADAL TRENDS AND INFLUENCES ON DISSOLVED ORGANIC CARBON DISTRIBUTION IN THE BARATARIA BASIN, LOUISIANA FROM IN-SITU AND LANDSAT/MODIS OBSERVATIONS

2.1. Introduction

The cycling of dissolved organic matter (DOM) and its major fraction—dissolved organic carbon (DOC) in an estuarine system is governed by multiple terrigenous sources and complex physical, photochemical, and biological processes (Bauer and Bianchi, 2011; Bauer et al., 2013; Miller and Moran, 1997). It is well known that terrestrially derived DOM is delivered to estuaries mainly through the rivers (Bianchi et al., 2007; Butman et al., 2016; D’Sa and DiMarco, 2009). Typically, estuaries are flanked by highly productive marshes that potentially leach DOM to estuaries and coastal oceans. Previous studies reported that most Atlantic and Gulf coast marshes in the U.S. have been considered as critical DOM sources to the adjacent shelf waters, likely due to water movement through the marshes washing off decaying detritus and soil accumulated carbon to estuarine waters (Bianchi et al., 2011b; Moran and Hodson, 1994; Peterson et al., 1994; Tzortziou et al., 2008). These traditional DOC sources have been significantly altered by several natural processes (e.g., climate change, meteorological events, wetland erosion) and anthropogenic activities (e.g., modifications to the land cover, land-use, and nutrient input), that eventually affect the magnitude, seasonal and annual variations, and long-term trends of DOC fluxes to ocean systems (Wilson and Xenopoulos, 2008; Tzortziou et al., 2015; Ren et al., 2016). This is likely the current status of the northern Gulf of Mexico (nGOM), where DOM is delivered not only from the Mississippi River (MR) but also potentially leached from over three million hectares of marshes (Bianchi et al., 2011b; Das et al., 2011). In addition, many estuarine-coastal areas of nGOM are now experiencing significant wetland loss and variations in land cover type, which are important factors influencing the biogeochemical processes of aquatic ecosystems (e.g., carbon cycling). The Barataria Basin (Figure 2.1a) is an example of such a dynamic wetland-estuary system (80 km to the west of MR delta) that is undergoing constant landscape change due to the combined effects of geological and man-made processes (Turner, 1997). Estuaries are known to deliver appreciable amounts of carbon to the Gulf waters (Feijtel et al., 1985), however, uncertainties exist due to the complex interactions between DOC and the ambient environment (natural and anthropogenic factors) in estuarine systems like the Barataria Basin. Furthermore, due to spatiotemporally-limited field observations of land-use/land-cover variations and corresponding in-situ DOC, it is difficult to resolve long-term influences of land variations on carbon cycling.

Given the important role of DOC in aquatic food web, biogeochemical cycles and climate change, it is essential to investigate the effects of natural and anthropogenic disturbance on DOC abundance at least from a regional perspective over various time scales - a task that cannot be achieved without the knowledge of DOC spatiotemporal distributions. Satellite remote sensing with its synoptic coverage over broad regions has provided efficient means to assess DOC abundance at high spatiotemporal resolution and revolutionized our understanding.

of long-term carbon dynamics in aquatic environments on regional and global scales. Although satellite sensors do not measure DOC directly, optical properties (absorption coefficients, spectral slope and fluorescence) of the colored part of the dissolved organic matter (CDOM) is an useful optical proxy for in-situ and remotely sensed estimates of DOC abundance at various spatial and temporal scales (Cao et al., 2018; D'Sa and Miller, 2003; Singh et al., 2010; D'Sa et al., 2014a; Fichot and Benner, 2012). Thus, different empirical algorithms (band ratios) have been developed to derive CDOM absorption coefficients at a specific wavelength (\( a_{\text{CDOM}} \)) for ocean color sensors, such as SeaWiFS (D'Sa et al., 2006; D'Sa et al., 2002; D'Sa, 2008), MODIS-Aqua (Mannino et al. 2014), VIIRS-NPP (Joshi et al. 2017), MERIS-Envisat (Tehrani et al., 2013) and Sentinel 3 OLCI (Toming et al., 2017), as also for land application sensors such as Landsat-5 TM and Landsat-8 OLI (Brezonik et al., 2005; Joshi and D'Sa, 2015; Kutser et al., 2016). However, for the relatively smaller waterbodies (e.g., estuaries, bays and lakes), the medium spatial resolution (250 m) MODIS data could provide more pixels and thus, allow better assessment of surface water features adjacent to the marsh fringes, shorelines and barrier islands (Miller and McKee, 2004); in addition, together with its relatively wider swath, nearly daily coverage and good sensitivity, MODIS meets the requirements to monitor ecosystem evolution at finer spatiotemporal resolution compared to other ocean color sensors. The availability of high spatial resolution (30 m in visible-NIR band) Landsat 5 TM data since 1985, can further provide valuable historical perspective to examine the variability and distribution of materials in coastal-estuarine waters. Better spatiotemporal resolution of satellite sensors could thus improve the accuracy of ag estimates, which is also crucial for remote sensing retrieval of DOC. However, relationships derived from empirical algorithms might only be suitable for the parameter within a specific time period due to limited field observations. These algorithms could thus be sensitive to alterations in the source and composition of DOM induced by highly dynamic estuarine environments (Zhu et al., 2014). Another key issue is that the ag-DOC relationships in river- and marsh-dominated estuarine waters generally exhibit seasonal and spatial variations due to complex sources and diverse degradation processes that occur in estuarine waters (Del Castillo and Miller, 2008; Joshi et al., 2017; Spencer et al., 2012).

Detection of dominant environmental forcing with optimized empirical ocean color algorithms under different environmental conditions are essential for achieving more accurate quantification of ag and DOC from space-based remote sensing, especially in optically complex coastal waters. In this study, both field and Landsat-5 TM/MODIS-Aqua match-ups acquired in Barataria Basin (Louisiana, USA) over different seasons between 2007–2012 are used to: (1) develop CDOM empirical algorithms more broadly applicable across significantly different hydrological/meteorological conditions in the estuary, (2) achieve long-term observations of the DOC concentrations (1985-2012) at a high spatiotemporal resolution of Landsat-5 TM and MODIS-Aqua, (3) investigate spatiotemporal variations in DOC associated with seasonal hydrological and meteorological events, and (4) assess the long-term trends of DOC in response to landscape dynamics in the Barataria Basin.

2.2. Data and Methods

2.2.1. Study Area

Barataria Basin (~4400 km²), located between the MR and the Bayou Lafourche (an abandoned river channel) in Southeast Louisiana, USA and south of New Orleans, is one of the most productive estuary-wetland systems in the nGOM (LACOAST, 2005) (Figure 2.1). The constructed levees along the MR and the closure of Bayou Lafourche during 1930s-40s significantly reduced freshwater and riverine sediment input to the Barataria Basin (Kesel,
As a result, the lower basin experienced critical wetland loss due to sediment and nutrient deprivation coupled with an increase in salt-water intrusion (Turner, 1997). The Davis Pond Freshwater Diversion (DPFD) with a maximum capacity of about 300 m$^3$s$^{-1}$ was made operational in 2002 to reintroduce sediment-laden MR water into the basin to slow wetland loss and limit salinity intrusion (Allison and Meselhe, 2010). Regions within the basin have been identified as saltwater marsh, brackish-intermediate marsh and freshwater marsh based on well-defined vegetative marsh units associated with different substrate types and salinity (Feijtel, 1985). Spanning from northwest to southeast along a fresh-marine salinity gradient, the upper low salinity section (0–2 psu) of the basin is covered by swamp forest-freshwater marshes; the middle Barataria Basin (2–10 psu) consists of intermediate-brackish marsh; and the lower high salinity basin (6–22 psu) is surrounded by the saltwater coastal marsh (Conner and Day, 1987) (Figure 2.1a). The lower Barataria Basin (Barataria Bay) is bounded to the south by a chain of barrier islands and connected by tidal passes to the nGOM (Figure 2.1b). Due to its proximity to the MR, variations in salinity and nutrients within Barataria Bay can be strongly influenced by the magnitude of MR discharge, wind regime and tidal cycles along the coast (Wiseman et al., 1990).

Figure 2.1. (a) MODIS-Aqua RGB image (February 12, 2011) of the MR deltaic plain region (southeast Louisiana) and the shelf region in the nGOM with Barataria Basin boundary outlined in red. (b) Barataria Basin with sampling locations (blue, black and orange circles indicate stations along the fresh, brackish and salt marsh areas; yellow stars represent the location of
meteorological stations in Paradis 7S, Marrero 9 SSW, and Grand Isle, respectively.

2.2.2. Data Collection

A total of 36 sampling sites along a marine-freshwater gradient spanning a 110 km long transect from the mouth of Barataria Basin (station 1; about 1 km offshore of Grand Isle) through Barataria Bay, Little Lake, Lake Salvador, and Lake des Allemands and into Bayou Chevreuil the upmost location (station 36) were sampled monthly between 2007–2012 (53 months) (orange/black/blue circles corresponding to lower/middle/upper basin, respectively; Figure 2.1b). Surface water samples collected monthly at these stations were filtered using pre-rinsed 0.2-µm Nuclepore membrane filters (Whatman GmbH) for absorption spectroscopic analysis and dissolved organic carbon (DOC) measurements. Yellow Springs Instruments (YSI) multi-probe field meter was used to obtain in-situ measurements of surface temperature and salinity. Meteorological data (precipitation and air temperature) (1985-2012) were obtained from NOAA’s National Climatic Data Center (NCDC) at three stations within the upper, the middle and the lower Barataria Basin, namely, Paradis 7 S, Marrero 9 SSW and Grand Isle (yellow stars; Figure 2.1). Wind speed and wind direction (2008-2011) were obtained from NOAA’s National Data Buoy Center (NDBC) at the Grand Isle station (GSL1, 20.265°N, 89.958°W). Mean daily MR discharge (2008-2011) at the DPFD (USGS 295501090190400) and Baton Rouge (USGS 07374000) was from the USGS Water Data. A total 88 scenes of Landsat-5 TM (1985-2011) and 65 MODIS-Aqua images (2002-2012) covering the entire basin were downloaded from the Landsat Data Archive (USGS) and NASA’s ocean color website, respectively.

2.2.3. Absorption Spectroscopy

CDOM absorbance ($A_{CDOM}$) spectra (250–750 nm) were measured using a 1-cm pathlength quartz cuvette on a Perkin Elmer Lambda-850 UV/VIS spectrophotometer at 2 nm intervals. The absorption coefficients of CDOM ($a_g$, same as $a_{CDOM}$) was calculated using the following equation (1.5). The spectra of $a_g$ were then corrected for scattering, temperature, and baseline drift by subtracting an average value of absorption between 700–750 nm for each spectrum (Joshi and D’Sa, 2015). The absorption coefficient at 355 nm ($a_g|355$) was used as a quantitative parameter of CDOM. The spectral slope $S$ between 275 nm and 295 nm ($S_{275–295}$) was calculated according to Helms et al., (2008). The absorption coefficient $a_g|355$ and spectral slope $S_{275–295}$ were then extracted from all the sample spectra for further analysis.

2.2.4. DOC Analysis

Seawater samples were first filtered under gentle vacuum through 0.2-µm Nuclepore membrane filters (Chow et al., 2005; Kolka et al., 2008) and then stored in acid cleaned, pre-combusted amber bottles with Teflon-lined caps in a refrigerator at 4 °C. DOC concentrations (mgL-1) were measured by High Temperature Catalytic Oxidation (HTCO) on a Shimadzu® TOC-5000A Analyzer, following the methods described in (D’Sa et al., 2016; Singh et al., 2010). The machine operates by combusting the water sample at 680 °C in a combustion tube filled with a platinum-alumina catalyst. DOC concentration was then obtained by subtracting dissolved inorganic carbon (DIC) from the total dissolved carbon (TDC).

2.2.5. Landsat Imagery Processing

Landsat-5 TM data (30 m resolution) were used in this study because the historical Landsat-5 TM data (from 1985) together with the MODIS-Aqua imagery can provide long-
term insights on the spatiotemporal variability of a target area at high temporal resolution. Landsat-5 TM images with < 10% cloud cover containing the northern (Path 22, Row 39) and the southern (Path 22, Row 40) Barataria Basin were downloaded from the USGS Landsat Data Archive. Scenes of Row 39 and 40 were further mosaicked using ENVI v 5.2 (ITT Visual Information Solutions, Inc.) image processing tool to create 88 Landsat scenes of the entire Barataria Basin. Radiometric calibration was then applied to the mosaicked images to convert digital numbers to the top-of-atmosphere (TOA) radiance at each spectral band. The raw TOA radiance images were then atmospherically corrected using the ENVI v 5.2 FLAASH (Fast Line of sight Atmospheric Analysis of Spectral Hypercubes) module (Joshi and D’Sa, 2015). The atmospherically-corrected surface reflectance ($\rho_{\text{Landsat}}$) was further used for the empirical algorithm development and the land cover classification.

2.2.6. MODIS Imagery Processing

MODIS 250 m medium resolution atmospherically-corrected surface reflectance ($\rho_{\text{MODIS}}$) was used instead of remote sensing reflectance ($R_{rs}$) to develop empirical algorithms in order to be consistent with Landsat algorithms, which are based on $\rho_{\text{Landsat}}$; further, these data meet the requirements of higher spatial resolution of the study area (Barataria Basin), which consist of many smaller waterbodies (e.g., Lac des Allemands, Little Lake and Lake Salvador). The atmospheric correction of MODIS data comprised of two major procedures. First, Level-L1B MODIS-Aqua images along with their corresponding geolocation files were input to the SeaDAS l2gen processor to obtain Rayleigh-corrected surface reflectance (selecting the rhos in product selector of Radiance/Reflectances) and then changing to 250 m resolution in Miscellaneous selector. The purpose of this step was to remove the contamination by Rayleigh scattering due to atmospheric gases. Aerosol scattering also contributes notably to the radiance at the top-of-atmosphere (D’Sa et al., 2002), particularly in the coastal-estuarine waters due to the elevated concentrations of aerosol particles from various terrigenous sources. Thus, the black-pixel correction method (Stumpf, 1992) was applied to the Rayleigh-corrected surface reflectance to reduce aerosol contamination. A black pixel in the image with extremely low reflectance value is generally from a “clear water” area (Kirk, 1994). Note that this method is considered to be most suited when atmospheric contributions over the entire study area are relatively constant, and the water is highly homogenenous (e.g., Case I open ocean). However, this method can also be applied in the optically-complex estuarine waters if the darkest pixel is carefully determined, which should be as close to the same longitude of the area of interest as possible, but in clear waters. Selection of the darkest pixels in this study was accomplished by first identifying darkest pixel in band 1 (620-670 nm) and then comparing the same pixel in band 2 (841-876 nm) to evaluate whether it is also the darkest pixel in band 2. Subsequently, the darkest pixel value in band 2 was subtracted from all other pixels over the entire Rayleigh-corrected reflectance image to remove the aerosol interference. Finally, the fully atmospheric-corrected reflectance ($\rho_{\text{MODIS}}$) values were obtained for MODIS.

2.2.7. Supervised Classification of Landsat Imagery

Atmospheric-corrected $\rho_{\text{Landsat}}$ images were imported into ERDAS IMAGINE 2016 software and cropped to the same size for further classification. Since environmental variations, such as seasonality, hydrological cycles, and episodic meteorological events (e.g., hurricanes), could introduce subtle changes in land classifications, it is advantageous to use Landsat 5 TM data obtained in an environmentally-stable season to reduce yearly bias when assessing long-term variations in land cover. In this study, a total of 30 of 80 Landsat 5 TM data were used for supervised classification, which were generally acquired in the fall season (September-
October) due to lower cloud cover, a relatively stable hydrodynamic regime, and a period with less energetic events (e.g., hurricanes and cold front passages). Signature files composed of six major land-cover types, namely: developed area (agriculture and urban), wetlands forest, fresh marsh, intermediate-brackish marsh, salt marsh and water area were generated by gathering several training pixels for each cluster. A maximum likelihood supervised classification routine resident in ERDAS IMAGINE along with signature files were jointly used to classify each Landsat scene into the six spectral clusters. Percentage of each cluster was calculated as (Wang and D’Sa, 2009):

\[
\text{Percentage (\%)} = \frac{\text{number of pixels in each cluster}}{\text{total number of classified pixels}} \times 100\% \quad (2.1)
\]

A post-classification smoothing operation using a 3×3 focal majority filter, was then applied to minimize the misclassified pixels. Eventually, some misclassified pixels (e.g., some urban and agricultural pixels misclassified as fresh marsh cover) were manually reclassified to the right class by referring to Landsat false-color imagery. In addition, in the hurricane-years (e.g., 1992 and 2005), the extracted percentage of land variations should be averaged pre- and post-hurricanes for these 6 clusters to obtain more accurate trends in land variations. To validate the classification accuracy, we generated 170 points in each scene, compared with the pixels in corresponding Landsat false-color image, and calculated the probability of misclassification to indicate classification accuracy (Nelson et al., 2002):

\[
\text{Accuracy (\%)} = \frac{\text{number of correctly classified pixels}}{\text{total pixels}} \times 100\% \quad (2.2)
\]

2.2.8. Wavelet Analysis

Wavelet analysis has been considered a feasible tool to detect spatiotemporal dependencies of biogeochemical parameters in aquatic environments (D’Sa, 2014b; Weigand et al., 2017), and potentially, to assess regionally important controlling factors for CDOM in the Barataria Basin. In addition to the traditional correlation analysis, wavelet analysis with the Morlet continuous wavelet transform (CWT) and wavelet transform coherence (WTC) were applied in this study to investigate the spatiotemporal dependency of monthly collected ag355 on the distinct freshwater sources. Based on a detailed description of wavelet analysis (Torrence and Compo, 1998; Grinsted et al., 2004) the computation of wavelet coherence (the square of the cross-spectrum normalized by the individual power spectra) and phase angle were conducted using a MATLAB package (Grinsted et al., 2004) to identify co-varying relationships between the time-series of two variables:

\[
R_x^2(B) = \frac{[4 \times (B^{-1} \times W_n^X(B))]^2}{[4 \times (B^{-1} \times W_n^X(B))]^2} \times [4 \times (B^{-1} \times W_n^Y(B))]^2 \quad (2.3)
\]

where A is a smoothing operator, B is the scale (period), \(W_n\) is the cross-wavelet transform, \(n\) is number of field observations, \(X\) is the time series \(x = [x_n]\), and \(Y\) is the time series \(y = [y_n]\).

Three groups of input datasets were defined in this study: (1) \(a_g 355_{-\text{LB}}\) – averaged \(a_g 355\) values of station 1–7 in the lower basin, frequently influenced by the MR plume waters, (2) \(a_g 355_{-\text{MB}}\) – averaged \(a_g 355\) values of station 17–25 in the middle basin strongly affected by the DPFD, and (3) \(a_g 355_{-\text{UB}}\) – averaged \(a_g 355\) values of station 30–34 in the upper basin with rainfall as a major freshwater source. In addition, WTC analysis requires equidistant and continuous data sets. Monthly water samples were obtained for this study at all stations during 2008–2011, except in January 2009, November 2009 and December 2011. Satellite-derived \(a_g 355\) were used for these three missing data points during 2008–2011. Monthly mean river discharge at Baton Rouge and the DPFD and cumulative daily precipitation for 20 days prior to water sample collection dates during 2008–2011 were calculated and considered as monthly
time-series of freshwater sources. With the knowledge of spatiotemporal correlations between CDOM and environmental variables such as meteorological events and hydrological cycles, CDOM algorithms for different conditions can be developed to reduce uncertainties associated with transient environmental disturbances and further achieve more reliable long-term estimates of satellite-retrieved CDOM and DOC.

2.3. Results and Discussion

2.3.1. Environmental Conditions

A previous study documented the influence of environmental forcing (e.g., MR discharge, freshwater diversions, and frontal passages) on CDOM in the Barataria Bay during 2010-2011 (Joshi and D'Sa, 2015). Present work extends to longer period (1985-2012) and broader area that includes the upper Barataria Basin, where precipitation replaces river discharge as a major freshwater source. Thus, environmental conditions during the sampling period (2008–2011) and for the whole study period (1985–2012) were assessed to better understand hydrological factors influencing DOM distribution and exchanges in the marshes, basin waters, and the nearshore Gulf waters (Figure 2.2). Mean daily discharge (m$^3$/s) of the MR at Baton Rouge during 2008-2011 showed strong seasonality, with high MR flow (>30,000 m$^3$/s) conditions in the spring and the early summer (April, May and June) and low river discharge (<15,000 m$^3$/s) during the fall and the late winter (colored circles on the plot show the field samples collection dates; Figure 2.2a). Large amounts of freshwater were released at the DPFD more frequently during 2008-2010, while DPFD discharge was low in 2011 (~109 m$^3$/s; Figure 2.2b). Significant flooding effects from MR discharge in 2011 (~42,000 m$^3$/s max, blue line; Figure 2.2a) and freshwater discharge from the DPFD associated with a record flow of ~250 m$^3$/s in 2010 (red line; Figure 2.2b) on CDOM distribution have been previously reported in the lower basin (Joshi and D'Sa, 2015). Furthermore, meteorological events like frontal passages (Chaichitehrani et al., 2014; Joshi and D'Sa, 2015) and tropical disturbances (Singh et al., 2010) also play important roles in modulating CDOM abundance and DOM composition in Barataria Basin via freshening events and salt water intrusions, respectively. Wind record at Grand Isle during 2008–2011 (Figure 2.2c) showed strong northerly winds occurring predominantly in the late fall and winter. These are generally associated with frequent outbreaks of cold fronts or frontal passages (between October and April) which are generally followed by a pattern of changes in surface wind speed and direction, barometric pressure, temperature and humidity (colder, drier and denser air masses) (Roberts et al., 1987; Feng and Li, 2010), making the wind regime directionally more variable during this period than the summer season, which is primarily dominated by weaker south-southeast winds except during hurricane events (Figure 2.2c). Frequent cold front passages are known to enhance flushing of the bays into the coastal and nearshore shelf environment (D’Sa and Ko, 2008) and further influence the local biogeochemical processes.
Figure 2.2. Time series of major environmental variables in the Barataria Basin. (a) Mean daily discharge (m$^3$s$^{-1}$) of the MR at Baton Rouge (2008–2011) station; pink boxes represent the high river discharge period of each year. (b) Mean daily discharge (m$^3$s$^{-1}$) at the DPFD; light blue boxes indicate the high freshwater discharge situations. (c) Mean daily wind speed (ms$^{-1}$) and direction recorded at the entrance of Barataria Bay; black boxes are the cold front conditions. Black, green, red and blue colors indicate year of 2008, 2009, 2010 and 2011, respectively. (d), (e) Averaged in-situ a$_g$355 (m$^3$) and DOC (mg L$^{-1}$) in Barataria Bay; orange, black and blue symbols represent lower, middle and upper part of the bay, respectively. (f) Annual precipitation (mm) during 1985–2012 at three stations at Paradis 7S, Marrero 9 SSW and Grand Isle meteorological stations, respectively. (g) Monthly average temperatures ($^\circ$C) at Paradis 7S during 1985–2012; red dashed line represents temperature anomaly ($^\circ$C). (h) Monthly cumulative precipitation (mm) at Paradis 7S during 1985–2012; red dashed line indicates precipitation anomaly (mm).

Precipitation and temperature are potentially important factors influencing DOM properties, especially in the upper Barataria Basin which is surrounded by swamp and fresh marsh, and where precipitation is the only hydrologic input. Cumulative annual precipitation obtained from the NOAA Weather Station (Paradis 7S) during 1985–2012 (Figure 2.2f) varied from 1000 to 2500 mm with relatively high annual totals observed in 1991 (~2500 mm), 1998 (~2100 mm) and 2004 (~2150 mm), in coincidence with the years of strong El Niño events during 1991-1992, 1997-1998 and 2004-2005 (Giese et al., 2011). In contrast, extremely low annual rainfall below 1000 mm were observed in 1996, 1999 and 2006 likely associated to the severe droughts in this area caused by the occurrence of La Niña (Mo et al., 2015). Monthly cumulative precipitation (Figure 2.2h) further shows that rainfall is fairly uniform in most years, but extremely heavy rainfall events (e.g. ~740 mm in December, 2009) generated by variable mechanisms (e.g. tropical disturbance, frontal events and air mass; Keim and Muller, 1993) were also observed in different seasons. In contrast, monthly mean air temperatures (Fig. 2g) displayed a regular pattern from the minima ~9 $^\circ$C during winter (December–February) to
the maxima of over 30 °C in summer (June–August) in the Barataria Basin and showed an overall warming trend (an increase of ~0.9 °C) since 1985 (dashed red line; Figure 2.2g).

2.3.2. Wavelet Analysis of $a_g$ 355 Spatiotemporal Variations

Freshwater inputs are expected to exert strong effects on the CDOM and DOC abundance in Barataria Basin. Peaks of $a_g$ 355 in lower part of bay (orange symbols; Figure 2.2d) were correspondingly observed after extremely high river discharge in 2008 and 2011. In contrast, $a_g$ 355 in middle Barataria Basin (black symbols; Figure 2.2d) appeared to be positively correlated with inflows from DPFD. However, the upper bay does not appear to be influenced by MR and DPFD (blue symbols; Figure 2.2d). It is thus critical to separately assess the spatiotemporal linkages of different freshwater sources (MR plume waters, the DPFD, and rainfall) and the monthly $a_g$ 355 data during 2008-2011. Wavelet analysis allows for analysis in time-frequency domain since the correlations will change spatially and temporally due to the complex landscape characteristics and meteorological conditions. Correlation (color) and phase angle (arrows) between time-series of monthly $a_g$ 355 and freshwater sources (MR, DPFD and rainfall) during 2008–2011 obtained from wavelet analysis are shown in Figure 2.3. Wavelet coherence ($R^2$) between monthly mean MR river discharge and $a_g$ 355_LB (Figure 2.3a) showed an overall higher value than the pair of monthly mean discharge at the DPFD and $a_g$ 355_LB (Figure 2.3b). Furthermore, a strong positive coherence ($R^2 > 0.8$) were observed around periodicity of 1 year, where $R^2$ values are evidently higher in flooding year of 2008 and 2011 than those observed in 2009 and 2010. High-frequency periodicities of 0.25–0.5 within the MR high flow periods (spring) in 2008, 2009 and 2011 showed clear seasonal variabilities ($R^2 \sim 0.7$) with arrows pointing down to the right indicating a positive correlation between $a_g$ 355_LB and the MR discharge with a slight time lag, which implies that high flow conditions usually occur once a year with abundant CDOM-laden waters in spring and early summer. In contrast, flow conditions rarely affected the CDOM abundance in the lower basin in the fall and winter of 2008 (0.5–1 year, Figure 2.3a), 2009 (1.5–2 year, Figure 2.3a) and 2011 (3.5–4 year, Fig. 3a). Interestingly, a negative correlation (arrows pointing to the left; Figure 2.4a) was observed during the fall and the winter in 2008 ($R^2=0.55$), which could be the disturbance from Hurricanes Gustav and Ike and frequent winter storms introducing abundant CDOM versus relatively low MR discharge. The R2 between the $a_g$ 355_LB and the DPFD discharge is fairly weak, indicating that the MR is the most important factor controlling CDOM compared to the DPFD in the lower basin. Moderate $R^2 (~0.55–0.6)$ around periodicities of 0.25–0.5 year appeared in the spring-summer season with variable phase relations (Figure 2.3b). In 2011, it showed a negative correlation (arrows pointing up to the left) between $a_g$ 355_LB and the DPFD discharge, which could be due to an overall low discharge at the DPFD versus especially high flows of the MR and elevated $a_g$ 355_LB in the lower basin.
Figure 2.3: Wavelet coherence between spatial sequences of freshwater sources and a$_g$355 at different locations in the Barataria Basin during 2008–2011. (a) a$_g$355_LB and monthly mean MR discharge at Baton Rouge. (b) a$_g$355_LB and monthly mean discharge at the DPFD. (c) a$_g$355_MB and monthly mean discharge at the DPFD. (d) a$_g$355_MB and monthly mean MR discharge at Baton Rouge. (e) a$_g$355_UB and 20-day cumulative precipitation at Paradis 7S prior to water sample collection. The colored legend indicates the wavelet squared coherence ($R^2$) and arrows indicate time lagging effects (pointing right is for in-phase relation; left: anti-phase; up: a$_g$355 leads discharge or rainfall 90°; down: a$_g$355 lags discharge or rainfall by 90°).

Coherence R2 between monthly mean a$_g$355_MB and the DPFD discharge (Figure 2.3c), reflects the response of a$_g$355 MB to the freshwater release at the DPFD in time-frequency domain. Higher coherence at high-frequency periodicities (0.25–0.4 year) with a positive correlation (arrows pointing to the right) appeared during high freshwater diversion at the DPFD in 2008, 2009 and 2010. In 2010, significant correlations with arrows pointing slightly up to the right indicates a positive relationship with a$_g$355 MB ahead of the freshwater release at the DPFD, which might due to earlier CDOM addition from other sources (MR or rainfall). Furthermore, high coherence around periodicity of 1 year was observed during 2010, which appears to correspond to the freshwater release at DPFD for several months following the DWH oil spill event in 2010 (Bianchi et al., 2011a). Additionally, the overall low $R^2$ with uncertain phase relations (Figure 2.3d) indicates the rare influence of the MR plume waters on CDOM abundance in the middle basin.
In the upper basin, positive relationships (arrows pointing down to right) between rainfall and ag355_UB at the periodicity of 0.25–0.5 (R² = 0.8–0.9) are quite evident in summer 2008 and fall-winter 2009 (Figure 2.3e); the downward arrows also implied that high-frequency, low-intensity precipitation events did not affect ag355 immediately, but with a slight time lag. Furthermore, there is another strong correlation at low frequency (periodicity of 1 year) during 2009–2010, which might be linked to the strong precipitation during winter 2009 and summer 2010 (Figure 2.2f) combined with other environmental factors that induced a strong and lasting effect on CDOM abundance in this area. In addition, the overall low R² between ag355_UB and discharge from the MR and the DPFD (not shown) indicate rainfall could be a major source of freshwater and CDOM within the upper Barataria Basin.

2.3.3. CDOM Optical Properties

Different hydrological and meteorological mechanisms modulating ag355 magnitude in each subsystem within Barataria Basin were observed from wavelet analysis during 2008–2011. As such, we categorized the monthly obtained ag355 and S275–295 into three different clusters based on meteorological and hydrological conditions: 1) normal conditions with calm wind (<4.5 ms⁻¹) and low MR discharge (<2.5×10³ m³s⁻¹; conservative conditions; black color), 2) high MR flow conditions (≥2.5×10³ m³s⁻¹; red color), and 3) cold front events (4.5 ms⁻¹; green color) (Figure 2.4). The mean value of ag355, S275–295, and salinity in the lower/middle/upper basin (2008–2011) under different conditions are shown in Table 2.1.

2.3.3.1. ag355–Salinity Relationships

During the normal conditions, an increasing salinity gradient was observed from the headwaters (0.21±0.03) to the entrance of the Barataria Basin near station 1 (25.59±2.83) (black symbols; Figure 2.4), with ag355 decreasing from a high of 15.51 ± 3.22 m⁻¹ to a low of 2.11 ± 0.91 m⁻¹ towards the open Gulf. Similar gradients of salinity and ag355 were observed during cold front events, with relatively fresher waters (17.21 ± 1.91) and higher ag355 values (4.20 ± 0.68 m⁻¹) at the lower basin stations (green stars; Figure 2.4a) compared to the normal conditions. In addition, the middle basin also experienced high levels of ag355 after the cold frontal passages with highest value reaching 15.2 m⁻¹ (green squares; Figure 2.4a). Thus, the occurrences of winter storm with increasing northerly winds combined with stronger ebb flows appear to efficiently transport CDOM-rich waters downstream, freshen the entire basin, and increase the role of the upper basin as a DOM source to the lower estuary and eventually to the shelf waters. In contrast, during spring river flood, when the fresh MR plume waters flow along the coast and into the basin, the surface salinity increases seaward except at the entrance of the Barataria Basin where fresher waters (10.85 ± 1.47) appear at marine end members (station 1-2; red stars in red circle, Figure 2.4a). Concomitantly, ag355 values adjacent to entrance showed higher values (4.99 ± 1.28 m⁻¹) compared to other conditions (red stars; Figure 2.4a). In addition, high discharge of DPFD following high MR flows also affected the middle basin by decreasing salinity and increasing ag355 values, but the extent of variations caused by DPFD in the middle basin was less compared to cold front events. CDOM contribution from deflected MR plume waters and frequent winter storms was observed and it could be differentiated based on environmentally categorized ag355–salinity relationships.
Table 2.1. Criterion for normal conditions, high MR discharge conditions and cold from events, mean salinity, $a_g 355$, and $S_{275-295}$ (mean ± SD) values in the lower, middle and upper basin between 2008-2011.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criterion</th>
<th>Salinity</th>
<th>$a_g 355$</th>
<th>$S_{275-295}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>MR discharge $&lt; 2.5 \times 10^3 \text{ m}^3\text{s}^{-1}$ &amp; Wind speed $&lt; 4.5 \text{ m} \text{s}^{-1}$</td>
<td>25.59 ± 2.83</td>
<td>2.11 ± 0.91</td>
<td>20.08 ± 1.11</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>1.42 ± 0.58</td>
<td>8.68 ± 2.67</td>
<td>18.58 ± 0.55</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>0.21 ± 0.03</td>
<td>15.51 ± 3.22</td>
<td>17.91 ± 1.25</td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>10.85 ± 1.47</td>
<td>4.99 ± 1.28</td>
<td>17.82 ± 0.55</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>1.15 ± 0.81</td>
<td>9.55 ± 2.38</td>
<td>18.06 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>0.16 ± 0.06</td>
<td>18.58 ± 3.01</td>
<td>16.39 ± 0.84</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>0.98 ± 0.88</td>
<td>11.81 ± 2.59</td>
<td>17.79 ± 0.61</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>0.13 ± 0.05</td>
<td>20.72 ± 4.78</td>
<td>17.03 ± 0.90</td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>17.21 ± 1.91</td>
<td>4.20 ± 0.68</td>
<td>18.31 ± 0.40</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
<td>0.98 ± 0.88</td>
<td>11.81 ± 2.59</td>
<td>17.79 ± 0.61</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
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</tr>
<tr>
<td></td>
<td>Upper</td>
<td>17.21 ± 1.91</td>
<td>4.20 ± 0.68</td>
<td>18.31 ± 0.40</td>
</tr>
<tr>
<td></td>
<td>Lower</td>
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<td>11.81 ± 2.59</td>
<td>17.79 ± 0.61</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>Upper</td>
<td>17.21 ± 1.91</td>
<td>4.20 ± 0.68</td>
<td>18.31 ± 0.40</td>
</tr>
</tbody>
</table>

Note: Wind data was referred to Weather Prediction Center (WPC) surface analysis archive from NOAA website (https://www.wpc.ncep.noaa.gov/archives/web_pages/sfc/). The hydrological conditions were based on the mean daily MR discharge at Baton Rouge (USGS 07374000).

2.3.3.2. $S_{275-295}$-Salinity Relationships

Unlike $a_g 355$, there was no consistent $S_{275-295}$ gradient from the freshwater to the marine end member (Figure 2.4b), although a general increasing trend in the spectral slope is observed at higher salinity range (10–32) under normal conditions. $S_{275-295}$ at the freshwater stations in Lac des Allemands (upper basin) were evidently higher 20–25 µm$^{-1}$ (black triangles; Figure 2.4b) under the normal conditions than the other two conditions, likely due to the strong degradation of CDOM associated with increased residence time of waters and weaker winds. The CDOM optical properties (lowest $S_{275-295}$ (8–13 µm$^{-1}$) versus highest $a_g 355$) observed in the upper basin (from des Allemands system to entrance of Lake Salvador; red triangles, Figure 2.4) appear to be associated with autochthonous sources of CDOM linked to algal-blooms triggered by abundant nutrients released from nearby agricultural catchments, living communities and fresh marshes (Singh et al., 2010). In the middle and lower basins below des Allemands system, $S_{275-295}$ obtained under normal conditions showed an increasing gradient seaward from station 25 to station 1, with apparently higher levels of $S_{275-295}$ (20.08 ± 1.11 µm$^{-1}$) observed at the marine end members, likely associated with enhanced photo-oxidation of CDOM caused by strong solar radiation and calm wind conditions (Joshi and D’Sa, 2015). In contrast, $S_{275-295}$ in the middle and lower basins presented fairly more constant and lower ranges of $S_{275-295}$ (15–20 µm$^{-1}$) during high MR discharge and the passage of cold fronts, that suggest meteorological and hydrological events led to potentially additional inputs of more aromatic and higher molecular weight CDOM to these estuarine waters.
Figure 2.4. (a) $a_g$ variations with salinity gradient along the transect of Barataria Bay. (b) $S_{275-295}$ versus salinity along the transect; red, green and black color represents high discharge from the MR, cold front and normal conditions, respectively; Stars, squares and triangles are corresponding to lower bay (station 1–10), middle part (station 11–25) and upper bay (station 26–35), respectively.

2.3.4. CDOM ($a_g$355) from Landsat and MODIS

2.3.4.1. Performance of $a_g$355 Empirical Algorithms for Landsat and MODIS

A total of 7 same-day pairs of Landsat and MODIS imagery (2007–2012) were used to compare the performance of the atmospheric correction for Landsat and MODIS. The ENVI-FLAASH atmospheric corrected $p_{\text{Landsat}}$ along with black pixels calibrated $p_{\text{MODIS}}$ using SeaDAS were separately averaged with 1x1, 3x3, 9x9 pixels at sampling sites and extracted from these 7 image pairs. The correlation coefficient ($R^2$), root mean square error (RMSE=$\sqrt{\frac{\sum_{i=1}^{N}(\text{Predicted}_i-\text{Actual}_i)^2}{N}}$) and mean relative error (MRE=$\frac{1}{n}\sum_{i=1}^{n}\frac{|\text{Predicted}_i-\text{Actual}_i|}{\text{Actual}_i}$) were calculated (supplementary Table 2.2) to compare the performance of Landsat and MODIS algorithms. Results were not too different, with the 3x3 Landsat pixel data showing the best performance (highest $R^2$ and lowest RMSE and MRE). Although the 9x9 pixel data for Landsat (270 m) and the 1x1 pixel data for MODIS (250 m) are expected to be the spatially optimized, the 9x9 Landsat pixel data appeared to present worst performance with lowest $R^2$ and highest errors (supplementary Table 2.2). Thus, the 1x1 pixel data were used for MODIS algorithms
in order to reduce differences of spatial resolution between Landsat and MODIS. The Green/Red (G/R) band ratio extracted from \( \rho_{\text{Landsat}} \) (3x3) and \( \rho_{\text{MODIS}} \) (1x1) showed good agreement (\( R^2=0.74, N=250 \)), with Landsat showing a slightly higher band ratio value than MODIS, especially during high MR flow conditions (red circles; Figure 2.5a). During cold front passages, both the Landsat and MODIS band ratio values were relatively equivalent in magnitude with data around 1:1 line (blue circles; Figure 2.5a); however, band ratios obtained under cold front conditions from both Landsat (0.72–1.46) and MODIS (0.66–1.42) displayed relatively lower ranges compared to other conditions (green circles; Figure 2.5b and 2.5c). In contrast, elevated G/R band ratio throughout the basin corresponding to smaller \( a_g \) was present under normal conditions for both sensors (black circles; Figure 2.5b and c), with a significantly higher band ratio (1.40–1.98) in the lower basin adjacent to the nGOM. Around 80% of pixels obtained during normal conditions had a band ratio (\( a_g \)), with the highest value reaching \( \sim 1.9 \). Further, the band ratio (1.25–1.5) extracted during high MR flow conditions in the lower basin was also associated with elevated \( a_g \) (\( >3.9 \text{ m}^{-1} \)). The high/low band ratios obtained during normal/cold front conditions likely revealed some disturbance in the red band. The comparison of band ratios between Landsat and MODIS implies that \( \rho_{\text{Landsat}} \) and \( \rho_{\text{MODIS}} \) were similar in magnitude, and a robust band ratio algorithm for the two sensors was suitable to generate long-term DOC time-series. Thus, a total of 10 Landsat and 20 MODIS imagery acquired in the Barataria Basin (±3 days of field data; supplementary Table 2.1) during 2007–2012 were used to generate empirical CDOM algorithms from G/R band ratio under different environmental conditions; note that the data from station 27-32 in Bayou des Allemands were not used in the algorithm due to the narrow water body and the potential for land contamination on the Landsat-5 TM 3x3 pixel data and the missing pixels for MODIS data. The major land features surrounding these stations were marsh forests, which likely introduce vegetation-type G/R ratio and further influence the satellite-retrieved \( a_g \) values. In addition, Bayou des Allemands is impacted by frequent algal-bloom events due to excessive nutrient inputs from surrounding areas (Singh et al., 2010; Dash et al., 2011). Thus, about 30 stations were available for each imagery to develop \( a_g \) algorithms in the absence of cloud effects or in-situ \( a_g \) measurements. Eventually, a total of 306 and 581 matchups were used in the \( a_g \) empirical algorithms for Landsat and MODIS, respectively (supplementary Table 2.3 and Figure 2.5). MODIS band ratio (G/R) was highly correlated \( a_g \) in power law relationships for the three conditions (\( R^2=0.82; \) Figure 2.5c); in comparison, relatively lower correlations were observed between Landsat-5 TM band ratio (G/R) and \( a_g \) (\( R^2=0.74; \) Figure 2.5b). The MODIS/Landsat \( a_g \) maps (Figure 2.6) were generated for each of the conditions based on separate coefficients as follows:

\[
\begin{align*}
\text{a}_g \text{ (m}^{-1}) & = 5.58 \times \left( \frac{\rho_{\text{MODIS}} (555)}{\rho_{\text{MODIS}} (645)} \right)^{-4.63} \text{[Cold front events; } R^2 = 0.82] \\
\text{a}_g \text{ (m}^{-1}) & = 7.63 \times \left( \frac{\rho_{\text{MODIS}} (555)}{\rho_{\text{MODIS}} (645)} \right)^{-2.67} \text{[High MR discharge; } R^2 = 0.83] \\
\text{a}_g \text{ (m}^{-1}) & = 10.87 \times \left( \frac{\rho_{\text{MODIS}} (555)}{\rho_{\text{MODIS}} (645)} \right)^{-4.37} \text{[Normal condition; } R^2 = 0.81] \\
\text{a}_g \text{ (m}^{-1}) & = 7.7 \times \left( \frac{\rho_{\text{MODIS}} (555)}{\rho_{\text{MODIS}} (645)} \right)^{-3.33} \text{[All MODIS data; } R^2 = 0.70] \\
\text{a}_g \text{ (m}^{-1}) & = 5.94 \times \left( \frac{\rho_{\text{Landsat}} (555)}{\rho_{\text{Landsat}} (666)} \right)^{-3.94} \text{[Cold front events; } R^2 = 0.79] \\
\text{a}_g \text{ (m}^{-1}) & = 8.28 \times \left( \frac{\rho_{\text{Landsat}} (555)}{\rho_{\text{Landsat}} (666)} \right)^{-2.14} \text{[High MR discharge; } R^2 = 0.73] \\
\text{a}_g \text{ (m}^{-1}) & = 7.63 \times \left( \frac{\rho_{\text{MODIS}} (555)}{\rho_{\text{Landsat}} (666)} \right)^{-2.67} \text{[Normal conditions; } R^2 = 0.72] \\
\text{a}_g \text{ (m}^{-1}) & = 8.35 \times \left( \frac{\rho_{\text{Landsat}} (555)}{\rho_{\text{Landsat}} (666)} \right)^{-2.45} \text{[All Landsat data; } R^2 = 0.65] 
\end{align*}
\]

The G/R band ratio is a useful proxy for estimating CDOM abundance in estuarine and coastal waters (Joshi and D’Sa 2015; Joshi et al. 2017b). However, CDOM abundance and
distributions in estuarine waters are highly dynamic and influenced by various environmental factors (hydrological and meteorological disturbances) that often introduce uncertainties in empirical algorithms based on spatiotemporally-constrained field observations. Thus, the time window within ±3 days used in this study could degrade the performance and accuracy of empirical algorithms, particularly for Landsat due to its 16-day repeat cycle; in contrast, time difference between MODIS-Aqua and in-situ measurements were generally less than for Landsat due to its nearly daily coverage, which likely improved the performance of MODIS $a_g$355 algorithm which exhibited better correlation than the Landsat algorithm. However, it is worth noting that the long-term monthly field observations in this study covered significantly more hydrological/meteorological conditions that allowed Landsat-5 TM and MODIS-Aqua empirical algorithms to be better tuned for the high MR flow, cold front and normal conditions, and also, likely reduced the errors due to the highly dynamic estuarine environment, thus leading to better spatiotemporal estimates of $a_g$355.
Better performance of the MODIS band ratio algorithms than Landsat could also be due to the narrower MODIS band widths in the red (620–670 nm; centered at 645 nm) and the green (545–565 nm; centered at 555 nm) bands. Red band (630-690 nm) of Landsat 5 TM centered at 665 nm being closer to the strong phytoplankton absorption in red (673 nm), is likely reduced more than the red band (645 nm) of MODIS, especially in spring-summer (high MR and normal conditions; red circles; Figure 2.5a), resulting in a higher Landsat band ratio during high MR flow conditions. The relatively small band ratio with similar magnitude for Landsat and MODIS during cold front events is likely related to stronger red reflectance from the more turbid waters along with weaker phytoplankton absorption. In contrast, normal conditions with low MR discharge and calm winds result in relatively clear waters with low levels of sediment, which correspond to lower reflectance in the red band and thus larger band ratio.

2.3.4.2. Satellite Observations of CDOM (a_g355) from Landsat and MODIS

Three image pairs of Landsat-5 TM and MODIS-Aqua corresponding to different conditions (normal, cold front, high MR discharge; Figure 2.6) were converted to a_g355 maps to examine spatial patterns of CDOM. The generated a_g355 maps revealed strong influences associated with plume waters during spring/summer flood period and frequent cold front events during winter/early spring. Maps of a_g355 generated from Landsat-5 TM/MODIS image pair acquired on November 11, 2011 under normal conditions during calm northwest winds (~2.2 ms^-1; Figure 2.6a and d), showed a decreasing gradient of a_g355 (15–1.9 m^-1) from the upper to the lower basin. a_g355 in Lac des Allemands, Lake Salvador, Little Lake and lower basin were around 11 m^-1, 15 m^-1, 12 m^-1 and 2 m^-1, respectively. In contrast, the cold front events contributed to a significant increase in CDOM in the upper and middle basins and its effect decreased along the transect into the lower basin. Landsat/MODIS image pair obtained on February 25, 2010 (Figure 2.6b and e) captured the passage of a strong cold front event (wind speed: ~6.5–6.8 ms^-1) that showed especially high values of ag355 throughout the basin (3.5–20 m^-1). The derived a_g355 maps from Landsat/MODIS image pairs obtained within ~3-hour time interval (Figure 2.6a and d; Figure 2.6b and e) showed a reasonable agreement in magnitude and short-term distribution patterns. Furthermore, two different instances of Landsat-5 TM (Figure 2.6c; April 01, 2011) and MODIS-Aqua (Figure 2.6f; May 20, 2008) images acquired during flooding events with similar intensity of southeasterly/southwesterly winds (daily mean=~2.5 ms^-1) displayed higher levels of a_g355 in the lower basin than the upper basin with the region adjacent to the nGOM presenting extremely high values (7–8 m^-1); the marsh fringes also showed extremely high a_g355 (~15 m^-1) which illustrated the movement of DOM out of the marsh. Additionally, algorithm failure was observed in the shelf waters for normal conditions (e.g., Figure 2.6a), which could be attributed to low water turbidity, and thus, very low red reflectance. In contrast, a_g355 algorithm performed better in the nGOM coastal waters during high MR flow conditions, with the Gulf waters presenting apparently higher levels of a_g355 in the range of (~3–4 m^-1), which implies that the G/R algorithm is more suitable for turbid waters (Joshi et al., 2018). Empirical algorithms of a_g355 for Landsat and MODIS were further applied according to different conditions to historical Landsat-5 TM
(from 1985) and MODIS-Aqua (from 2002) data to obtain long-term observations of CDOM in the Barataria Basin.

Figure 2.6. Barataria Basin Landsat-5 TM and MODIS-Aqua CDOM imagery based on empirical G/R band ratio algorithms with appropriate coefficients. (a), (b), and (c) Landsat-derived CDOM \(a_{g,355}\) maps for November 11, 2011, February 25, 2010 and April 01, 2011, respectively. (d), (e), and (f) display MODIS-derived CDOM \(a_{g,355}\) maps for November 11, 2011, February 25, 2010 and May 18, 2008, respectively. White arrows indicate the wind vectors (wind speed and direction).

2.3.5. Satellite Assessment of DOC

2.3.5.1. \(a_{g,355}\)-DOC Relationships from Field Observations

DOC concentrations were strongly correlated to \(a_{g,355}\) \(R^2 > 0.75\), Figure 2.7), with the highest (0.69) and the lowest slope (0.53) for \(a_{g,355}\)-DOC linear relationships observed under
the cold front and high MR discharge conditions, respectively. Relatively lower R² values under the normal conditions indicate the influence of different sources and sinks of DOC and CDOM. However, differences in the slope and intercept under these three conditions were minimal. Thus, a general \( a_{g,355} \)-DOC relationship were developed for all data to convert the Landsat/MODIS-derived long-term \( a_{g,355} \) maps (1985–2012) to DOC imagery as:

\[
\text{DOC (mg L}^{-1}\text{)} = 0.63 \times a_{g,355} \text{ (m}^{-1}\text{)} + 2.47 \quad \text{[All data; } R^2 = 0.80]\]

(2.12)

Figure 2.7. \( a_{g,355} \)-DOC relationships under normal (black), cold front (green) and high MR flow (red) conditions based on in-situ measurements at station 1-36 (excluding 27-32) during 2009-2011.

2.3.5.2. DOC from Landsat and MODIS \( a_{g,355} \)

Landsat and MODIS derived \( a_{g,355} \) imagery were converted to DOC maps using Eq. (11). The Landsat- and MODIS-extracted DOC values at stations 1-26 and 33-36 agreed reasonably well with in-situ measurements of DOC; MODIS algorithms displayed higher R² ~0.73 but lower RMSE ~2.33 than Landsat (R²=0.69; RMSE=1.86) (Figure 2.8a). Further, DOC extracted from a total of 16 Landsat/MODIS same-day image pairs within 3 hours over the study period (supplementary Table 2.1) were used to compare and assess Landsat and MODIS derived DOC concentrations (Figure 2.8b). DOC values at station 33 (blue circles; Figure 2.8b), station 25 (black circles; Figure 2.8b), and station 6 (orange circles; Figure 2.8b), were used to represent DOC levels in the upper, the middle and the lower basin, respectively. It was found that DOC extracted from 16 pairs of Landsat/ MODIS (supplementary Table 2.1) correlated highly with each other (R²=0.65, N=445) in different parts of the Barataria Basin; however, it showed that MODIS-derived DOC were slightly higher than the Landsat-derived DOC, which was likely associated with the 3-hour time interval between Landsat and MODIS and the resulting differences in DOC distributions. In addition, the relatively poorer spatial resolutions and narrower bandwidth of MODIS could also contribute to the differences in algorithm performance compared to Landsat. However, there were no obvious differences in magnitude and spatial distributions between Landsat and MODIS extracted DOC; thus, DOC derived from 88 scenes of Landsat and 65 MODIS imagery were used to generate long-term DOC time series (Figure. 2.8c); the blue, black and orange curves represent mean DOC concentrations in the upper (stations 33–36), the middle (stations 17–25) and the lower bay (stations 1–7), respectively. Note that if both Landsat and MODIS data were available on the same day and month (yellow color; supplementary Table 2.1), mean DOC values averaged
from Landsat and MODIS were used to represent the DOC value in the time series for that particular month, otherwise, Landsat or MODIS derived values were used to represent the DOC concentrations since both showed similar magnitudes of DOC retrieval. It was observed that only 2-5 cloud-free Landsat 5 TM images were available yearly during 1985-2001 (supplementary Table 2.1) due to the relatively lower temporal resolution (16-day repeat coverage), and thus, 2-5 Landsat-DOC were obtained per year before 2001 (Figure 2.8c); this could contribute to yearly-biased DOC time series due to the uneven temporally distributed satellite data. In contrast, the addition of MODIS (higher temporal resolution) combined with Landsat achieved nearly monthly monitoring of DOC between 2002-2012 in the study area. Furthermore, cloud coverage and sunglint effects on either Landsat or MODIS during summer (June-August), resulted in very limited data, hence, yearly biases were likely reduced before and after 2001 as satellite-data were mainly obtained during winter, spring and fall seasons.

![Figure 2.8 Landsat- and MODIS-derived DOC versus in-situ DOC](image)

**Figure 2.8.** Landsat- and MODIS-derived DOC versus in-situ DOC; black square and red cross represent DOC concentrations from MODIS and Landsat, respectively. (b) A comparison between satellite-derived DOC of Barataria Bay from 16 image pairs of Landsat-5 TM and MODIS-Aqua acquired within ±3 hrs at station 33, station 25 and station 6, respectively. (c) Long-term distribution patterns of mean DOC in the upper, middle, and lower Barataria Basin from 1985 to 2012; blue, black and orange symbols and lines represent data in the upper, middle and lower Barataria Basin, respectively.

Time-series DOC showed apparently lower values in the lower basin (orange circles; Figure 2.8b-c) compared to that in the upper/middle basin (blue/ black symbols; Figure 2.8b-
c). Further, the upper basin generally displayed relatively higher DOC levels than the middle basin (Figure 2.8c). It reasons that frequent algal blooms in the highly eutrophic Lac des Allemands, the major waterbody in the upper Barataria Basin, contributes to abundant DOC in the upper basin (Day et al. 1977). However, a comparison of DOC derived from 16 pairs of MODIS and Landsat imagery acquired within 3 hours (supplementary Table 2.1) did reveal occurrences of DOC in middle basin (black triangles; Figure 2.8b) higher than in the upper basin (blue circles; Figure 2.8b) and corresponded to data points derived from Landsat/MODIS image pairs obtained on 10/20/2003, 10/09/2005, 09/26/2006 and 11/18/2008 (supplementary Table 2.1). Some of these data were obtained under normal conditions with calm wind regime and low precipitation, which suggest the likely important role of rainfall and wind on modulating DOC abundance in the upper basin; furthermore, lingering effect of hurricanes that impacted the region in 2005 and 2008 could have contributed to higher DOC levels in the middle bay later in the fall. Overall, DOC distribution in the three regions showed seasonality and irregular fluctuations likely caused by seasonal meteorological and local hydrological events. Order 3 polynomial trend-lines with highest correlation coefficients (solid lines; Figure 2.8c) were added to investigate trends in DOC variation in Barataria Basin regardless of the short-term seasonal fluctuations. In the upper basin, the DOC concentrations (blue solid line; Figure 2.8c) increased gradually from 1985 to 2012, but were relatively flat during 2010–2012. Interestingly, DOC in the upper bay showed especially high concentrations associated with heavy precipitation coinciding with the 1998 El Niño year. In the middle basin, DOC showed a sharp increase between 1985–2010, with especially high rate during 1985–2002. The short-term fluctuations between DOC time-series (1985–2012) in the upper and middle basin displayed subtle differences. Time series DOC fluctuations in the lower basin showed apparent differences with DOC in the upper/middle basins. DOC trend in the lower basin (orange solid line; Figure 2.8c) increased from 1985 to 2006 by 41% and decreased from 2007 to 2012 by 28%. Higher levels of DOC were observed between 1992-1993 and 2005-2006, likely due to the disturbance from Hurricanes Andrew and Katrina. High decline rate during 2010–2012, likely implies the occurrence of some events which reduced carbon flux in this area (e.g., the DWH oil spill events starting from April, 2010). Previous studies based on field observations, have reported that heavy oiling influenced the marsh plant health, weakened the soil in the Barataria Basin (McClenachan et al. 2013; Silliman et al. 2012) and changed fluorescent properties of DOM related to oil contamination even two to three years after the Deep Water Horizon (DWH) oil spill event (D’Sa et al., 2016). This event could have further contributed to variations in composition and abundance of DOM released from marsh to surrounding waters.

2.3.5.3. Satellite-Derived Spatiotemporal Patterns of DOC

DOC imagery obtained between the years 1985–2012 (Figure 2.9) under normal conditions, MR flooding periods, and cold front events were used to assess environmental effects on the spatiotemporal distributions, seasonality, year-to-year variations and long-term trends of DOC along the wetland-estuary interface in the Barataria Basin. More importantly, application of these algorithms (equation 2.2–2.10) to multi-year satellite Landsat and MODIS imagery across different seasons, allowed, for the first time, an assessment of DOC spatiotemporal response to hurricanes (e.g., Hurricane Andrew and Katrina) and extreme precipitation events in the Barataria Basin.

Generally, the shelf waters in the summer yielded higher levels of DOC concentration (3.5–5.0 mg L⁻¹; Figure 2.9b, e, l and p) than in the winter (2.4–3.6 mg L⁻¹; Figure 2.9a, h and m), likely due to DOC from autochthonous sources, such as phytoplankton. Elevated discharge of the MR with high nutrient loading during spring and the spread of the river plume waters
support extensive phytoplankton blooms along the Louisiana-Texas coast in the spring and summer (Malcolm and Durum 1976; Turner and Rabalais 1991).

Figure 2.9. Landsat and MODIS-derived DOC imagery of Barataria Basin (1985–2012, with corresponding dates shown) under normal, high MR flow and cold front conditions. Red arrows indicate the mean daily wind speed and direction.

The prevailing southerly winds can further transport the coastal waters through the tidal passes into the lower Barataria Basin, thus elevating DOC concentration in the bay (Ho and Barrett 1977). Our results agreed reasonably well with Benner et al., 1992 observation of phytoplankton being an important DOC source in the MR plume and Gulf shelf region during the summer (July–August) compared to winter (February). In contrast, most of DOC imagery acquired under normal conditions (Figure 2.9a, c, g, h and j) were in the fall and showed relatively elevated DOC concentrations (7.5–11.5 mg L⁻¹) in the middle/upper basin decreasing along the basin transect into the lower bay (2.5–5.5 mg L⁻¹). More remarkably, DOC imagery of October 05, 1992 (one month after Hurricane Andrew; Figure 2.9c) and October 16, 2005 (one month after
Hurricane Katrina and Rita; Figure 2.9j), showed fairly high DOC concentrations even in the absence of strong winds and high river discharge; DOC ranged from (7.5–9.5 mg L$^{-1}$) in Lac des Allemands, (9.8 to 11.5 mgL$^{-1}$) in Lake Salvador and (4.5–7.5 mg L$^{-1}$) in the lower basin after Hurricane Katrina (Figure 2.9j). Furthermore, the corresponding two cold front cases (two months after Hurricane Andrew and Katrina; Figure 2.9d and k) suggest a pulsed elevation of DOC. DOC map after Hurricane Andrew on November 06, 1992 (wind speed $=7.5$ m s$^{-1}$; Figure 2.8d), showed the DOC concentration approaching 16 mgL$^{-1}$ in the middle basin and greater than 9.5 mgL$^{-1}$ throughout the lower basin; similar sharp increase of DOC was also observed during a cold front event on November 17, 2005 after Hurricane Katrina (Figure 2.9j). These two cases indicate that winter storms after hurricanes could additionally transfer detritus and soil organic material from marshes into the water column, resulting in more abundant DOC-laden waters flushing seaward through the entire basin that eventually gets transported into the Gulf waters. Previous studies suggested that much of the carbon exported from marshes is recycled within estuaries, being buried in estuarine sediments instead of outwelling (Bauer et al. 2013; Day et al. 1977; Lane et al. 2016). During cold front passages, however, bottom sediment resuspension and its transport into the Gulf waters have been documented (D’Sa and Ko 2008; Joshi and D’Sa 2015); DOC trapped in sediments could also be released during these resuspension events and increasingly exported to the shelf waters. Another strong cold front passage (wind speed$=8.2$ m s$^{-1}$ combined with extremely high precipitation ($\sim710$ mm) captured on December 21, 2009 (Figure 2.9m) also profoundly increased DOC concentrations in the lower basin ($\sim8.0–9.0$ mg L$^{-1}$) and its transfer to the Gulf waters (as indicated by high DOC plumes at the passes), but DOC magnitude was relatively lower than after the two hurricanes. Further, DOC imagery during high MR flow conditions obtained on June 10,1996 (Figure 2.9f), April 14, 2004 (Figure 2.9i) and April 01, 2011 (Figure 2.9o) showed an inverted spatial gradient of DOC generally decreasing from the lower to the middle basin with the region adjacent to MR plume waters presenting extremely high values ($\sim6.5–9.2$ mg L$^{-1}$). Marsh fringes around the lower basin displayed especially high levels of DOC ($\sim9.5–10.5$ mg L$^{-1}$), which likely imply deep flooding of the salt marshes caused by the high flows with prevailing southerly winds flushing abundant organic materials into the waters of the lower basin.

2.3.5.4. The Temperature/Precipitation Effects on DOC

Temperature and rainfall are two important climatic factors that influence the vegetation type and organic carbon accumulation on the land surface that could further modulate DOC abundance in the waters of Barataria Basin. Satellite-retrieved DOC concentration in the upper, the middle and the lower basin were separately regressed on the monthly mean air temperature at Paradis 7S (Figure 2.10a-c) and 20-day cumulative precipitation at Paradis 7S (upper basin), Marrero 9 SSW (middle basin) and Grand Isle (lower basin) during 1985-2012 (Figure 2.10d-f). Temperature was inversely correlated to DOC with $R^2$ for the upper and middle basin were much higher $R^2$ (0.42; Figure 2.10a-b) than that of the lower basin (0.16; Figure 2.10c), illustrating more obvious DOC seasonality in the upper/middle basins. The negative correlation between temperature and DOC further reasonably agreed with field and satellite observations that DOC in the upper/middle basin was highest during the winter and with little fluctuation throughout the summer. One reasonable explanation is that marsh vegetation in coastal Louisiana generally reaches its peak in late summer (August), and then senesces in winter (Couvillion and Beck, 2013; Day, 1973); high winter DOC values could be associated with leaching of DOM from these dead plants. In addition, frequent winter storm, stronger north winds combined with heavy rainfall during this period tends to support the DOM transport from the marshes to adjacent waters, the lower basin, and even the GOM due to decreased water levels and strong ebb flows (Feng and Li,
Meanwhile, the benthic flora dominate aquatic production during winter (Day, 1973) and benthic fluxes of DOC to the overlying water column might be another possible reason for high DOC during winter. In contrast, DOC in the lower basin generally showed a peak during spring linked to high MR discharge periods, and relatively lower DOC levels in fall-winter (except during cold front events), and thus poorly correlated with air temperature ($R^2=0.16$; Figure 2.10c) due to more complicated controlling factors in the lower basin.

The precipitation record was, however, more variable than temperature (Figure 2.2e and f), with no apparent relationship between precipitation and DOC in middle/lower basin ($R^2 < 0.06$; Figure 2.10e-f); the poor correlations further confirmed results from wavelet analysis (section 3.3) that fresh water sources of the MR and the DPFD exert greater influence on the distribution of DOC in the lower and middle basins. The weak correlation ($R^2<0.17$; Figure 2.10d) between precipitation and DOC in the upper basin could be due to rainfall, which is a major freshwater source within the upper Barataria basin. Overall, DOC response to precipitation is very minor in the lower basin and the coast, but increases substantially in the upper basin. These relationships indicate that the higher amounts of DOC concentrations may enter the upper Barataria Basin during low temperatures and high precipitation in the winter.

Figure 2.10. DOC concentrations (mg L$^{-1}$) vs. air temperature (°C) and 20-day cumulative precipitation (mm) in the Barataria Basin. (a), (b) and (c) DOC vs. temperature in upper, middle and lower basin, respectively. (d), (e) and (f) DOC vs. 20-day precipitation in upper, middle and lower basin, respectively.
2.3.6. Effects of Land Cover Change on DOC Distributions

2.3.6.1. Supervised Classification and Accuracy of Land Cover Types in Barataria Basin

In each classified Landsat 5-TM imagery of Barataria Basin, 240 points were generated and were compared to corresponding Landsat false-color image to estimate the accuracy of supervised classification in the Barataria Basin. Among these 240 points in each scene, 40 pixels in Landsat 5 TM false-color imagery were initially selected for each cluster (developed area, fresh marshes, brackish marshes, salt marshes, forest area and water area) and then compared with the same pixels in corresponding classified Landsat 5 TM imagery. The selected 9 scenes of Landsat 5 TM imagery for validation were generally in the fall (September-October) due to lower cloud cover, a relatively stable hydrodynamic regime, and a period with less energetic events (e.g., hurricanes). The selected classified pixels on Landsat-5 TM imagery agreed well with classification categories (average accuracy of 82.59%; Table. 2.2), with the highest (87.50%) and lowest (77.50%) accuracy observed on October 19, 1997 and October 20, 2003, respectively. Category of water area displayed best performance with 100% accuracy for all Landsat imagery. Salt marsh category in the lower basin also showed relatively high accuracy (80.28%). However, fresh marsh in the upper basin showed lower accuracy (68.25%) with misclassification in developed areas (crop land) or interference by intermediate-brackish marsh pixels. Category of developed area, intermediate-brackish marsh and forest area showed moderate accuracy of 79.16%, 81.11% and 80.28%, respectively.

Table 2.2. Classification accuracy for comparisons between classification imagery to Landsat TM false-color imagery (30-m resolution) for a total of 170 pixels.

<table>
<thead>
<tr>
<th>Date</th>
<th>Developed Area</th>
<th>Fresh marsh</th>
<th>Brackish marsh</th>
<th>Salt marsh</th>
<th>Forest area</th>
<th>Water area</th>
<th># of total pixel</th>
<th>Accuracy (%)</th>
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<td>32/40</td>
<td>30/40</td>
<td>30/40</td>
<td>33/40</td>
<td>30/40</td>
<td>40/40</td>
<td>195/240</td>
<td>81.25</td>
</tr>
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<td>31/40</td>
<td>29/40</td>
<td>29/40</td>
<td>31/40</td>
<td>32/40</td>
<td>40/40</td>
<td>192/240</td>
<td>80.00</td>
</tr>
<tr>
<td>02/08/1992</td>
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<td>31/40</td>
<td>35/40</td>
<td>33/40</td>
<td>31/40</td>
<td>40/40</td>
<td>202/240</td>
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</tr>
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<td>31/40</td>
<td>36/40</td>
<td>30/40</td>
<td>40/40</td>
<td>199/240</td>
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<td>30/40</td>
<td>36/40</td>
<td>34/40</td>
<td>33/40</td>
<td>40/40</td>
<td>210/240</td>
<td>87.50</td>
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<td>24/40</td>
<td>30/40</td>
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<td>30/40</td>
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</table>

2.3.6.2. DOC Variations of Land Cover during 1985-2011

Classification results from Landsat-5 TM acquired on August 31, 1985 and October 05, 1992 (Figure 2.11d) was in reasonable agreement with a previous study (Nelson et al. 2002) using Landsat-5 MSS imagery obtained on the same day covering the upper Barataria Basin. Our study extended both the spatial and temporal coverage to a broader area using a 27-year (1985-2011) time-series data that revealed the long-term, although coarse-scale rates of land-cover variations in the Barataria Basin (Figure 2.11a-i). The extracted percentage of each cluster within the Basin are shown for the study period (Figure 2.12a). The percentage of water area differences (black line; Figure 2.12a) showed a gradual increase from 45.96% to 49.95% between August 1985 to September 2011 (Figure 2.11a-i); this increase in water area appears to be associated mainly with conversion of salt marsh to open waters (Figure 2.11, 2.12a) and
to a lesser degree the fluctuations in areas of shallow ponds and small lakes in the upper basin. Percentage increase of water area (~9%) during 1985-2011 reasonably agreed with Couvillion et al., 2017 that percentage decrease of total land area derived from Landsat-5 TM normalized difference water index (NDWI) in the Barataria Basin was ~11% during 1985-2010 (note however, that the area of interest in the two studies were not exactly the same). Further, the salt marsh showed a decrease from 10.05% to 8.21% during 1985-2011, and a relatively lower loss rate during 2007-2011 which appears to be related to the massive deposition of inorganic sediments in the Louisiana coastal wetlands from Hurricanes Katrina and Rita in 2005 (Turner et al., 2006). These hurricanes related deposition events predominantly of inorganic sediments from offshore likely contributed to wetland stability (Turner et al., 2006). Sedimentation of the salt marsh have also been shown to occur during winter storms and hurricane conditions (Leonardi et al., 2017). However, these meteorological processes are not sufficient to maintain the elevation of the marsh under the combined effects of soil compaction and sea level rise in the Barataria estuary (Wilson and Allison, 2008). Overall, the decrease of salt marsh in the Barataria Basin is related to human intervention in natural sedimentation regime, wherein, following the completion of the artificial levee system after the 1927 flood, riverine sediments deposition ceased due to unconstrained overbank flooding (Baumann et al., 1984).

Figure 2.11. Landsat-5 TM images of Barataria Basin land cover classification during 1985-2011; pink, orange, green, light yellow, brown and black color represent developed area, fresh marsh, forest area, brackish marsh, salt marsh and water area, respectively.
Wetland forest area in the Barataria Basin also showed an overall decreasing trend from 23.45% to 17.83% during 1985-2011 mainly due to conversion of agricultural land, urbanization along the levee, and overall land subsidence caused by compaction and sea level rise (Nelson et al., 2002). Correspondingly, human developed area including urban and crop land (pink color; Figure 2.11) increased from 3.56% to 6.03% (pink line; Figure 2.12a), primarily at the expense of forest area, and to a lesser degree of fresh marsh. The levees, which were once covered with forests of hardwood trees have been extensively developed and converted to agricultural, residential, and industrial areas (pink color; Figure 2.11). Furthermore, freshwater marsh in the upper basin increased from 10.51% to 12.34% and varied quite differently from the deteriorating pattern of the saline coastal margin, which could be due to the rich nutrients and sediments delivered to the wetlands by the Davis Pond freshwater diversion.

In addition to the general trends of different land cover variations, year-to-year fluctuations caused by extreme weather events were also captured (Figure 2.11 and Figure 2.12a). Percentages of fresh marsh (orange line), marsh forests (green line), and salt marsh (brown line) all declined during 1991-1992 due to Hurricane Andrew in September 1992. Regardless of the general trend (Figure 2.12a), the fresh marsh showed a substantial decrease from 11.46% to 10.89%, as also indicated by the classification imagery of February 08, 1992 (Figure 2.11c) and September 1992 (Figure 2.11d), respectively. The higher declining rate of fresh marsh, also confirms that salt marsh communities appear to be more resilient to hurricanes than fresh marshes (Barras, 2007); this has been attributed to the generally heavier clay-like soils in saltwater or brackish marshes, which deposit more easily than the unconsolidated decomposing plants in fresh marsh (DeLaune and White, 2012). Further, the soils trapped in weakly-rooted fresh marshes are more easily scoured away, further leading to vegetation loss and, eventual land erosion (Cahoon, 2006). Similar effect was observed after Hurricane Katrina and Rita in September 2005 (Figure 2.12a). However, after the strong hurricane years of 1992 and 2005, fresh marsh displayed an increasing trend along with the relatively lower decline of salt marsh during 1992–1993 and 2005–2006; this phenomenon further supported the previous conclusion that hurricanes could potentially ruin marshes by scouring and eroding the sedimentation or, conversely, prevent marsh collapse by introducing abundant sediment and nutrients (Stone et al., 1997). The sediment deposition and nutrient addition is critical in slowing the land loss rate and marsh flooding. In comparison, little fresh marsh and salt marsh loss occurred after Hurricanes Gustav and Ike in 2008 (Figure 2.12a), which likely indicates that these specific impacts on marsh elevation dynamics associated with hurricanes were interactively determined by type and location of marshes, as well as intensity, track and forward speed of storms (Guntenspergen et al. 1995).

2.3.6.3. Effects of Land Cover Variations on DOC Concentrations

To better understand DOC-landscape dynamics, annual mean DOC concentrations (Figure 2.12b) during 1985–2011 were calculated by averaging the DOC values derived from all of the Landsat and MODIS imagery acquired within a year. Third order polynomial trend-lines in the upper, the middle and the lower Barataria Basins (Figure 2.12b; $R^2$ of 0.21, 0.34 and 0.63, respectively) represent the long-term variations of DOC. DOC in the upper/middle basins showed consistently increasing trends regardless of fluctuations caused by extreme weather events. In the lower basin, DOC exhibited an elevated trend during 1985–2005 and then slightly declined during 2007–2012. Following the catastrophic hurricane years of 1992 and 2005, DOC values showed pulsed increases, with largest increase in the upper and middle basins compared to the lower basin. The percentage of salt marsh appeared to have slightly increased and then stabilized for a number of years following these hurricanes. These results
support the hypothesis that hurricanes can play an important role in wetland sedimentation and limit land loss (Turner et al., 2006; 2007). Variations of land cover percentage (Figure 2.12a) during 1985–2011 were further regressed on annual mean DOC concentrations (Figure 2.12c-d). Significant negative correlation was observed between annual mean DOC concentration and salt marsh percentage during 1985–2012 with $R^2$ of 0.54 (Figure 2.12c), which likely implies the removal of organic-rich materials from submerged salt marshes into estuarine water bodies. In contrast, annual mean DOC during 1985–2011 in the upper basin were positively correlated (low $R^2$ of 0.29) to percentage of human developed area, but increased ($R^2$ of 0.49) when DOC values for the hurricane years of 1992 and 2005 (data in blue dashed circle; Figure 2.12d) were excluded; hurricanes, thus have potential to trigger rapid and huge carbon outflows originally sequestered in soils by scouring and eroding large areas of the marsh.

![Figure 2.12](image)

(a) Percentage of five classified land cover Landsat-5 TM images in Barataria Basin during 1985–2011; pink, orange, green, light yellow, brown and black color correspond developed area, fresh marsh, forest area, brackish marsh, salt marsh and water area, respectively. (b) Annually averaged DOC concentrations in the Barataria Basin during 1985–2012; blue/black/orange color represents DOC in the upper/middle/lower basin. (c) Correlation between annually averaged DOC in the lower basin and salt marsh percentage. (d) Correlation between annually averaged DOC in the upper basin and percentage of developed area.

The salt marshes in the lower Barataria estuary are highly productive and are considered to be a crucial DOC source to estuarine waters. The healthy plants and decomposition of dead organic matter in salt marshes could jointly leach high amounts of DOC into the adjacent water column (Day et al., 1977). Thus, salt marsh degradation and vegetation loss caused by erosion, saltwater intrusion and soil waterlogging is expected to reduce DOC levels in the lower Baratara Basin (Duan et al., 2017). However, increased DOC concentrations accompanying the salt marsh loss in the lower basin observed in our study suggest the soil loss in the salt marsh as an important DOC source. The top marsh soil (~50 cm) within living root zone, which
contains especially abundant organic matter, is most geomorphically unstable and easily eroded (DeLaun et al. and Reddy, 2008). Further, vegetation inundation results in die-off and organic carbon undergoes complex cycling; part of the soil organic carbon can be chemically decomposed, and part can be buried in estuarine sediment or outflows as DOC and DIC into estuarine waters (Alewell et al., 2009; Pendleton et al., 2012). Wilson and Allison, (2008) reported that sediment yields within per meter shoreline length to estuarine areas of Barataria Bay was $1.7 \text{ m}^3\text{yr}^{-1}$ with organic matter accounting for 0.09 MT, which is a potential contribution of organic carbon to the bay and its export to the shelf waters that could also contribute to the summer hypoxia. The negative correlation between salt marsh percentages and DOC concentrations from space-based remote sensing observations (Figure 2.12c) is also supported by other studies that suggest large amounts of previously stored carbon could potentially be released when salt marshes collapse (Davidson and Janssens, 2006; DeLaun and White, 2012; Lane et al., 2016; Wilson and Allison, 2008). In contrast, the positive relation between DOC and percentage of developed area demonstrated that urban and agricultural activities in the surrounding man-made levees could be another possible reason for elevated DOC concentration that could further affect the natural chemistry of basin waters. Lac des Allemands, a major water body in the upper basin and the headwater of Barataria Basin receives drainage from a number of bayous and canals rich in nitrogen and phosphorous (Stow et al., 1985) which results in highly eutrophic ecosystem with high productivity and frequent cyanobacteria blooms (Day et al., 1977) which could contribute to DOC in Lac des Allemands (Singh et al., 2010). Furthermore, the elevated autochthonous production of DOC caused by eutrophication in the upper basin might also increase the role of this area as a source of nutrients and DOC to the lower estuary; this is reasonably supported by a weak positive correlation ($R^2=0.19$; not shown here) observed between percentage of developed area and mean DOC in the lower basin.

2.4. Conclusions

The combined effect of natural processes and human perturbations on long-term (1985–2011) variations of DOC in the Barataria Basin was assessed from in-situ measurements (2008-2011) and satellite observations (1985–2012) of CDOM absorption coefficient ($a_{355}$) and DOC concentrations. Water is the major medium for DOM transport among the waterbodies and marshes within the Barataria Basin and its movement is governed by complicated environmental factors. Primary analysis of various $a_{355}$–salinity relationships under distinct meteorological and hydrological conditions allow inferences regarding water movement and hence DOM transport. Increasing salinity seaward with a pronounced gradient during normal conditions was observed; this gradient becomes more obvious during winter storms since freshwaters driven by strong northwest frontal passages flush waters from the upper basin to the shelf, thus freshening the basin. A deviation in the general freshwater-marine gradient was observed during high flow conditions of the MR and the effects of prevailing southern winds on the plume waters; under these conditions, salinity of marine end members were slightly lower than some stations within in the bay. The $a_{355}$–salinity relationships revealed strong riverine input of CDOM associated with the MR plume waters in the lower basin during spring/summer flood period, and elevated CDOM linked to frequent cold front events during winter/early spring.

Landsat-5 TM and MODIS-Aqua imagery over the Barataria Basin were combined with monthly collected in-situ measurements during 2008–2012 to develop empirical $a_{355}$ algorithms under normal, high MR flow and cold front conditions. The band ratio (G/R) of Landsat-5 TM and MODIS-Aqua were highly correlated with $a_{355}$ in power law relationships.
with different coefficients for the three conditions. Empirical algorithms for MODIS performed better ($R^2 > 0.81$) than those of Landsat ($R^2 = 0.72–0.79$). The CDOM–DOC relationships along the transect in the Barataria Basin were also assessed and applied to time-series Landsat-5 TM (1985–2011) and MODIS-Aqua data (2002–2012) to investigate a 28-year long-term trend of DOC in Barataria Basin. DOC in the lower basin, generally displayed spring peak linked to the high MR discharge periods and relatively lower levels in fall-winter (except cold front events), and were thus poorly correlated to air temperature. In contrast, negative correlation between temperature and DOC in the upper/middle basin indicated highest DOC during winter associated with decaying marsh plants along with frequent winter storm. DOC–precipitation relationships illustrated that DOC response to the precipitation is low in the lower basin, but becomes significant in the upper basin. During winter, high precipitation and low temperature, results in high amounts of DOC concentrations entering the upper Barataria Basin.

More importantly, percentage of 27-year land cover variations (1985–2011) derived from Landsat-5 TM supervised classification was further linked to annually mean DOC concentrations (1985–2011) to investigate DOC–landscape dynamics in the Barataria Basin. Inverse correlation between DOC concentration and salt marsh percentage during 1985–2011 signifies that loss of salt marshes could be considered as a potential DOC source in the lower Barataria Basin. In contrast, the positive relations between DOC in the upper basin and percentage of developed area demonstrated that increasing nutrient-rich runoff from urban and agricultural activities strengthen the export of DOC to the waterbodies in the upper basin. Even though with known uncertainties in the Landsat-5 TM/MODIS-Aqua derived DOC concentrations and percentage of land cover variations, the primary linkage between spatiotemporal DOC abundance and land cover type is a scientific priority for understanding increasing anthropogenic influences associated with estuaries (e.g., wetland loss, land-cover variations, levee construction, eutrophication) on carbon sources, sinks, and cycling in the estuary-shelf system.
CHAPTER 3. FLOODWATER IMPACT ON GALVESTON BAY PHYTOPLANKTON TAXONOMY, PIGMENT COMPOSITION AND PHOTO-PHYSIOLOGICAL STATE FOLLOWING HURRICANE HARVEY FROM FIELD AND OCEAN COLOR (SENTINEL 3A-OLCI) OBSERVATIONS

3.1. Introduction

Phytoplankton, which forms the basis of the aquatic food web, is crucial to marine ecosystems and plays a strong role in marine biogeochemical cycling and climate change. Phytoplankton contributes approximately half of the total primary production on Earth, fixing ~50 GT of carbon into organic matter per year through photosynthesis; however, various phytoplankton taxa affect differently the carbon fixation and export (Sathyendranath et al., 2014). Chlorophyll a (Chl a), an essential phytoplankton photosynthetic pigment, has been considered a reliable indicator of phytoplankton biomass and primary productivity in aquatic systems (Bracher et al., 2015). Phytoplankton also contain several accessory pigments such as chlorophyll-b (Chl b), chlorophyll-c (Chl c), photosynthetic carotenoids (PSC) and photo-protective carotenoids (PPC) that are either involved in light harvesting, or in protecting Chl a and other sensitive pigments from photodamage (Fishwick et al., 2006). Some of PSCs and PPCs are taxa-specific and have been considered as bio-marker pigments: e.g., fucoxanthin (PSC) for diatoms, peridinin (PPC) for certain dinoflagellates, alloxanthin (PPC) for cryptophytes, zeaxanthin (PPC) for prokaryotes (e.g. cyanobacteria), and the degradation products of Chl a, namely, divinyl Chl a and divinyl-Chl b for prochlorophyte (Jeffrey and Vest, 1997). High-Performance Liquid Chromatography (HPLC) which can efficiently detect and quantify several chemo-taxonomically significant chlorophylls and carotenoids, when coupled with these taxa-specific pigment ratios, allow phytoplankton taxonomic composition to be quantified based on a pigment concentration diagnostic procedures such as CHEMTAX (Mackey et al., 1996). Furthermore, phytoplankton pigments with distinct absorption characteristics strongly influence the light absorption by phytoplankton (Bidigare et al., 1990; Ciotti et al., 2002; Briacud et al., 2004). As such, phytoplankton absorption spectra has been used to infer underlying pigments and also phytoplankton taxonomy by Gaussian-decomposition (Hoepffner and Sathyendranath, 1991; Lohrenz et al., 2003; Ficek et al., 2004; Chase et al., 2013; Moisan et al., 2013; Wang et al., 2016; Moisan et al., 2017). More importantly, phytoplankton optical properties (absorption and backscattering) bearing the imprints of different pigments and cell-size are important contributors to reflectance in a waterbody (Gordon et al., 1988). Morel and Prieur, (1977) first reported the feasibility of calculating the phytoplankton absorption coefficients and other inherent optical properties (IOPs) from measured subsurface irradiance reflectance based on the simplified radiative transfer equation. Improvements in semi-analytical inversion algorithms to derive IOPs from in-situ and remotely sensed reflectance spectra have been reported (Roesler and Perry, 1995; Hoge and Lyon, 1996; Lee et al., 1996; Garver and Siegel, 1997; Carder et al., 1999; Maritorena et al., 2002; Roesler and Boss, 2003; Chase et al., 2017). Roesler et al., (2003) further modified an earlier IOP inversion algorithm used in Roesler and Perry, (1995) by adding a set of 5
species-specific phytoplankton absorption spectra, and derived phytoplankton taxonomic composition from the field measured remote sensing reflectance.

Phytoplankton pigment composition varies not only between taxonomic groups but also with photo-physiological state of cells and environmental stress (e.g., light, nutrients, temperature, salinity, turbulence and stratification) (Suggett et al., 2009). The photosynthetic pigment field is an important factor influencing the magnitude of fluorescence emitted by phytoplankton, with active fluorometry commonly used to obtain estimates of phytoplankton biomass (D’Sa et al., 1997). Advanced active fluorometry termed as fast repetition rate (FRR; (Kolber et al., 1998)) and analogous techniques such as the fluorescence induction and relaxation (FIRE; Suggett et al., 2008) allows for the simultaneous measurements of the maximum PSII photochemical efficiency (Fv/Fm); where Fm and Fo is maximum and minimum fluorescence yield and Fv is variable fluorescence obtained by subtracting Fo from Fm) and the effective absorption cross section (σPSII) of a phytoplankton population; these have been used as diagnostic indicators for the rapid assessment of phytoplankton health and photo-physiological state linked to environmental stressors. Considerable effort has been invested to achieve a deeper understanding of the impacts of environmental factors and phytoplankton taxonomy on photosynthetic performance of natural communities from field and laboratory fluorescence measurements (Kolber et al., 1988; Geider et al., 1993; Schützler et al., 1997; Behrenfeld and Kolber, 1999; D’Sa and Lohrenz, 1999; Holmboe et al., 1999; Moore et al., 2003). Furthermore, knowledge of photo-physiological responses of phytoplankton in combination with information on phytoplankton taxonomic composition could provide additional insights on regional environmental conditions.

Synoptic mapping of aquatic ecosystems using satellite remote sensing has revolutionized our understanding of phytoplankton dynamics at various spatial and temporal scales in response to environmental variabilities and climate change. It has also provided greater understanding of biological response to large events such as hurricanes in oceanic and coastal waters (Babin et al., 2004; Acker et al., 2009; D’Sa, 2014; Farfan et al., 2014; Hu and Feng, 2016). Although the primary focus of ocean color sensors has been to determine the Chl a concentration and related estimates of phytoplankton primary production (Mitchell, 1994; Behrenfeld and Falkowski, 1997), more recently, several approaches have been developed based on phytoplankton optical signatures to derive spatial distributions of phytoplankton functional types (PFTs) (Alvain et al., 2005; Nair et al., 2008; Hirata et al., 2011), phytoplankton size classification (Ciotti et al., 2002; Hirata et al., 2008; Brewin et al., 2010; Devred et al. 2011), and phytoplankton accessory pigments (Pan et al., 2010; Pan et al., 2011; Moisan et al., 2013; Moisan et al., 2017; Sun et al., 2017). The basis of these satellite-based remote sensing algorithms have relied on distinct spectral contributions from phytoplankton community composition (e.g., taxonomy, size structure) to remote sensing reflectance (Rrs, sr-1); however, these studies have all been confined to open ocean and shelf waters. In contrast, satellite studies of phytoplankton pigments have been limited in the optically complex estuarine waters where the influence from wetlands, rivers, and coastal ocean make phytoplankton communities highly variable and complex.

In this study, field bio-optical measurements and ocean color remote sensing data (Sentinel-3A OLCI) acquired in Galveston Bay, a shallow estuary along the Gulf coast (Texas, USA; Figure 3.1), are used to investigate the spatial distribution of phytoplankton pigments, taxonomic composition, and their photo-physiological state following the extreme flooding of the Houston Metropolitan and surrounding areas due to Hurricane Harvey and the consequent biological impact of the floodwater discharge into the bay. The paper is organized as follows: section 2 describes the field data acquisition and laboratory processing, section 3 presents the algorithms and methods used to distinguish phytoplankton groups, retrieve spatial distribution of pigments, and calibrate phytoplankton physiological parameters. Results and discussions
(section 4 and 5), and summary (section 6) addresses the main contributions and findings of this paper.

Figure 3.1. Sentinel-3A OLCI RGB image (October 29, 2017) with locations of sampling sites in Galveston Bay acquired on September 29 (red asterisk), October 29 (green circles) and October 30 (blue solid squares), 2017, respectively.

3.2. Data and Methods

3.2.1. Study Area

Galveston Bay (GB), a shallow water estuary (~2.1 m average depth), encompasses two major sub-estuaries: San Jacinto Estuary (also divided as Upper GB and Lower GB), and Trinity Estuary (Trinity Bay) (Figure 3.1). It is located adjacent to the heavily urbanized and industrialized metropolitan areas of Houston, Texas (Dorado et al., 2015). A deep (~14 m) narrow Houston Ship Channel connects the bay to the GoM through a narrow entrance, the Bolivar Roads Pass. Tidal exchange between GB and the GoM occurs through the entrance channel with diurnal tides ranging from ~0.15 to ~0.5 m. The major freshwater sources to GB are the Trinity River (55%), the San Jacinto River (16%), and Buffalo Bayou (12%) (Guthrie et al., 2012). The San Jacinto River was frequently observed to transport greater amounts of dissolved nutrients into GB than the Trinity River (Quigg, 2011); however, the negative relationship between nitrate concentrations and salinity observed in the mid-bay area (adjacent to Smith Point) (Santschi, 1995), indicated Trinity River to be a major source of nitrate in GB. The catastrophic flooding of Houston and surrounding areas associated with Hurricane Harvey resulted in strong freshwater inflows into GB from the San Jacinto River (>3300 m$^3$s$^{-1}$; USGS 08067650) on August 29, 2017 and the Trinity River (>2500 m$^3$s$^{-1}$; USGS 08066500 site at Romayor, Texas) on August 30, 2017, respectively. Although the discharge from the two rivers in the upstream returned to normal conditions (~50–120 m$^3$s$^{-1}$) in about 2 weeks after the Hurricane passage, salinity remained low for over a month following the hurricane passage (D’Sa et al., 2018).

3.2.2. Sampling and Data Collection

Surface water samples were collected at a total of 34 stations during two surveys on September 29 and October 29–30, 2017 (Figure 3.1). Samples at stations 1 to 14 (red asterisk
on top of green circle; Figure 3.1) along the Trinity River transect were collected repeatedly on September 29 and October 29, 2017, respectively. Additional 9 sampling sites (blue squares; Figure 3.1) around the upper bay and in the East Bay were sampled on October 30, 2017. The surface water samples were stored in coolers and filtered on the same day. The filter pads were immediately frozen and stored in liquid nitrogen for laboratory absorption spectroscopic and HPLC measurements of the samples. An optical package equipped with a conductivity-temperature-depth recorder (Sea-Bird SBE) and a Fluorescence Induction and Relaxation System (FIRe; Satlantic Inc) was used to obtain profiles of salinity, temperature, pressure, and phytoplankton physiological parameters ($F_v/F_m$ and $\sigma_{PSII}$). Measurements of backscattering were also made at each station using the WETLabs VSF-3 (470, 530, 670 nm) backscattering sensor (D’Sa et al., 2006). Included in the optical package was also a hyperspectral downwelling spectral irradiance meter (HyperOCR, Satlantic). The irradiance data from HyperOCR were processed using Prosoft 7.7.14 and the photosynthetically Active Radiation (PAR) were estimated from the irradiance measurements. The above-water reflectance measurements were collected using a GER 1500 512iHR spectroradiometer in the 350-1050 nm spectral range. At each station, sky radiance, plate radiance, and water radiance were recorded (each repeated three times) and processed to obtain above-water remote sensing reflectance (Joshi et al., 2017). A total of 43 Sentinel-3A OLCI full resolution mode, cloud free level-1 images were obtained over GB between August 01, 2016-December 01, 2017 from the European Organization for Meteorological Satellites (EUMESAT) website and pre-processed using Sentinel-3 Toolbox Kit Module (S3TBX) version 5.0.1 in Sentinel Application Platform (SNAP). These Sentinel-3A OLCI data were further atmospherically corrected to obtain remote sensing reflectance ($R_{rs,OLCI}$, sr$^{-1}$) using Case-2 Regional Coast Color (C2RCC) module version 0.15 (Doerffer and Schiller, 2007). River discharge information during August, 2016-December, 2017 was downloaded from the USGS Water Data (USGS) for Trinity River at Romayor, Texas (USGS 08066500) and the west flank of the San Jacinto River (USGS 08067650). Individual pictures of microplankton (10 to 150 µm) recorded by an Imaging FlowCytobot (IFCB) located at the entrance to Galveston Bay were downloaded (http://dq-cytobot-pc.tamug.edu/tamugifcb) for pigment validation.

3.2.3. Absorption Spectroscopy

Surface water samples were filtered through 0.2-µm nuclepore membrane filters and the colored dissolved organic matter (CDOM) absorbance (ACDOM) were obtained using a 1-cm path length quartz cuvette on a Perkin Elmer Lambda-850 UV/VIS spectrophotometer equipped with an integrating sphere. The Quantitative Filter Technique (QFT) with 0.7-µm GF/F filters were used to measure absorbance of particles (Atotal) and non-algal particles (ANAP) inside an integrating sphere at 1 nm intervals from 300 to 800 nm. The absorption coefficients of CDOM ($a_{CDOM}$), NAP ($a_{NAP}$), particles (atotal) and phytoplankton ($a_{phy}$) were calculated using the following equation 1.5-1.7, the $a_{CDOM}$ were corrected for scattering, temperature, and baseline drift by subtracting an average value of absorption between 700-750 nm for each spectrum (Joshi and D’Sa 2015) and the path length correction for filter pad was applied according to (Stramski et al. 2015).

3.2.4. Pigment Absorption Spectra

The water samples were filtered with 0.7-µm GF/F filter. The filter pads were stored in liquid nitrogen until transferred into 30 ml vials containing 10 ml cold 96% ethanol (Ritchie, 2006). The vials were spun evenly to ensure full exposure of the filter pad to the ethanol and then kept in the refrigerator (in the dark) overnight. The pigment solutions at room-temperature
were poured off from vials into 1 cm cuvette and measured on a Perkin Elmer Lambda-850 UV/VIS spectrophotometer to obtain pigment absorbance spectra (Apig), while, 90% ethanol was used as a blank (Thrane et al., 2015). The total absorption coefficients of pigments apig(λ) were calculated as follow:

\[
apig(\lambda) = 2.303 \times \frac{Apig(\lambda)}{L} \times \frac{V_{ethanol}}{V_{filtered}}
\]

where L is the path length in meters, Vethanol is the volume of ethanol, and Vfiltered is the filtered volume of the water samples.

3.2.5. HPLC Measurement

Water samples were filtered through 0.7-µm GF/F filters and immediately frozen in liquid nitrogen for HPLC analysis using the methods reported by Barlow et al., (1997). The detected pigments along with their abbreviations are listed in Table 1. Diagnostic biomarker pigments are marked in bold letters (Table 3.1).

Table 3.1. Pigments information acquired from HPLC samples in Galveston Bay.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Primary Pigment (PPig)</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chlorophylls</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[TChl a]</td>
<td>Total chlorophyll a (TChl a)</td>
<td>[Chlide a]+[DVChl a]+[Chl a]</td>
</tr>
<tr>
<td>[TChl b]</td>
<td>Total chlorophyll b (TChl b)</td>
<td>[DVChl b]+[Chl b]</td>
</tr>
<tr>
<td>[TChl c]</td>
<td>Total chlorophyll c (TChl c)</td>
<td>[Chl c]+[Chl c]+[Chl c]</td>
</tr>
<tr>
<td><strong>Carotenoids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Caro]</td>
<td>Carotenes†</td>
<td>[ββ-Car]+[βε-Car]</td>
</tr>
<tr>
<td>[Allo]</td>
<td>Alloxanthin</td>
<td></td>
</tr>
<tr>
<td>[Buta]</td>
<td>19'-Butanoyloxyfucoxanthin</td>
<td></td>
</tr>
<tr>
<td>[Diadino]</td>
<td>Diadinoxanthin</td>
<td></td>
</tr>
<tr>
<td>[Diat]</td>
<td>Diatoxanthin</td>
<td></td>
</tr>
<tr>
<td>[Fuco]</td>
<td>Fucoxanthin</td>
<td></td>
</tr>
<tr>
<td>[Hexa]</td>
<td>19'-Hexanoyloxyfucoxanthin</td>
<td></td>
</tr>
<tr>
<td>[Peri]</td>
<td>Peridinin</td>
<td></td>
</tr>
<tr>
<td>[Zea]</td>
<td>Zeaxanthin</td>
<td></td>
</tr>
<tr>
<td>[Neo]</td>
<td>Neoxanthin</td>
<td></td>
</tr>
<tr>
<td>[Lut]</td>
<td>Lutein</td>
<td></td>
</tr>
<tr>
<td>[Viola]</td>
<td>Violaxanthin</td>
<td></td>
</tr>
<tr>
<td>[Pras]</td>
<td>Prasinoxanthin</td>
<td></td>
</tr>
<tr>
<td>[Anthera]</td>
<td>Antheraxanthin</td>
<td></td>
</tr>
</tbody>
</table>

Note: (1) [Chl b], [Allo], [Fuco], [Peri], [Zea], [Buta] and [Hexa] are considered as diagnostic pigments for PFTs (Moisan et al., 2017).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Pigment Sum</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[TChl]</td>
<td>Total Chlorophyll (TChl)</td>
<td>[TChl a]+[TChl b]+[TChl c]</td>
</tr>
<tr>
<td>[PPC]</td>
<td>Photoprotective Carotenoids (PPC)</td>
<td>[Allo]+[Diadino]+[Diat]+[Zea]+[Caro]+[Viola]</td>
</tr>
<tr>
<td>[PSC]</td>
<td>Photosynthetic Carotenoids (PSC)</td>
<td>[Buta]+[Fuco]+[Hexa]+[Peri]+[Lut]+[Pras]</td>
</tr>
<tr>
<td>[PPS]</td>
<td>Photosynthetic Pigments (PPS)</td>
<td>[PSC]+[TChl]</td>
</tr>
<tr>
<td>[AP]</td>
<td>Total Accessory Pigments (AP)</td>
<td>[PPC]+[PSC]+[TChl b]+[TChl c]</td>
</tr>
<tr>
<td>[TP]</td>
<td>Total Pigments (TP)</td>
<td>[AP]+[TChl a]</td>
</tr>
<tr>
<td>[DP]</td>
<td>Total Diagnostic Pigments (DP)</td>
<td>[PSC]+[Allo]+[Zea]+[T Chl b]</td>
</tr>
</tbody>
</table>
3.2.6. FIRe Measurements

An in-situ Fluorescence Induction and Relaxation System (FIRe, Satlantic Inc.) was used to characterize phytoplankton photosynthetic physiology during the two surveys in GB. The FIRe is based on illuminating a sample with an intense flash of light to instantaneously saturate the reaction centers of photosystem II (PSII); under these light conditions, reaction centers do not accept electrons and most of the absorbed light energy is dissipated as fluorescence. The fundamental parameter measured by FIRe is fluorescence yield $F(t)$, which is the emitted fluorescence divided by the irradiance intensity (no unit). In contrast to strong flashes, dark adaption enables all reaction centers of PSII to be open with least fluorescence emitted, thus, resulting in minimal fluorescence yield ($F_o$). Maximum fluorescence yield ($F_m$) can be obtained after sufficient irradiation when all reaction centers are closed. Maximum photochemical efficiency, which quantify the potential of converting light to chemical energy for the PSII reaction centers (Moore et al., 2006), was calculated as $(F_m - F_o)/F_m = F_v/F_m$. The functional absorption cross section $\sigma_{PSII}$ ($\text{Å}^2\text{quantum}^{-1}$) measures the capability of reaction centers to absorb light from the ambient environment. The FIRe was deployed at a slow descent rate, with 12 and 20 vertical profiles obtained during the first and second surveys, respectively. All measurements were programmed using standard protocols of single saturating turn-over (ST) flash saturation of PSII (Kolber et al., 1998). Flashes were generated from highly uniform blue LEDs at 455 nm with approximately 30 nm half-bandwidth. Chl a fluorescence was stimulated using saturating sequence of 80 1.1 µs flashes applied at 1 µs intervals, 8 sequences were averaged per acquisition, and the fluorescence signal was detected at 668 nm. All data were processed using standard FIReCom software (Satlantic). In addition, samples of 0.2-µm filtered sea water at each station were used as ‘blank’ to remove the background fluorescence signals (Cullen and Davis, 2003); in this step, the fluorescence from the filtered samples (without phytoplankton) were subtracted from in-situ fluorescence signals to get more accurate values of $F_v/F_m$.

3.2.7. Retrieving Phytoplankton Groups from Above-water $R_{rs}$

A fundamental relationship that links sub-surface remote-sensing reflectance ($r_{rs}$) and the IOPs was expressed using a quadratic function developed by (Gordon et al., 1988):

$$r_{rs} = g_1 * u(\lambda) + g_2 * u(\lambda)^2; u(\lambda) = \frac{b_p}{a_{total} + b_p}$$

(3.2)

where, the parameters $g_1$ (~0.0788) and $g_2$ (~0.2379) are values for turbid estuarine waters (Joshi and D'Sa, 2018); $r_{rs}$ is the sub-surface remote sensing reflectance that were obtained from above-water remote sensing reflectance ($R_{rs}$) using (Lee et al., 2002):

$$r_{rs} = \frac{R_{rs}}{0.52 + 1.7 \times R_{rs}}$$

(3.3)

The total backscattering coefficient $b_p$ is comprised of water (bbw) and particulates including both organic and inorganic particles ($b_{bp}$), while the total absorption coefficients ($a_{total}$) can be further separated into four sub-constituents $a_w$, $a_{phy}$, $a_{NAP}$ and $a_{CDOM}$ (Roesler and Perry, 1995) as indicated by equation 1.1.

The IOP inversion algorithm for retrieving IOPs from $R_{rs}$ require known spectral shape (eigenvector) of each component in Eq. 1.1 to estimate the magnitude (eigenvalues) of each component (Table 3.2). The spectral shape can be adjusted by changing the values of slope based on characteristics of the study area. It is worth noting that a single averaged phytoplankton eigenvector does not provide species information whereas a set of several species-specific phytoplankton eigenvectors allow estimates of species composition. IOPs inversion algorithm applied in this study makes use of mass-specific phytoplankton absorption
spectra of 10 groups namely, dinoflagellate, diatom, chlorophyte, cryptophyte, haptophyte, prochlorophyte, raphidophyte, rhodophyte, red cyanobacteria and blue cyanobacteria; these were obtained from Dierssen et al. (2006) and Dutkiewicz et al. (2015) as eigen vectors rather than using one average \( a_\text{phy} (\lambda) \) spectrum. Subsequently, the inversion algorithm iterates repeatedly to minimize the difference between modeled \( R_{rs} \) and in-situ measured \( R_{rs} \) \((R_{rs,\text{in situ}})\) until a best fit is achieved while allowing for alterations of all parameters listed in Table 3.2 (Chase et al., 2017). The absolute percent errors between modeled and measured values of \( R_{rs} \), aphy, aCDOM, aNAP and bbp were calculated as:

\[
\% \text{error} = \frac{|X_{\text{modeled}} - X_{\text{measured}}|}{X_{\text{measured}}} \times 100
\]  

Table 3.2. Parameters and eigenvectors used in the semi-analytical inversion algorithm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>Slope</th>
<th>Eigenvalue</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{\text{CDOM}} (\lambda) )</td>
<td>( a_{\text{CDOM}} (\lambda) = M_{\text{CDOM}} \times \exp^{-S_{\text{CDOM}} \times (\lambda - \lambda_0)}; \lambda_0 = 443 )</td>
<td>( S_{\text{CDOM}} )</td>
<td>( M_{\text{CDOM}} )</td>
</tr>
<tr>
<td>( a_{\text{NAP}} (\lambda) )</td>
<td>( a_{\text{NAP}} (\lambda) = M_{\text{NAP}} \times \exp^{-S_{\text{NAP}} \times (\lambda - \lambda_0)}; \lambda_0 = 443 )</td>
<td>( S_{\text{NAP}} )</td>
<td>( M_{\text{NAP}} )</td>
</tr>
<tr>
<td>( a_{\text{phy}} (\lambda) )</td>
<td>( a_{\text{phy}} (\lambda) = \sum \text{Chl}<em>a_i \times a</em>{\text{phy}i}; a_{\text{phy}i} ) is the spectral shape of each phytoplankton group.</td>
<td>( \text{Chl}_a_i )</td>
<td></td>
</tr>
<tr>
<td>( b_{\text{bbp}} (\lambda) )</td>
<td>( b_{\text{bbp}} (\lambda) = B_{\text{bbp}} \times (\lambda_0 / \lambda)^{5_{\text{bbp}}}; \lambda_0 = 443 )</td>
<td>( S_{\text{bbp}} )</td>
<td>( B_{\text{bbp}} )</td>
</tr>
</tbody>
</table>

Note: \( a_{\text{phy}i}(\lambda) \) for 10 different groups of phytoplankton used in this study were extracted from (Dierssen et al., 2006) and Dutkiewicz et al., (2015).

3.2.8. Retrieving Pigments from Sentinel 3-OLCI \( R_{rs} \)

3.2.8.1. Reconstruction of Pigment Absorption Spectrum by Multiple Linear Regression

Total pigment absorption spectra \( a_{\text{pig}} (\lambda) \) obtained during both surveys (Eq. 3.1), were modeled as a third order function of HPLC measured Chl a (Chl _a_HPLC) concentration at each station as (Moisan et al., 2017):

\[
a_{\text{pig}} (\lambda) = C_3 \times (\text{Chl}_a_{\text{HPLC}})^3 + C_2 \times (\text{Chl}_a_{\text{HPLC}})^2 + C_1 \times \text{Chl}_a_{\text{HPLC}} + C_0
\]  

where vector coefficient \( C=[C_3, C_2, C_1, C_0] \), are wavelength-dependent coefficients that range from 400 to 700 nm at 1 nm interval; these were further applied to Sentinel-3A OLCI Chl a to calculate \( a_{\text{pig,OLCI}} \) at each pixel as:

\[
a_{\text{pig,OLCI}} (\lambda) = C_3 \times (\text{Chl}_a_{\text{OLCI}})^3 + C_2 \times (\text{Chl}_a_{\text{OLCI}})^2 + C_1 \times \text{Chl}_a_{\text{OLCI}} + C_0
\]  

where Chl _a_OLCI is Sentinel-3A OLCI derived Chl a concentration (259×224 pixels); the obtained image represents the value of \( a_{\text{pig,OLCI}} \) at a certain wavelength and 301 images of \( a_{\text{pig,OLCI}} \) can be obtained in the 400-700 nm wavelength range at 1 nm interval.

3.2.8.2 Satellite Retrieval of Pigments using Non-Negative Least Square Inversion Model

The \( a_{\text{pig,OLCI}} \) is a mixture of \( n \) pigments with known absorption spectra \( a_i(\lambda), i = 1, 2, \ldots, n \) at wavelength \( \lambda \) (nm); thus, \( a_{\text{pig,OLCI}}(\lambda) \) can be considered as a weighted sum of individual component spectrum (Thrane et al., 2015) at each image point as:

\[
a_{\text{pig,OLCI}} (\lambda) = x_1 \times a_1 (\lambda) + x_2 \times a_2 (\lambda) + \ldots x_n \times a_n (\lambda)
\]  

where \( A(\lambda) = [a_1 (\lambda), a_2 (\lambda), \ldots a_n (\lambda)] \) represent the mass-spectral spectra of 16 pigments (Chl a, Chl b, Chl c1, Chl c2, pheophytin-a, pheophytin-b, peridinin, fucoxanthin, neoxanthin, lutein, violaxanthin, alloxanthin, diadinoxanthin, diatoxanthin, zeaxanthin, and β-
carotenoid), which are the in-vitro pigment absorption spectra over pigment concentrations and can be extracted from supplementary R scripts of Thrane et al., (2015). The vector coefficient \( X = [x_1, x_2, \ldots x_n] \) correspond to the concentrations (µg L\(^{-1}\)) of these distinct pigments; note that \( X \) cannot be negative, therefore, non-negative least squares (NNLS) was used to guarantee positive solutions of \( X \) (Moisan et al., 2013; Thrane et al., 2015). Eq. 3.7 can be further expressed as:

\[
\begin{bmatrix}
  a_{\text{pig}(400)_{\text{OLCI}}} \\
  a_{\text{pig}(401)_{\text{OLCI}}} \\
  \vdots \\
  a_{\text{pig}(700)_{\text{OLCI}}}
\end{bmatrix} =
\begin{bmatrix}
  x_1 \\
  x_2 \\
  \vdots \\
  x_n
\end{bmatrix}
\times
\begin{bmatrix}
  a_1(400), a_2(400), \ldots a_n(400) \\
  a_1(401), a_2(401), \ldots a_n(401) \\
  \vdots \\
  a_1(700), a_2(700), \ldots a_n(700)
\end{bmatrix}
\]

\[ (3.8) \]

3.2.9. Processing Approach

Sentinel 3A-OLCI pigment maps were generated using the processing pathway 1 (Fig. 2) that includes the following: 1) developing empirical relationships between HPLC-measured Chl a and Rrs\(_{\text{insitu}}\) band ratio for Sentinel 3A-OLCI band 9 (673 nm) and band 11 (709 nm) to generate Sentinel 3A-OLCI Chl a maps, 2) converting Chl a concentration to a\(_{\text{pig,OLCI}}(\lambda)\) maps, and subsequently decomposing a\(_{\text{pig,OLCI}}(\lambda)\) into individual pigment spectra to generate phytoplankton pigment maps for GB. In processing pathway 2, phytoplankton taxonomic composition at each sampling station was obtained from a 10-species IOP inversion model, which take R\(_{\text{Rs,insitu}}\) as input and estimates Chl a concentration of each phytoplankton group (Figure 3.2). Finally, CDOM-corrected FIRe measurements of F\(_r\)/F\(_m\) and \( \sigma_{\text{PSII}} \) were combined with phytoplankton taxonomy to assess photosynthetic physiology of different phytoplankton groups.
Figure 3.2. Flowchart showing the three processing steps for: (1) retrieving pigments spatial distribution maps from OLCI, (2) distinguishing phytoplankton groups, and (3) assessing phytoplankton physiological parameters and their linkages to taxonomic groups.

3.3. Results

3.3.1. Phytoplankton Taxonomy and Physiological State from Field Observations

3.3.1.1. Measurements of Above Water Remote Sensing Reflectance

Above-water remote sensing reflectances ($R_{rs,insitu}$) from the two surveys (Figure 3.3) reflect the influence of the absorbing and scattering features of water constituents. Low reflectance (~675 nm) caused by Chl a red light absorption and maximum reflectance at green wavelength (~550 nm) were observed. Obvious dips at ~625 nm versus reflectance peaks ~650 nm were observed in spectra during both surveys, which could be attributed to cyanobacteria modulation of the spectra (Hu et al., 2010). The reflectance peak around 690–700 nm was obvious at most sampling sites except at stations 13 and 14 adjacent to the nGOM and were likely due to the effect of Chl a fluorescence (Gitelson, 1992; Gilerson et al., 2010). The peak position at stations with lower Chl a concentration (~5 µg L$^{-1}$) were observed at 690–693 nm; however, the peaks shifted to longer wavelengths of 705 and 710 nm for station 23 and 19 with extremely high Chl a concentrations of ~31 and 50 µg L$^{-1}$, respectively (Figure 3.3).

![Figure 3.3. $R_{rs,insitu}$ spectra at stations in GB on September 29, and October 29-30, 2017; vertical bars represent Sentinel-3A OLCI spectral bands.](image)

3.3.1.2. Performance of IOP Inversion Algorithm

The IOP inversion algorithm was applied to $R_{rs,insitu}$ data (Figure 3.3) obtained during the two surveys in GB. The mean errors for modeled $a_{CDOM}$, $a_{NAP}$, $a_{phy}$ and $b_{bp,470}$ at all wavelengths for the 34 stations were 5.86%, 6.83%, 12.19% and 10.79%, respectively (Table 3.3). A total of 8 phytoplankton groups (dinoflagellate, diatom, chlorophyte, cryptophyte, haptophyte, prochlorophyte, raphidophyte, and blue cyanobacteria) were spectrally detected from IOP inversion algorithm. The sum of 8 eigenvalues of Chl$\text{a}$ (Table 3.2) represents the modeled total Chl a ($T\text{Chla}_{\text{mod}}$) of the whole phytoplankton community. The $T\text{Chla}_{\text{mod}}$ is better correlated with HPLC-measured total Chl a ($T\text{Chla}_{\text{HPLC}}$) for survey 2.
(green circle; Figure 3.4a) with $R^2 \sim 0.92$, compared to survey 1 (red color; Figure 3.4a). In addition, the TChl $a_{\text{mod}}$ appear to be slightly higher than TChl$_a$-HPLC for survey 2. The modeled $a_{\text{DOM}}$ ($a_{\text{DOM}_{\text{mod}}}$) are in close agreement with spectrophotometrically measured aCDOM at 412 nm (Figure 3.4b), with $a_{\text{DOM}}$ obtained on September 29, 2017 much higher than that on October 29-30, 2017. The modeled $b_{\text{bp}}$ ($b_{\text{bp}_{\text{mod}}}$) are well correlated with in-situ $b_{\text{bp}}$ ($b_{\text{bp}_{\text{insitu}}}$) at 470 nm (Figure 3.4c) with higher $R^2(0.81)$ observed on September 29, 2017. In addition, both modeled and field-measured $b_{\text{bp}}$ showed stronger backscattering at most stations on September 29, 2017 than those on October 29-30, 2017.

Table 3.3. Error statistics over all wavelengths and sampling stations (N=301×34=10234; 12 and 22 stations on Sep 29 and Oct 29-30, 2017) from semi-analytical IOP inversion algorithm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Min. error (%)</th>
<th>Max. error (%)</th>
<th>Mean error (%)</th>
<th>$R^2$(Sep)</th>
<th>$R^2$(Oct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{ST_{\lambda}}, \lambda \in [400,700]$</td>
<td>0.005</td>
<td>40.12</td>
<td>18.71</td>
<td>0.90</td>
<td>0.89</td>
</tr>
<tr>
<td>$a_{\text{DOM}}(\lambda), \lambda \in [400,700]$</td>
<td>0.042</td>
<td>11.20</td>
<td>5.86</td>
<td>0.92</td>
<td>0.94</td>
</tr>
<tr>
<td>$a_{\text{KAP}}(\lambda), \lambda \in [400,700]$</td>
<td>0.001</td>
<td>11.46</td>
<td>6.73</td>
<td>0.90</td>
<td>0.91</td>
</tr>
<tr>
<td>$a_{\text{HY}}(\lambda), \lambda \in [400,700]$</td>
<td>0.001</td>
<td>36.42</td>
<td>12.19</td>
<td>0.84</td>
<td>0.85</td>
</tr>
<tr>
<td>$b_{\text{bp}}(\lambda), \lambda = 470$ nm</td>
<td>0.057</td>
<td>40.22</td>
<td>10.79</td>
<td>0.81</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Figure 3.4. (a) Validation of TChl $a_{\text{mod}}$ via HPLC-measured TChl $a$; individual %Chl $a$ of each detected taxa versus corresponding %DP shown with (d) cryptophyte, (e) chlorophyte, (f) cyanobacteria, (g) diatom, (h) dinoflagellate, and (l) haptophyte; red and green dots indicate
the samples on September 29 and October 29-30, 2017, respectively. Comparison between in-situ measurements and modeled results with (b) $a_{CDOM}$ (412) and (c) $b_{DP}$ (470).

The Chl a percentage (%Chl a), which is $\text{Chl}_a/\text{TChl}_a$, were also compared with diagnostic pigment percentage (%DP), which is specific DP for each phytoplankton group over the sum of DP ($\sum \text{DP}$). The DP for diatom (fucoxanthin), dinoflagellate (peridinin), cryptophytes (alloxanthin), chlorophyte (Chl b), haptophyte (19'-hexanoyloxyfucoxanthin), and cyanobacteria (zeaxanthin) referred in (Moisan et al., 2017) were used in this study. The $R^2$ between %Chl a and %DP for different phytoplankton groups range from 0.15 to 0.81 (Figure 3.4). The %Chl a of cryptophyte is between 5%-42% and well correlated with alloxanthin/$\sum \text{DP}$ ($R^2=0.62-0.72$; Figure 3.4d) for both surveys. In addition, the cryptophyte %Chl a at station 19 and 23 on October 30, 2017 was highest (~40%) in coincidence with the highest value of alloxanthin/$\sum \text{DP}$ (Figure 3.4d). Furthermore, relationship between chlorophyte %Chl a and Chl b/$\sum \text{DP}$ ($R^2=0.55$; Figure 3.4e) showed that chlorophyte during survey 1 contributed higher fraction to the whole phytoplankton community compared to survey 2. The %Chl a of cyanobacteria highly correlated with zeaxanthin/$\sum \text{DP}$ with $R^2$ larger than 0.7 (Figure 3.4f) for both surveys. Low %Chl a of dinoflagellate in coincidence with low peridinin/$\sum \text{DP}$ ($R^2=0.78$) were observed at stations along the transect, however, increased contribution of dinoflagellate appeared adjacent to the entrance during both surveys (Figure 3.4g).

3.3.1.3. Variations in Phytoplankton Community Structure

Reconstruction of the phytoplankton absorption coefficients spectra revealed variations in phytoplankton community structure (Figure 3.5) even several weeks after Hurricane Harvey. The modeled aphy spectra ($a_{phy,mod}$) at stations 6, 13, 17 and 19 (Figure 3.5a-f) yielded spatiotemporal differences of phytoplankton taxonomic composition in GB.

Figure 3.5. Reconstruction of phytoplankton absorption coefficients spectra at station 6 (a) and 13 (b) on September 29, 2017, at station 6 (c) and 13 (d) on October 29, 2017 and at 17(e), and 19 (f) on October 30, 2017 based on the mass specific absorption spectra of different phytoplankton groups including diatom, chlorophyte, dinoflagellate, cryptophyte,
cyanobacteria (blue), haptophyte, prochlorophyte and raphidophyte presented using different colors.

The strong absorption peak around 625 nm induced by cyanobacteria was observed at most of the stations for both modeled results and in-situ measurements (Figure 3.5a, 5c and 5e) except at stations adjacent to the entrance (Figure 3.5b and d). The $a_{\text{phy}}$ at station 6 was primarily dominated by group of cyanobacteria (blue line) and chlorophyte (green line) on September 29, 2017 (Figure 3.5a); in contrast, the spectrum of chlorophyte contributed very little at station 6 on October 29, 2017 (green line; Figure 3.5c). Furthermore, the shape of spectra for samples obtained at station 13 showed strong dinoflagellate-modulation versus extremely low cyanobacteria contribution during survey 1 (red line; Figure 3.5b). However, small-size group like haptophyte and prochlorophyte displayed increasing proportions at station 13 on October 29, 2017 (Figure 3.5d). Station 17 in the East Bay was dominated by cyanobacteria (blue line; Figure 3.5e) and cryptophyte (pink line; Figure 3.5e) absorption spectra, whereas, on October 30, 2017, the main spectral features at station 19 in the upper GB was from cryptophyte (pink line) and chlorophyte (green line; Figure 3.5f).

The corresponding taxa-specific %Chl a derived from IOPs inversion algorithm for the two surveys on September 29 and October 29-30, 2017 are shown in Figure 3.6a and b, respectively. Cyanobacteria (blue bars) and chlorophyte (green bars) constituted over 55% of the phytoplankton communities during survey 1 (September 29, 2017; Figure 3.6a). In addition, chlorophyte, known to proliferate in freshwater environments, showed higher fraction than that observed in survey 2 (green color; Figure 3.6). Further, chlorophyte together with diatoms (purple color; Figure 3.6a) accounted for ~60% of TChl a mod at many stations (e.g., station 7, 8 and 9) with a well-mixed water column (inferred from salinity profiles; not shown) on September 29, 2017. Cryptophyte, haptophyte and raphidophyte became a minor component of the community and accounted in total to ~25% of TChl a mod (Figure 3.6a).

Figure 3.6. Phytoplankton taxonomic compositions detected from IOPs inversion algorithm on a) September 29 and b) October 29-30, 2017 in Galveston Bay; phytoplankton groups are represented in different colors as shown in the legend.
Furthermore, contribution by dinoflagellate group to TChla_mod was low inside the bay, but showed increasing %Chl a (~30%) in higher salinity waters adjacent to the nGOM (red color; Figure 3.6a). Cyanobacteria (blue color; Figure 3.7) exhibited a slightly elevated percentage during survey 2 (~60 days after hurricane passage, October 29-30, 2017) and were quite abundant at station 16, 17 and 18 in East Bay where the water was calm and stratified as observed from salinity profiles. In addition, cyanobacteria were not prevailing adjacent to the nGOM (Station 12, 13 and 14) and close to San Jacinto (station 19, 20, 21, 23 and 24), where cryptophyte (pink color) and chlorophyte (green color) showed dominance (Figure 3.6b). The %Chl a of chlorophyte obtained at stations along the Trinity River transect decreased by ~10% on October 29-30, 2017 compared to that on September 29, 2017. Small size groups like haptophyte and prochlorophyte increased on October 29-30, 2017 and were more abundant adjacent to the nGOM, accounting for more than 25% of the TChla_mod.

3.3.1.4. Environmental Conditions and Physiological State of Phytoplankton Community

The surface salinity presented a pronounced seaward increasing gradient along the transect (station 3-14) during both the surveys (Figure 3.7a) with primarily lower salinity throughout the bay during survey 1 in comparison to survey 2, which indicated the freshening impact was still ongoing even 4 weeks after Hurricane Harvey. The salinity was ~15 at station 16 and decreasing when going further into East Bay (~10 at station 17 and 18; Figure 3.7a). In upper GB, salinity at station 19-24 did not vary significantly (~15), increasing along with the distance away from the San Jacinto River mouth with highest value (~17.5) at station 24. During both surveys, lowest Chl a (Figure 3.7b) were observed adjacent to the nGOM, and the highest Chl a were closest to the river mouth. The photosynthetically Active Radiation (PAR) which were calculated from down-welling irradiance (not shown here) decreased significantly with depth, but surface PAR (Figure 3.7c) were similar in magnitude at all stations. Pigment ratios including TChl a/TP (0.58-0.68), PSC/Chl a (0.07-0.26) and AP/TP (0.34-0.42) were obtained from HPLC measurements and shown in Figure 3.7d, e and f, respectively.
Figure 3.7. Phytoplankton taxonomic compositions detected from IOP inversion algorithm on September 29 and October 29-30, 2017 in Galveston Bay; phytoplankton groups are represented in different colors as shown in the legend.

The CDOM calibrated and 0-0.5m depth averaged photosynthetic parameters $F_v/F_m$ varied from 0.41 to 0.64 (Figure 3.7g), while $\sigma_{PSII}$ was in the range of 329-668 Å² quantum⁻¹ (Figure 3.7h). The highest $\sigma_{PSII}$ and lowest $F_v/F_m$ appeared adjacent to the nGOM (station 12-14). Conversely, values of $F_v/F_m$ at stations 7-9 with a well-mixed water column were high with low values of $\sigma_{PSII}$. Both $F_v/F_m$ and $\sigma_{PSII}$ did not directly correlate with Chl a, (e.g., high Chl a ~51 µg L⁻¹ at station 19 corresponded to a relatively low level of $F_v/F_m$~0.45, versus high $\sigma_{PSII}$ ~550 Å² quantum⁻¹). However, the stations with high $F_v/F_m$ coincided with the high fraction of Chl a (Chl a/TP) and low fraction of AP (AP/TP) (Figure 3.7d and f). In contrast, $\sigma_{PSII}$ showed an overall positive relationship with AP/TP, but altered negatively with Chl a/TP during both surveys. The lowest (highest) value of $\sigma_{PSII}$ ($F_v/F_m$) were observed at station 9 corresponding to the highest Chl a/TP value (~0.64) on October 29, 2017. The highest AP/TP and PSC/Chl a were obtained from stations adjacent to the nGOM.

3.3.1.5. $F_v/F_m$ and $\sigma_{PSII}$ Taxonomic Signatures

Distinct pigments housed within phytoplankton light-harvesting antennae can strongly influence PSII light-harvesting capability and the photosynthetic quantum efficiency of phytoplankton (Lutz et al. 2001). In this study, we observed an inverse relationship ($R^2$~0.63-0.81; Figure 3.8a and d) between the $F_v/F_m$ and $\sigma_{PSII}$, that appeared related to taxonomic signals during surveys 1 and 2 in GB. Stations 1-9 along the transect were considered as well-mixed group with no dominance by any particular group (black circles; Figure 3.8a-c); stations 10-14 close to the entrance were however, strongly dominated by dinoflagellate and haptophyte (red symbol; Figure 3.8a-c) during survey 1. This well-mixed group displayed low values of
σ_{PSII} (~390-439 Å² quantum⁻¹), and high levels of Fᵥ/Fₘ (~0.42-0.65) with Fᵥ/Fₘ approaching 0.65 at station 9 on September 29, 2017 (Fig. 8a). However, enhanced contributions of dinoflagellate and haptophyte around the entrance corresponded to a decline of Fᵥ/Fₘ (0.3-0.4) against an increase of σ_{PSII} (500–600 Å² quantum⁻¹) during survey 1. Furthermore, samples obtained from survey 2 at station 1-9, station 10-14, station 16-18 and station 19-24 were considered as well-mixed (black), dinoflagellate-haptophyte dominated (red), cyanobacteria dominated (blue) and cryptophyte-chlorophyte dominated (green), respectively. Stations 16-17 dominated by cyanobacteria (blue triangles; Figure 3.8d) showed high level of Fᵥ/Fₘ (0.5–0.6) and relatively low values of σ_{PSII} (300–400 Å² quantum⁻¹). The Fᵥ/Fₘ and σ_{PSII} of cryptophyte-chlorophyte dominated stations showed a moderate level of Fᵥ/Fₘ (0.4–0.5) and σ_{PSII} (580–680 Å² quantum⁻¹). More importantly, tight positive relationships existed between measurements of Fᵥ/Fₘ and Chl a/TP (R²~0.31-0.63; Figure 3.8b and e). On the other hand, σ_{PSII} were positively correlated with PSC/Chl a with R²~0.6 (Figure 3.8c and f). The PSC/Chl a of cyanobacteria dominated group (blue symbols), and well mixed group (brown symbols) were relatively low. Highest PSC/Chl a and lowest Chl a/TP was observed for the dinoflagellate-haptophyte dominated group, corresponding to the lowest σ_{PSII} and highest Fᵥ/Fₘ. In addition, cryptophyte-chlorophyte dominated group had high levels of PSC/TChl a (~0.18-0.26) and slightly higher Chl a/TP compared to dinoflagellate-haptophyte dominated group. Overall, well-mixed groups with high proportion of large-size phytoplankton (e.g., diatoms and chlorophyte) showed higher Chl a/TP along with larger Fᵥ/Fₘ and smaller σ_{PSII} than those stations with high fraction of dinoflagellate and pico-populations (Figure 8c and f).

Figure 3.8. a, d) σ_{PSII} against Fᵥ/Fₘ; b, e) Fᵥ/Fₘ versus Chl a/TP; and c, f) σ_{PSII} versus PSC/Chl a on September 29 and October 29-30, 2017 respectively. The data points identified by dominant taxa with black, red, green and blue symbols denoting well-mixed, dinoflagellate-haptophyte dominated, cryptophyte-chlorophyte dominated, and cyanobacteria dominated groups, respectively.

3.3.2. Satellite Observations of Phytoplankton Pigments
3.3.2.1 An OLCI Chl a Algorithm and its Validation

Blue to green band ratio algorithms have been widely used to study Chl a in the open ocean and shelf waters (D’Sa et al., 2006; Blondeau-Patissier et al., 2014); however, these bands generally fail in estuarine waters due to strong blue absorption by the high levels of CDOM and suspended particulate matter, especially after flooding events associated with hurricanes (D’Sa et al., 2011; D’Sa et al., 2018; Joshi and D’Sa, 2018). The percentage contribution by CDOM fluorescence (blank) to maximum fluorescence yield ($F_m$) obtained from in-situ FIRe (Figure 3.9a) demonstrated that Chl a fluorescence was strongly influenced by high amounts of CDOM fluorescence in GB, especially during the first survey (September 29, 2017), when the bay was under strong freshwater influence (red triangles; Figure 3.9a). The CDOM fluorescence signal constituted ~ 25 % in the region adjacent to the nGOM (stations 12-14), between 25%-50% in the upper GB, and up to ~65% in Trinity Bay, which implied that blue and even green band are highly contaminated by CDOM and might not be the most suitable bands for estimating Chl a in GB. However, an increase in peak height near 700 nm and its shift towards longer wavelength (Figure 3.3) can be used as a proxy to estimate Chl a concentration (Gitelson, 1992). The C2RCC atmospheric-corrected $R_{rs,OLCI}$ at each of the sampling sites were further compared with $R_{rs,insitu}$ (Figure 3.3) at phytoplankton red absorption (~673 nm) and Chl a fluorescence (~700 nm) bands (Figure 3.9b). The C2RCC performed overall better for the second survey on October 29-30, 2017 (green and blue symbols; Figure 3.9b) than the first survey on September 29, 2017 (red triangles; Figure 3.9b) when stations 1, 3 and 4 (circled triangles; Figure 3.3c) adjacent to the Trinity River mouth were included; these stations were the last sampling sites in the afternoon (~4:30 pm) and under somewhat cloudy conditions. The time difference between satellite pass and in-situ measurements, sky conditions and shallow water depth also likely introduced more errors at these locations. The $R^2$ between $R_{rs,OLCI}$ and $R_{rs,insitu}$ at red and near infrared (NIR) bands was 0.89 when the data from station 3 and 4 were excluded, suggesting good usability of these two bands for Chl a empirical algorithms in GB. Thus, the higher the Chl a concentration, the stronger the red light absorption, resulting in higher reflectance at 709 nm; consequently, negative correlations were observed between Red/NIR band ratio and Chl a. The ratio of Red (~673 nm) and NIR (709 nm) reflectance bands from in-situ measurements were overall highly correlated with HPLC-measured Chl a with $R^2$ ~ 0.96, 0.94 and 0.98 on September 29, October 29 and October 30, 2017, respectively (Figure 3.9c). The Sentinel-3A OLCI Chl a maps (Figure 3.10a-c) were generated for all data based on the relationship between Chl a and the Red and NIR band ratio as:

$$\text{Chl a (µg L}^{-1}) = 216.38 \times \exp (-2.399 \frac{R_{rs}(673)}{R_{rs}(709)})$$

(3.10)

The OLCI-derived Chl a (Figure 3.10a-c) showed a good spatial agreement with Chl a HPLC (Figure 3.10d-f). In addition, a comparison of this algorithm with that of Gilerson et al. (2010) revealed slightly better performance (not shown) inside of GB and especially in the area adjacent to the shelf.
Figure 3.9. a, d) $\sigma_{\text{PSII}}$ against $F_v/F_m$; b, e) $F_v/F_m$ versus Chl a/TP; and c, f) $\sigma_{\text{PSII}}$ versus PSC/Chl a on September 29 and October 29-30, 2017 respectively. The data points identified by dominant taxa with black, red, green and blue symbols denoting well-mixed, dinoflagellate-haptophyte dominated, cryptophyte-chlorophyte dominated, and cyanobacteria dominated groups, respectively.

The Chl a concentration on September 29, 2017 was overall higher than that on October 29-30, 2017 through the entire bay. East Bay displayed very high Chl a concentration, with highest value (>30 $\mu$g L$^{-1}$) observed on September 29, 2017 (Figure 3.10a). The narrow shape and shallow topography of East Bay results in relatively higher water residence time (Rayson et al. 2016); thus, the reduced exchange with shelf waters likely lends the East Bay vulnerable to eutrophication. The average Chl a concentration on October 29-30, 2017 were ~15 $\mu$g L$^{-1}$ along the transect (station 1-11) and ~4-6 $\mu$g L$^{-1}$ (station 12-14) close the entrance of GB. In addition, Chl a adjacent to San Jacinto River mouth (>16 $\mu$g L$^{-1}$) was higher than that in Trinity Bay, which might suggest that San Jacinto inflow had higher nutrient concentrations than Trinity as also previously reported (Quigg et al. 2010). Furthermore, the OLCI-Chl a maps on October 29 and 30, 2017 showed extremely high Chl a concentration in a narrow area adjacent to the San Jacinto River mouth, with Chl a approaching ~ 40 $\mu$g L$^{-1}$ at station 19 (Figure. 3.10c).
Figure 3.10. Chl a concentration generated based on in-situ band ratio (R_{673}/R_{709}) algorithm with (a), (b) and (c) representing Chl a distribution on September 29, October 29 and October 30, 2017, respectively; (c), (d) and (f) show the validation between HPLC-measured Chl a and OLCI-derived Chl a on September 29, October 29 and October 30, 2017, respectively.

3.3.2.2. Long-term Chl a Observations in Comparison with Hurricane Harvey Event

OLCI-derived Chl a maps between August, 2016-November, 2017 (Figure. 3.11a1-a15) and time series of averaged Chl a values in the areas of Trinity Bay, East Bay and adjacent to the nGOM (Figure 3.11b) revealed regionally different responses of Chl a to freshwater discharge from the San Jacinto and the Trinity Rivers (Figure 3.11b). Due to the relatively much higher discharge from the Trinity River, the spatial distribution of Chl a in the bay (Figure 3.11) generally indicates its greater influence than the San Jacinto River. During the winter, and spring in 2017, phytoplankton Chl a peaks ~32 µg L^{-1} in Trinity Bay (Figure 3.11b) were observed after high inflows from both rivers (Figure 3.11a5-a8). Chla then slightly decreased to ~20 µg L^{-1} in summer (July and August, 2017). Generally, Chl a showed overall lower value (~10 µgL^{-1}) between September-December, 2016 compared to 2017 in the absence of meteorological and hydrological events (Figure 3.11a1-a4). However, with the East Bay less directly affected by river discharge, Chl a levels remained fairly constant in the range of ~18-24 µg L^{-1} before hurricane. In contrast, extremely high river discharge (~3300 m^{3}s^{-1}) induced by Hurricane Harvey in late August, 2017, elevated Chla in both Trinity and East Bay to higher levels as observed on September 14, 2017 (~30-35 µg L^{-1}; Figure 3.11a11) compared to mean state of fall season in 2016. Chl a then continuously decreased through September to October, 2017 in Trinity and East Bay and were relatively low (≤10 µg L^{-1}) in November, 2017 under no additional pulses of river discharge. Concentration of Chla adjacent to the entrance of GB exhibiting much lower values year round than that of the Trinity and East Bay, and also showed slight positive responses to the enhanced river discharge and the hurricane-induced flooding events. In addition, Chl a concentrations always displayed low values along the Houston Ship Channel.
Figure 3.11. (a1-a15) OLCI-derived Chl a shown for the period of August 31, 2016-October 01, 2017. (b) Trinity River discharge at Romayor, Texas (USGS 08066500, black line) and the west flank of the San Jacinto River (USGS 08067650; blue line); the green, red and gray lines/symbols represent the mean of Chl a at stations 1-7 in Trinity Bay, at stations 17-18 in East Bay and at stations 12-14 close to the entrance of GB corresponding to 43 cloud free Sentinel 3A-OLCI images (colored symbols; dated symbols correspond to images a1-a15).

3.3.2.3. Reconstruction of Total Pigment Absorption Spectra from OLCI-derived Chl a

The reconstructed apig(λ) based on the third order function of Chl a_HPLC (gray lines; Figure 3.12a and b) agreed well with the spectrophotometrically measured apig(λ) (black lines; Figure 3.12a and b) during both surveys (R²=0.86; Figure 3.12c). The R² for modeled versus measured apig(λ) are between 0.76 and 1.00 from 400 to 700 nm with averaged R² of whole spectra reaching ~ 0.82 on September 29, 2017 and ~0.89 on October 29-30, 2017, respectively. The vector coefficients C = [C₁, C₂, C₃, C₄] were further applied to Eq. (3.6) to generate apig_OLCI(λ) based on OLCI-derived Chl a images on July 06 (Figure 3.11a), September 29 (Figure 3.10a), October 29-30 (Figure 3.10b-c), and Nov 25 (Figure 3.11a15), 2017, respectively; these contained 259×224 pixels in each image. The a_{pig,OLCI}(λ) at each pixel was retrieved at 1 nm interval, and thus 301 images of a_{pig,OLCI}(λ) representing each wavelength were obtained over GB.
Figure 3.12. Spectrophotometrically measured and multi-regression fitted $a_{\text{pig}}(\lambda)$ spectra acquired on (a) September 29 and (b) October 29-30, 2017 in GB. Gray and black lines represent modeled and measured results, respectively. (c) Comparison between modeled and spectrophotometrically measured $a_{\text{pig}}(\lambda)$ for all data with color representing wavelength.

3.3.2.4. Accuracy of phytoplankton pigment retrievals from Sentinel 3A-OLCI

The reconstructed $a_{\text{pig,OLCI}}(\lambda)$ was spectrally decomposed into 16 individual pigment spectra at each pixel based on Eq. (7). A comparison of all data between HPLC-measured pigments and NNLS algorithm inverted pigments showed that $R^2$ ranged from a low of 0.40 for diatoxanthin to 0.96 for Chl a and RMSE was in the range of 0.103-0.584 (Table 3.4). The NNLS-modeled Chl a also correlated well with OLCI-derived Chl a ($R^2=0.98$; Figure 3.13a), with each exhibiting similar quantitative and spatial patterns. For the other 15 simultaneously simulated pigments, $R^2$ of only 7 pigments were greater than 0.650 (Table 3.4). In addition, the produced RMSE were less than 0.3 for most of pigments, except zeaxanthin, violaxanthin, diatoxanthin and diadinoxanthin. Further, those pigments with relatively lower RMSE, their slopes were very close to 1 and y-intercepts approached to 0. Five NNLS-derived versus HPLC measured diagnostic pigments including alloxanthin, Chl b, zeaxanthin, fucoxanthin and peridinin are shown in Figure 13. The $R^2$ between NNLS-derived and HPLC-measured pigments for surveys 1 and 2 was highest for alloxanthin (0.91; Figure 3.13b). For the other pigments $R^2$ was 0.854 for Chl b (Figure 3.13c), 0.689 for zeaxanthin (Figure 3.13d), 0.645 for fucoxanthin (Figure 3.13e) and 0.566 for peridinin (Figure 3.13f), respectively.

Table 3.4. Correlation between HPLC-measured pigment concentration with NNLS-modeled pigments.

<table>
<thead>
<tr>
<th>Pigment</th>
<th>$R^2$</th>
<th>slope</th>
<th>intercept</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl a</td>
<td>0.963</td>
<td>0.878</td>
<td>0.099</td>
<td>0.125</td>
</tr>
<tr>
<td>Chl b</td>
<td>0.854</td>
<td>0.791</td>
<td>0.091</td>
<td>0.214</td>
</tr>
<tr>
<td>Chl c₁</td>
<td>0.701</td>
<td>0.842</td>
<td>0.112</td>
<td>0.199</td>
</tr>
<tr>
<td>Chl c₂</td>
<td>0.626</td>
<td>0.884</td>
<td>0.134</td>
<td>0.103</td>
</tr>
<tr>
<td>Pheophythin a</td>
<td>0.812</td>
<td>0.841</td>
<td>0.097</td>
<td>0.114</td>
</tr>
<tr>
<td>Pheophythin b</td>
<td>0.783</td>
<td>0.632</td>
<td>0.112</td>
<td>0.145</td>
</tr>
<tr>
<td>Peridinin</td>
<td>0.566</td>
<td>0.649</td>
<td>0.081</td>
<td>0.246</td>
</tr>
<tr>
<td>Fucoxanthin</td>
<td>0.625</td>
<td>0.651</td>
<td>0.383</td>
<td>0.189</td>
</tr>
<tr>
<td>Neoxanthin</td>
<td>0.691</td>
<td>0.627</td>
<td>0.142</td>
<td>0.279</td>
</tr>
<tr>
<td>Lutein</td>
<td>0.742</td>
<td>0.651</td>
<td>0.109</td>
<td>0.298</td>
</tr>
<tr>
<td>Violaxanthin</td>
<td>0.426</td>
<td>0.456</td>
<td>0.415</td>
<td>0.389</td>
</tr>
<tr>
<td>Alloxanthin</td>
<td>0.912</td>
<td>0.592</td>
<td>0.107</td>
<td>0.227</td>
</tr>
<tr>
<td>Diadinoxanthin</td>
<td>0.512</td>
<td>0.446</td>
<td>0.721</td>
<td>0.396</td>
</tr>
<tr>
<td>Diatoxanthin</td>
<td>0.401</td>
<td>0.423</td>
<td>0.693</td>
<td>0.423</td>
</tr>
<tr>
<td>Zeaxanthin</td>
<td>0.689</td>
<td>0.516</td>
<td>0.802</td>
<td>0.584</td>
</tr>
</tbody>
</table>
3.3.3. Spatiotemporal Variations of Diagnostic Pigments

Flooding due to Hurricane Harvey not only enhanced Chl a, but also affected the phytoplankton pigments composition. NNLS-retrieved pigment maps for July, September, October, and November, 2017 including those of alloxanthin, chl b, zeaxanthin, fucoxanthin and peridinin (Figure 3.14) showed different levels of variations before and after the hurricane event. Alloxanthin, which is unique to cryptophytes (Wright and Jeffrey, 2006) exhibited same spatial distribution patterns (Figure 3.14a-e) with Chl a. Alloxanthin was especially low (~0.5 µg L⁻¹, Figure 3.14a) in the major basin area on July 06, 2017 before the hurricane and slightly elevated (~0.7 µg L⁻¹, Figure 3.14b) in September and October, 2017 after the hurricane passage. Furthermore, extremely high alloxanthin (~3.5 µg L⁻¹, Figure 3.14c-d) was observed adjacent to San Jacinto River mouth on October 29-30, 2017, which coincided with the high %Chl a of cryptophyte at stations 19 and 23 (Figure 3.6b). The bloom with high concentration of alloxanthin on October 29, 2017 (~3.5 µg L⁻¹; Figure 3.14c) then extended to a broader area on October 30, 2017 (Figure 3.14d).

Chl b is abundant in the group of chlorophyte (green algae) (Hirata et al., 2011) and the spatial distributions of Chl b (Figure 3.14a-e) also showed strong correlations with Chl a on July 06, 2017, September 29, October 29-30 and November 25, 2017. The NNLS-derived Chl b exhibited overall low values (~0.5-2 µg L⁻¹; Figure 14a) before the hurricane and showed obvious elevation throughout the bay after the hurricane and eventually decreasing to pre-hurricane level by November 25, 2017. Furthermore, Chl b concentrations observed on September 29, 2017 were higher than that on October 29-30, 2017, which corresponded to a decline of chlorophyte percentage derived from the IOP inversion algorithm (Figure 3.6). More importantly, images obtained from IFCB at the entrance to GB also detected freshwater species...
Chlorophyte (Pediastrum duplex; Figure 3.14g) on September 29, 2017. However, this species was rarely observed in IFCB images for the other dates (Figure 3.14a–e). In addition, Chl b concentrations approached ~2.8 µg L\(^{-1}\) in the bloom area and the corresponding green discoloration of water was also observed during the field survey on October 30, 2017.

Zeaxanthin is known as taxa-specific pigment for prokaryotes (cyanobacteria) (Moisan et al., 2017; Dorado et al., 2015) and NNLS-derived zeaxanthin maps (Figure 3.14a–e) displayed significantly different patterns with Chl a, exhibiting low concentrations in the areas where the Chl a were high. For example, zeaxanthin was especially low in the bloom area on October 29–30, 2017, which agreed well with low %Chl a of cyanobacteria at stations 19 and 23 (Figure 3.6), thus indicating that this localized algal bloom event was not associated with cyanobacteria. In addition, zeaxanthin was high ~3.0 µg L\(^{-1}\) (Figure 3.14a), and remained elevated on October 29–30, 2017 (Figure 3.14b–d). Zeaxanthin eventually decreased to very low values (~1.2 µg L\(^{-1}\); Figure 3.14e) on November 25, 2017.

Fucoxanthin is a major carotenoid found in diatoms (Hirata et al. 2011; Moisan et al. 2017) and the NNLS-derived fucoxanthin maps (Figure 3.14a–e) showed highly similar distribution patterns with Chl a. Maps of fucoxanthin showed low concentrations on July 06, 2017 (~1.5 µg L\(^{-1}\); Figure 3.11a), and displayed a large increase on September 29, 2017 (~1.6-3.0 µg L\(^{-1}\); Figure 3.11b). Diatom group detected from IFCB were dominated by marine species before the hurricane, but subsequently shifted to freshwater species (e.g., Pleurosigma; Figure 3.14g) and then back to marine species after October, 2017. Overall, fucoxanthin concentrations in GB were relatively higher during survey 1, which corresponded to the higher %Chl a of diatom (Figure 3.6) compared to survey 2. Although, fucoxanthin decreased to low values on November 25, 2017 (~1.6 µg L\(^{-1}\); Figure 3.11e), it accounted for higher fraction of phytoplankton diagnostic pigments compared to other dates in July, September and October, 2017.

Peridinin, a primary bio-marker pigment for certain dinoflagellates (Örnólfsdóttir et al. 2003), also displayed significantly distinct patterns in comparison to Chla (Figure 3.14a–e). On July 06, 2017, peridinin was ~0.24-0.36 µg L\(^{-1}\), accounting for high proportion of the diagnostic pigments; meanwhile, diversity of marine dinoflagellate species observed from IFCB at this time was also high (Figure 3.14f). However, peridinin decreased (~0.001-0.05 µg L\(^{-1}\)) after the hurricane, with freshwater dinoflagellate species (Ceratium hirundinella; Figure 3.14g) detected from IFCB on September 29, 2017. In addition, maps of peridinin during both surveys (Figure 3.14b–d) presented higher concentration (~0.3 µg L\(^{-1}\)) in higher salinity waters adjacent to the bay entrance, which agreed well with the increasing fraction of dinoflagellate at stations 10-14 detected from IOP inversion model (Figure 3.6). In contrast, peridinin showed low concentrations in both GB and shelf waters (Figure 3.14e), with dinoflagellate species rarely observed from IFCB on November 25, 2017 (Figure 3.14l).
Figure 3.14. Sentinel-3 OLCI derived maps of diagnostic pigments for Galveston Bay. Simulated $a_1$=e_1) alloxanthin, $a_2$=e_2) Chl b, $a_3$=e_3) zeaxanthin, $a_4$=e_4) fucoxanthin, and $a_5$=e_5) peridinin concentrations. a, b, c, d and e represent columns (maps for July 06, September 29, October 29-30 and November 25, 2017) and 1-5 represent rows (pigments), respectively; (f), (g), (h) and (l) are the corresponding IFCB data for July 06, September 29, October 29-30 and November 25, 2017, respectively; note that IFCB pictures of fresh water species including chlorophyte and cyanobacteria that appeared on September 20-30, 2017 have been zoomed in for better clarity.

3.4. Discussion

3.4.1. Performance of the Semi-Analytical IOP Inversion Algorithm

The residuals between $R_{rs,insitu}$ and $R_{rs,mod}$ on September 29 and October 29-30, 2017, are negative in the blue (400-450 nm) and red (610-630 nm) spectral range at most
stations, whilst keeping positive ∼700 nm, which could be attributed to a number of factors. First, the underestimation near 700 nm by the IOP inversion model is possibly induced by the absence of a fluorescence component in the IOP inversion model; thus, \( R_{rs,insitu} \) containing fluorescence signals were generally higher than \( R_{rs,mod} \) near 700 nm. Second, in the range of 610-630 nm, the absorption was overestimated at most of the stations; in this spectral range, the shape of spectra was strongly modulated by cyanobacteria absorption. Thus this overestimation at ∼620 nm is likely introduced by the input absorption spectrum (eigenvector) for cyanobacteria since all of input \( a^*_{\phi} (\lambda) \) are general absorption spectral shapes for different phytoplankton groups. However, the spectra of \( a^*_{\phi} (\lambda) \) can vary in magnitude and shape associated with package effects under different environmental conditions (e.g., nutrient, light and temperature) even for the same species (Bricaud et al. 2004). More detailed absorption spectra of phytoplankton under different conditions (e.g., high/low light and nutrients) could improve the performance of the IOP algorithm. Furthermore, the role of scattering might be another key factor to explain differences between \( R_{rs,insitu} \) and \( R_{rs,mod} \) for the whole spectra. The quantity and composition of suspended materials including phytoplankton, sediment and minerals will collaboratively determine \( b_{bp}(\lambda) \) in both shape and magnitude.

However, the input eigenvector of \( b_{bp}(\lambda) \) in the present study was not divided into detailed sub-constituents and was a sum spectrum based on a power law function (Table 3.2). In reality, \( b_{bp}(\lambda) \) spectra are not smooth and regular, and thus, the \( bbp(\lambda) \) value of phytoplankton and sediment might introduce errors to the whole spectrum due to their own scattering characteristics.

3.4.2. Distributions of NNLS-Retrieved Phytoplankton Pigments from Sentinel-3A OLCI

The NNLS-inversion algorithm showed relatively higher \( R^2 \) for those pigments that better correlated with HPLC-measured Chl a (e.g., Chl b, and alloxanthin), which was reasonably consistent with Moisan et al., 2017; this outcome could potentially be attributed to the fact that the NNLS pigment inversion algorithm was developed based on the relationship between HPLC-measured Chl a and spectrophotometer-measured \( a_{pig}(\lambda) \). For instance, pigments that were relatively poorly correlated with HPLC-measured Chl a, such as fucoxanthin, diatoxanthin and diadinoxanthin on October 29-30, 2017, the OLCI-derived concentrations in cryptophyte-chlorophyte algal bloom area showed higher concentrations than those of HPLC measurements (e.g., values in gray circle; Figure 3.13e), thus, resulting in lower \( R^2 \). However, in previous studies (Moisan et al. 2017; Pan et al. 2010), satellite-derived fucoxanthin appeared better correlated with HPLC-measured fucoxanthin compared to this study; it reasons that, fucoxanthin, generally one of the most abundant diatom biomarker pigments in coastal waters and along with its long-term measurements in their study area (United States northeast coast), agreed very well with Chl a. In contrast, the cryptophyte-chlorophyte algal bloom area with extremely high Chl a appeared to disturb the correlations between Chl a and fucoxanthin in this study. Also, pigments with apparent high values in algal bloom areas, such as Chl b, Chl c, alloxanthin, lutein, showed higher \( R^2 \) with RMSE less than 0.3. Thus, in-situ measurements of Chl a and \( a_{pig}(\lambda) \) in waters with stronger gradients in magnitude and greater variations in phytoplankton community structures could potentially increase the challenge of applying NNLS-inversion algorithms in optically-complex estuarine waters. Further, the highly dynamic estuarine environment could as well contribute to additional uncertainties in the validation of inverted pigments due to variations such as turbulence, turbidity or light field that are likely to occur during the time interval between in-situ and Sentinel 3-OLCI (∼4 hours) observations. HPLC measurements also cannot detect extremely low pigment concentrations; for example, HPLC-measured peridinin were 0.001
µgL⁻¹ at several stations, however, OLCI-derived peridinin showed higher and variable values at these stations (data in gray circles; Figure 3.13f); this could thus increase the RMSE of the NNLS-inverted peridinin. It was also found that the slope of all pigments were smaller than 1, which demonstrate that NNLS-inverted pigments were relatively smaller than HPLC measurements, especially for those stations located in the algal bloom area; this could most likely be attributed to the underestimation of Chl a values by the Sentinel 3-OLCI empirical algorithms in the algal bloom area. Algal bloom dominated by cryptophyte group, which is also known to cause red tides worldwide, to some degree, could increase red reflectance and thus increase ratio values of Red/NIR and decrease estimated Chl a values. Therefore, reliable estimates of satellite Chl a is crucial for the accuracy of retrieved pigments. The goal of the empirical Chl a algorithm for Sentinel 3A-OLCI is to obtain more accurate estimation of surface Chl a concentration, which is better for retrieving other accessory pigments. However, the primary limitation of Chl a empirical algorithms in this study was that the derived relationships between Red/NIR and Chl a in GB may only be valid within a specific time period due to temporally-limited field observations versus highly dynamic estuarine environments. Therefore, a Chl a empirical algorithm that is more broadly applicable over a longer time period will largely improve the accuracy of retrieved pigments over a series of remote sensing images and can be more useful for spatiotemporal studies of phytoplankton functional diversity. More importantly, the highly similar absorption spectra of many carotenoids are another key issue limiting the accuracy of spectral decomposition techniques. Although the 16 input pigment spectra used in this study were selected from (Thrane et al., 2015), which were correctly identified from unknown phytoplankton community structure with low error rate reported from Monte Carlo tests, the potential effects of aliasing spectra of some pigment pairs (e.g., fucoxanthin vs peridinin, diadinoxanthin vs lutein, β-Carotene vs zeaxanthin) could still be a factor. Thus, the reported errors/R² for retrieved total carotenoids in Trane et al., 2015 were apparently lower/higher than those of modeled total chlorophylls, which showed consistency with this study. Although the predicted pigments showed a range of R² and RMSE with known uncertainties, all are within the acceptable range and could be useful for studying the spatiotemporal responses of PFTs to environmental variations, especially in such optically-complex estuaries.

The derived maps of phytoplankton diagnostic pigments appeared to be reasonably correlated with HPLC-measured diagnostic pigments and showed overall agreement with extracted phytoplankton taxonomic compositions detected from the IOP inversion algorithm. The retrieved diatom-specific fucoxanthin maps however, showed high concentrations compared to other pigments adjacent to the entrance (Figure 3.13b4 and c4), which contradicted with diatom %Chl a calculated from IOP inversion algorithm that Chl a fraction of diatom was relatively uniform at stations 12-14 (Figure 3.6b). (Nair et al., 2008) concluded that fucoxanthin can occur in other phytoplankton types (e.g. raphidophyte and haptophyte). Fucoxanthin and/or fucoxanthin derivatives such as 19'-hexanoyloxyfucoxanthin can also replace peridinin as the major carotenoid in some dinoflagellates (e.g., Karenia brevis; Jeffrey and Vest, 1997). The elevated contributions from groups of dinoflagellate, haptophyte and prochlorophyte adjacent to the entrance (stations 10-14; Figure 3.6b) along with high concentrations of fucoxanthin likely suggest the presence of elevated fractions of haptophyte and dinoflagellate, and further implies that fucoxanthin is an ambiguous marker pigment for diatoms. This could also explain the poor correlation between inverted %Chl a and %DP observed for the groups of diatom and haptophyte (Figure 3.4g and l). These results also further suggest the inherent limitations of using DP-type comparison between major biomarker pigments and phytoplankton groups because the major assumption for DP-type methods is that diagnostic pigment of distinct phytoplankton groups are uncorrelated to each other. This assumption is invalid in that concentrations of major biomarker pigments are significantly correlated with each other and
also may vary in time and space under some external environmental stress (e.g., temperature, salinity, mixing, light and nutrient) (Latasa and Bidigare, 1998).

3.4.3. Response of Phytoplankton Taxa to Environmental Conditions

Previous studies showed diatoms to be the most abundant taxa in GB, and tend to be more dominant during winter/spring, corresponding to periods of high fresh water discharge and nutrient-replete conditions (Dorado et al., 2015; Örnólfsdóttir et al., 2004a); transition from chain-forming diatoms such as Chaetoceros and rod-like diatoms pre-flood to small cells, such as Thalassiosira and small pennate diatoms were generally observed during high river discharge periods (Anglès et al., 2015; Lee, 2017). In contrast, cyanobacteria were the most abundant species during the warmer months (Jun-Aug) when river discharge was relatively low (Örnólfsdóttir et al., 2004b). Further, phytoplankton groups in GB responded differentially both taxonomically and spatially to the freshening events due to their contrasting nutrient requirements and specific growth characteristics. For instance, most phytoplankton taxa (e.g., diatom, chlorophyte and cryptophyte) can be positively stimulated by fresh inflows due to their relatively rapid growth rate (Paerl et al., 2003); however, Roelke et al. (2013) also documented that cyanobacteria and haptophytes in the upper GB were not sensitive to nutrient-rich waters from both rivers, due to the extra nutrients obtained from N2-fixation abilities and mixotrophic characteristics, respectively. In the lower part of GB, dinoflagellates and cyanobacteria are known to be more dominant during the low river discharge due to their preference for higher phosphorus (P) compared to some other groups, and to low turbulence (Lee, 2017) and thus, generally inversely related to the fresh inflows (Lee, 2017; Roelke et al., 2013).

Perturbations following Hurricane Harvey affected the phytoplankton taxonomic composition with alterations in phytoplankton community structure observed as the GB system transitioned from marine to freshwater then to marine system (Figures 3.6 and 3.14). Higher fraction of zeaxanthin and peridinin and the presence of large and slow-growing marine dinoflagellates detected from IFCB pre-hurricane (July 06, 2017) indicate that both cyanobacteria and dinoflagellates were the main groups of phytoplankton community during summer, and likely associated with warmer temperature and lower river flow (Lee, 2017). Later, massive Chla observed in September, 2017 and the decline of Chla to background state in October, 2017, were likely associated with the hurricane-induced high river discharge and the resulting variations in nutrient concentration and composition. Higher fractions of diatom and chlorophyte accompanied with increasing fucoxanthin and Chl b on September 29, 2017, to some extent agreed well with measurements of Steichen et al. (2018) two weeks following Hurricane Harvey that freshwater species (diatom, green algae and cyanobacteria) appeared immediately following the flooding event. Greater abundance of diatom and chlorophyte during survey 1 in comparison to survey 2 were likely due to their rapid growth rates, enhanced nutrient uptake rates, and tolerance of low salinity and high turbulence under high nutrient loading conditions following the freshwater inflows (Roy et al., 2013; Santschi, 1995). Therefore, it is not surprising that Chl b concentrations showed very low values in July and November, 2017, when river discharge was correspondingly low. Cyanobacteria, which normally prefer low salinity conditions, also showed specific responses to this flood event. On September 29, 2017, zeaxanthin slightly increased compared to summer season in July, 2017. The decline of diatoms and chlorophyte versus slightly increased cyanobacteria observed on October 29-30, 2017, could be attributed to the relatively slow growth rates of cyanobacteria compared to that of chlorophytes and diatom (Paerl et al., 2003); cyanobacteria appeared to have lagged behind these groups in terms of responding to enhanced freshwater discharge when longer residence times were again restored. In contrast, the presence of green algae and cyanobacteria could as well be explained by the clarity and turbidity gradient of water. Quigg
et al., (2010) reported that when turbidity was relatively high, chlorophyte dominated over cyanobacteria with biomass ratio of chlorophyte/cyanobacteria greater than 2, which supported our observations that chlorophyte dropped off whilst cyanobacteria increased during survey 2 on October 29-30, 2017. In addition, highest cyanobacteria percentage in East Bay suggest that calm and stratified waters may accelerate cyanobacteria growth as the buoyancy regulation mechanism of cyanobacteria is possibly restricted by the water mixing (Roy et al., 2013). Peridinin, which initially decreased in September and then increased in the lower GB on October 29-30, 2017, suggest that dinoflagellates showed overall preference for high-salinity waters. Furthermore, previous IFCB observations from Biological and Chemical Oceanography Data Management Office (BCO-DMO) showed that algal blooms after hurricanes in the nGOM were initially dominated by diatoms, and subsequently transitioned to blooms of dinoflagellates, likely associated with nutrient ratios and chemical forms of nutrient supplied by the flood waters and rainfall (Heisler et al., 2008). In addition, high concentrations of peridinin observed along the Houston Ship Channel, might provide evidence that the ballast water addition from shipping vessels likely promote harmful species of dinoflagellates (Steichen et al., 2015). Finally, low concentrations of all pigments on November 25, 2017 with relatively higher fraction of fucoxanthin compared to previous dates (Figure 3.14), indicate the major role of marine diatoms at that time and further confirms that diatoms can be found under a wide range of inflows in GB.

The localized cryptophyte-chlorophyte bloom that occurred ~60d after Hurricane Harvey on October 29-30, 2017, was captured by both satellite and in-situ measurements. This bloom might not be associated with the flooding events of Hurricane Harvey, and could be linked to nutrient-rich runoff flowing into GB, reflecting sensitivity and rapid response of phytoplankton community to nutrient input in GB. In shallow and turbid estuaries, human activities are altering the environment and causing phytoplankton changes in diversity and biomass to occur more frequently. Dugdale et al., (2012) reported that variations of phytoplankton community in San Francisco estuary could be attributed to anthropogenically-elevated concentration of ammonium, which restrain the uptake of nitrate, thus reducing the growth and reproduction of larger diatoms and shifting towards smaller species (e.g., cryptophyte and green flagellate). Furthermore, ‘pink oyster’ events related to alloxanthin of cryptophyte in GB occurred more frequently from September through October in recent years (Paerl et al., 2003). The eastern side of Houston Channel in mid bay region was reported as the area most heavily impacted by the intense ‘pink oyster’ events. Previous studies and present observations both suggest that this cryptophyte-chlorophyte dominated bloom could be promoted by the nutrient-driven eutrophication from Houston Ship Channel, urbanization and industrialization along the upper San Jacinto River complex.

3.4.4. Photo-Physiological State of Natural Phytoplankton Community

In this study, the CDOM-corrected FV/FM and \( \sigma_{PSII} \) likely represented a composite of both phytoplankton taxonomy and physiological stress (e.g., nutrient and mixing). Typically, lowest N and P concentrations were measured closest to the nGOM (Quigg et al., 2009). Phytoplankton community living close to nGOM were usually in poor nutrient conditions and would be expected to maximize their light harvesting (increase in \( \sigma_{PSII} \)) due to nutrient stress. Simultaneously, phytoplankton cells might experience a decline of functional proportion of reaction centers of PSII (RCII), which means decrease in \( F_v/F_m \). The observed low levels of \( F_v/F_m \) and Chl a/TP versus high values of \( \sigma_{PSII} \) and AP/TP adjacent to the nGOM showed agreement with previous studies that the fraction of carotenoids to be higher for nutrient-poor cultures (Schütter et al., 1997; Holmboe et al., 1999). In contrast, phytoplankton in well-mixed waters (station 7-9) might experience abundant nutrients due to the resuspension of cyclonic
gyre around Smith Points; as such, their photosynthetic machinery were likely healthier. Aiken et al. (2004) documented that the Chl a/TP ratio was relatively higher when plants were in good growing conditions, which is similar to the observations in this study that phytoplankton have higher fraction of Chl a accompanying higher rate of photosynthetic efficiency ($F_v/F_m$) under nutrient replete conditions. Overall, the spatial pattern of $F_v/F_m$ and $\sigma_{PSII}$ in GB could be mainly attributed to physiological stress of nutrient and hydrodynamics conditions since the light availability (PAR) during the sampling period did not spatially vary significantly at the surface. Furthermore, FIRe measurements ($F_v/F_m$ and $\sigma_{PSII}$) also presented a taxonomic signal super-imposed upon environmental factors. Each cluster with different dominant taxa (well mixed group, chlorophyte & cryptophyte, cyanobacteria, and dinoflagellate & haptophyte) displayed different physiological characteristics. The taxonomic sequence of eukaryotic groups from high $F_v/F_m$, low $\sigma_{PSII}$ to low $F_v/F_m$, high $\sigma_{PSII}$ in the present observations showed potential effects of phytoplankton cell size corresponding to diatoms, chlorophyte, and cryptophyte, dinoflagellate and haptophyte. The prokaryote (cyanobacteria) had relatively high values of $F_v/F_m$ and low values of $\sigma_{PSII}$; this agreed with $F_v/F_m$ for some species of nitrogen-fixing cyanobacteria that can range from 0.6 to 0.65 (Berman-Frank et al., 2007). Yet, it is difficult to separate the contributions from environmental factors and taxonomic variations to the changes of FIRe fluorescence signals since all these parameters are inter-related. Different phytoplankton groups/sizes will display distinct physiological traits ($F_v/F_m$ and $\sigma_{PSII}$) when experiencing considerable environmental pressures. Thus, effects of physiological stress on $F_v/F_m$ and $\sigma_{PSII}$ variations for natural samples can only be determined when taxonomic composition can be excluded as a contributor (Suggett et al., 2009).

3.5. Conclusions

Field measurements (salinity, pigments, optical properties and physiological parameters) and ocean color observations from Sentinel-3A OLCI were used to study the effects of extreme flooding associated with Hurricane Harvey on the phytoplankton community structures, pigment distributions and their physiological state in GB. Flooding effects made the entire GB transition from saline to freshwater then back to a more marine influenced system. The band ratio (Red/NIR) of $R_{ST}$ was negatively correlated with HPLC-measured Chl a in an exponential relationship ($R^2 > 0.93$). The satellite-retrieved Chl a maps yielded much higher Chl a a concentration on September 29, 2017 compared to October 29-30, 2017 with lowest Chl a observed adjacent to the shelf waters. Phytoplankton taxonomic composition was further retrieved from Rrs_insitu using a 10-species IOP inversion algorithm. Phytoplankton community generally dominated by estuarine marine diatoms/dinoflagellates before flood events, was altered to freshwater species of diatom, green algae (chlorophyte) and cyanobacteria during survey 1. It also showed an increase of small-size species including cryptophyte, haptophyte, prochlorophyte and cyanobacteria accompanied by a decline of chlorophyte and diatoms during survey 2.

Phytoplankton diagnostic pigments were retrieved using an NNLS inversion model based on Sentinel-3A OLCI Chl a maps also confirmed spatiotemporal variations of phytoplankton taxonomy. The NNLS-retrieved diagnostic pigment maps showed overall spatiotemporal agreement with HPLC measurements with $R^2$ ranging from 0.40 (diatoxanthin) to 0.96 (Chl a) during both surveys. Alloxanthin, Chl b, and fucoxanthin exhibiting similar patterns with Chla, showed different levels of increase after Hurricane Harvey. In contrast, NNLS-derived zeaxanthin and peridinin presented significantly low values in the area where Chla concentrations were high. Further, maps of zeaxanthin and peridinin displayed relatively higher fraction on July 06, 2017 before the hurricane compared to other diagnostic pigments. However, peridinin decreased post-hurricane on September 29, 2017 and then increased a bit...
on October 29-30, 2017. Ultimately, concentration of Chl a and all biomarker pigments decreased to low levels in November, 2017 when the typical environmental conditions of GB was restored.

Finally, the retrieved phytoplankton taxonomic compositions from IOP inversion algorithm were linked with FIRe-measured photosynthetic parameters ($F_v/F_m$ and $\sigma_{PSII}$) to assess the effects of physiological stress and taxonomic contributions on phytoplankton photosynthetic performance. An inverse relationship between the $F_v/F_m$ and $\sigma_{PSII}$ were observed during both surveys. Phytoplankton community in well-mixed waters (around Smith Point) showed high $F_v/F_m$ against low $\sigma_{PSII}$; in contrast, the area with poor nutrient conditions (adjacent to the shelf waters), showed low $F_v/F_m$ and elevated $\sigma_{PSII}$. Taxonomic signatures of $F_v/F_m$ and $\sigma_{PSII}$ revealed diverse physiological characteristics with dinoflagellate-haptophyte group showing the lowest $F_v/F_m$ versus the highest $\sigma_{PSII}$, whereas prokaryote of cyanobacteria-dominated group showed high values of $F_v/F_m$ and low values of $\sigma_{PSII}$. Overall, this study using field and ocean color data combined with inversion algorithms provided novel insights on phytoplankton response to an extreme flood perturbation in a turbid estuarine environment based on taxonomy, pigment composition and physiological state of phytoplankton.
CHAPTER 4. BIOLOGICAL RESPONSE OF APALACHICOLA BAY AND THE SHELF WATERS TO HURRICANE MICHAEL USING OCEAN COLOR INVERSION MODELS

4.1. Introduction

Projections of increased intensity of hurricanes in a warming climate remains a major concern in terms of threats to human lives in expanding coastal communities and its economic consequences (Emanuel, 2005). Hurricanes also impact the natural cycles of local waters such as increases in primary production (Lin et al., 2003; McKinnon et al., 2003; Babin et al., 2004). This enhanced primary production has been attributed to increases in the mixed-layer depth, decreases in sea-surface temperature (SST), breakdown in water column stratification, and upwelling (Williams et al., 2001; Davis and Yan, 2004; Black and Dickey, 2008). Consequently, an increase in the intensity and frequency of hurricanes could potentially have dramatic regional effects on coastal biogeochemical cycles. Moreover, enhanced hurricane activity, coupled with higher precipitation events (Emanuel, 2013, 2017), could result in greater storm surge flooding, higher discharge from rivers and coastal watersheds, and increased nutrient, particulate and dissolved organic carbon (POC and DOC) loading, potentially driving large-scale changes in coastal ecosystems (Paerl et al., 1998; McKinnon et al., 2003; Liu et al., 2019a).

Ocean-color satellite remote sensing offers the capability for synoptic monitoring of the marine environment over large spatial scales, at frequent intervals, and during severe weather conditions. Most ocean-color studies have shown greater chlorophyll a concentrations (Chl a, an indicator of phytoplankton biomass) in oceanic, shelf and coastal waters following hurricane events (Yuan et al., 2004; Babin et al., 2004; Miller et al., 2006; Yanshaw et al., 2008). The passage of numerous hurricanes on both east and west coasts of Mexico and the US east coast resulted in distinct increases in surface Chl a (Davis and Yan 2004; Farfan et al. 2014). Satellite studies in the nGoM have reported changes in Chl a that have been linked to a decrease in SST (Walker et al., 2005). While phytoplankton community responses to hurricane passage are important to estuarine food web dynamics (Paerl et al., 2001), their effects on phytoplankton composition using satellite ocean color have been limited. Optical inversion algorithms such as the non-negative linear square (NNLS) algorithm have been developed to estimate phytoplankton pigment composition from satellite ocean color data (Moisan et al., 2017). The NNLS algorithm for example uses information on the in-vivo spectral absorption coefficients of phytoplankton and pigments in combination with standard MODIS Chl a product to obtain phytoplankton pigment maps of northeastern US shelf waters (Moisan et al., 2017). A similar technique based on in-vitro absorption properties of algal pigments and satellite-estimated Chl a, from a Red to NIR band ratio empirical algorithm, has also generated pigment composition maps in GB, using the Sentinel-3A OLCI data with higher spectral and spatial resolution (Liu et al., 2019a). Ocean color remote sensing is however, often limited by cloud cover especially during and after hurricanes and numerical modeling approaches, in

combination with ocean color, have allowed for a better understanding of the physical-biogeochemical interactions associated with hurricane passages in the coastal ocean (Chen et al., 2009; D’Sa et al., 2011).

The nGoM has been impacted by hurricanes with increasing frequency and intensity that have affected many coastal ecosystems in the region (Turner et al., 2006; Keim et al., 2007). Most recently, Hurricane Michael made its track along the northeastern Gulf of Mexico (neGoM), before making landfall as a Category 5 hurricane on October 10, 2018, just west of Apalachicola Bay (ApB), a shallow, sub-tropical, bar-built, and river-dominated estuary on the Florida Panhandle. It then moved rapidly inland depositing large amounts of precipitation before weakening to a tropical storm over Georgia. A storm surge of ~2.5 m was recorded in ApB which sustained severe damage due to the storm surge and intense winds. In this study, we used a combination of the outputs of a high-resolution numerical ocean model and satellite ocean color data to assess the phytoplankton response in northwest Florida shelf waters following the hurricane passage.

4.2. Materials and Methods

4.2.1. Study Area

The path of Hurricane Michael through the nGoM and its landfall as a strong Category 5 hurricane strongly impacted the north Florida shelf and coastal waters including ApB, an elongated shallow estuary with an average depth ~3 m and area of ~540 km² (Figure 4.1). ApB, a highly productive estuary is designated as a National Estuarine Research Reserve, is well known for its oyster harvest that in the past accounted for ~10% of the nation's oyster production (Wilber, 1992; Havens et al., 2013).

![Figure 4.1. Study area. Apalachicola Bay (ApB) and the surrounding shelf waters with the main Apalachicola River and the smaller Carabelle River flowing into the bay. Circles denote the location of the river stage station (Sumatra, FL, United States), meteorological station (LM) and the water quality monitoring station at Cat Point (CP) in ApB. Inset shows the northeast Gulf of Mexico region comprising ApB showing track of hurricane Michael (red line).](image)

A major source of freshwater to the bay, Apalachicola River (AR) is the third largest river in the northern GOM with the greatest discharge of any Florida river, and a drainage basin of ca.
48,500 km² that extends into Georgia (Livingston, 2013). Another source of freshwater to the bay, albeit considerably smaller, is from the blackwater Carrabelle River (Figure 4.1). Water exchange between the relatively fresh bay and saline Gulf waters occur through a few passes (Indian Pass, West Pass, East Pass and Sikes Cut) located between several barrier islands that separate the bay from the Gulf waters (Figure 4.1). The neGoM region impacted by the hurricane considered in this study includes the northwest Florida shelf, which is broadly sloping south of Big Bend and tapers narrower northwest of Cape San Blas (Figure 4.1). Shelf waters are generally stratified from April to November due to seasonally weaker winds and surface heat gain (He and Weisberg, 2002); eddies associated with the Loop Current, located adjacent to the shelf edge (Walker et al., 2011), can also impact the hydrodynamics of this region.

4.2.2. Bio-optical Measurements

A total of 425 measurements of in-situ phytoplankton absorption spectra aphy(λ) and Chl a concentrations between 2006 to 2016 were also obtained from the NASA SeaBASS archive.

4.2.3. NCOM Ocean Circulation Model and Flux Calculations

The Navy Coastal Ocean Model (NCOM), based on the Princeton Ocean Model (POM) uses a nested modeling approach (Ko et al., 2008) with a high-resolution (~ 250 m) estuarine model for ApB (Figure 4.2c). This model is nested within a lower 1.5 km resolution neGoM regional model (Figure 4.2b) that connects the deep Gulf to the coast - and then to ApB (Joshi et al., 2017). The estuarine model is driven by realistic tides and real-time river flows and to a lesser extent by winds, evaporation and rainfall which are from a high-resolution regional weather forecast model, the coupled ocean/atmosphere mesoscale prediction system (COAMPS).

Figure 4.2. NCOM model outputs. (a) Sea level variations from model simulations and the NOAA National Ocean Service (NOS) tide gauge station located in Apalachicola, Florida; (b) model simulation of surface elevation superimposed by surface currents and air pressure for...
October 10, 2018 during Hurricane Michael landfall just east of ApB. (c,d) Sea surface salinity (SSS) and superimposed by de-tided surface currents on October 4 and 13, 2018.

4.2.3. Ocean Colore Satellite Data Processing

Sentinel-3 OLCI full resolution mode (300 m) cloud-free images for October 13 and 17, 2018 over neGoM were obtained from the European Organization for Meteorological Satellites (EUMETSAT) and pre-processed using the Sentinel-3 Toolbox Kit Module (S3TBX) version 5.0.1 in Sentinel Application Platform (SNAP). The OLCI data were then atmospherically corrected using the Case-2 Regional Coast Color (C2RCC) module to obtain remote sensing reflectance ($R_{RS,OLCI}, sr^{-1}$). The Sentinel-3 OLCI data were then used to estimate Chl a using the OLCI Case2R neural net standard algorithm along with phytoplankton pigment compositions.

4.2.4. Derive Phytoplankton Pigment Composition from Sentinel-3A OLCI

Phytoplankton pigment compositions were estimated using the NNLS inversion algorithm (Liu et al., 2019a) with a focus on the neGoM shelf waters (Figure 4.3; bio-optical analysis). Our goal was to obtain spatiotemporal distributions of some pigment ratios specific to algal-bloom species using a previously developed technique to study a hurricane-induced phytoplankton bloom event which appeared to be comprised of mixed algal blooms dominated by different species as indicated by the contrasting colors observed in post-hurricane enhanced true color (ERGB) satellite imagery of the shelf waters (supplementary Figure 4.1 and Figure 4.4a). Thus, Sentinel-3A OLCI pigment maps for October 13, 2018 were generated using the bio-optical analysis processing pathway (Figure 4.3.) in a series of steps.

![Figure 4.3](image-url)

Figure 4.3. Schematic diagrams. Processing pathway of bio-optical analysis for generation of Chl a and phytoplankton pigment maps of the northwest Florida shelf waters from Sentinel-3 OLCI imagery.
Initially, a total of 425 in-situ measurements including phytoplankton absorption spectra aphy(λ) and Chl a concentrations acquired from SeaBASS during 2006-2012 (Figure 4.4a; location shown by pins) were interpolated at 1 nm interval from 400 to 700 nm (Figure 4.4c), and modeled as a third order function of in-situ Chl a concentrations (Liu et al., 2019a) to obtain the wavelength-dependent coefficients. We then further applied these coefficients to Sentinel-3A OLCI Chl a to generate satellite-derived phytoplankton absorption spectrum (a_{phy,OLCI}) at each pixel (1851×1038). Since ~ 80% variations in the shape and magnitude of in-vivo a_{phy}(λ) by phytoplankton cells are attributed to the pigment composition (Ciotti et al., 2002), their concentrations were estimated by reconstructing a_{phy,OLCI} spectra using mass-specific absorption spectra of different pigments based on non-negative least square (NNLS) inversion algorithm (Liu et al., 2019a). In addition, pigment packaging effect is another important factor influencing the absorption spectra of phytoplankton; thus, a_{phy}(λ) was normalized at 675 to minimize pigment packaging effects (Moisan et al., 2017) before spectrum reconstruction. A total of 22 mass-specific pigment spectra obtained from different published sources were included in this study. In-vivo mass-specific absorption spectra of 14 pigments including Chl a, Chl b, divinyl (DV)-Chl a, DV-Chl b, Chl c, peridinin (peri), fucoxanthin (fuco), 19′hexanoyloxyfucoxanthin (19′hexa-fuco), 19′butanoyloxyfucoxanthin (19′buta-fuco), alloxanthin, diadinoxanthin (diadino), zeaxanthin, and α-carotenoid and β-carotenoid (β-caro) were obtained from Bricaud et al. (2004). Furthermore, total Chl a consists of active intact Chl a plus breakdown products called “pheopigments”, mostly pheophytin, which modify a_{phy}(λ) between 400 and 435 nm – due to a shift in the maximal absorption of pheophytin-a toward shorter wavelengths (Kiefer and SooHoo, 1982). Generally, healthy phytoplankton have mostly active Chl a, but a fraction of pheopigments increases with increasing senescence of algal cells (Mitchell and Kiefer, 1988; Bianchi and Canuel, 2011). Thus, spectra of pheophtytins-a and –b were also included in the NNLS inversion algorithm (Thrane et al., 2015) due to the algal blooms detected in the enhanced RGB image (Fig. 4.4a). In addition, the in-vitro absorption spectra of 5 other chloroplast carotenoids including violaxanthin, lutein, neoxanthin, diatoxanthin, and dinoxanthin were obtained from Thrane et al. (2015). However, in-vivo spectra were generally measured using the filter techniques and thus, the absorption spectra from pure pigment in vitro are not the best illustration of the pigment absorption spectra contained in phytoplankton cellular complexes in vivo (Lutz et al., 2001) due to a slight shift in absorption peak (Bidigare et al., 1990). Therefore, the absorption maxima of these 5 in-vitro absorption spectra were shifted to longer wavelength by +10 nm to in-vivo positions (Bidigare et al., 1990; Kirk, 1994). The mass-specific absorption spectra of phycocerythrin and phycocyanin (Cook et al., 2017), were also included in the NNLS inversion algorithm to generate phytoplankton pigments maps (Figure 4.5).

**4.3. Results**

**4.3.1. Hydrodynamic Conditions in ApB**

A comparison between model and tide-gage sea level at NOAA NOS Apalachicola station (id 2359170) for the month of October 2018 showed the model to simulate realistic sea levels (Figure 4.2a) with diurnal patterns of sea level variations and westerly surface currents before the hurricane (Figure 4.2c). Both model simulation and tide gage showed increasing sea levels by October 6 and storm surge at landfall. The model, however, underestimated the peak storm surge (~ 2.5 m) measured by the tide gauge likely due to coarser and therefore weaker hurricane winds predicted by COAMPS -used to drive the model. The coastal response to the hurricane was the generation of a storm surge, which appeared to peak on October 10, close to
landfall and just west of ApB (Figures 4.2a-b). The storm surge was greatest to the right (east) of the hurricane track including ApB region with strong wind-driven coastally directed currents; both winds and currents showed decreasing trends eastward along the Florida coast into the Big Bend area. Coastal water levels, however, decreased to low or negative levels to the left (west) of the storm track with southward-directed currents appearing to deliver low salinity waters from the various bays (e.g., St Andrews Bay, Choctawhatchee Bay) - likely delivering large amounts of freshwater, nutrients, and organic matter to the coast. Coastal currents, which were predominantly westward and mild before the hurricane (Figure 4.2c), were highly variable in both intensity and direction just before, during, and following the hurricane (Figures 4.2b–d). Three days following the hurricane’s landfall, currents were directed mostly southeastward in the coastal waters around ApB, likely due to relaxation of storm surge and prevailing easterly winds (Figure 4.2b) that pushed water out of ApB. Model simulation of salinity within the bay showed a strong influence of freshwater discharge from the AR and Carrabelle Rivers before the hurricane (October 4; Figure 4.2c). Salinity increased substantially during the hurricane due to a storm surge that brought high salinity water into ApB. After the hurricane on October 13 low salinity waters extended well beyond the bay’s barrier islands and into more open Gulf waters (Figure 4.2d).

4.3.2. Bio-Physical Response of Shelf Waters to Hurricane Michael

Factors that could contribute to the distinct colors observed in the OLCI ERGB imagery in shelf waters, especially southwest and east of ApB after passage of the storm (Figure 4.4a) include sediment resuspension, CDOM-rich or bloom waters. Thus, an algal bloom index (ABI, mWcm⁻²μm⁻¹sr⁻¹) which has been used by Florida Fish and Wildlife Conservation Commission (FWC) for routine monitoring of red tide along the Florida Coast is adapted in this study for the Sentinel-3A OLCI atmospheric-corrected normalized water leaving radiance (Lwn at band 8–665 nm, band 10–681 nm and band 12–754 nm); the ABI which is based on the MODIS normalized fluorescence line height (nFLH) product, was further modified to reduce the contaminations from CDOM-rich waters and suspended sediments according to Hu and Feng, (2016) as:

$$ABI = \frac{Lwn_{681} - 1.005 \times (Lwn_{665} + (Lwn_{754} - Lwn_{665}) \times \frac{681 - 665)}{754 - 665})}{1 + (Rrs_{560} - 0.0015) + 80}$$

(4.1)

The Sentinel-3 OLCI-derived ABI imagery indicated that most areas along the Florida Coast with high ABI ~ 0.08-0.09 (white arrows; Figure 4.4c) coincided with medium (~10,000-100,000 cells L⁻¹) to high (>100,000 cells L⁻¹) concentrations of Karenia brevis reported in the statewide red tide status map from FWC for the month of October 2018 (white arrows; Figure 4.4d). For example, dark-reddish color in ERGB image (arrow 1; Figure 4.4a) with Chl a concentrations reaching ~10.5 mg L⁻¹ (Figure 4.5a) in the areas southwest of ApB was likely due to the presence of a red tide bloom (K. brevis); these type of waters have been associated with strong light absorption by K. brevis cells (Hu and Feng, 2016). Corresponding reflectance spectral profiles in the red tide area (arrow 1; Figure 4.4a) showed overall low reflectance but a strong fluorescence signal (red line; Figure 4.4b). However, along the Big Bend Coast of Florida stretching from Apalachee Bay (Wakulla County) to Anclote Key (Pasco County), ABI showed moderate levels ~0.055 (red circle; Figure 4.4c) while K. brevis cell concentrations were very low (0-1000 cells L⁻¹) or not present (Figure 4.4d). It likely indicates that other species dominated the phytoplankton community along the Big Bend Coast, such as nitrate-assimilating diatom, which generally show dominance in the nutrient-rich river plume waters or during strong upwelling events (Qian et al. 2002; Chakraborty and Lohrenz 2015; such events associated with
Hurricane Michael (Figure 4.2a) likely contributed to elevated phytoplankton biomass along the coast and shelf waters (Figure 4.5a and c).

Figure 4.4. Sentinel-3A OLCI imagery and field absorption spectra. (a) OLCI enhanced RGB imagery (ERGB) of 13 Oct 2018 with arrows indicating dark features associated with high absorption due to red tide and bright features related to coccolithophore bloom. (b-inset) OLCI-derived $R_{rs}$ spectra corresponding to red tide and coccolithophore bloom locations in the imagery. (c) OLCI algal bloom index (ABI) of 13 Oct 2018 with white arrows indicating waters in bloom status. (d) Statewide map of archived status of red tide Karenia brevis in October, 2018 acquired from Florida Fish and Wildlife Conservation Commission (FWC) with colors circles representing the cell concentrations of K. brevis. (e) A total of 425 $a_{phy}$(λ) spectra acquired from NASA SeaBASS archive with locations shown as colored pins in (a); blue dotted lines drawn to show spectra in the range 450–470 nm. (f) Comparison between modeled and in-situ measured $a_{phy}$(λ) for all data across all wavelength with color representing wavelength.

However, the extremely bright milky-white color (arrow 2, Figure 4.4a) could be attributed to the coccolithophore Emiliania huxleyi, with its high reflectance across the visible spectrum induced by their detached coccoliths (Brown and Yoder 1994). The E. huxleyi bloom area displayed relatively lower Chl a (~3.5 mg L$^{-1}$; Figure 4.6c) but much higher reflectance compared to the K. brevis bloom (Figure 4.4b). This coccolithophore bloom area (white circle; Figure 4.4c) which was completely masked in the modified ABI due to its high reflectance at 560 nm as well as the reflectance threshold method (Joshi and D’Sa 2020) suggests the potential of these techniques to differentiate between highly reflective and absorbing bloom waters. A sequence of cloud-free Sentinel-3 OLCI derived Chl a imagery obtained before (October 06), and immediately following the hurricane (October 13) indicated a relatively large increase in Chl a in the shelf waters (~3.1 to ~7.5 mg m$^{-3}$) before decreasing to lower values (~4.1 mg m$^{-3}$) by October 17, 2018 (Figure 4.5a, c, e). This increase was mainly associated with large scale algae blooms (Figure 4.5c) which nearly dissipated within a week (Figure 4.5e). Within ApB, Chl a values which were elevated before the hurricane (~11.2 mg m$^{-3}$ on October 06) showed a slight increase to ~14.5 mg m$^{-3}$ on October 13 before decreasing to ~12.5 mg m$^{-3}$ by October 17, 2018 (Figure 4.5b, d, f); these satellite estimates however, have not been previously validated for these estuarine waters.
4.3.3. The Pigment Inversion Algorithm Performance

The inversion model used an extensive set of field bio-optical data ($a_{\text{phy}}(\lambda)$ spectra and Chl a, $N = 425$; Figure 4.4e) obtained in the neGoM ranging from coastal ocean to estuaries including CDOM, sediment-rich and red-tide waters (Figure 4.4a-pin locations) to optimize regional tuning and obtain robust parameterization of Chl a-$a_{\text{phy}}(\lambda)$ relationship for the neGoM waters. The $a_{\text{phy}}(\lambda)$ showed large variations in magnitude (0.01–1.497 m$^{-1}$ at 440 nm and 0.008–1.253 m$^{-1}$ at 675 nm) while Chl a varied from $\sim$ 0.12 mg m$^{-3}$ in offshore waters to an average of $\sim$ 12.67 mg m$^{-3}$ in the various neGOM estuaries across different seasons; however, extremely high values reaching $\sim$ 77 mg m$^{-3}$ were observed in red tide bloom waters. The aphy($\lambda$) spectra obtained in red-tide area displayed a small peak in the range of 450–470 nm (blue dotted lines; Figure 4.4e), likely attributed to the presence of fucoxanthin; in contrast, at lower Chl a levels corresponding to pico-phytoplankton dominated groups, $a_{\text{phy}}(\lambda)$ were steep were 450–470 nm range but lifted $\sim$ 490 nm, probably due to the absorption of zeaxanthin. The modeled $a_{\text{phy}}(\lambda)$ agreed well with the spectrophotometrically measured $a_{\text{phy}}(\lambda)$ for all data across the whole spectra ($R^2 = 0.84$, Figure 10f).

![Image](image_url)  
Figure 4.5. Sentinel-3A OLCI-derived Chl a maps. (a,c,e) Chl a standard product of shelf waters for 06, 13, and 17 October 2018 with corresponding maps (b,d,f) of ApB and nearshore coastal waters. (g) Total Chl derived from the NNLS inversion algorithm for October 13, 2018; (h) comparison of OLCI-derived Chl a standard product vs. NNLS-derived Chl a for October 13, 2018.
The vector coefficients were further applied to Sentinel-3A OLCI Chl a maps to generate 301 sentinel-3A OLCI aphy images \((a_{phy,OLCI})\), representing aphy values at each wavelength (400–700 nm at 1 nm interval). However, since the parameterization for Chl a-aphy correlation is optimized for the neGOM, it could show limitations when applied to other areas wherein phytoplankton communities show large seasonal and taxonomic differences, or where the algal blooms are not associated with red tide species, K. brevis; thus uncertainties could be introduced in satellite-derived aphy. The \(a_{phy,OLCI}(\lambda)\) was then spectrally decomposed into 22 mass-specific pigment spectra at each pixel using NNLS technique to obtain the concentrations of 22 pigments. The NNLS-inversed Chl a (Figure 4.5g) exhibited exactly the same spatial patterns with Sentinel-3A OLCI Chl a product but showing slightly lower values \((R^2=0.99; \text{Figure } 4.5h)\). In this study, the limitation is the lack of HPLC measurements during the study period, and thus, parameters associated with uncertainties (e.g., MAE, RMSE, and \(R^2\)) for the estimated pigments cannot be calculated at this time. However, the modeled \(a_{phy}(\lambda)\) (Figure 4.5f) and NNLS-inversed Chl a (Figure 4.5g) showed acceptable range for predicting pigment compositions compared to Moisan et al. (2017) and Liu et al. (2019a), in which a similar NNLS-algorithm has been used and validated for estimation of phytoplankton pigments.

4.3.4. Satellite-derived Pigment Distributions in shelf waters following Hurricane Michael

Most photosynthetic type-1 dinoflagellates contain a chloroplast with peridinin as the major carotenoid; however, fucoxanthin and/or fucoxanthin derivatives such as 19’hexa-noyloxyfucoxanthin (19’hexa-fuco) can also replace peridinin as the major carotenoid in the genus Karenia (5 species, 8 strains) - type-2 dinoflagellates (Jeffrey and Vesk, 1997). Fucoxanthin, a carotenoid largely used to trace diatoms (Bianchi and Canuel, 2011), was found to be the major carotenoid in \(K. \text{ brevis, } K. \text{ mikimotoi, and } K. \text{ selliformis}\) (Zapata et al., 2012). HPLC analysis of a \(K. \text{ brevis}\) culture, obtained in Galveston Bay and Florida Coast (Örnólfsdóttir et al., 2003), showed Chl a, Chl c3, Chl c1c2, fuco, 19’buta-fuco, 19’hexa-fuco, diadino, gyro, and \(\beta\)-carotenoid (\(\beta\)-caro) – with no peridinin detected. Further HPLC analyses are clearly needed to examine for regional differences in pigment composition of \(Karenia\) spp.

![Figure 4.6. Sentinel-3A OLCI-derived maps of diagnostic pigments and ratios for October 13, 2018. Pigment maps of (a) 19’hexa-fuco, (b) fuco, (c) pert, (d) 19’hexa-fuco:Chl a, (e) fuco:Chl a, (f) peri:Chl a.](image-url)
In this study, the NNLS-inversed 19′hexa-fuco, fuco, and peri (Figures 4.6a–c) showed differences in distribution patterns and magnitude from estuarine to coastal waters and bloom areas. Values of 19′hexa-fuco (range of 0.001–0.9 mg L\(^{-1}\)) were obviously higher in the bloom areas in the midshelf waters than estuarine waters, which is consistent with Chakraborty and Lohrenz, (2015) that haptophytes (coccolithophores) were more prevalent at midshelf resulting in an order of magnitude higher ratio of 19′hexa-fuco to total accessory pigment than inner shelf waters. In contrast, fucoxanthin displayed the same pattern as the Chl a map, decreasing from estuarine to shelf waters (Figures 4.5a, 4.6b), which is likely attributed to the presence of diatoms. Diatoms are more abundant prevalent in the N and Si-rich estuarine/shelf waters of the NGoM compared to offshore waters (Qian et al., 2003). In contrast, dinoflagellates, which tend to have higher P demands, will generally increase in abundance with decreasing ratios of N:P and Si:P, resulting in a compositional shift from a diatom-to dinoflagellate-dominated community (Paerl, 1997; Heisler et al., 2008). Along these lines, the carotenoid peridinin, found in Type-I dinoflagellates, exhibited substantially different patterns compared to the distributions of Chl a and fuco (Figure 4.6c); peri displayed extremely low concentrations in estuarine waters (~0.001 mg L\(^{-1}\)), but elevated in shelf waters. Consistent with more P-limited estuarine environments vs. more N-limited oceanic waters (Paerl, 1997). Moreover, extremely low concentration of peri (~0.001 mg L\(^{-1}\)) observed in bloom areas, indicated algal blooms were not associated with Type 1 dinoflagellates. Furthermore, the fringing area of the red tide, dark in color (black arrow 1; Figure 4.4a) with extremely high ABI (Figure 4.4c) and Chl a (Figure 4.5a), showed relatively lower values of 19′hexa-fuco (~0.6 mg L\(^{-1}\), white arrow; Figure 4.6a), compared to the adjacent coccolithophore-dominated area (~0.85 mg L\(^{-1}\); Figure 4.6a). In contrast, values of fuco (~2.3 mg L\(^{-1}\)) at the edge of red tide (white arrow; Figure 4.6b), were as high, as found in estuarine waters, with the mean value of the red tide dominated area (~2.0 mg L\(^{-1}\)) higher than the coccolithophore dominated area (~1.5 mg L\(^{-1}\)). Although fuco is a common biomarker for diatoms, the absence of 19′hexa-fuco suggests that \textit{K. brevis} accounted for a major proportion of the phytoplankton community - with minor only contributions from diatoms (black arrow 1; Figure 4.4a). This supports previous work which showed that \textit{K. brevis} have higher phosphorus demands than diatoms and are generally found in waters with very low DIN:PO4 (~4) (Walsh et al., 2006). Some bloom-forming dinoflagellates (e.g., \textit{K. brevis}) share several of the same pigment markers as bloom-forming haptophytes (e.g., \textit{E. huxleyi}) (Zapata et al. 2004); thus, specific pigment to Chl a ratios including 19′hexa-fuco (Figure 4.6d), fuco (Figure 4.6e), and peri (Figure 4.6f) could help in discriminating \textit{Karenia} species from 19′hexa-fuco-containing haptophytes. In the red tide area, fuco:Chl a varied from 0.24 to 0.30 and was lower than in coccolithophore bloom (~0.45). These ratios are within the range of previously reported fuco:Chl a values for \textit{K. brevis} (0.31) and haptophytes (0.58) (Örnólfsdóttir et al. 2003). Furthermore, 19′hexa-fuco:Chl a ratios had a higher mean value (~0.4) in coccolithophore bloom (~0.4) than the red tide area (~0.15) (Figure 4.6d), consistent with previous studies (Örnólfsdóttir et al. 2003; Zapata et al. 2004, 2012). More specifically, higher 19′hexa-fuco:Chl a ratios are found in strains of type-6 haptophytes (\textit{E. huxleyi}) than type-2 dinoflagellate (\textit{Karenia} species).

### 4.4. Discussion

#### 4.4.1. Hurricane Impact on Phytoplankton Composition in Shelf Waters

The wind field and precipitation associated with Hurricane Michael caused a complex response in the coastal and shelf waters that led to reduced salinity and surface temperatures (as indicated by model outputs—not shown). This was likely due to enhanced water column mixing, upwelling and transport of coastal waters over a large area of the northwest Florida
shelf, and elevated levels of organic matter in the shelf waters. Surface currents appeared to transport cooler coastal waters eastward alongshore and then steered westward by the presence of an eddy at the shelf edge that led to a strong biological response with spatially distinct distribution patterns in the shelf waters (Figures 4.4 and 4.5).

Observations of pigment ratios from the bio-optical inversion algorithm, ERGB image and the reflectance spectra in algal boom areas from Sentinel-3A OLCI and in-situ measured *K. brevis* cell concentration from FWC jointly suggest that shelf waters southwest of ApB was a mixed algal bloom of *K. brevis* and *E. huxleyi*, with fringing area more dominated by *K. brevis*. The coccolithophore *E. huxleyi* flourished in shelf waters east side of ApB, broadly extending to K. brevis bloom area. It is widely agreed that red tide of *K. brevis* near shore in the eastern GOM originate 15–65 km offshore in deep shelf waters due to the initial phosphorus-rich nutrients at low DIN/PO4 ratios supplied by benthic sediments and recycled estuarine/ground water (Waters et al., 2015). Accumulated *K. brevis* seeds at the bottom of the Florida shelf which then upwell inshore by wind and tidal currents, often bloom in the estuarine-coastal surface waters (Hu et al., 2006); these are further enhanced by high dissolved organic nitrate (DON) from a variety of sources including land-based nutrients carried by estuarine waters, decomposing dead fish and nutrient inputs from N2-fixation from Trichodesmum blooms, which generally co-occur with *K. brevis* blooms on the West Florida shelf (Walsh et al., 2006). In this study, the areas southwest of ApB were strongly influenced by hurricane-induced flux of organic matter out of bays which likely favor those species capable of assimilating organic forms of nutrients (e.g., *K. brevis*) rather than species more reliant on inorganic nutrients (e.g., diatoms) (Anderson et al., 2008; Heisler et al., 2008). To our knowledge, this is first time synchronous blooms of *K. brevis* and *E. huxleyi* were found in mid-shelf waters following Hurricane Michael. *E. huxleyi* is well-known as one of the more cosmopolitan coccolithophore species, forming extensive blooms from polar to tropical regions, in both open ocean and coastal shelf waters (Holligan et al., 1993). The particularly competitive ability of *E. huxleyi* at high N:P ratios, observed in cultures (Riegman et al., 2000) and eutrophic coastal waters with high N and P, but low silica (Si) concentrations (Yunev et al., 2007) may in part, explain for its rapid appearance after the passage of Hurricane Michael. Thus, low ratios of Si:N and Si:P could be a possible reason that coccolithophores outcompeted other phytoplankton species, such as diatoms, in this hurricane-impacted nutrient-rich environments.

More interestingly, MODIS ERGB imagery of October 11 and 12, 2018 (Supplementary Figure 4.1) indicated that the K. brevis bloom expanded rapidly into areas dominated by the *E. huxleyi* bloom especially west of ApB and the area closer to where Hurricane Michael made landfall. Also notable was a small area south of ApB on October 11 (light pink, Supplementary Figure 4.1) that expanded eastward by October 12 (dark pink/red due to greater absorption) revealing the rapid and intense growth of *K. brevis* bloom following the hurricane passage. Previous studies using MODIS images acquired in the western English Channel also observed similar phenomenon of *K. mikimotoi* development along coccolithophore blooms, which captured both dinoflagellate and coccolithophores blooms spanning across different seasons during 2002–2006 (Garcia-Soto et al., 1995; Garcia-Soto and Pingree, 2009). However, the statewide red tide status map acquired one week before Hurricane Michael (October 1–6, 2018) from FWC detected low concentrations of *K. brevis* (~ 10,000-100,000 cells L\(^{-1}\)) adjacent to Dune Lakes in Walton, Panama City Beach and Apalachicola. With NCOM model results indicating plumes of these coastal waters with elevated DOM being transported into the mid-shelf region where satellite imagery detected algal blooms suggest that *K. brevis* did not initiate from coccolithophore bloom, but were likely transported into the bloom regions where hydrographic and nutrient conditions appears to create ecological preferences for *K. brevis* on the northwest Florida Coast. In fact, a previous study in this same area (McCulloch et al., 2013)
documented the presence of gyroxanthin dinoflagellates (*K. brevis*) in near-surface and near-bottom shelf waters in this area and further suggested that under light and nutrient conditions typical of summer, *K. brevis* coastal blooms could originate from concentrated near-bottom populations during upwelling conditions (McCulloch et al., 2013). Upwelling conditions and strong offshore currents during hurricane landfall (Figure 4.2b) and subsequent transport of these coastal waters to the shelf strongly suggest that these coastal and estuarine waters with elevated organic nutrients and entrained seed populations of *K. brevis* conjointly led to a phytoplankton bloom including that of *K. brevis* (Figures 4.4a, 4.5, and 4.6). Previous field measurements of the Florida shelf waters acquired in 2004 and 2005 hurricane season also showed that nutrient loading was an order of magnitude greater than pre-hurricane (Neely et al., 2006); following Hurricane Michael, the coastal plume likely contained high nutrients transported from the estuaries and bays along the northwest Florida coast that likely contributed to the intensive phytoplankton bloom. Further, estuarine additions of dissolved organic matters in the shelf waters associated with the hurricane could have provided more favorable light-shield environment (Walsh et al., 2003) for the shade-adapted *K. brevis*. The identification of algal bloom pigment composition from the high spectral and spatial resolution Sentinel-3A OLCI imagery using inversion techniques (e.g., Moisan et al., 2017; Liu et al., 2019a) could revolutionize our understanding of phytoplankton spatiotemporal response to environmental variabilities.

### 4.5. Conclusions

In this study, the bio-optical responses of ApB and northwest Florida shelf waters were examined following the passage of Hurricane Michael through the neGoM in October 2018. A combination of pre-hurricane ocean color data from Sentinel-3A OLCI and the outputs of a high-resolution ocean model (NCOM) provided a robust assessment of the hurricane’s impact on the bio-optical properties of shelf waters. Water discoloration in a true color imagery obtained 3 days following the hurricane landfall (October 13) along with high surface Chl a concentrations indicated the presence of distinct algal blooms in the normally oligotrophic offshore waters. Observations of Sentinel-3A OLCI derived pigment ratios from the bio-optical inversion algorithm, and the shape of reflectance spectra in the algal boom areas suggested that shelf waters southwest of ApB was a mixed algal bloom of *K. brevis* and *E. huxleyi*, with fringing area mainly dominated by *K. brevis*; the area east/southeast of ApB, in contrast appeared to be dominated by coccolithophore *E. huxleyi*. The presence of a cyclonic loop current eddy along the shelf edge likely limited the response of deep waters to the hurricane passage. This study revealed a varied but shorter-term impact on the biogeochemistry and the ecosystem of ApB and surrounding shelf waters during Hurricane Michael. Additional longer-term studies of the hurricane impacts are warranted due to the socio-economic importance of the northwest Florida coast and shelf waters.
CHAPTER 5. BIOGEOGRAPHICAL TRENDS IN PHYTOPLANKTON COMMUNITY SIZE STRUCTURE USING OPTIMIZED SENTINEL 3-OLCI CHLOROPHYLL AND SEMI-ANALYTIC/INVERSION APPROACHES IN THE ESTUARINE-SHELF WATERS OF THE NORTHERN GULF OF MEXICO

5.1. Introduction

Phytoplankton, which forms the foundation of the marine food web, sequesters ~10 Gigatonnes of carbon per year from the atmosphere to the oceanic deep waters worldwide via the biological pump (Finkel et al., 2010; Rabalais et al., 2002). Phytoplankton’s diverse morphological characteristics (size and shape), and different biogeochemical functions (e.g., silicification, calcification, and nitrogen fixation) (Sathyendranath et al., 2014) result from a complex interplay of environmental stressors (e.g. light, temperature and nutrients), and thus to heterogeneous phytoplankton communities across different oceanic regions (Acevedo-Trejos et al., 2015). Phytoplankton cell size is arguably one of the most important factors affecting their physiological and ecological functions including growth rate, nutrient uptake, sinking velocity, light absorption, photosynthetic rate, and grazing (Finkel and Irwin, 2001; Uitz et al., 2008). Phytoplankton cell size which range over several orders of magnitude, have been classified into: i) picophytoplankton - organisms with spherical diameter less than 2 µm, ii) nanophytoplankton in the range of 2–20 µm, and iii) microphytoplankton that range from 20–200 µm (Beardall et al., 2009). Thus, phytoplankton size fractions (PSFs), which are crucial indicators of phytoplankton community dynamics, play a cascading role in structuring marine food web (Mouw et al., 2016) and altering the magnitude of carbon fixation and export into the ocean’s interior (Beardall and Raven, 2004; Falkowski et al., 2003). In turn, subtle variations in PSFs are expected to influence atmospheric carbon dioxide concentrations, and likely alter global surface temperatures and climatic processes. Generally, microphytoplankton (e.g., diatoms), which are more prevalent in turbulent and nutrient-rich waters (e.g., upwelling), contribute significantly to carbon export to deep waters (Agustí et al., 2017); in comparison, phytoplankton in small size (e.g., some cyanobacteria and small flagellates) living in stratified and oligotrophic waters are quickly remineralized within the euphotic zone (Falkowski et al., 2003). Such observations of phytoplankton biogeography have been observed from field data (Hirata et al., 2011; Maranón et al., 2015), satellite observations (Brewin et al., 2010) and modelling simulations (Prowe et al., 2012) at the global ocean scale. However, these are simplifications of more complex scenarios in estuarine-coastal ecosystems, where waters are affected by continuous physical, chemical, and biological interactions from both the natural (e.g., hurricanes and flooding discharge) and anthropogenic pressures (e.g., landscape dynamics and nutrient loading). For instance, active hydrodynamics along with circulation patterns (Loop Current) in the northern Gulf of Mexico (nGoM) provides an dynamic scenario to investigate mesoscale responses of phytoplankton size structures to environmental variabilities. The phytoplankton taxonomy composition and size fractions in the nGoM have been reported to be modified by freshwater inflows associated with variability in hydrological and meteorological forcings at various temporal and spatial scales (Chakraborty and Lohrenz, 2015; D’Sa et al., 2019; D’Sa et al., 2018; Gomez et al., 2018; Liu et al., 2019; Williams et al., 2015). However, comprehensive mechanisms underlying the biogeographically-different distributions phytoplankton community size structures in the nGoM is still poorly understood.

Satellite ocean color has been shown to be an effective tool to monitor the spatio-temporal distribution and variations of phytoplankton. Over the past 3 decades, chlorophyll a (Chl a) products have been considered as a reliable proxy to estimate phytoplankton biomass
and productivity in open ocean and coastal waters. However, its application has been limited in smaller estuarine water bodies due to low spatial resolution of current ocean color sensors (e.g., MODIS and VIIRS) and poor algorithm performance in optically-complex waters (e.g., OC4, based on blue/green band ratios). More important, Chl a alone is not sufficient to illustrate dynamics of phytoplankton community. Recently, growing efforts have been made in mapping PSFs from satellites. Ciotti et al., (2002) characterized PSFs in a sample via decomposing phytoplankton absorption spectra into small and large phytoplankton fractions. Later, the concept in Ciotti et al., (2002) has been applied to different inherent optical properties (IOPs) inversion algorithms to retrieve PSFs (Ciotti and Bricaud, 2006; Zhang et al., 2015). PSFs can also be retrieved from satellite via partitioning the phytoplankton biomass of each size based on empirical relationships between Chl a concentrations of each size class and total Chl a, which is determined from large high performance liquid chromatography (HPLC) dataset (Brewin et al., 2012; Brewin et al., 2010; Hirata et al., 2011). Furthermore, the correlation between the phytoplankton groups and environmental factors (e.g., sea surface temperature and irradiance) were used to determine PSFs in Brewin et al., (2015) and Ward (2015). However, satellite algorithms relevant to phytoplankton have been mostly confined to the open ocean and shelf waters and very limited in the optically complex estuarine waters where the influence from wetlands, rivers and coastal ocean make phytoplankton communities highly variable and complex. Thus, high-resolution satellite products on PSFs in estuarine-coastal ecosystems are urgently required for identifying the drivers of phytoplankton community dynamics and associated food webs and to assess climate-driven interactions from regional to global scales.

In this study, a large in-situ dataset acquired in inland, estuarine and coastal waters of the nGoM and ocean color remote sensing data (Sentinel 3A/B-OLCI) are used to better understand the fundamental mechanisms that create compelling differences in phytoplankton community size structures in the nGoM. The paper is organized as follows: Sect. 2 presents the in-situ/field and satellite data used for algorithm development and validation, and the procedures of two satellite algorithms including a Chl a adaptive algorithm and a PSF algorithm based on Empirical Orthogonal Functions (EOFs). Results and discussions (Sect. 3) and conclusions (Sect. 4) address the main contributions and findings of this work.

5.2. Data and Methods

5.2.1. Study Area

The Gulf of Mexico (GoM; Figure 5.1b) is a large productive marine ecosystem, strongly influenced by injected warm Caribbean waters or the Loop Current (LC) (Chang and Oey, 2012). The intrusion and retraction of the LC and eddy shedding (i.e., separation of warm rings from the LC) dominate the circulation patterns in the GoM. The northern Gulf of Mexico (nGoM) is bordered by the Gulf Coast of United States including coastlines of Florida, Alabama, Mississippi, Louisiana, and Texas. Notable chains of barrier islands from Florida to eastern Louisiana and eastern Texas separate the nGoM from the US mainland by narrow bodies of water such as lagoons, bays and estuaries. The estuarine-coastal ecosystem in the nGoM is experiencing pressures from both natural processes and human activities. Extreme meteorological and hydrological events, such as hurricanes and floodwater discharge from mainly the Mississippi and Atchafalaya Rivers increase the export of terrestrial dissolved and particulate matter, potentially altering the biogeochemistry of estuaries and coastal waters. Moreover, anthropogenic disturbances (e.g., coastal eutrophication and morphological modifications) often adversely influence water quality, leading to the occurrence of harmful algal blooms and hypoxic events (Rabalais et al., 2002). Many northern Gulf estuaries are showing signs of nutrient pollution as the Gulf-wide Eutrophication Survey documented that
hypereutrophic (Chl a > 60 mg m\(^{-3}\)) conditions were observed in seven estuaries (e.g., Barataria Bay and Tampa Bay) and high Chl a (20-60 mg m\(^{-3}\)) were reported in 18 estuaries (e.g., Atchafalaya Bay and Mobile Bay) (Scavia and Bricker, 2006).

Figure 5.1. Sampling locations of in-situ/field data obtained in estuarine-coastal waters of the US East Coast and the northern Gulf of Mexico. Blue and orange symbols represent historical data from SeaBASS; green symbols indicate a comprehensive new dataset obtained in 2019.

5.2.2. SeaBASS Dataset

The in-situ bio-optical measurements in estuarine-coastal waters of the US East Coast and the northern Gulf of Mexico (blue symbols, Figure 5.1b) including paired Chl a and above-water remote sensing reflectance (R\(_{rs}\)) compiled from NASA’s SeaWiFS Bio-optical Archive and Storage System (SeaBASS) (Supplementary Table 5.1). A total of 394 measurements of above-water R\(_{rs}\) (sr\(^{-1}\)) were calculated and calibrated from downwelling spectral irradiance E\(_{s}\) (\(\mu W\ cm^{-2}\ nm^{-1}\)) and water leaving radiance L\(_{w}\) (\(\mu W\ cm^{-2}\ nm^{-1}\ sr^{-1}\)) collected just above water using a Satlantic Hyperpro Profiler equipped with a downward looking Hyper OCR radiance collector and upward looking Hyper OCR irradiance collector. E\(_{w}\) was collected on deck with a skyward irradiance collector. The rest of the above-water Rrs measurements (N=399) obtained from field portable spectroradiometers (e.g., GER 1500) were calculated by measurements of the upwelling radiance (L\(_{u}\), \(\mu W\ cm^{-2}\ nm^{-1}\ sr^{-1}\)) from water surface to the downwelling radiance (L\(_{d}\), \(\mu W\ cm^{-2}\ nm^{-1}\ sr^{-1}\)) collected from a Spectralon reference panel (e.g., white target with a reflectance factor of 0.99). Further, of the total, 298 Chl a are from HPLC measurements and the rest are fluorometric Chl a. A concurrent dataset (793 measurements) of above-water R\(_{rs}\) and Chl a (blue asterisk, Figure. 5.1b), was also compiled for the development of an adaptive Chl a algorithm (Chl a AD). SeaBASS data also contained 264 pairs of phytoplankton absorption coefficients (a\(_{phy}\)) and HPLC measurements (orange cross, Figure
5.1b) that were used for developing phytoplankton size fraction algorithms. More details regarding data calibration can be referred to each of the datasets obtained from SeaBASS website.

5.2.3. Field Data Collection

A total of 114 surface water samples (green symbols, Figure 5.1b) were collected along the Louisiana Coast on the R/V Pelican (July 16-21, 2019), and in the estuarine-coastal waters of Barataria Basin (June 18-19 and September 10-11) and Atchafalaya Basin (June 13-14, August 15-16 and September 13-14, 2019) on the R/V Acadiana for validation purpose. The filter pads were immediately frozen and stored in liquid nitrogen for laboratory absorption spectroscopic analysis and HPLC measurements. Profiles of salinity, temperature, and pressure were obtained using a conductivity–temperature–depth recorder (SBE; Sea-Bird Scientific) at each station. The above-water reflectance at 41 of 114 stations were collected using a GER 1500 512iHR spectroradiometer in the 350–1050 nm spectral range and processed to obtain \( R_{rs} \) (Joshi et al., 2017).

5.2.4. Satellite Data Processing

Ocean and Land Color Instrument (OLCI) on board ESA Sentinel-3A/B satellite launched in Feb, 2016, has a large swath width (~1270 km) covering the entire nGoM at high temporal resolution (nearly 3-day repeat cycle). Further, OLCI spatial resolution (300 m) meet the requirements of monitoring water dynamics in smaller waterbodies (e.g., Barataria and Atchafalaya Basins) in the nGoM. In this study, a total of 157 Sentinel-3A/B-OLCI full resolution mode, largely cloud free images were obtained over the past four years (October 01, 2016-January 05, 2020) in the nGoM. Of these, 8 OLCI imagery corresponded to research cruise days on June 13, June 19, July 16-July 19, August 15, September 04, and 14, respectively. Sentinel-3 Toolbox Kit Module (S3TBX) version 5.0.1 in Sentinel Application Platform (SNAP) version 5.0 was used to preprocess images. The Case 2 Regional Coast Color (C2RCC) atmosphere correction module were then applied to Sentinel 3A/B-OLCI top of atmosphere (TOA) radiances (\( \mu W \text{ cm}^{-2} \text{ nm}^{-1} \text{ sr}^{-1} \)) to obtain atmospheric-corrected \( R_{rs,OLCI} \) (Liu et al., 2019b).

5.2.5. Chl a adaptive Algorithm

Standard satellite Chl a products based on blue/green band ratios (OC3 and OC4, O’Reilly et al., 2000) are often inaccurate in inland-estuarine waters due to the strong contamination from colored dissolved organic matter (CDOM) or non-algal particles (NAP) in the blue part of the spectrum. It was reported that when CDOM absorption coefficients (\( a_{CDOM} \)) at 440 nm is larger than 10 m\(^{-1} \), the combined absorption of CDOM and pure water (\( a_{w} \)) could exceed the absorption of Chl a ~100 mg m\(^{-3} \) at all visible wavelengths (Gilerson et al., 2010). In contrast, algorithms utilizing red/NIR ratios are known to more accurately assess very high Chl a in optically-complex estuarine waters (Gitelson et al., 2007); however, limitations have been reported in these algorithms due to the phytoplankton absorption peak in the red wavelength being dominated by the combined \( a_{CDOM} \) and \( a_{w} \) absorption at lower Chl a (< 1 mg m\(^{-3} \)) (Schalles, 2006). At Chl a > 1 mg m\(^{-3} \), substantial overlap of diverse optically-active water constituents could contribute at wavelengths below 550 nm (Schalles, 2006). Furthermore, stronger red absorption peak due to Chl a compared to the combined absorption of CDOM, sediments and water only occur at high Chl a (> 10 mg m\(^{-3} \)) (Dall'Olmo and Gitelson, 2006). It is thus critical to define the threshold and criteria for adaptive selection of
best performing Chl a algorithms to optimally estimate Chl a from turbid coastal waters to the clear open ocean in a satellite image.

The processing pathway of the adaptive Chl a algorithm is summarized in the following 5 steps: i) The red/NIR ratios extracted from in-situ Rrs at OLCI bands \( \frac{R_{\text{RS} 665}}{R_{\text{RS} 709}} \) and \( \frac{R_{\text{RS} 674}}{R_{\text{RS} 709}} \) are linked to Chl a to achieve regional parameterization of Chl a algorithms based on red/NIR ratios and to further define a threshold for applying red/NIR Chl a algorithms; 2) Sentinel 3A/B-OLCI standard neural-network Chl a product (Chl a\(_{\text{NN}}\)) is selected as the initial input and then replaced by Chl a values estimated from red/NIR algorithm when the threshold defined in 1 is satisfied; 3) pixels meeting criteria for applying red/NIR algorithm but showing spectral characteristics of coccolithophore blooms in coastal waters are forced back to Chl\(_{\text{NN}}\) values; and 5) replacing Chl a\(_{\text{NN}}\) by Chl a values estimated from OC4 algorithm (Chl a\(_{\text{OC4}}\)) when the pixels show oceanic clear water spectral characteristics.

5.2.6. Phytomplankton size fraction algorithms for Sentinel 3A/B-OLCI

5.2.6.1. Retrieve a\(_{\text{phy}}\) from a Multi-regression Model

A total of 264 in-situ phytoplankton absorption spectra a\(_{\text{phy}}\)(\(\lambda\)) obtained from SeaBASS during 2008–2017 (orange crosses; Figure 5.1b) were interpolated at 1 nm interval from 400 to 700 nm and modeled as a third order function of Chl a concentration via multi-regression (MR) model (Liu et al., 2019b; D’Sa et al., 2019) to obtain the wavelength-dependent coefficients. We then further applied these spectral coefficients to Sentinel-3A OLCI Chl a\(_{\text{AD}}\) products to generate OLCI phytoplankton absorption spectra at each pixel (MR-a\(_{\text{phy,OLCI}}\)).

5.2.6.2. Retrieve a\(_{\text{phy}}\) from modified QAA-V algorithm

The standard quasi-analytical algorithm (Lee et al., 2002) was tuned as QAA-V to improve its performance in retrieving IOPs in optically-complex estuarine-coastal waters (Joshi and D’Sa, 2018). The QAA-V optimized for VIIRS, was then calibrated for other satellite sensors, such as Sentinel 3-OLCI, and showed overall better estimation of total absorption and backscattering coefficients (\(a_{t,\text{nw}}\) and \(b_{t,\text{nw}}\)) compared to the standard QAA algorithms (Joshi and D’Sa, 2018), especially in blue wavelength. Important modifications to the QAA algorithm include the use of thresholds (\(\rho\)) based on green/red band ratio (e.g., \(\rho \leq 0.25\) indicates estuarine waters) defined for various water types from turbid estuaries to clear open ocean (Joshi and D’Sa, 2020). The IOPs estimated from QAA-V have been further been used to quantify a variety of important biogeochemical parameters (e.g., SPM, POC and DOC) in the optically complex waters of Galveston Bay following Hurricane Harvey (D’Sa et al., 2018). In this study, QAA-V was applied to Sentinel 3A/B-OLCI to obtain \(a_{t,\text{nw}}\) and \(b_{t,\text{nw}}\) and further estimate QAAV-a\(_{\text{phy,OLCI}}\) using the following steps: i) reconstruct Rrs spectrum at blue wavelength (including 412, 442, 490 and 510 nm) in optically complex waters (when \(\rho \leq 0.25\)) due to the frequently observed negative values from in-situ data obtained in Barataria Basin (BB), Atchafalaya Basin (AB) and Galveston Bay (GB); ii) estimate combined CDOM+NAP absorption coefficient at 442 nm \(a_{d(442)}\) from standard QAA algorithm, which works well for open ocean but highly overestimate \(a_{d(442)}\) values in the estuarine waters of the nGoM; iii) a \(R_{\text{RS} 560}/R_{\text{RS} 674}\) OLCI band ratio (in-situ) was highly correlated with \(a_{d(442)}\) and \\(\text{d}(442)\) in an exponential relationship given by

\[
a_{d(442)}G/R = 6.82 \times \exp \left( -0.75 \times \frac{R_{\text{RS,insitu}(560)}}{R_{\text{RS,insitu}(674)}} \right) \tag{5.1}
\]
iv) Replace $a_{dg442}$ values estimated from standard QAA when $\rho \leq 0.25$ with $a_{dg442}$ determined from iii) to overcome the overestimates of $a_{dg442}$ in estuaries. v) QAA-V-aphy_OLCI was then calculated at each OLCI wavelength from the equation

$$a_{phy}(\lambda) = a_{t, nw}(\lambda) - a_{dg}(\lambda)$$

(5.2)

5.2.6.3. Phytoplankton size fraction model based on empirical orthogonal functions (EOFs)

Empirical Orthogonal Function (EOF) analysis, which is also known as principal component analysis (PCA), is widely used in the climate, oceanographic and meteorological sciences (Pritchard and Somerville, 2009). Typically, EOF analysis is used to study possible spatio-temporal patterns of variability by computing the eigenvalues and eigenvectors of a spatially-weighted time-series data (Monahan et al., 2009). The time series of each mode are calculated by projecting the extracted eigenvectors onto the spatially-weighted anomalies, which is basically the same as principle components of the PCA. The calculated eigenvalues represent the percent variance of each mode (eigenvectors). By construction, the EOF patterns and the principal components are mutually uncorrelated, which likely represent different phenomena that are strongly influenced by distinct stressors and can be studied individually. The magnitudes of eigenvalues show the relative importance of each new set of time series data. More recently, EOF has been used in spectrophotometry to achieve dimensional reduction, and thus, obtain the dominant signals (“modes”) of spectra and associated temporal and spatial patterns (Bracher et al., 2015; Taylor et al., 2013). In this study, EOF is used to detect the spectral modes $a_{phy}$ acquired at different sampling sites in the nGoM from estuaries to the open ocean. Before applying EOF analysis, we demean aphy by subtracting the spectral mean and further normalize it to the spectral standard deviation, which is finally called $a_{phy, demean}^{std}$ in order to reduce the uncertainties introduced from phytoplankton size and pigment packaging effects (Wang et al., 2015). It assumes that the original data in the spectral space can be expressed in a matrix form as:

$$a_{phy, demean}^{std}(p, \lambda) = \begin{bmatrix}
a_{11} & a_{12} & \cdots & a_{1\lambda} \\
a_{21} & a_{22} & \cdots & a_{2\lambda} \\
\vdots & \vdots & \ddots & \vdots \\
a_{p1} & a_{p2} & \cdots & a_{p\lambda}
\end{bmatrix}$$

(5.3)

where $\lambda = 301$ is maximum index for the spectra in the range of 400-700 nm at 1 nm interval; $p$ is maximum index for position, which represents a total of 264 sampling sites. Next, the variance of the spectral data was examined by projecting a series of spectral vectors at given location onto any unit vector $E$ in Euclidean space with $\lambda$-dimensions, which are the eigenvectors (EOFs).

$$E(\lambda) = \begin{bmatrix}
E_1 \\
E_2 \\
\vdots \\
E_\lambda
\end{bmatrix}$$

(5.4)

Each projection (principle component) is calculated as $PC = Z(t) \cdot E(\lambda)$, where $Z(t)$ is any row in the original data matrix $a_{phy, demean}^{std}(p, \lambda)$, and given by

$$Z(t) = \begin{bmatrix}
z_{t1} \\
z_{t2} \\
\vdots \\
z_{t\lambda}
\end{bmatrix}$$

(5.5)

where $t=1,2, \cdots, p$

Finally, the original data set can be constructed by
\[ a_{\text{phy std}}(p, \lambda) = Z(t) \cdot E(\lambda) = Z_{t1} \cdot E_1 + Z_{t2} \cdot E_2 + \cdots Z_{tK} \cdot E_{\lambda} \]  

(5.6)

Next, the phytoplankton size fraction model for Sentinel 3-OLCI is built based on the first EOFs \((E_\lambda, E_{\lambda-1}, E_{\lambda-2}, \text{and } E_{\lambda-3})\) with following steps: i) Infer phytoplankton size fraction \(f\) in micro- and pico-size from HPLC measurements based on \((f_{m, \text{HPLC}} \text{ and } f_{p, \text{HPLC}}; \text{Hirata et al. } 2011)\). ii) Determine the regression coefficients between HPLC-derived \(f\) and first 4 PCs from a log transformed linear model expressed as \((\text{Wang et al., } 2015)\):

\[
f = \frac{1}{1 + \exp \left[- \left( C_0 + \sum_{i=1}^{k} C_i \cdot PC_i \right) \right]} \quad (k \text{ is the number of PCs})
\]  

(5.7)

iii) Implement exactly the same EOF algorithm on the OLCI-derived \(a_{\text{phy}}\) using the two different methods (Sect. 2.6.1 and 2.6.2) with eight OLCI visual wavebands (412, 442, 490, 510, 560, 620, 665, 674 and 681 nm) in order to derive OLCI-estimated EOFs. v) The regression coefficient \(C_0\) and \(C_i\) obtained from Eq. (7) are then applied to OLCI-extracted PCs to estimate phytoplankton size fraction from Sentinel 3-OLCI \((f_{m, \text{OLCI}}, f_{n, \text{OLCI}} \text{ and } f_{p, \text{OLCI}})\).

### 5.2.7. Processing Approach

Sentinel 3-OLCI phytoplankton size fraction maps generated using the processing pathway 1-3 (Figure 5.2) includes the following: (1) Atmospheric correction of Sentinel 3-OLCI; (2) Chl a adaptive algorithm; (3) OLCI-derived \(a_{\text{phy}}\) from Multi-regression model and QAA-V algorithm; (4) EOF algorithm on in-situ \(a_{\text{phy}}, MR\)- and QAA-V-retrieved \(a_{\text{phy,OLCI}}\) to obtain OLCI-PCs. Finally, coefficients between PCs and HPLC-calculated size fractions obtained from in-situ data were applied to OLCI-PCs to generate the phytoplankton size fraction maps for Sentinel 3-OLCI.
Figure 5.2. Processing chain showing the three steps as follows: (1) atmospheric-correction of Sentinel 3A-OLCI data, (2) development of Chl a adaptive algorithm, and (3) phytoplankton size fraction algorithm based on EOF concept.

5.3. Results and Discussion

5.3.1. The Chl a Adaptive Algorithm (Chl a_AD)

A series of atmospheric-corrected $R_{rs,OLCI}$ spectra were derived from a broad range of water types from Sentinel 3A-OLCI imagery (Figure 5.3) that demonstrate diverse optical properties in the nGOM. The spectra in the clear offshore waters (red box b, Figure 5.3a) indicate an oligotrophic condition with high blue and strongly decreasing reflectance with increasing wavelength, and virtually negligible signal above 600 nm due to the sharp increase in water absorption (Figure 5.3b). Therefore, the spectral criteria 1 for defining clear oceanic pixels are: 1) $R_{rs,412}>R_{rs,510}$ and 2) $R_{rs,490}>R_{rs,510}>R_{rs,560}>R_{rs,620}$. Coccolithophore bloom waters were frequently masked on the inner shelf of the nGOM by the NASA standard algorithm (not shown), which appear bright milky-white (red box c, Figure 5.3a), with high reflectance across the visible spectrum (Figure 5.3c) induced by their detached coccoliths (Brown and Yoder, 1994); the spectral criteria 2 for detecting coccolithophore waters are: 1) $R_{rs,412}<R_{rs,442}<R_{rs,490}$, 2) $R_{rs,442}>R_{rs,620}$, and 3) $\max(R_{rs}(\lambda))=(R_{rs,490}$ or $R_{rs,510}$ or $R_{rs,560}$) (Joshi and D’Sa, 2020). In comparison, extremely turbid sediment-rich waters in Atchafalaya Basin (AB) and adjacent to Mississippi River plume areas (red boxes d and e; Figure 5.3a) showed obvious increasing reflectances in red to NIR wave bands with reflectance maxima frequently observed near 650 nm (Figure 5.3d). However, these spectra in the turbid AB environment did not show noticeable phytoplankton absorption and fluorescence features in the red and NIR wavebands. In contrast, spectra from turbid algae-laden waters in Galveston Bay (GB; red box e in Figure 5.3a) presented larger Chl a absorption features near 670 nm and higher peaks near 700 nm (Figure 5.3e). In addition to sediment, CDOM also plays a vital role in modulating the water colors; for example, dark-brownish waters observed in Barataria Bay (BB) typically have enhanced light absorption due to very high CDOM (Joshi and D’Sa, 2015). As such, the OLCI-extracted spectra from BB showed extremely low reflectance, most notably in the blue and green wavebands, with a subdued peak centered near 700 nm. Further, an examination of 157 Sentinel 3A/B-OLCI images of the nGOM, showed an average of 4745 negative values out of 1,843,222 pixels in OLCI blue wavebands (400, 412, 442, and 490 nm; Figure 5.3f and 5.3g), with most pixels located in BB. More interestingly, the number of pixels with this type of spectrum was positively correlated to the mean 3-day wind speed before the satellite acquisition date ($N=66, R^2=0.69$; Figure 5.3h); these pixels with negative values are likely linked to the resuspension of CDOM from bottom waters during cold front events (Joshi and D’Sa, 2015). CDOM-type Rs spectra showing overall low reflectance ($\leq 0.04\text{sr}^{-1}$; Figure 5.3f) with a peak near 700 nm, would likely introduce large errors in Chl a estimates using the red/NIR algorithms. Thus, these CDOM-rich pixels (criteria 3 given by: (1) $R_{rs,709}\geq R_{rs,681}\geq R_{rs,674}\geq R_{rs,665}\geq R_{rs,620} \geq R_{rs,560}$ and (2) $[R_{rs,510}\leq 0 \text{ or } R_{rs,490}\leq 0 \text{ or } R_{rs,412}\leq 0 \text{ or } R_{rs,400}\leq 0])$, would be excluded from the red-NIR Chl a algorithm. In addition to BB, the Lac des Allemands (a smaller CDOM-rich but hypereutrophic lake in the upper Barataria Basin) experiences frequent cyanobacteria blooms dominated by N-fixing Anabaena spp. (Dash et al., 2011; Ren et al., 2009). Correspondingly, $R_{rs}$ spectra from Lac des Allemands, showed overall low reflectances but distinctive phytoplankton features (Figure 5.3g). Generally, strong CDOM absorption in blue regions could reduce the photosynthetic efficiency of most eukaryotic phototrophs. However, several studies reported that cyanobacteria use blue light less efficiently than red light for photosynthesis because their phycobilisomes (PBS) are
mostly associated with photosystem II (PSII) but do not absorb blue photons (Arnon et al., 1974).

Figure 5.3. Reflectance spectra derived from atmospheric-corrected Sentinel 3A-OLCI imagery acquired on April 24, 2017 revealing diverse water types in the nGOM including (b) pixels in clear oceanic waters in the nGoM, (c) pixels indicate coccolithophore bloom masked by NASA standared algorithm, (d) pixels locate in turbid aquatic environment including Mississippi River plume and Atcharfalaya Basin, (e) pixels in algae-laden turbid waters in GB, (f) CDOM-rich pixels in BB and (g) high-Chl a pixels combined with high CDOM. (h) Relationship between averaged wind speeds prior to satellite data acquision and percentage of pixels with negative values in blue-green wavebands. (l) Comparison between in-situ $R_{rs}$ and reconstructed $R_{rs}$ with color representing wavelength.

The problematic pixels with negative values are due to the atmosphere correction failure over highly CDOM-rich waters. Thus, in-situ $R_{rs}$ obtained in nGoM estuaries (AB, BB and GB) were used to reconstruct $R_{rs,OLCI}$ in the blue wavebands; in-situ hyperspectral $R_{rs}$ at specific OLCI blue wavebands when multi-regressed with in-situ $R_{rs}$ corresponding to other OLCI visible wavebands showed good performance ($R^2$=0.96; Figure 5.3l). Subsequently, the coefficients were applied to corresponding $R_{rs,OLCI}$ to obtain reconstructed $R_{rs,OLCI}$ at blue wavelength when $\rho$$\leq$0.25 in order to replace problematic pixels in estuaries. The reconstructed $R_{rs,OLCI}$ at blue wavelength (Figure 5.3l) showed overall reasonably low values ($\leq$ 0.01 sr$^{-1}$), which are consistent with the spectral values at longer wavebands (560 nm $\sim$0.02 sr$^{-1}$; Figure 5.3f). Most of the missing pixels (black arrows) at blue wavebands observed in the original data ($R_{rs}$412 and $R_{rs}$490; Figure. 5.4a-b) were restored with very low positive values by multi-regression spectral reconstruction. Thus, additional pixels in estuaries are available that can be further used as input for the QAA-V algorithm. In addition, high values at $R_{rs}$412 nm observed in AB have been reconstructed with reasonable lower values at 412 nm (Figure. 5.4a-b).
5.3.2. Performance of Chl a Adaptive Algorithm

5.3.2.1. Identifying Thresholds for Applying red/NIR Chl a Algorithm

The goal of this section is to regionally tune red/NIR Chl a algorithms from large-scale field measurements of above-water Rrs and Chl a (N=793) acquired in inland, estuarine, and coastal turbid productive waters of the US East Coast and the northern Gulf of Mexico, in order to more accurately define the threshold for applying red/NIR algorithms for the estimation of Chl a. The red/NIR model was applied as $\text{Chl a} \propto \frac{R_{\text{rs,insitu(red)}}}{R_{\text{rs,insitu(NIR)}}}$. The red wavelengths were chosen as 665 nm or 674 nm and NIR band is 709 nm, which correspond to OLCI wavebands 8, 9 and 11, respectively (Figure 5.5a-b). The in-situ red/NIR band ratios showed overall good agreement with Chl a in a negative exponential relationship ($R^2 = 0.70$, $N = 793$; Figure 5.5a-b); however, very scattered data points are observed in log-scale when Chl a < ~7 mg m$^{-3}$, corresponding to red/NIR ratios > ~1.5, which is considered as an important threshold for applying red/NIR algorithms in this study.

Previous work has recommended maximum threshold of Chl a (~10 mg m$^{-3}$) for applying NIR/red algorithms (Dall’Olmo and Giteson, 2006), which corresponds to a NIR/red ratio value of approximately 0.75 (red/NIR~1.33). Gilerson et al., (2010) further concluded that two-band algorithm based on NIR/red ratio performs well when the ratio is in the range of 0.6-2.2 (corresponding to 0.45-1.67 for red/NIR), which reasonably agreed with the thresholds found in this study (Figure 5.5). It was documented that CDOM absorption and backscattering terms could be generally smaller than the contribution from water absorption when Chl a $\geq$ 5 mg m$^{-3}$ (Gilerson et al., 2010). However, at Chl a< 5 mg m$^{-3}$, when red/NIR band ratio > 1.67, the variations in CDOM absorption and backscattering have been proved to introduce additional uncertainties in predicting Chl a (Gilerson et al., 2010). In this study, band ratio of 674nm/709nm in the range 0.48-1.49 was highly correlated with Chl a (N=365, $R^2$~0.804; Figure 5.4a); in comparison, relatively lower correlations were observed between 665nm/709nm band ratio and Chl a (N=361, $R^2$~0.798; Figure 5.4b), which is likely due to greater contribution by Chl a absorption at wavelength of 674 nm than at 665 nm in the waters with high Chl a.
Figure 5.5. Parameterization of (a) and (b) algorithms based on red/NIR ratios using Sentinel 3A/B-OLCI wavebands (665, 674, and 709 nm); color symbols represent data acquired from different areas, corresponding to information listed in supplementary Table 5.1.

5.3.2.2. Chl a Adaptive Algorithm Validation

The OLCI Chl a _NN is the initial input for Chl a _AD, and the performance of the adaptive Chl a algorithm for each step is presented in this section. Once the red/NIR ratio threshold in the 0.48-1.5 range is applied, estuarine pixels were selected for the red/NIR algorithm; however, some oceanic pixels with very low Chl a levels are also in this specific red/NIR ratio range (red colors; Figure 5.6a). As such, criterion 1 defining clear oceanic pixels (Sect. 3.1) is used to avoid the application of red/NIR algorithm on clear water pixels (Figure 5.6b). Further, the NASA standard algorithm mask for coccolithophore pixels (blue arrows), were still present (Figure 5.6b), but in the absence of in-situ data, validation of the Chl a algorithms in coccolithophore-bloom waters could not be conducted. Thus, coccolithophore-bloom pixels identified from spectral criteria 2 (Sect. 3.1) are also excluded when applying red/NIR algorithm and forced back to the initial values of Chla_NN. Finally, the red/NIR algorithms were applied in the areas marked in red color (Figure 5.6c). Further, Chl a _NN in the oceanic pixels detected from criterion 1 (purple areas; Figure 5.6c) were replaced with Chla_OC4 values due to the better performance of OC4 algorithm in the open ocean (Figure 5.7c-d). In the coastal waters (blue areas, Figure 5.6c), in-situ Chl a obtained on the same day as the Sentinel 3A-OLCI (gray symbols) during June 13-September 04, 2019 were used to separately test the accuracy of Chl a_OC4 and Chl a_NN products (Figure 5.7a and 5.7b). Chl a estimates using the Neural Network (NN) algorithm was observed to be more accurate (N=19, R^2=0.71) than the OC4 algorithm (N=19, R^2=0.14), which displayed obvious overestimation of Chl a (gray symbols; Figure 5.7a-b); thus, Chl a_NN values were kept in the coastal zone. The last step is to detect the very high CDOM-affected pixels based on spectral criteria 3 (Figure 5.3f) and mask those CDOM-rich pixels as NaN. For the satellite image acquired on October 30, 2017 with stable environmental conditions (calm winds and low river discharge), there were few pixels with CDOM-rich spectra detected and thus not shown here.
Figure 5.6. Performance of Chl a adaptive algorithm in the nGoM for an image obtained on October 30, 2017: (a) pixels with red/NIR ratio in the range of 0.48-1.5 is in red color; (b) estuarine and coccolithophore-bloom waters with red/NIR ratio in the range of 0.48-1.5 (blue arrow); (c) estuaries (red), coastal zone (blue) and open ocean (purple) are applied with red/NIR, NN and OC4 Chl a algorithms, respectively. (d), (e) and (f) are maps of Chl a _OC4, Chl a_NN and Chl a_AD, respectively.

Figure 5.7. Comparison between the performance of (a) Chl a_AD and (b) Chl a_NN using in-situ Chl a obtained from 4 estuaries, namely, ApB, BB, GB and AB in the nGoM. Validation of Sentinel 3A/B-OLCI standard (a) Chl a_OC4 and (b) Chl a_NN products in coastal waters using in-situ Chl a obtained from stations in shelf waters of nGoM.
Distinct differences in Chl a distributions and concentrations were observed in estuaries between Chl a_OC4, Chl a_NN and Chl a_AD Chl a maps (Figure 5.6d-f). Chl a_AD presents stronger gradients for estuarine to oceanic waters; in contrast, Chl a_NN displayed very homogeneous values in estuaries (e.g., BB, Figure 5.6e). In-situ Chl a obtained (±1 day of satellite data) from different estuarine-coastal zones of the nGoM including Apalachicola Bay (ApB; July 6-7, 2016), BB (October 5-6, 2016) and GB (September 29, and October 29-30, 2017), AB and shelf waters (June 13-14, August 14-15, and September 3-4, 2019), BB and shelf waters (June 13-14, and September 10-11, 2019) and Louisiana shelf waters (July 16-21, 2019) were used to validate and compare the performances of Chl a_AD and Chl a_NN. It showed that Chl a_AD agreed well with the in-situ Chl a with higher $R^2$ (~0.84) and lower RMSE (~3.145; Figure 5.7b) compared to Chl a_NN ($R^2$=0.39, RMSE=6.443; Figure 5.7a). It is clear that most high Chl a values were underestimated by Chl a_NN algorithm (data in black dashed circle); in contrast, Chl a_NN in AB (red triangles) totally overestimated Chl a ~2 times greater than in-situ Chl a (Figure 5.7a).

5.3.3. Seasonal Variability of Chl a in the nGoM

5.3.3.1. Multi-year Chl a Response to River Discharge

Time-series Chl a encompassing the OLCI dataset (October, 2016-January, 2020) were extracted and averaged in the lower BB and AB (Figure 5.1c-d) using the Chl a_AD and Chl a_NN algorithms (Figure 5.8a-b). The Chl a_AD time series (black circles) in the lower BB indicated that increased freshwater discharge from Mississippi River (blue line) to be a major environmental driver for elevated Chl a (Figure 5.8a). Mean Chl a_AD in BB between 2016-2019 was ~20 mg m$^{-3}$ and showed positive response to high MR discharge (blue line) in May-June, 2017 and February-June, 2019 (Figure 5.8a). Lower Chl a were observed during low freshwater discharge (e.g., January and November, 2017, July, 2018 and November, 2019 (Figure 5.8a). In contrast, average Chl a_NN (red circles) extracted from the same area in BB generally underestimated Chl a and showed very minor variations in the time-series (red circles, Figure 5.8a)

In AB, differences between Chl a_AD and Chl a_NN were smaller across the time series (Figure 5.8b) with overall lower mean Chl a (~15 mg m$^{-3}$) than in BB. Although, this difference suggests that Chl a_NN likely performs better in AB compared to BB, examination of paired Chl a_AD and Chl a_NN maps in AB reveal Chl a distribution patterns to some extent to be opposite; for example, Chl a_NN showed highest values close to river mouth, where both in-situ Chl a and aphy showed low values. In contrast, Chl a_AD presented higher values on the leading edge of the plume, at greater distance from the river mouth. This contrasting pattern could be explained by the distribution of seawater constituents near large river mouths such as Atchafalaya River (AR) and AB estuary, wherein freshwater discharge delivers high nutrient concentrations to estuaries and bays, but also accompanying high levels of sediments and CDOM that can reduce light penetration. However, sediment loads will decrease and CDOM diluted with distance from the river mouth, which allows light penetration to increase in the presence of elevated nutrients resulting in high phytoplankton in plume-edge regions which is detected by the Chl a_AD (black circles; Figure 5.8b). Chl a enhancement was also observed in both BB and AB post-Hurricane Barry (green dashed line), with AB showing greater and longer duration Chl a response (Figure 5.8a-b). An assessment of Chl a_AD and Chl a_NN at different Chl a concentrations was conducted by considering percentage of Chl a > 20, 15 and 10 mg m$^{-3}$ in a single image (land-, cloud- and NaN-pixel excluded) (Figure 5.8c-d). It was observed that the percentage of Chl a > 20 mg m$^{-3}$ from Chl a_AD (black bars) was on average ~80 times higher than Chl a_NN product (red bars), implying significant limitations of the NN
algorithm in estimating Chl a in highly productive estuaries (Figure 5.8c). Based on the Chl a NN maps acquired between October, 2016 and January 2020, it is found that Chl a NN products generally showed saturation at Chl a reaching ~22 mg m\(^{-3}\) (supplementary Figure 5.1). In comparison, Chl a AD performed better at predicting Chl a in high-biomass and algal-bloom waters, showing strong Chl a gradients from estuaries to coastal waters. The percentage of Chl a > 15 mg m\(^{-3}\) showed similar patterns with less differences observed between Chl a NN and Chl a AD (Figure 5.8d), which indicates that Chl a NN estimated most of the high-biomass waters in the range of ~15-20 mg m\(^{-3}\).

Figure 5.8. Comparison between mean Chl a extracted from Chl a NN and Chl a AD for two estuarine waters in the nGoM. (a) Barataria Bay, (b) Atchafalaya Basin; with blue, black and red colors represent river discharge, averaged Chl a AD and Chl a NN, respectively. (c) and (d) are the percentages of Chl a > 20, and 15 mg m\(^{-3}\) with black and red bars representing Chl a AD and Chl a NN, respectively.

5.3.3.2. Mean Seasonal Chl a Trends in the nGoM

In this study, we define spring to be from March to May, summer from June to August, fall (autumn) from September to November, and winter from December to February, to obtain the seasonally-averaged Chl a AD products between October 2016 to January, 2020. Averaged Chla AD maps over different seasons displayed apparent seasonality and spatially decreasing gradients from estuaries to the coastal ocean with much higher averaged-Chl a in the estuaries than that on the inner- and mid-shelf (Figure 5.9). Temporally, Chl a in estuaries during late winter and spring was higher than that in summer and fall (Figure 5.9). Mean Chla AD maps over different seasons (Figure 5.9) from October 2016 to January, 2020 displayed apparent seasonality and spatially decreasing gradients from the estuaries to coastal ocean with much
higher Chl a in the estuaries and decreasing on the inner (isobath<20 m) and mid-shelf (isobath<100 m) before transitioning to very low values (~0.5 mg m$^{-3}$) in the oligotrophic waters of the nGOM (inner, mid and offshore waters are defined in Swarzenski et al., 2008). Temporally, Chl a in estuaries during spring was higher than that in other seasons (Figure 5.9).

Overall highest Chl a values with strong offshore cross-shelf gradients were observed in the spring season (Figure 5.9a) and is primarily related to the high river discharge. A total 49 Chl a_AD images were used to obtain the mean spring Chl a map. Chl a in estuaries (AB ~19.1 mg m$^{-3}$, BB ~26.4 mg m$^{-3}$, GB ~22.1 mg m$^{-3}$ and Lake Pontchartrain, LP ~16.3 mg m$^{-3}$) was higher than that on the inner shelf (~12.3 mg m$^{-3}$) and mid-shelf (~4.5 mg m$^{-3}$) from March-May (Table 5.1). Frequent algal blooms in the Louisiana Bight (LB) and the easternmost Louisiana and Texas Coast (LATEX) were observed in spring, with mean Chl a approaching ~21 mg m$^{-3}$ (Fig. 5.9a) due to the abundant nutrients from the Mississippi River discharge (Twilley, 1996). The overall high Chl a during spring in the estuaries, inner shelf and mid-shelf support field studies, satellite observations and conceptual models that show enhanced phytoplankton biomass due to increased nutrient loading in the nGOM. The magnitude and duration of the high Chl a biomass and algal blooms along the LATEX shelf during the spring season has been shown to play an important role on the areal extent of the hypoxic zone. For example, the extremely wet spring of 2019 and associated flooding in large areas of the Mississippi River watersheds, resulted in a large-scale ‘dead zone’, which was bigger than the 5-year average recorded size of 1.49×10$^{10}$ m$^2$ (Lindsey et al., 2019). More accurate satellite estimates of Chl a biomass would be critical inputs to models to better predict the areal extent and severity of hypoxic zones in the nGOM (Beck et al., 2017).

As spring transitions into summer, decreasing river discharge (Figure 5.8a-b) and nutrient loading results in lower Chl a levels on the inner (~9.1 mg m$^{-3}$) and the mid-shelf (~2.1 mg m$^{-3}$) (Table 5.1; Figure 5.9b). In estuaries, Chl a in AB (~14.2 mg m$^{-3}$) and BB (~19.2 mg m$^{-3}$) showed obvious decrease than in GB (~19.4 mg m$^{-3}$) and LP (~13.4 mg m$^{-3}$). In the distal end of AB however, a high Chl a band was frequently observed in 13 out of 31 summer Chl a_AD maps, as also in the averaged summer Chl a (black arrow; Figure 5.9b), a feature
that has been previously reported (D’Sa, 2008); this could be due to the inner shelf circulation on the LATEX shelf, but needs further investigation. The eastward current resulting from a southern wind regime during summer in the GoM, likely bring high-biomass waters in AB upcoast to shelf waters. Correspondingly, Chl a in coastal area adjacent to EMS showed relatively higher values in summer compared to other seasons (Figure 5.9b). During fall, average Chl a values (calculated from 40 cloud-free Chl a_AD images between 2016-2019; Figure 5.9c) further declined in the estuaries (~12 mg m\(^{-3}\)) and the inner shelf waters (~5 mg m\(^{-3}\)); for example, average Chl a in BB, AB and LP were ~13.5, 10.9 and 6.2 mg m\(^{-3}\), respectively (Table 5.1; Figure 5.9c). This could be attributed to the relatively stable hydrodynamic regime, a period with less energetic events (e.g., hurricanes and cold front passages) and low river discharge, with Chl a a declining dramatically in the LB to ~2 mg m\(^{-3}\).

Table 5.1. Mean seasonal Chl a in different estuaries and shelf waters in the nGoM

<table>
<thead>
<tr>
<th>Season</th>
<th>AB (mg m(^{-3}))</th>
<th>BB (mg m(^{-3}))</th>
<th>GB (mg m(^{-3}))</th>
<th>LP (mg m(^{-3}))</th>
<th>Inner shelf (mg m(^{-3}))</th>
<th>Midshelf (mg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>19.1</td>
<td>26.4</td>
<td>22.1</td>
<td>16.3</td>
<td>12.3</td>
<td>4.5</td>
</tr>
<tr>
<td>Summer</td>
<td>14.2</td>
<td>19.2</td>
<td>19.4</td>
<td>13.4</td>
<td>9.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Fall</td>
<td>10.9</td>
<td>13.5</td>
<td>15.6</td>
<td>6.2</td>
<td>5.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Winter</td>
<td>19.5</td>
<td>16.3</td>
<td>12.6</td>
<td>7.5</td>
<td>6.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Satellite imagery obtained during winter revealed high Chl a after frontal passages in the nGOM (from a total of 16 out of 37 Chl a_AD maps obtained up to 2-days after cold fronts used for calculating winter-averaged Chl a). Mean Chl a calculated from the remaining images obtained under relatively stable meteorological conditions showed overall low Chl a with no obvious Chl a variations in the inner and mid-shelf waters from fall to winter. In contrast, Chl a in estuaries were apparently higher (e.g., ~20 mg m\(^{-3}\) in AB; Figure 5.9d) compared to that in the fall season (Figure 5.9c); this is likely due to nutrient release from bottom sediments in the shallow estuarine waters during cold front events. It was also observed that the number of CDOM-rich pixels was positively correlated to wind speed (as shown in Fig. 3b for negative pixels), which likely implies that winds, in addition to modulating estuarine circulation and optical properties, also influence phytoplankton community dynamics in these waters (Lohrenz et al., 2008). In addition, wetlands serving as another source and transformer of nutrients and other chemical constituents, could also significantly affects downstream water quality and ecosystem, especially during cold fronts (Bauer et al., 2013). For example, stronger north winds combined with heavy rainfall during the winter storms have been reported to have flushed over three million hectares of marshes along the coasts, loading nutrient-rich waters downstream to the estuaries and enhancing primary productivity (Justić et al., 1993).

5.3.4. The Phytoplankton Size Fraction (PSF) Algorithm Performance

5.3.4.1. \(a_{phy}\) from Sentinel 3-OLCI based on Multi-regression

An extensive suite of SeaBASS data including aphy (m\(^{-1}\)) and HPLC (mg m\(^{-3}\)) obtained across different seasons in the nGoM was used to regionally train the aphy-Chl a relationship to obtain the spectral coefficients between aphy and Chl a (N=264, 2008-2017); the modeled aphy was highly correlated with in-situ aphy (\(R^2=0.82\); Figure 5.10a), with an overall greater scatter in the blue than the red wavelengths. The spectra obtained from high-Chl a samples however, showed an apparent peak at ~490 nm, which is likely due to the absorption of zeaxanthin, a common pigment in cyanobacteria. Next, the spectral coefficients were applied to OLCI-Chl a_AD maps to generate MR-\(a_{phy, OLCI}\) maps at 301 wavelengths (400–700 nm at
1 nm interval). The limitation of this method is that the Chl a-aphy correlation will be optimally suitable for the nGoM because of phytoplankton taxonomic differences in other areas.

5.3.4.2. EOFs from in-situ and MR-\( a_{\text{phy,OLCI}} \) Spectra

We performed EOF analysis on the demeaned and normalized in situ aphy (\( a_{\text{phy,demean}} \)), a matrix with 301 columns and 264 rows, to detect the variability patterns (modes) of \( a_{\text{phy,demean}} (p, \lambda) \). The first four PCs together explain 98.17% of all variations in \( a_{\text{phy,demean}} \), which implies the original spectra have been reduced from a 264 \( \times \) 301 matrix to a 264 \( \times \) 4 matrix with a minimal loss of information (1.83%). The cumulative proportions showed that the first mode explained 87.7% variability of the \( a_{\text{phy,demean}} \) spectra (blue line; Figure 5.10c), with two negative peaks present at 440 and 675 nm that could be attributed to the absorption of Chl a. The PC1 was negatively correlated with micro-phytoplankton fraction \( f_m \), but positively related to pico-phytoplankton \( f_{pico} \) (Table 5.2). The second mode (red line; Figure 5.10c) accounted for 7.5% of the variance and correlated with \( f_{micro} \) and \( f_{pico} \) in a positive and negative relationship, respectively (Table 5.2). A stronger peak with positive variance was observed in 660-690 nm (Figure 5.10c), and thus, the higher the peak of \( a_{\text{phy,demean}} \), the larger the size of phytoplankton. Several small peaks and troughs corresponding to different phytoplankton pigments were also observed from EOF2; for example, the peak at \( \sim 490 \) nm with negative variance possibly represents zeaxanthin, which is a pigment for pico-phytoplankton. The third component explains an additional 1.99% for a cumulative total of 98.17%. This mode displayed an apparent broad peak in the range of 450-500 nm (green line; Figure 5.10f), which coincidently correspond to the absorption peaks from fucoxanthin, peridinin, Chl b and DV-Chl b in this range; however, contribution of each pigment at this peak is unknown. The negative/positive coefficient (Table 5.2) between PC3 and \( f_{micro}/f_{pico} \) likely indicates that this broad peak is from pico- or nano-size phytoplankton, such as chlorophyte (green algae), which are mostly found in small size fractions, in particular the pico-phytoplankton and nano-phytoplankton (Tragin and Vaulot, 2018). The spectrum of the fourth mode (pink line; Figure 5.10c) appears as a broad and positive peak in the 500-550 nm range, with very minor variations due to the absence of strong pigment absorption in this range. Thus, it is reasonable to assume that PC4 showed poor correlation with either micro- or pico-phytoplankton.

The same EOF algorithm was then applied to the MR-\( a_{\text{phy,OLCI}} \), which was also demeaned and normalized. The average EOFs extracted from a total of 157 MR-\( a_{\text{phy,OLCI}} \) maps (MR-EOFs) showed high similarity with the EOFs obtained from 267 in-situ \( a_{\text{phy}} \) spectra at specific OLCI wavebands, accounting for 94.28% variance (Figure 5.10d). However, slight differences in magnitude were observed, which could be mainly attributed to the uncertainties of OLCI-estimated \( a_{\text{phy}} \). As mentioned in Sect. 3.4.1, the modeled \( a_{\text{phy}} \) spectra (Figure 5.10a) are more scattered at the blue-green wavelength compared to red wavelength, which is likely due to the limited in-situ data pairs (Chl a and \( a_{\text{phy}} \)) in such optically-complex waters. Furthermore, the coefficients \( C_i \) (Table 5.2) obtained in Sect. 3.4.2 were applied to the first four MR-EOFs (colored lines; Figure 5.10d) to generate maps of phytoplankton size fractions (\( f_{micro} \), \( f_{nano} \) and \( f_{pico} \)). The modeled \( f_{micro} \) (brown squares; \( R^2 = 0.87 \); RMSE=0.11), and \( f_{pico} \) (green triangles; \( R^2 = 0.76 \); RMSE=0.13) agreed well with corresponding HPLC-calculated size fractions (Figure 5.10e-f). The modeled \( f_{nano} \) showed relatively lower \( R^2 \) but higher RMSE (purple circles; Figure 5.10g) because it receives uncertainties from both \( f_{micro} \) and \( f_{pico} \).
Figure 5.10. (a) A total of 264 in-situ aphy spectra from SeaBASS. (b) Comparison between in-situ $a_{\text{phy}}$ and modeled $a_{\text{phy}}$ from multi-regression with colors representing wavelengths. (c) Averaged MR-EOFs extracted from in-situ aphy spectra. (d) Averaged EOFs extracted from a total of 157 MR-aphy_OLCI. (e), (f) and (g) are the validation of EOF-modeled $f_{\text{micro}}$, $f_{\text{nano}}$ and $f_{\text{pico}}$ from in-situ data obtained in summer, 2019.

Table 5.2. Coefficients $C_i$ for different size fractions and principle components from in-situ data

<table>
<thead>
<tr>
<th>$a_{\text{phy}}$-mean $(p, \lambda)$</th>
<th>Size</th>
<th>EOF 1</th>
<th>EOF 2</th>
<th>EOF 3</th>
<th>EOF 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro</td>
<td>-1.27</td>
<td>2.34</td>
<td>-1.38</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Pico</td>
<td>1.17</td>
<td>-2.29</td>
<td>1.34</td>
<td>-0.68</td>
<td></td>
</tr>
</tbody>
</table>

5.3.4.2. EOFs from QAAV-aphy_OLCI

Following QAA-V algorithm in Joshi and D’Sa, (2018), $a_t\text{nw}$ and $b_{bt\text{nw}}$ were estimated from atmospheric-corrected Rs_r_OLCI with replacement of reconstructed Rs in estuaries. Further, an empirical algorithm based on green to red ratio (Eq.5.1; Figure 5.11a) was established for estimating $a_{\text{dg}}(442)_{G/R}$ in estuaries to avoid using blue wavelength, due to greater uncertainties from atmospheric correction and sky light influence (Joshi and D’Sa, 2015). The green/red ratio was well correlated with $a_{\text{dg}}(442)$ in a negative exponential relationship (Figure 5.11a). In contrast, strong overestimations of $a_{\text{dg}}(442)$ from the standard QAA algorithm ($a_{\text{dg}}(442)_{QAA}$), which is primarily based on OLCI wavebands of 412 and 442 nm were observed in the nGoM. Thus, $a_{\text{dg}}(442)_{QAA}$ in optically-complex estuarine waters when $\rho \leq 0.25$ were replaced by $a_{\text{dg}}(442)_{G/R}$. Finally $a_{\text{phy}}(\lambda)$ was determined by subtracting $a_{\text{dg}}(\lambda)$ from $a_t\text{nw}$, and defined as QAAV-aphy_OLCI. It was found that QAAV-aphy_OLCI showed overall higher values in blue wavebands, especially at 412 and 442 nm, when compared with in-situ $a_{\text{phy}}$ ($R^2=0.64$; Figure 5.11b). The overestimations of QAAV-aphy_OLCI could be mainly attributed to the following factors: (1) the coefficients used in QAA-V which are specifically calibrated for Sentinel 3-OLCI in Joshi and D’Sa, (2018), are needed for further parameterization based on larger-scale in-situ data, (2) the absorption and scattering coefficient
of pure water which depend on temperature, salinity, and wavelength, are obtained from Water Optical Properties Processor, (WOPP version 2; Röttgers et al., 2016) based seasonally-averaged water temperature (T) and salinity (S) in the nGoM; this could still introduce uncertainties when estimating $a_{\text{dG}}$ and $b_{\text{bt.1,0}}$ due to the differences of S and T in different estuaries and coastal zones. (3) More in-situ data are required in estuaries to better reconstruct the Rrs in the blue part of the spectrum to generate a more robust relation between $a_{\text{dG}}(442)$ and the G/R ratio.

Figure 5.11. (a) Exponential relationship between $a_{\text{dG}}(442)$ and Rrs ratio (560nm/674nm). (b) Comparison between in-situ $a_{\text{phy}}$ and QAAV-$a_{\text{phy,OLCI}}$ at specific OLCI wavebands, with colors indicating wavelength. (c) Averaged QAAV-EOFs extracted from a total of QAAV-$a_{\text{phy,OLCI}}$ imagery. d), e) and f) are the validation of modeled $f_{\text{micro}}$, $f_{\text{nano}}$ and $f_{\text{pico}}$ from in-situ data obtained in summer, 2019.

The first four modes (Figure 5.11c) derived from QAAV-$a_{\text{phy,OLCI}}$ explained a total of 89.5% variability and showed spectral similarity but larger variance compared to EOFs from in-situ and MR-$a_{\text{phy}}$. When coefficients $C_i$ is applied to QAAV-EOFs, the results (Figure 5.11d-e) showed overestimations (underestimations) of $f_{\text{micro}}$ ($f_{\text{pico}}$), and thus, reduced estimates for $f_{\text{nano}}$ ($R^2=0.38$; Figure 5.11f). It is observed that EOF 2 in 665 nm (red line) and EOF 4 in 500-550 nm range (pink line) are 0.3 and 0.25, respectively, displaying apparent higher variance than those detected from in-situ $a_{\text{phy}}$ (Figure 5.11c), which could be the major reason for the overestimations of $f_{\text{micro}}$.

5.3.5. Response of Phytoplankton Size Fractions (PSFs) to Hurricane Barry

Maps of phytoplankton size fractions ($f_{\text{micro}}$, $f_{\text{pico}}$ and $f_{\text{nano}}$) were generated based on MR-EOFs due to its better performance compared to QAAV-EOFs. A series of Sentinel 3-OLCI images (July 04-September 14, 2019) acquired pre- and post-Hurricane Barry were used to generate Chl a_AD (Figure 5.12a1-a7) and PSFs maps (Figure 5.12b1-b7, c1-c7 and d1-d7). Corresponding daily altimetry-derived sea surface height (SSH) data were also downloaded
from NOAA CoastWatch to facilitate the understanding of environmental variability within this period (Figure 5.12e1-e7). On July 04, 2019, Chl a values showed moderate levels (~15.8 mg m\(^{-3}\); Figure 5.12a1) in the estuaries of the nGoM except the Mississippi Sound (MS), which experienced an algal bloom (EPA advisory). Values of \(f_{\text{micro}}\) displayed a strong decreasing gradient from estuaries (~0.78) to offshore waters (~0.15; Figure 5.12b1). In comparison, nanophytoplankton fraction showed low values in estuaries ~0.21 but increased their contributions in the western midshelf and offshore waters ~0.42 (Figure 5.12b1). Conversely, \(f_{\text{pico}}\) showed exactly opposite patterns with \(f_{\text{micro}}\), displaying highest values (~0.92; Figure 5.12d1) in the eastern midshelf/offshore waters, which coincidently meets the warm Loop Current waters (Figure 5.12c1). SS map obtained on July 9, 2019 (two days pre Hurricane Barry; not shown) captured a clockwise rotating ring of warm water (warm core ring) separating from the main loop current. Hurricane Barry made landfall as a category 1 hurricane along the Louisiana Coast on July 13, 2019 and caused significant flooding with more than 20 inches of rainfall in Louisiana and Mississippi (Li et al., 2020). On July 17 2019, four days following the hurricane landfall, an increase in Chl a, \(f_{\text{micro}}\) and \(f_{\text{nano}}\) from the estuaries to offshore waters were observed, but \(f_{\text{pico}}\) significantly decreased in midshelf and offshore waters. More importantly, an apparent increase/decrease of \(f_{\text{nano}}/f_{\text{pico}}\) was revealed along the hurricane's path (black line; Figure 5.12c1) on July 17-19, 2019 (Figure 5.12c2-d2, c3-d3 and c4-d4), where a wake of colder water with low SHH values were observed (Figure 5.12e2-e4). Algae bloom developed adjacent to the Mississippi Delta (MD) with Chl a reaching 42 mg m\(^{-3}\) on July 18, 2019 (Figure 5.12a1), agreed well with in-situ observations (~46.5 mg m\(^{-3}\)). This algae bloom showed strong dominance of microphytoplankton, with extremely high \(f_{\text{micro}}\) (~0.95; Figure 5.12b1) observed in this area. HPLC analysis in this MD bloom station on July 18, 2019 indicated the dominance of diatoms with highest fucoxanthin concentrations (~13.62 mg m\(^{-3}\)) that accounted for ~65% of diagnostic pigments (Figure 5.13). In addition, \(f_{\text{nano}}\) showed a substantial increase in the midshelf and offshore waters, approaching ~0.54 around the hurricane track (black line; Figure 5.12c3). In contrast, \(f_{\text{pico}}\) showed continuous decline in the midshelf and offshore waters with higher values observed coincidently in the nutrient-poor warm core eddy waters (Figure 5.12e3). One day later (July 19), a strong increase in Chl a was observed in AB (~24.7 mg m\(^{-3}\)) and the adjacent shelf waters (~12.8 mg m\(^{-3}\)), where Hurricane Barry landed (Figure 5.12a1). More interestingly, an algal bloom with Chl a ~18.5 mg m\(^{-3}\) (black arrow; Figure 5.12a4) formed, which appeared to be isolated by low-biomass shelf waters. HPLC measurement at this station showed comparable Chl a (~19.67 mg m\(^{-3}\)) that also revealed a considerable increase in 19\(^{\prime}\)hexa-fuco and Chl c, which are specific to coccolithophore (Zapata et al., 2004). Furthermore, the milky blue-green waters observed at this station during the cruise had a typical coccolithophore R\(_a\) spectrum; coccolithophore have also been previously reported to be generally dominant in offshore waters of the nGoM (Chakraborty and Lohrenz, 2015). Thus, higher fraction of 19\(^{\prime}\)hexa-fuco (~11%; Figure 5.13) together with the water color at this station jointly suggested that this coccolithophore bloom that formed in the shelf waters was most likely transported from offshore waters by the hurricane and further nourished by the nutrient-rich deeper cold waters. Additionally, \(f_{\text{micro}}\) in the bloom area showed high values (~0.71; Figure 5.12b1), which is reasonable since coccolithophores are spherical cells about 5–100 micrometers (Moheimani et al., 2012). Concurrently, \(f_{\text{nano}}\) and \(f_{\text{pico}}\) slightly decreased and increased on July 19 compared to July 18 in the midshelf and offshore waters (Figure 5.12c4-d4). Approximately two weeks after Hurricane Barry (July 30, 2019), while \(f_{\text{pico}}\) increased in the shelf waters (Figure 5.12d5), Chl a (Figure 5.12a5), \(f_{\text{micro}}\) (Figure 5.12b5) and \(f_{\text{nano}}\) (Figure 5.12c5) all showed an overall decrease.
Figure 5.12. Time-series Sentinel-3A OLCI-derived maps of Chl a_AD, PSFs, and altimetry-derived SSH in the nGoM during July 04-September 14, 2019. (a1-a7) Chl a_AD, (b1-b7) \( f_{\text{micro}} \), (c1-c7) \( f_{\text{nano}} \), (d1-d7) \( f_{\text{pico}} \), and (e1-e7) SHH. Panels 1-7 represent maps for July 04, July 16, July 18, July 19, July 30, September 04 and September 14, 2019, respectively.

Chl a returned to normal low levels by September, 2019 (Figure 5.12a6-a7) with reasonable decline of large-size phytoplankton due to the depleted nutrient conditions (Figure 5.12b6-b7 and c6-c7). Thus, picophytoplankton was prevalent and outcompeted the larger-size phytoplankton with high \( f_{\text{pico}} \) approaching ~0.9 (Figure 5.12d6-d7) in the offshore, midshelf.
and even reaching the inner shelf waters. HPLC measurements obtained at the same stations in both BB and AB during July and September, 2019 showed obvious decreasing fraction of fucoxanthin (representing diatoms; brown bar) and alloxanthin (specific to cryptophyte; pink bar) but clear elevation of zeaxanthin, which is a biomarker pigment for cyanobacteria (blue bar; Figure 5.13). Finally, the time-series size fraction maps, especially $f_{\text{pico}}$ (Figure 5.12 d1-d7) clearly captured the slowly west-southwestward drift of the warm core eddy, and demonstrated their potential in interpreting ocean circulation and the crucial role of loop current in the biology of the GoM.

Figure 5.13. Percentage of biomarker pigments including Chl b, alloxanthin (allo), fucoxanthin (fuco), peridinin (peri), zeaxanthin (zea), Chl c3 and 19’hexa-fuco calculated from HPLC measurements in Barataria shelf, Barataria Bay, Atchafalaya Basin, MD bloom, and shelf bloom area.

5.3.6. Seasonality of Phytoplankton Size Fractions (PSFs)

A total of 49, 31, 40 and 37 OLCI Chl a_AD imagery (2016-2019), respectively were used for calculating the seasonal-averaged phytoplankton size fractions between October 01, 2016 and January 05, 2020 (Figure 5.14). Highest $f_{\text{micro}}$ and $f_{\text{nano}}$ were observed from the estuaries to offshore waters in the spring season (Figure 5.14a1-a2) that could be attributed to overall high river discharge. In addition, apparent higher fraction of nanophytoplankton (~0.58; Figure 5.14a2) was observed in the western midshelf waters, which could be associated with the downcoast currents on the LATEX shelf, carrying cool low-salinity but nutrient-rich water from the Mississippi and Atchafalaya Rivers westward along the LATEX coast (Zavala-Hidalgo et al., 2003). Further, $f_{\text{pico}}$ showed lowest values in the eastern offshore waters, which were generally influenced by the LC intrusion. In summer, $f_{\text{micro}}$ declined from the estuaries to the offshore waters due to decreased river discharge (Figure 5.14b1); in comparison, $f_{\text{nano}}/f_{\text{pico}}$ showed obvious decline (~0.11)/increase (~0.87) in offshore waters (Figure 5.14b2-b3) likely due to the LC and warm core eddies, which were known to reach maximum extension in summer but are less intrusive in other seasons (Delgado et al., 2019). A statistically significant peak in LC eddy separation events occur in the months of August and September (Hall and Leben, 2016).
Figure 5.14. Seasonally-averaged OLCI PSF maps in (a1-a3) spring, (b1-b3) summer, (c1-c3) fall and (d1-d3) winter (2016-2020) in the nGoM. Panels 1-3 represent maps for $f_{\text{micro}}$, $f_{\text{nano}}$ and $f_{\text{pico}}$, respectively.

The eddy-driven anticyclonic circulation could further deepen the nutricline and result in oligotrophic surface water, which allowed the small-size phytoplankton to outcompete large-size phytoplankton during summer (Biggs et al., 1996). In the fall season, $uf_{\text{micro}}$ showed overall lowest levels in the estuaries (Figure 5.14c1), and corresponded to the extremely low river discharge and relatively calm regime. In contrast, fractions of nano-phytoplankton (Figure 5.14c2) slightly increased compared to that of summer, which could be attributed to the weakened loop current in the fall. Also, the area with the highest $f_{\text{pico}}$ (~0.85; Figure 5.14c3) in offshore waters moved slightly westward, which likely corresponds to the west-southwestward shift of warm core eddies towards Texas or Mexico at about 2 – 3 miles per day (Chang and Oey, 2012). Finally, in the winter season, $f_{\text{micro}}$ started to increase in response to elevated river discharge and the frequent cold fronts in estuaries and inner shelf waters. In midshelf and offshore waters, apparent enhancement/decline of $f_{\text{nano}}/f_{\text{pico}}$ was observed, which contrasts with the warm season. In winter, stronger northerly winds and lower surface temperatures, favor the offshore flow of nutrients, likely contributing to higher fraction of...
nano-phytoplankton in shelf waters. Further, decreased $f_{\text{pico}}$ again likely correlated with the retraction of the LC and the dissipation LC eddies, which are generally strong from summer to fall and weaker from winter to spring (Chang and Oey, 2012).

5.4. Conclusions

The ability to observe the spatio-temporal distribution (including phenology) and variability of PSFs is a scientific priority for understanding the marine food web, and ultimately predicting the ocean's role in regulating climate and responding to climate change at various time scales. The seasonal variations of Chl a and PSFs in the nGoM are complex and closely associated with environmental variabilities (e.g., river discharge, hurricanes, LC and eddies) at various temporal and spatial scales. This study attempts to develop appropriate satellite algorithms to reveal some patterns in the seasonality of Chl a and PSFs and further investigate their response and linkages to extreme coastal events. Main contribution of this study can be summarized as:

i) Estuarine Chl a algorithms based on red/NIR ratio are regionally parameterized for the nGoM in this study. It is found that the algorithm utilizing the OLCI band 674 nm presented better performance ($R^2=0.804$; RMSE=3.923) than using the 665nm band ($R^2=0.798$ and RMSE=4.044), indicating that the addition of 674 nm is an advantage of Sentinel 3A/B-OLCI for predicting Chl a. A threshold ($0.48 \leq \frac{\text{red}(674\text{ nm})}{\text{NIR}(709\text{ nm})} \leq 1.5$) is also determined for applying the red/NIR algorithm to high biomass estuarine waters and some algae-bloom shelf waters. Further, an adaptive scheme was used to combine red/NIR algorithms with other standard Chl a algorithms (NN, OC4) to optimally extract Chl a in diverse water types. This adaptive methodology showed superior performance ($R^2=0.84$) in the nGoM compared to any single algorithm, and thus, could be extended to many other productive coastal and estuarine waters. Chl a AD maps generated from this adaptive scheme were then used to obtain OLCI-aPhy from a regionally-tuned 3rd order function of Chl a based on Multi-regression (MR); the modeled aPhy is highly correlated with in-situ data, with aPhy showing greater scatter in blue than red wavelengths ($R^2=0.82$). Furthermore, OLCI-aPhy is also estimated from an estuarine-tuned QAA-V algorithm, which also shows slight overestimation in the blue wavebands ($R^2\sim0.64$). Finally, an EOF-based algorithm is applied to OLCI-aPhy derived from these two different methods to retrieve PSFs from Sentinel 3-OLCI. Results indicate better performance MR-EOF in estimating $f_{\text{micro}}$ ($R^2=0.87$), $f_{\text{nano}}$ ($R^2=0.76$) and $f_{\text{pico}}$ ($R^2=0.64$) compared to QAAV-EOF.

ii) A case study utilizing time-series of OLCI Chl a AD and PSFs obtained pre- and post Hurricane Barry is conducted to investigate the biological response to the hurricane from estuaries to offshore waters in the nGoM. Strong algal blooms with extremely high Chl a ($\sim46.5$ mg m$^{-3}$) and $f_{\text{micro}}$ ($\sim0.93$) contribution were observed in estuaries adjacent to MD and Wax Lake Delta (WLD) one-week after Hurricane Barry. HPLC analysis indicated the strong dominance of diatoms linked to hurricane-induced algae blooms in the estuaries of the nGoM. In comparison, $f_{\text{nano}}$ and $f_{\text{pico}}$ substantially increased and declined in midshelf and offshore waters in response to the hurricane. More importantly, $f_{\text{nano}}$ and $f_{\text{pico}}$ showed apparent increase and decline along the hurricane track associated with the wake of colder nutrient-rich water along the hurricane's path. An algae bloom with Chl a $\sim18.5$ mg m$^{-3}$ formed near Barry’s track on inner/midshelf region but was isolated by the low-biomass shelf waters; HPLC revealed considerable increase of 19’hexa-fuco and Chl c$_3$, which are specific to coccolithophore. In addition, milky blue-green water color was observed in the field in the bloom area, which supports the physical and chemical environment following Hurricane Barry to be favorable for the growth and dominance of coccolithophores in shelf waters. Overall, it is observed that nutrients brought up by cyclonic wind of hurricanes could promote
phytoplankton blooms in the shelf waters; in estuarine waters, nutrients are often directly from river runoff or released from the resuspension of sediments in the shallow waters.

iii) The spatiotemporal response of Chl a and PSFs revealed complex linkages to environmental variabilities with ecological implications in the nGOM. Results showed that the seasonally-averaged Chl a and \( f_{\text{micro}} \) in the estuaries and inner shelf waters of the nGoM are mainly controlled by regional wind regime and freshwater inflows from river discharge, with highest/lowest values observed in spring/fall. In comparison, Chl a and PSFs dynamics in the midshelf and offshore waters of the nGoM are strongly influenced by LC expansion, eddy shedding, and retraction, with especially stronger effects on nano- and pico-phytoplankton fractions. Highest \( f_{\text{pico}} \) and lowest \( f_{\text{nano}} \) are observed in the midshelf and offshore waters in summer due to the strongest LC intrusion in this season. In this study, areas with highest \( f_{\text{pico}} \) always coincidently matched the area with LC and warm core eddy, indicating the potential of \( f_{\text{pico}} \) to be used to additionally map and interpret the LC and its eddies.
CHAPTER 6. SUMMARY AND CONCLUSION

The bio-geochemical responses and linkages to environmental variabilities in the estuarine-coastal waters are assessed in the nGoM. Many estuaries flowing into the GoM play a crucial role in the GoM biogeochemical cycling and ecosystem dynamics. This study explores how the optically active constituents (e.g., CDOM and different phytoplankton groups) impact the light field in optically-complex waters, and in turn, how the field optics and remote sensing techniques can facilitate the study of carbon cycling and phytoplankton community dynamics. Bio-optical field measurements acquired in different shallow estuaries of the GoM combined with satellite algorithms developed for different sensors (e.g., Landsat 5-TM, Aqua-MODIS and Sentinel 3-OLCI) are used to investigate the biogeochemical responses and linkages to environmental variabilities including river discharge, cold fronts, and strong meteorological events such as hurricanes. The major outcomes of this dissertation are listed below:

6.1. The Role of Land-ocean Interactions in Coastal Carbon Cycling

Coastal carbon dynamics is far more complex compared to open ocean environments due to its proximity to land, experiencing both geomorphologic and ecological disturbances from environmental variabilities (e.g., sea-level rise, climate change, pollution, nutrient enrichment and land-use change). The external source of carbon in the coastal ocean subsystem is governed not only by riverine input but also by the highly productive tidal wetlands and estuaries, where dissolved and particulate matter transition from land to ocean. However, many estuarine-coastal systems are continuing to experience significant wetland loss and variations in land cover type due to the combined effects of physical, geological, climatic and anthropogenic influences, which result in uncertainties in quantifying the magnitude and variability of coastal carbon fluxes from land to ocean. Furthermore, it is difficult to resolve long-term influences of landscape dynamics on carbon cycling due to spatiotemporally-limited field observations of land variations. Thus, remote sensing observations with high spatiotemporal resolution advanced our ability to monitor the patterns and processes associated with coastal carbon cycles, which is important for understanding carbon exchange across air-sea-land environments. In this study, dissolved organic carbon (DOC) algorithms for two satellite sensors (Landsat and MODIS) are developed and used to study long-term (1985-2012) DOC variations in Barataria Basin, a dynamic wetland-estuary system (80 km to the west of MR delta) undergoing constant landscape change in the nGoM.

To assess the DOC dynamics, monthly measurements of DOC concentrations and CDOM absorption were obtained over a three-year period (2008-2011) along a transect encompassing the upper, middle and lower regions of the Barataria Basin estuary. While CDOM absorption coefficient at 355 nm ($\alpha_{g,355}$) generally decreased and spectral slope at 275-295 nm ($S_{275-295}$) increased along the transect from the upper to lower basin, deviations were observed associated with hydrologic and meteorological influences. An application of wavelet analysis to the time-series of $\alpha_{g,355}$ and various freshwater sources revealed a spatiotemporal resonance of $a_{g,355}$ with freshwater input from the Mississippi River (MR), the controlled freshwater discharge from the Davis Pond freshwater diversion, and rainfall in the lower, middle and upper basins, respectively. Field measurements and Landsat/MODIS data spanning across different seasons between 2008-2011 were used to develop optimized $a_{g,355}$ empirical algorithms for the high river flow, cold front, and normal conditions. Power law models relating a band ratio (green/red) of a satellite sensor to $a_{g,355}$ showed good performance for the MODIS-Aqua ($R^2$~0.81-0.83, N=581) and Landsat-5 TM ($R^2$~0.72-0.79, N=304) imagery. $a_{g,355}$-DOC relationships ($R^2$~0.77-0.84, N=306) applied to historical Landsat-5 TM (1985-306).
and MODIS-Aqua imagery (2002-2012) showed strong environmental influences on multi-decadal CDOM and DOC spatiotemporal trends. Satellite-derived DOC agreed reasonably well with in-situ measured DOC (averaged $R^2=0.71$; RMSE=2.13). While the time-series DOC showed seasonality and decreasing gradients from the upper to lower basin, an overall increase in DOC was observed in the upper and middle basins from 1985 to 2012. However, in the lower basin, DOC increased from 1985 to 2006 but decreased from 2007 to 2012, likely due to the impact of two major hurricanes in 2005. We also have done supervised land classification work across this complex wetland-estuary interface for Landsat data to obtain long-term land cover variations (1985–2011). This study revealed linkages between DOC and environmental variations (e.g., seasonality, hydrological cycles, and episodic meteorological events), as well as first time addressed how land use/land loss are impacting the long-term DOC trends and distributions in this dynamic and narrow land-ocean interface from remote sensing observations. The relationships between satellite-derived DOC and land cover variations (1985–2011) along the wetland-estuary interfaces derived from Landsat-5 TM supervised classification showed an increase in DOC with corresponding increase in developed area in the upper basin, while in the lower basin, DOC increased by 41% ($R^2=0.54$) between 1985-2006 corresponding to a 17% decrease in salt marsh area; this indicates soil loss in the salt marsh is an important DOC source in the wetland-estuary system, which implying strong land use/land loss impact on the long-term DOC trends in Barataria Basin.

6.2. Phytoplankton Community Dynamics to Environmental Changes

Diverse morphological characteristics (size and shape), physiological requirements (light, nutrients and temperature) and biogeochemical functions (e.g., silicification, calcification, and nitrogen fixation) of phytoplankton result in complex nature of phytoplankton community dynamics and the marine food web in aquatic ecosystems. Phytoplankton community in the estuarine-coastal system is characterized by rapid dynamics driven by both natural (e.g., hurricanes and flooding related discharge) and anthropogenic pressures (e.g., nutrient loading). The ability to observe the spatial-temporal variations of diverse phytoplankton groups (including their phenology) provides a scientific priority for understanding phytoplankton’s response to environmental stressors and investigating the structure of aquatic food web, and predicting the phytoplankton's role in shaping the structure of aquatic food web and ultimately regulating climate change on various time scales. Coastal zones are especially vulnerable to the threats from climatic processes and major human activities that caused by eutrophication, harmful algal blooms, hypoxia, and deteriorated water quality. However, satellite algorithms relevant to phytoplankton have been confined to the open ocean and shelf waters and very limited in the optically complex estuarine waters where the influence from wetlands, rivers and coastal ocean make phytoplankton communities highly variable and complex. Thus, high-resolution satellite products on phytoplankton community composition in the estuarine-coastal ecosystem are urgently required for identifying the drivers of phytoplankton composition and assessing climate ecosystem interactions from regional to global scales.

In a series of studies, we developed satellite algorithms for mapping phytoplankton taxonomy, and size fraction and detecting dominant species of algal blooms in the estuarine-coastal system of the nGoM. By synthesizing satellite and field observations, we assessed and proved the importance of meteorological/hydrological effects on phytoplankton community dynamics. The satellite algorithms have been validated by field/in-situ data acquired in inland, estuarine and coastal waters of the nGoM from extensive research cruises. The satellite algorithms were applied to study phytoplankton community responses to three recent hurricanes including Hurricane Harvey (2017), Hurricane Michael (2018) and Hurricane Barry.
(2019) and the extreme flooding events of Mississippi River (MR) in the nGoM. We found that
the hurricane’s effects on phytoplankton community dynamics depend on background nutrient
conditions, as well as the intensity, track and translational speed of storms. 1) Strong flooding
associated with Hurricane Harvey (2017) shifted the dominance of phytoplankton community
in Galveston Bay from cyanobacteria and dinoflagellate to diatom and chlorophyte, and
recovered to normal condition within 2 months. 2) High levels of organic matters delivered
from estuaries to shelf waters after Hurricane Michael (2018) fuelled a red tide mixed with
coccolithophore bloom that was reported for the first time in the nGoM. 3) The physical and
chemical environments after hurricanes are favorable for the growth and dominance of
coccolithophores in shelf waters. 4) High freshwater discharge due to Hurricane Barry (2019)
pushed large-size phytoplankton originally living in estuaries to offshore waters, nano-/pico-
size phytoplankton in offshore waters increased/decreased after the hurricane. In addition to
phytoplankton in response to hurricanes, it was also found that microphytoplankton dominate
in estuaries and inner shelf waters of the nGoM and are mainly controlled by regional wind
regime and freshwater inflows from river discharge, with highest/lowest values observed in
spring/fall. In comparison, phytoplankton size fraction (PSF) dynamics in the midshelf and
offshore waters of the nGoM are strongly influenced by the Loop Current (LC) expansion,
eddy shedding, and retraction. Maps of picophytoplankton fraction suggest the dominance of
small-size phytoplankton in the warm waters of LC and warm core eddies in the nGoM, which
can be in turn used to interpret LC dynamics.
**APPENDIX A**

**SUPPLEMENTARY MATERIAL FOR CHAPTER 2**

Supplementary Table 2.1. Multi-satellite imagery of Landsat 5 TM and Aqua-MODIS used for algorithm development and land cover classification in this study.

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<td></td>
</tr>
<tr>
<td>2010/04/26</td>
<td>MODIS</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2010/10/07</td>
<td>Landsat</td>
<td>28</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2010/10/07</td>
<td>MODIS</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2010/11/06</td>
<td>MODIS</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2010/11/06</td>
<td>MODIS</td>
<td>Cold front 14 MODIS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010/11/08</td>
<td>Landsat</td>
<td>Cold front 9 Landsat</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010/12/14</td>
<td>MODIS</td>
<td>Normal 15 MODIS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011/01/22</td>
<td>MODIS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
* Satellite data in red color represent Landsat 5-TM and Aqua-MODIS acquired on same day; a total of 16 image pairs of Landsat/MODIS were obtained during 2002-2011.
* Satellite data number in 1st column marked in yellow color represents data acquired within same month and are averaged to obtain mean state of that particular month.
* Satellite data marked with green color indicate imagery acquired within ±3 days of field data during 2007-2012; there are 10 Landsat and 20 MODIS images used for algorithms development.
* A total of 30 image were used for land type classification and most of them were obtained in fall (September-October), if Landsat imagery not available during September-October, data from other season were used.

Supplementary Table 2.2. Performance of Landsat/MODIS algorithms developed based on 1x1, 3x3, and 9x9 pixels data.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Landsat</th>
<th>MODIS</th>
<th>RMSE</th>
<th>MRE</th>
<th>RMSE</th>
<th>MRE</th>
</tr>
</thead>
<tbody>
<tr>
<td>R²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cold front</td>
<td>1*1</td>
<td>0.8081</td>
<td>2.4582</td>
<td>0.0764</td>
<td>0.8203</td>
<td>2.5840</td>
</tr>
<tr>
<td>3*3</td>
<td>0.7938</td>
<td>2.4540</td>
<td>0.0747</td>
<td>0.8189</td>
<td>2.7109</td>
<td>0.0708</td>
</tr>
<tr>
<td>High MR</td>
<td>1*1</td>
<td>0.7145</td>
<td>2.1901</td>
<td>0.0852</td>
<td>0.8331</td>
<td>1.6925</td>
</tr>
<tr>
<td>3*3</td>
<td>0.7286</td>
<td>2.5244</td>
<td>0.0935</td>
<td>0.8356</td>
<td>1.7440</td>
<td>0.0721</td>
</tr>
<tr>
<td>Normal</td>
<td>1*1</td>
<td>0.7197</td>
<td>2.4747</td>
<td>0.0930</td>
<td>0.7961</td>
<td>2.6043</td>
</tr>
<tr>
<td>3*3</td>
<td>0.7197</td>
<td>2.4747</td>
<td>0.0930</td>
<td>0.7961</td>
<td>2.6043</td>
<td>0.0810</td>
</tr>
</tbody>
</table>

Note: number marked with gray color represent highest R² or lowest error.

Supplementary Table 2.3. Summary of matchups for Landsat/MODIS data and in-situ measurements of ag355 used in Landsat/MODIS empirical algorithms.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Landsat</th>
<th>MODIS</th>
<th>Landsat</th>
<th>MODIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>2008/07/13</td>
<td>30</td>
<td>2007/10/26</td>
<td>27 (station 26, and 33-36 due to clouds)</td>
</tr>
<tr>
<td></td>
<td>2008/09/27</td>
<td>30</td>
<td>2008/10/20</td>
<td>23 (station 6, 8, 11-12, 14-15, 18 and 21 due to clouds)</td>
</tr>
<tr>
<td></td>
<td>2010/12/14</td>
<td>30</td>
<td>2011/02/12</td>
<td>30</td>
</tr>
<tr>
<td>Date</td>
<td>Count</td>
<td>Details</td>
<td>Date</td>
<td>Count</td>
</tr>
<tr>
<td>------------</td>
<td>-------</td>
<td>-------------------------------------------------------------------------</td>
<td>------------</td>
<td>-------</td>
</tr>
<tr>
<td>2008/10/01</td>
<td>30</td>
<td></td>
<td>2011/11/11</td>
<td>30</td>
</tr>
<tr>
<td>2011/02/12</td>
<td>30</td>
<td></td>
<td>2012/03/05</td>
<td>30</td>
</tr>
<tr>
<td>2011/11/11</td>
<td>30</td>
<td></td>
<td>2012/06/02</td>
<td>30</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>110</strong></td>
<td></td>
<td><strong>Total</strong></td>
<td><strong>228</strong></td>
</tr>
<tr>
<td>2008/02/04</td>
<td>21</td>
<td>(station 22-26, 33-36 due to clouds)</td>
<td>2007/11/23</td>
<td>30</td>
</tr>
<tr>
<td>2008/02/07</td>
<td>30</td>
<td></td>
<td>2007/12/04</td>
<td>30</td>
</tr>
<tr>
<td>2008/12/18</td>
<td>25</td>
<td>(station 26 and 33-36 due to clouds)</td>
<td>2008/12/18</td>
<td>30</td>
</tr>
<tr>
<td>2010/02/25</td>
<td>30</td>
<td></td>
<td>2010/01/22</td>
<td>30</td>
</tr>
<tr>
<td>2010/02/25</td>
<td>30</td>
<td></td>
<td>2010/02/25</td>
<td>30</td>
</tr>
<tr>
<td>2010/11/08</td>
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<td></td>
<td>2010/11/08</td>
<td>30</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
<td></td>
<td><strong>Total</strong></td>
<td><strong>235</strong></td>
</tr>
<tr>
<td>2008/03/23</td>
<td>30</td>
<td></td>
<td>2008/04/13</td>
<td>30</td>
</tr>
<tr>
<td>2009/04/11</td>
<td>6</td>
<td>(station 1-23 due to clouds)</td>
<td>2009/04/14</td>
<td>30</td>
</tr>
<tr>
<td>2009/06/30</td>
<td>30</td>
<td></td>
<td>2010/04/08</td>
<td>28</td>
</tr>
<tr>
<td>2011/03/16</td>
<td>30</td>
<td></td>
<td>2011/04/05</td>
<td>30</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>96</strong></td>
<td></td>
<td><strong>Total</strong></td>
<td><strong>118</strong></td>
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<tr>
<td><strong>Total number</strong></td>
<td><strong>12</strong></td>
<td><strong>306</strong></td>
<td><strong>Total number</strong></td>
<td><strong>20</strong></td>
</tr>
</tbody>
</table>
APPENDIX B
SUPPLEMENTARY MATERIAL FOR CHAPTER 4

Supplementary Figure 4.1. MODIS enhanced RGB imagery (ERGB) of 11 and 12 Oct 2018.
Appendix C
SUPPLEMENTARY MATERIAL FOR CHAPTER 5

Supplementary Table 5.1. Field/in-situ data obtained from SeaBASS (Chl a and $R_{rs}$) and used in for regional-training red/NIR ratio-based Chl a algorithm in the nGoM.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Location</th>
<th>Investigator(s)</th>
<th>Experiment</th>
<th>n</th>
<th>N</th>
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<tr>
<td>*</td>
<td>Northwest Florida</td>
<td>Chuanming Hu</td>
<td>SWFL</td>
<td>16</td>
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<tr>
<td></td>
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<td>Big_Bend</td>
<td>50</td>
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<td></td>
<td>Tampa_Bay</td>
<td>87</td>
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<tr>
<td></td>
<td>Chesapeake Bay</td>
<td>Rick Gould</td>
<td>2009_Oct_Chesapeake</td>
<td>29</td>
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<tr>
<td>△</td>
<td></td>
<td>Chuanming Hu</td>
<td>GEO-CAPE</td>
<td>42</td>
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<tr>
<td></td>
<td></td>
<td>Alex Gilerson</td>
<td>Bio_optics_Chl_polarization</td>
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<tr>
<td></td>
<td></td>
<td>Cota Glenn</td>
<td>Chesapeake Light Tower</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Margaret Mulholland</td>
<td>GEO-CAPE</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>△</td>
<td>Southwest Florida &amp; Lake Okeechobee</td>
<td>Kendall Carder</td>
<td>Okeechobee</td>
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<td>Red_tide</td>
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<td></td>
<td>EcoHAB</td>
<td>16</td>
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<tr>
<td>○</td>
<td>Mobile Bay</td>
<td>Don Johnson</td>
<td>CoJet 3,4,5,6</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mississippi Sound</td>
<td>Rick Gould</td>
<td>CoJet 7</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>△</td>
<td>Northern GOM shelf</td>
<td>Antonio Mannino &amp; Michael Novak</td>
<td>GEO-CAPE</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Mississippi Delta shelf waters</td>
<td>Rick Gould</td>
<td>Optical Layers</td>
<td>2</td>
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<tr>
<td>△</td>
<td>Horn Island</td>
<td>Robert Arnone</td>
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<td>14</td>
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<td>2</td>
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<tr>
<td>△</td>
<td>Lake Bourne</td>
<td>Sherwin Ladner</td>
<td>NGLI Lake</td>
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<td></td>
<td>Atlantic Coast of New Jersey</td>
<td>Robert Arnone</td>
<td>LEO</td>
<td>7</td>
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<td>+</td>
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<td>Eurico D’Sa &amp; Christopher Osburn</td>
<td>BluCAR</td>
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<td>Eurico D’Sa</td>
<td>Hurricane Harvey</td>
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<td>Eurico D’Sa &amp; Christopher Osburn</td>
<td>BluCAR</td>
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<tr>
<td>△</td>
<td>North Carolina Coast</td>
<td>Stumpf Rick</td>
<td>North Carolina Coast</td>
<td>32</td>
<td>32</td>
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</table>

Total N = 744
Supplementary Figure 5.1. In-situ measurements and satellite data used to test the performance of Chl a_NN and Chl a_AD in two contrasting estuaries, Atchafalaya and Barataria inner shelf waters, respectively; with left (right) column for Chl a_AD (Chl a_NN) obtained on 06/13, 06/19, 07/18, 08/15, 09/04 and 09/14, 2019, respectively. The black symbols indicate asmapleing site of the match-up field data.
APPENDIX D
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Multi-decadal trends and influences on dissolved organic carbon
distribution in the Barataria Basin, Louisiana from in-situ and
Landsat/MODIS observations
Author: Bingqiang Liu, Eulice J. D’Sa, Shankar Joshi
Publication: Remote Sensing of Environment
Publisher: Elsevier
Date: July 2019
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Biogeochemical Response of Apalachicola Bay and the Shelf Waters to Hurricane Michael Using Ocean Color Semi-Analytic/Inversion and Hydrodynamic Models

Eurico J. D’Sa*, Iuhan D. Joshi†,†, Bingqing Liu†, Dong S. Ko†, Christopher L. Osburn† and Thomas S. Bunch†

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*Correspondence: Eurico J. D’Sa edsa@lsu.edu
Specialty section: This article was submitted to Marine Biogeochemistry, a section of the journal Frontiers in Marine Science
Received: 26 May 2019 Accepted: 12 August 2019 Published: 28 August 2019

Hurricanes are increasingly being recognized as important episodic drivers in ocean biogeochemical cycling; however, spatiotemporal response of their impacts on coastal and estuarine ecosystems are limited. Hurricane Michael, which made landfall just west of Apalachicola Bay (ApB) on October 10, 2018 as a Category 5 hurricane with sustained winds of 255 km h⁻¹, caused widespread damage to the northwest Florida coast, and adverse effects on oyster reefs and water quality in ApB due to winds and coastal flooding associated with a strong storm surge. The impact of wind forcing and retreating storm surges on coastal and shelf biogeochemical properties remains, however, largely unknown. In this study, we use a combination of pre-hurricane field observations, ocean-color satellite imagery and the outputs (salinity, currents, sea surface height, and temperature) of a nested high-resolution three-dimensional hydrodynamic model (NCOM) to examine the biogeochemical response of ApB and the surrounding shelf waters to Hurricane Michael. MODIS-derived optical proxies (e.g., absorption of colored dissolved organic matter or CDOM and particle backscattering coefficients) of dissolved and particulate organic carbon (DOC and POC) were derived for a series of clear-sky imagery (prior to and following the hurricane) using a combination of estuarine-tuned semi-analytic and empirical algorithms. Following the hurricane, spatiotemporal distribution of both DOC and POC in ApB and the nearshore coastal waters showed a strong response to storm surge, increasing river discharge, currents, and wind field. Average flux estimates of organic carbon exported from ApB between October 5–21, 2018 to the coastal ocean were much greater for DOC (0.86 × 10⁵ kg C d⁻¹) than POC (0.21 × 10⁵ kg C d⁻¹) and increased with increasing river discharge and the wind field. A bio-optical inversion algorithm applied to Sentinel-3A OLCI imagery of 13 October, 2018 immediately following the hurricane’s passage, showed a strong, week-long biological response with spatially distinct phytoplankton blooms.
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Department of Oceanography and Coastal Sciences
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dissolved organic matter, and suspended sediments. *Limnology and Oceanography*, 51, 2646-2659


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VITA

Bingqing Liu was born in Shanghai, China. She received the B.S. and M.S. degrees in oceanography from Shanghai Ocean University (SHOU), Shanghai, China, in 2012 and 2015, respectively. In 2014, she joined the University of Washington, Seattle, WA, USA, as a visiting student and participated in research related to physical processes of oceanic internal waves. Soon after completing her master studies in May, 2015, Bingqing Liu joined the Department of Oceanography and Coastal Sciences, Louisiana State University as a Ph.D. student in August, 2015 under the supervision of Dr. Eurico D’Sa. Her Ph.D. topic is related to marine optics and ocean color remote sensing, including developing satellite algorithms to monitor phytoplankton community dynamics, and water quality (e.g., algal blooms, turbidity, CDOM), and land-ocean interactions in the coastal zones (e.g., land use change). During the second year of her PhD program, she was selected to participate in a NASA sponsored summer class “Calibration & Validation for Ocean Color Remote Sensing”, conducted by the University of Maine, with the goal of preparing a new generation of oceanographers trained in the use of optics to study the oceans.