Bio-optical properties in waters influenced by the Mississippi River during low flow conditions

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Abstract

Spatial and temporal patterns of bio-optical properties were studied in the Northern Gulf of Mexico during cruises in April and October of 2000, a year during which the discharge volume from the Mississippi River was unusually low. Highly variable surface Chl a concentrations (0.1 to 17 mg m⁻³) and colored dissolved organic matter (CDOM) absorption (0.07 to 1.1 m⁻¹ at 412 nm) were observed in the study region that generally decreased with increasing salinity waters, being highest nearshore and decreasing at offshore stations. The optical properties of absorption, scattering, and diffuse attenuation coefficients reflected these distributions with phytoplankton particles and CDOM contributing to most of the spatial, vertical, and seasonal variability. The diffuse attenuation coefficient Kd(λ) and spectral remote sensing reflectance Rrs(λ) were linear functions of absorption and backscattering coefficients a(λ) and b(λ) through the downward average cosine l_d and the ratio of variables f/Q at the SeaWiFS wavebands for waters with widely varying bio-optical conditions. Although various Rrs(λ) ratio combinations showed high correlation with surface Chl a concentrations and CDOM absorption at 412 nm, power law equations derived using the Rrs(490)/Rrs(555) and Rrs(510)/Rrs(555) ratios provided the best retrievals of Chl a concentrations and CDOM absorption from SeaWiFS reflectance data.

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1. Introduction

The Mississippi River system ranks among the top 10 rivers in length, freshwater discharge, and sediment delivery (Milliman & Meade, 1983) and thus exerts a strong influence on the biological, chemical, and physical properties of the Northern Gulf of Mexico (Del Castillo et al., 2001; Muller-Karger, Walsh, Evans, & Meyers, 1991). A seasonally varying discharge of fresh water and nutrients from the Mississippi River influences the spatial and temporal distribution of carbon fluxes and primary productivity in the Northern Gulf of Mexico (Dinnel & Wiseman, 1986; Lohrenz et al., 1999; Rabalais et al., 1996; Redalje, Lohrenz, & Fahnsteniel, 1994). Recent outbreaks of hypoxia over large areas of Louisiana and Texas coastal waters have been attributed to high levels of primary productivity in surface plume waters that are sustained by nutrients from the Mississippi River (Rabalais & Turner, 2001). While satellite remote sensing provides the potential to describe and monitor the variability of bio-optical properties (e.g., phytoplankton biomass) and the oceanic carbon fluxes, there is still a need to evaluate currently used or to develop regional ocean color algorithms for coastal regions as those influenced by the Mississippi River.

Ocean color algorithms developed to estimate biological variables such as Chl a have been used in both case I and case II waters (O’Reilly et al., 1998) and are based on the premise that other in-water constituents such as colored dissolved organic matter (CDOM) and detrital material co-vary with Chl a, the primary pigment used to represent phytoplankton concentrations. However, the ability of these algorithms to accurately estimate bio-optical variables in coastal waters is not very clear as in-water constituents such as CDOM and suspended sediments may not co-vary with Chl a (Carder et al., 1991; Tassan, 1994), although still
influencing the water leaving radiance. The contribution of particulate and dissolved constituents to the variability of optical properties and ocean color in coastal waters requires a better understanding of the linkages between the concentration of these constituents, the inherent optical properties (IOPs) of absorption and scattering coefficients, and the apparent optical properties (AOPs) such as the spectral attenuation for downward irradiance $K_d(\lambda)$ and remote sensing reflectance $R_{rs}(\lambda)$. Knowledge of these relationships is important for characterizing the marine optical environment and developing remote sensing ocean color algorithms for coastal waters.

In this study, we present results of bio-optical measurements obtained during two research cruises conducted in the coastal margin influenced by the Mississippi River in April and October of 2000. While river discharge in spring and fall generally corresponds to high/low flow periods, the discharge for the study year was unusually low compared to previous years. We evaluate the spatial and temporal variability of the bio-optical properties and the relationships between the IOPs (absorption, scattering and backscattering coefficients) and the AOPs ($K_d(\lambda)$ and $R_{rs}(\lambda)$) within the context of low discharge. This data may provide an understanding of the baseline effect of the Mississippi River on the regional coastal waters. The properties of the two main AOPs of importance to remote sensing, $K_d(\lambda)$ and $R_{rs}(\lambda)$, are discussed and analyzed in relation to absorption and scattering in an attempt to examine closure between the AOPs and IOPs based on field data. We also derive empirical relationships between the ratios of $R_{rs}(\lambda)$ and in-water constituents such as Chl $a$ concentrations and CDOM absorption and compare estimates obtained using these local algorithms with the standard ocean chlorophyll OC4v4 algorithm (O’Reilly et al., 1998) on a SeaWiFS image of the region.

2. Methods and data

2.1. Study site

The study site is located in the Northern Gulf of Mexico (Fig. 1) in waters largely influenced by the Mississippi River. Most of the River discharge flows westward onto the Louisiana–Texas shelf (Dinnel & Wiseman, 1986). Two research cruises using the RV Pelican were undertaken in spring (5–13 April) and fall (24 October–1 November) of 2000. Stations were occupied in the plume waters of the main flow of the Mississippi River (Southwest Pass) to the outer shelf, the inner shelf, as well as some open ocean locations in the Gulf of Mexico (station locations shown in

Fig. 1. Study site showing location of bio-optical stations occupied in the Northern Gulf of Mexico during research cruises in April and October of 2000. Bio-optical properties of four representative stations (squares) during the April cruise and two stations (circles) in October are noted for further discussion in the text.
While a full suite of bio-optical measurements was made during the April cruise, in-water bio-optical data were obtained at only four stations during the October cruise. However, remote sensing reflectance $R_{s}(\lambda)$ measurements using an above-water radiometer were made at all the stations (Fig. 1) during both cruises. Although river flow is generally high during spring, the average discharge volume for the 2 months prior to the spring 2000 cruise was about 45% lower than the previous years (discharge data are from the U.S. Army Corps of Engineers monitoring station at Tarbert Landing, Mississippi). The fall cruise was conducted during a period usually considered as a low-flow period of river discharge. Overall, river discharge was much lower for the year, and therefore, the results presented here may be considered as prevailing under such conditions.

Ocean color SeaWiFS satellite imagery was obtained for one clear day in spring (e.g., April 8), while three images of the region were obtained for the fall experiment. The satellite data were obtained from the Goddard Distributed Active Archive Center and processed using NASA’s SeaDAS (version 4.1) software.

### 2.2. Bio-optical measurements

Bio-optical measurements were obtained using an optical profiling package that integrated a number of optical instruments within a metal cage. Discrete water samples were obtained immediately after the optical cast with a rosette sampler equipped with 10-l Niskin bottles. The bio-optical package contained sensors for measurements of conductivity and temperature (SBE-19, Seabird), stimulated chlorophyll fluorescence (Wetstar, WetLabs), absorption/attenuation at nine wavebands (ac-9, WetLabs), downwelling spectral irradiance and upwelling spectral radiation at seven channels (OCI and OCR-200, Satlantic), and backscattering at two spectral bands (Hydroscat-2, HOBLabs). A data acquisition and power unit (Mpak3, WetLabs) was used to integrate and archive the data collected from the different instruments in the bio-optical package. Subsequently, upon transfer of the data to a desktop computer, a separate software program was used to unpack into separate files the data corresponding to individual instruments. A program was then used to depth-align the data based on time stamps referenced to the CTD depth. The data were then separated into downcast and upcast segments and averaged into 0.5- or 1-m bins for further processing and analysis.

The ac-9 consists of dual, 25-cm pathlength flow tubes for measurement of in-water absorption and attenuation at nine 10-nm wide spectral wavebands (412, 440, 488, 510, 532, 555, 650, 676, and 715 nm). Optically clean water from a Nanopure system (Infinity UV/UF, Barnstead) was used to calibrate the ac-9 during the cruise (Twardowski, Sullivan, Donaghay, & Zaneveld, 1999). Software was written to implement three additional corrections (temperature, salinity, and scattering) to the ac-9 data (Pegau, Gray, & Zaneveld, 1997; Zaneveld, Kitchen, & Moore, 1994). Particulate scattering coefficient $b_{p}(\lambda)$ was calculated as the difference between the corrected attenuation and absorption. The ac-9 data were generally binned at 1-m depth intervals, but at stations with shallow depths (<20 m), binning was set to 0.5 m. The deployment of the bio-optical package at each station was repeated for dissolved or CDOM absorption measurements using a 0.2-μm Supercap cartridge filter (Gelman Sciences) that was attached to the intake tubes of the ac-9 meter. The difference between unfiltered (particulate plus dissolved absorption or $[a_{p}(\lambda) + a_{cdom}(\lambda)]$) and filtered (dissolved absorption or $a_{cdom}(\lambda)$) profiles can be attributed to particulate absorption, $a_{d}(\lambda)$. Scattering data from the Hydroscat-2 sensor were obtained during the October cruise only and were processed using software (Hydrolab, HOBLabs) that generated the uncorrected backscattering coefficients at two wavelengths of 442 and 589 nm. The ac-9 derived absorption and scattering values were then used to correct the backscattering data $b_{p}(\lambda)$ (here, $b_{p}$ is the sum of backscattering due to particulates $b_{bp}$ and pure water $b_{bw}$) to account for losses due to attenuation of some backscattered light in the water between the instrument and the detection volume. The 440- and 442-nm central wavebands for the ac-9 and the Hydroscat measurements were interpolated to the 443-nm waveband to match the SeaWiFS waveband (band 2). The change in values due to this shift was insignificant for the absorption and scattering data.

Vertical profiles of spectral downwelling irradiance $E_{d}(\lambda)$ and upwelling radiance $L_{u}(\lambda)$ at seven 10-nm wavebands (412, 443, 490, 510, 555, 665, and 683 nm) were processed to calculate the diffuse attenuation coefficients for downwelling irradiance $K_{d}(\lambda)$ and upwelling radiance $K_{u}(\lambda)$. These coefficients were determined as the slope of $\ln E_{d}(\lambda)$ or $L_{u}(\lambda)$ versus depth. An 11-point moving linear regression of $\ln E_{d}(\lambda)$ versus depth was used to obtain vertical profiles of $K_{d}(\lambda)$ and $K_{u}(\lambda)$. Values of $K_{d}(\lambda)$ and $K_{u}(\lambda)$ at the shallowest depth were then used to estimate $E_{d}(\lambda,0^{-})$ and $L_{u}(\lambda,0^{-})$ just beneath the sea surface. Based on known values of Fresnel reflectance at the water–air interface for upwelling radiance and downwelling irradiance, the subsurface values $E_{d}(\lambda,0^{-})$ and $L_{u}(\lambda,0^{-})$ were extrapolated to values just above the sea surface (Mueller & Austin, 1995). Remote sensing reflectance $R_{s}(\lambda,0^{-})$ or $R_{rs}(\lambda)$ was then calculated as

$$R_{rs}(\lambda) = \frac{L_{u}(\lambda,0^{-})/E_{d}(\lambda,0^{-})}{1},$$

where $L_{u}(\lambda,0^{-})$ is the water-leaving radiance measured in the nadir direction just above the sea surface and $E_{d}(\lambda,0^{-})$ is the downwelling irradiance incident on the sea surface.

In addition to the in-water derived values of $R_{s}(\lambda)$, we also derived $R_{s}(\lambda)$ from above-water measurements of signals proportional to surface and sky radiance, and radiance reflected from a horizontal plaque with known bi-directional reflectance (Mobley, 1999). Above-water remote sensing reflectance measurements of $R_{s}(\lambda)$ from 400 to 825 nm at 1-nm spectral resolution were obtained using a GER.
1500 (Geophysical and Environmental Research) 512-channel, fiber optic system adapted for field operations. Following SeaWiFS protocols (Mueller & Austin, 1995), replicate radiance spectra of the sea surface were measured with the fiber-optic radiometer at 30°, followed by the sky radiance and the radiance reflected from a 10% reference Spectralon plaque ( Labsphere), and the data processed for determination of above-water \( R_s(\lambda) \).

2.3. Discrete water sample analysis

Water samples at discrete depths were collected using a CTD rosette multi-bottle array system (General Oceansics Model 1015-12). Water samples collected from CTD casts immediately following optical profiles were used for correlation with optical measurements. Discrete water samples were analyzed for: (1) Chl \( a \) and selected pigments using high performance liquid chromatography or HPLC, (2) particulate \( \alpha_p(\lambda) \) and detrital \( \alpha_d(\lambda) \) absorption coefficients using the quantitative filter pad technique (Kishino, Takahashi, Okami, & Ichimura, 1985; Mitchell & Kiefer, 1988), and (3) CDOM absorption \( \alpha_{cdom}(\lambda) \) using a multiple path-length capillary waveguide (Miller, Belz, Del Castillo, & Trzaska, 2002). Water samples collected from Niskin bottles were filtered through GF/F glass fiber filters and frozen/stored in liquid nitrogen for laboratory analysis of pigments and particle absorption. Chlorophyll \( a \) used in this study and determined from HPLC represents chlorophyll \( a \) and derivatives (chlorophyllide \( a \), chlorophyll \( a \), allomers and epimers). Measurements of CDOM absorption were carried out with a waveguide using pre-rinsed 0.2-μm Nuclepore nylon filters and verified with spectrophotometric measurements using a Perkin-Elmer ultraviolet/visible (UV/VIS) Lambda-18 dual beam spectrophotometer.

3. Results and discussion

3.1. Spatial and seasonal variability in the bio-optical properties

One of the consequences of the Mississippi River flow into the Northern Gulf of Mexico is the density stratification, with lower salinity waters overlying a more saline oceanic water body. At most stations sampled during the April cruise (Fig. 1), the overlying surface plume waters had salinity values that varied spatially from lows in the 20 to 33 psu, while in the underlying oceanic waters, salinities varied from 33 to 36.4 psu. Example stations close to the Mississippi River outflow into the Gulf of Mexico (st. 192, near SW Pass), a mid-shelf station (st. 46) and an off-shore station (st. 24), are shown as representing the range of bio-optical properties at the study site during the spring cruise. High Chl \( a \) concentrations were associated with lower salinity surface plume waters with concentrations varying from highs of about 17 mg m\(^{-3}\) at station 192 (Fig. 2(a)) to lows of <0.2 mg m\(^{-3}\) at the weakly stratified offshore stations (st. 24 and 122). High surface Chl \( a \) concentrations and CDOM absorption at stations with lower salinities (e.g., Fig. 2(a) and (b)) strongly attenuated the light field thus potentially restricting primary production to near surface waters. In comparison, a weakly stratified surface layer (e.g., station 24, Fig. 2(c)) was associated with low surface Chl \( a \) concentrations of about 0.2 mg m\(^{-3}\), which increased with depth to about 0.7 mg m\(^{-3}\) at up to 25 m and then again decreases. An examination of inorganic nutrient concentrations (Powell, LUMCON, personal communication) indicated elevated levels of nutrient concentrations (>3 μM NO\(_3\)) at most stations with high Chl \( a \) concentrations in the river plume, while at the two offshore stations (st. 24 and 122), nitrate concentrations in surface waters were relatively low (0.14 and 0.19 μM NO\(_3\), respectively).

Vertical profiles of particulate plus CDOM and CDOM absorption and scattering coefficients (determined from ac-9 measurements) at the 440 nm waveband (Fig. 2(d)–(f)) at the same three representative stations show a strong resemblance to Chl \( a \) profiles, higher values in surface waters that decrease with depth. These high values of absorption were all associated with lower salinity waters and high surface Chl \( a \) concentrations. At the nearshore station (st. 192), a near-surface [\( \alpha_p(440) + \alpha_{cdom}(440) \)] maximum of 1.5 m\(^{-1}\) decreased rapidly to about 0.3 m\(^{-1}\) at a depth of 10 m. Spatially, surface values of [\( \alpha_p(440) + \alpha_{cdom}(440) \)] further decreased to 0.5 m\(^{-1}\) at the mid-shelf station (Fig. 2(e)) and to about 0.13 m\(^{-1}\) at the offshore station 24. Surface \( \alpha_{cdom}(440) \) varied from a high of about 0.4 m\(^{-1}\) (nearshore station 192) to about 0.01 m\(^{-1}\) at station 24. Particulate scattering \( b_p(440) \) at stations 192 and 46 also showed surface highs (4 and 1.6 m\(^{-1}\)), reflecting higher phytoplankton concentrations at these two stations. In contrast, surface scattering was relatively low (~0.2 m\(^{-1}\)) at station 24 (surface Chl \( a \) concentration <0.2 mg m\(^{-3}\)). Subsurface and near-bottom highs in scattering unrelated to phytoplankton concentrations were observed at all three stations. Spectrally, both the absorption and scattering typically decreased with increasing wavelengths. In the case of CDOM, the spectra showed an exponential decrease in absorption with increasing wavelength, an expected trend (Miller et al., 2002) with slopes of the log-linearized absorption spectra, \( S \), in the range 0.014 to 0.017.

Seasonality of the Mississippi River discharge is observed to strongly influence the hydrographic and bio-optical properties of waters in the Northern Gulf of Mexico. This is illustrated by the variability in bio-optical properties at closely located stations (st. 192 and 34 near SW Pass) and mid-shelf stations (st. 46 and 70) sampled in April and October of 2000, respectively (Table 1). A higher volume of river discharge in spring results in lower salinity and temperature values observed at both the nearshore and mid-shelf stations. Seasonal changes (April to October 2000) in hydrographic conditions were greatest at the mid-shelf location where surface salinity changed from 29.48 to 36.0...
psu and temperatures from 22.5 to 25.8 °C. Biological and optical properties were also directly influenced by the seasonal flow of the Mississippi River. While at the near-shore stations surface Chl $a$ concentrations and absorption and scattering coefficients were lower in October, the mid-shelf stations (Table 1) experienced the greatest change. Here, average surface Chl $a$ concentration decreased from 5.57 mg m$^{-3}$ to a low of 0.43 mg m$^{-3}$, and surface absorption (particulate plus CDOM) at 443 nm decreased from 0.55 to 0.062 m$^{-1}$, respectively. Surface values of other variables such as CDOM absorption, scattering, and diffuse attenuation coefficient $K_d$(443) also decreased significantly at the mid-shelf location.

### 3.2. Absorption and scattering characteristics

Particulate absorption due to phytoplankton cells and detrital material generally dominated the absorption field.
However, CDOM absorption also formed an important though variable component of the total absorption, varying from less than 25% of the absorption field at the nearshore stations to greater than 50% at the offshore stations. Also, at the turbid nearshore stations, detrital material contributed a large fraction (about 40%) to the particulate absorption while being negligible at the offshore stations. The particulate scattering coefficient \( b_p \) (where appropriate, we drop the \( k \) argument for brevity), as derived from field measurements with the ac-9, varied over a large range (e.g., \( b_p(443) \) varied from 3.55 \( m^{-1}/C_0 \) near SW Pass to about 0.2 \( m^{-1}/C_0 \) at the offshore station 24). Spectrally, scattering decreased in a similar fashion (Gould, Arnone, & Martinolich, 1999), with increasing wavelength from 412 to 715 nm (not shown). However, the backscattering coefficient \( b_b(\lambda) \) is the variable that directly influences ocean color variability and is most often used in inversion models. From simultaneous measurements of \( b_b(443) \) and \( b_p(443) \) at various stations during the October cruise, we obtained a relationship (Fig. 3(a)) between \( b_b(443) \) and \( b_p(443) \) given by

\[
b_b(443) = 0.00069 + 0.01799b_p(443) \quad (r^2 = 0.98). \tag{2}
\]

A similar value for the slope (0.01829) was obtained by Gould et al. (1999) using Petzold’s values of \( b_b \) that were applicable over a wide wavelength range (400 to 600 nm) and samples that were obtained from different oceanic regions. Similarity in the relationship between scattering and backscattering obtained by these two studies are interesting in that these parameters are also dependent on particle size, shape, and composition (i.e., index of refraction). However, an examination of Fig. 3(a) suggests that a nonlinear fit may also be applicable, especially for the mid-range data. A general cubic-polynomial equation (\( b_b = a_0 + a_1b_p + a_2b_p^2 + a_3b_p^3 \)) showed a strong fit to the data (coefficient of determination of 0.98) with values of coefficients being \( a_0 = 0.00248 \), \( a_1 = 0.01 \), \( a_2 = -0.0036 \), and \( a_3 = -0.00041 \). The intercept, \( a_0 = 0.00248 \), which represents the backscattering by pure water \( b_{bw}(443) \) is about the same value (0.002406 \( m^{-1} \)) as that obtained by Smith and Baker (1981). Based on the assumption that the relationship between \( b_b \) and \( b_p \) would also be valid temporally for the same waters, we

### Table 1

<table>
<thead>
<tr>
<th>Surface properties (0–3 m)</th>
<th>Spring 2000 (April 5–13)</th>
<th>Fall 2000 (October 24–31)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW Pass (st. 192)</td>
<td>Mid-shelf (st. 46)</td>
<td>SW Pass (st. 34)</td>
</tr>
<tr>
<td>Salinity (psu)</td>
<td>23.35</td>
<td>29.48</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>21.76</td>
<td>22.50</td>
</tr>
<tr>
<td>Chl a (mg m(^{-3}))</td>
<td>17.34</td>
<td>5.57</td>
</tr>
<tr>
<td>TSM (mg/l)</td>
<td>7.0</td>
<td>13.5</td>
</tr>
<tr>
<td>CDOM abs. ( \delta_{cdom}(443) ) (m(^{-1}))</td>
<td>0.45</td>
<td>0.26</td>
</tr>
<tr>
<td>Scattering, ( b_p(443) ) (m(^{-1}))</td>
<td>3.55</td>
<td>1.63</td>
</tr>
<tr>
<td>Backscattering ( b_b(443) ) (m(^{-1}))</td>
<td>0.065</td>
<td>0.031</td>
</tr>
<tr>
<td>Attenuation coeff. ( K_d(443) ) (m(^{-1}))</td>
<td>1.18</td>
<td>0.89</td>
</tr>
<tr>
<td>Nitrate + Nitrite (µM)</td>
<td>11.52</td>
<td>4.29</td>
</tr>
</tbody>
</table>

Fig. 3. (a) Backscattering \( b_b \) at 443 nm (m\(^{-1}\)) plotted as a function of particulate scattering \( b_p \) at the same waveband measured for three stations during the October 2000 cruise. The solid line represents the least-squares regression fit to the data; (b) particulate backscattering \( b_{bp} \) (m\(^{-1}\)) as a function of wavelength at four stations (Fig. 1) derived from scattering measurements.
use the linear relationship of Eq. (2) to derive $b_{bp} (\lambda)$ from $b_p (\lambda)$ for the April cruise. Typical surface spectral $b_{bp} (\lambda)$ values (Fig. 3(b)) for four stations (st. 192, 46, 24, and 207) varied by an order of magnitude from about 0.003 m$^{-1}$ at the offshore station (st. 24) to $> 0.06$ m$^{-1}$ at the two nearshore stations (st. 192 and 207). Under the low flow regime of the Mississippi River, both suspended sediments and phaeopigments were relatively low suggesting phytoplankton biomass to be the dominant factor determining backscattering. HPLC pigment analysis showed higher levels of the carotenoid fucoxanthin, indicative of diatoms at these stations.

Observed spatial and vertical changes in the magnitude of the water column attenuation coefficient for downward irradiance $K_d (\lambda)$ were primarily influenced by particulate and CDOM absorption (D’Sa, Miller, McKee, & Trzaska, 2002). Estimated at the 10% light level, $K_d (443)$ was linearly related to total absorption $(a = a_w + a_p + a_{cdom})$ at 443 nm (Fig. 4) determined at the same optical depth. Here, absorption due to pure water $a_w$ was obtained from Pope and Fry (1997). The diffuse attenuation coefficient $K_d$ has been expressed as a function of absorption and backscattering coefficients $a$ and $b_h$ using the two-stream irradiance model (Aas, 1987) through the approximation

$$K_d = (a + b_h) / \mu_d,$$

where $\mu_d$ is the cosine of the mean downwelling light field and the absorption $a$ and backscattering $b_h$ coefficients are the sum of components representing the contribution of various in-water constituents. The various components of absorption are due to pure water, particulates, and dissolved materials, while backscattering comprised of pure water backscatter and particulate backscatter. From field determinations of $a$, $b_h$, and $K_d$ at the 10% light level, we also observe that $(a + b_h)$ and $K_d$ are linearly related (Fig. 4) for stations comprising a variety of optical conditions. From Eq. (3), the slope (0.65) in Fig. 4 represents the mean cosine $\mu_d$, which on neglecting the effects of $b_h$ reduces $\mu_d$ to a value of 0.61. As observed in Fig. 4, while the $b_h$ contribution to this formulation appears to be negligible at the offshore stations with low absorption values, it is quite significant at the nearshore stations with higher absorption. The mean cosine $\mu_d$ has been modeled for a variety of solar zenith angles ($0–90^\circ$), scattering to absorption ratios (1–20) and water depths (Bannister, 1992). Modeled values of $\mu_d$ have been shown to vary from 0.8 at surface to an asymptotic value of 0.65 at the 0.1% light level for a sun zenith angle of 30° and a $b/a$ value of 4 (Bannister, 1992). For stations at our study site, the $b/a$ ratio at the 10% light level varied from a high of about 9.7 at coastal stations (st. 157 and 91) to a low of about 1.23 at the offshore station 24. A comprehensive examination of $\mu_d$ as a function of depth and the IOPs (Berwald, Stramski, Mobley, & Kiefer, 1995; McCormick, 1995) and the relationship between $K_d$ and Chl a concentrations (Morel & Maritorena, 2001) will be useful in further characterizing the bio-optical properties of these waters.

### 3.3. Remote sensing reflectance relationship to absorption and backscattering

Spectral remote sensing reflectances $R_{rs}(\lambda)$ determined from measurements with an in-water radiometer were variable in shape and magnitude (Fig. 5). Reflectance spectra of the nearshore and mid-shelf stations (st. 192, 207, and 46) show well-pronounced maxima in the green spectral band, while the offshore station 24 shows maximal reflectance at 490 nm. The relative role of absorption and scattering appear to control the reflectance spectra at these stations. While absorption due to phytoplankton and CDOM is strong at the nearshore and mid-shelf stations, enhanced

![Fig. 5. Typical remote sensing reflectance spectra $R_{rs}(\lambda)$ determined from measurements using an in-water radiometer at four stations at the study site in April of 2000.](image-url)
backscattering (Fig. 3(b)) due to suspended particles (phytoplankton, detrital, and suspended sediments) contributed to the large $R_a(\lambda)$ values (>0.005) at the green wavebands. We also observe the signature associated with solar-stimulated Chl $a$ at 683 nm at these stations. At the offshore station 24, backscattering contribution by particulate material is minimal (Chl $a < 0.2$ mg m$^{-3}$), while the relatively higher CDOM levels (0.1 m$^{-1}$ at 443 nm) at this station results in lower $R_{ns}(\lambda)$ values in the blue spectral region.

Ocean color is usually understood in terms of remote sensing reflectance $R_a(\lambda)$, which is defined as the ratio of the upwelling radiance and downwelling irradiance (Eq. (1)). $R_{ns}(\lambda)$ has been related to the irradiance reflectance just beneath the surface $R(0^-)$ through the approximation given by (Mobley, 1994),

$$R_{ns}(\lambda) \approx 0.54 \frac{R(0^-)}{Q},$$

where $Q$ is the ratio of upwelling irradiance to upwelling radiance (Morel & Gentili, 1996). The subsurface irradiance reflectance $R(0^-)$ defined as the ratio of upwelling irradiance to downwelling irradiance has been related through modeling studies to the absorption $a(\lambda)$ and backscattering $b_b(\lambda)$ coefficients of seawater through the approximation (Gordon, et al., 1988; Morel & Gentili, 1996)

$$R(0^-) \approx \frac{f b_b}{(a + b_b)},$$

where $f$ is a variable that depends upon the solar zenith angle, the optical properties of seawater, and light wavelength (Morel & Gentili, 1991). From Eqs. (4) and (5), $R_{ns}(\lambda)$ relates to the IOPs of absorption and backscattering through the approximation given by

$$R_{ns}(\lambda) \approx 0.54 \left[ \frac{f}{Q} \right] \left[ \frac{b_b}{(a + b_b)} \right]$$

The $f/Q$ ratio above, although being dependent on the geometric conditions (solar-zenith angle and the viewing angle), wavelength, and the bio-optical state (Morel & Gentili, 1996), varies to a lesser degree than $f$ and $Q$ individually.

Using Eq. (6), we examine the spectral relationship between $R_{ns}(\lambda)$ and concurrent surface (0–3 m average) estimates of backscattering and absorption coefficients at the SeaWiFS wavebands (Fig. 6). The criteria for choosing the 0–3 m surface average for the IOPs and Chl $a$ were based on the observation that the lower salinity surface mixed layer in the study region, while variable, was generally greater than 3 m. We observe that $R_{ns}$ and $b_b/(a + b_b)$ are linearly related ($r^2 > 0.8$) at the 490 and 555 nm wavebands (Fig. 6) as well as at the 412, 510, and 683 nm wavebands. From Eq. (6), the slope divided by 0.54 gives the ratio $f/Q$ and lies between 0.09 and 0.12 (Fig. 7) over the spectral range of 412 to 683 nm. These $f/Q$ values derived from our field studies fall well within the range modeled for various solar-zenith angles, the viewing angle, wavelength, and the bio-optical state (Morel & Gentili, 1996). While the solar-zenith angle has been shown to strongly affect value of $f/Q$, this was not observed in our data since most of our field measurements were done within 2 h of midday. Although surface values of Chl $a$ concentrations varied widely (0.2 to >17 mg m$^{-3}$) at the study site, it did not contribute greatly to the $f/Q$ variability. A similar range in the field determinations of $f/Q$ ratio (Reynolds, Stramski, & Mitchell, 2001) in the Southern Ocean suggests a narrow range in its variability. High correlations between the independently measured reflectances and the IOPs (backscattering and absorption) and the low $f/Q$ variability suggest a measure of closure in our field determinations of AOPs and IOPs for waters with considerable range in absorption and scattering properties.

3.4. Remote sensing reflectance algorithms

Remote sensing reflectance $R_{ns}(\lambda)$ were determined using both in-water and above-water radiometers during the April 2000 cruise. A comparison of the ratios of
The application of color ratios of water-leaving radiances or remote sensing reflectances to estimate Chl $a$ concentrations is based on the absorption characteristics of Chl $a$ which absorbs more blue light than green. The operational SeaWiFS ocean chlorophyll algorithm (OC4), for example, uses a four-band (443, 490, 510, and 555 nm) maximum band ratio formulation (O’Reilly et al., 1998). Regression analysis of the log-transformed reflectance ratios and Chl $a$ for the four bands used in the OC4 algorithm indicates high correlations between the $R_{rs}(\lambda)$ ratios and Chl $a$ ($r^2>0.8$) for all the bands (Fig. 9). For the same range in Chl $a$ concentrations, however, the range in $R_{rs}(\lambda)$ ratio values decreases with increasing wavebands (i.e., $R_{rs}(443)/R_{rs}(555) > R_{rs}(490)/R_{rs}(555)$ and $> R_{rs}(510)/R_{rs}(555)$). The $R_{rs}(443)/R_{rs}(555)$ ratio is expected to give the most precise estimates at lower Chl $a$ concentrations, the $R_{rs}(510)/R_{rs}(555)$ ratio at higher Chl $a$ concentrations while the $R_{rs}(490)/R_{rs}(555)$ ratio in the Chl $a$ range between the other two ratios (O’Reilly et al., 1998). However, in the presence of variable and relatively high CDOM absorption in the region, the effect of shifts in the ratio selection is not clear, although for our data set, it was observed that the OC4 algorithm would predominantly select the $R_{rs}(510)/R_{rs}(555)$ band ratio. With $R_{rs}(490)/R_{rs}(555)$ ratio providing a higher dynamic range for the same range in Chl $a$ concentrations, we propose the use of this single band ratio for estimating
Chl $a$ from remote sensing data for the study region. The power law equation derived from field measurements (Fig. 9(b)) is given by

$$\text{Chl} \ a = 1.629 (R_{rs}(490)/R_{rs}(555))^{-2.551}. \quad (7)$$

We also derived empirical relationships between CDOM absorption at 412 nm and the ratios of reflectances $R_{rs}(412)/R_{rs}(510)$, $R_{rs}(443)/R_{rs}(510)$, and $R_{rs}(510)/R_{rs}(555)$ (Fig. 10) and obtained high correlations in all cases (Miller & D’Sa, 2002).

Empirical relationships derived from field data were applied to SeaWiFS imagery of April 8, 2000 to retrieve Chl $a$ concentrations and CDOM absorption. These retrieved values were compared to a limited set of in situ measured values. Similar trends in Chl $a$ retrievals (Fig. 11) were observed using the power law Eq. (7) and the standard operational OC4v4 algorithm. Similarly, we evaluated empirical relationships between the reflectance band ratios and $\alpha_{\text{cdom}}(412)$ and applied these relationships (Fig. 10) to retrieve CDOM absorption from SeaWiFS satellite data. The closest retrievals of CDOM absorption to in situ values were obtained using the $R_{rs}(510)/R_{rs}(555)$ band ratio (not shown). While the $R_{rs}(443)/R_{rs}(510)$ band ratio was found suitable in other regions (Kahru & Mitchell, 2001), in terms of dynamic range (Fig. 10), the $R_{rs}(412)/R_{rs}(510)$ is the optimal band ratio for the application. However, we observed larger CDOM absorption retrieval errors for these ratios. This may be attributed to lower water-leaving radiances and greater extrapolation errors due to atmospheric correction (Gordon & Wang, 1994) at these wavebands (412 and 443 nm) than at the 510-nm waveband. A
validation with a larger data set will help determine the optimal waveband ratio.

4. Conclusions

River-impacted coastal margins influenced by large rivers such as the Mississippi River are highly dynamic regions where the use of global ocean color algorithms may not be appropriate for accurate retrieval of bio-optical variables such as phytoplankton biomass. In developing local ocean-color remote sensing algorithms or parameterizations of bio-optical models, there is a need to understand the processes and mechanisms that influence the ocean color or the remote sensing signal. In this work, we have examined the concentrations and distribution of optically active in-water constituents such as Chl \( a \) and CDOM in relation to the IOPs (absorption and scattering coefficients) and AOPs (diffuse attenuation coefficient \( K_d \) and the remote sensing reflectance \( R_s(\lambda) \)) under very low discharge conditions of the Mississippi River. Surface stratification resulting from lower salinity river plume waters overlying more saline oceanic waters was observed to be a major factor influencing the bio-optical properties in the region, varying both spatially and temporally. CDOM absorption at 412 and 443 nm, while variable, formed a significant component of the total absorption field at these wavebands. The combination of absorption and particle backscattering strongly influenced the remote sensing reflectance signal. Semi-analytic algorithms (Carder, Chen, Lee, & Hawes, 1999; Garver & Siegel, 1997) are based on the formulation relating irradiance reflectance or remote sensing reflectance to absorption and backscattering (Gordon et al., 1988). The linear relationship between the AOPs (\( K_d \) and \( R_s \)) and absorption and backscattering for the SeaWiFS wavebands, and the derived \( f/Q \) and \( \mu_d \) values that lie within the modeled ranges, suggests the potential for development of new or parameterization of existing models for this region of study. These results also formed the basis for the robust relationships between \( R_s(\lambda) \) ratios and surface Chl \( a \) concentrations and CDOM absorption that we obtained for a bio-optically complex, river-impacted coastal region. The acquisition of a larger data set of bio-optical variables under more typical flow conditions will allow the refinement of the above algorithms for the estimation of Chl \( a \) and CDOM absorption for this coastal region.

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