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Chapter 6

BIO-OPTICAL PROPERTIES OF COASTAL WATERS

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1. Introduction

Coastal waters are generally characterized by large variations in biological, physical and chemical properties and are an important source of dissolved and particulate matter for the open ocean. In highly productive coastal waters, a significant fraction of organic matter produced in surface waters reach the bottom sediments of coastal margins and become buried (Hedges and Keil, 1995). River dominated coastal margins present additional complexities due to large inputs of freshwater that vary seasonally and carry constituents such as suspended sediments, organic matter, and nutrients. As such, uncertainties exist in the contribution of coastal carbon flux rates to the biogeochemical carbon cycle (Wollast, 1991). Repeated, synoptic coverage with satellite remote sensing provides the capability for understanding and monitoring of many coastal processes. The development of numerous bio-optical algorithms provides a bridge between ocean color remote sensing and concentrations of seawater constituents and has been useful, for example, in studies of oceanic carbon cycling through its ability to obtain estimates of phytoplankton biomass and its derived primary productivity (Platt et al., 1988; Muller-Karger et al., 1991). Monitoring water quality parameters such as clarity, suspended sediment concentrations and presence of harmful algal blooms are also some of the other applications of ocean color remote sensing (Carder and Steward, 1985; Tassan, 1994; Kahru and Mitchell, 1998; Stumpf et al., 1999). However, the complexity of optical properties still presents difficulties in the use of ocean color remote sensing in coastal waters.

Oceanic waters have been commonly classified as Case 1 or Case 2 waters (Morel and Prieur, 1977; Gordon and Morel, 1983). Case 1 waters have been defined as those for which phytoplankton and their associated derived products are the main influence on the optical field, while in Case 2 waters, additional seawater constituents such as suspended sediments and dissolved organic matter that may not co-vary with phytoplankton, influences the optical field. Coastal and inland water bodies are optically complex and often referred to as Case 2 waters (Sathyendranath, 2000). Until recently, most studies have focused on Case 1 waters where generally reliable estimates of phytoplankton chlorophyll are being obtained. In contrast, estimates of various in-water constituents from ocean color remote sensing of Case 2 waters are often not accurate due to poor performance of standard algorithms (Darecki and Stramski, 2004). For example, in interpreting the CZCS data of the Orinoco River plume, Hochman et al., 1994 concluded that as much as 50% of the remotely sensed chlorophyll biomass within the plume could be an artifact due to colored dissolved organic matter (CDOM). Large variations in CDOM-to-chlorophyll ratios were reported for measurements conducted in

the northern Gulf of Mexico (Carder et al., 1989) with potential effects on both empirical and semi-analytic ocean color algorithms. In many coastal regions including those influenced by rivers, the often complex interactions of the physical, chemical and biological processes and lack of knowledge of the optical properties have hampered the routine use of ocean color remote sensing in these waters.

One of the keys to improving the accuracy of estimates of the seawater constituents from ocean color remote sensing is the need for a better understanding of the coastal bio-optical properties (Bukata et al., 1981; Carder et al., 1989, 1991; Sathyendranath et al., 1989; Gallegos et al., 1990; Blough et al., 1993; Doerffer and Fisher, 1994; Bukata et al., 1995; Arrigo et al., 1998; Gould et al., 1999; Reynolds et al., 2001; Twardowski and Donaghay, 2001; Babin et al., 2003; Hamre et al., 2003). The optically significant seawater constituents such as chlorophyll (chlorophyll *a*), CDOM (generally denotes the colored material that passes through a 0.2 μm filter) and suspended particulate material (SPM) determine the inherent optical properties (IOPs) such as spectral absorption $a(\lambda)$, scattering $b(\lambda)$, and backscattering $b_b(\lambda)$ coefficients that are important for characterizing the marine optical field. In turn, these variables influence the apparent optical properties (AOPs) that define the in-water radiation field. The three most commonly studied AOPs of interest in remote sensing include the diffuse attenuation coefficient $K_d(\lambda)$, irradiance reflectance $R(\lambda)$, and the remote sensing reflectance $R_{rs}(\lambda)$. Empirical and semi-analytic bio-optical algorithms have been developed mainly for oceanic Case 1 waters to estimate both these IOPs as well the seawater constituents from the apparent optical properties (AOPs) such as remote sensing reflectance that is generally derived from ocean color satellite sensors (Gordon et al., 1988; O'Reilly et al., 1998; Carder et al., 1999). Empirical band-ratio algorithms, for example, are derived by statistical regression of radiance or reflectance ratios versus chlorophyll. The more complicated semi-analytic ocean color algorithms (Garver and Siegel, 1997; Carder et al., 1999) have resulted from a better understanding of the relationship between remote sensing reflectance, inherent optical properties such as backscattering and absorption, and in-water constituents. Bio-optical studies in various coastal waters have demonstrated the need for local empirical (Kahru and Mitchell, 2001; D'Sa et al., 2002a) and semi-analytic algorithms (Reynolds et al., 2001) in order to obtain better estimates of various in-water constituents.

Here we examine various relationships between the AOPs, IOPs and seawater constituents, generally limiting our discussion to coastal waters. Recent developments in instrumentation for *in situ* measurements of IOPs such as absorption and backscattering coefficients of seawater have provided better insight into the optical properties of coastal waters. We review some of the instrumentation and methods used in studies of coastal waters and examine linkages between the physical and bio-optical properties and the relationship between the various seawater constituents and the IOPs and AOPs. We interpret R_{rs} spectra and examine semi-analytic and empirical algorithms used for estimating the seawater constituents such as chlorophyll and CDOM (see also Twardowski et al., Chapter 4; Muller-Karger et al., Chapter 5; Del Castillo, Chapter 7). Finally, we identify potential areas of research that need to be addressed to obtain a better understanding of the bio-optical properties of coastal waters.

2. Background

The process of light absorption and scattering by the various seawater constituents such as particulate and dissolved organic matter are described by the inherent optical properties (IOPs). The apparent optical properties (AOPs) of seawater such as the

vertical attenuation coefficient for downward irradiance or the irradiance reflectance are mainly determined by the inherent optical properties (Kirk, 1994). However, in comparison to the IOPs (e.g., absorption coefficient $a(\lambda, z)$, and backscattering coefficient $b(\lambda, z)$), routine radiometric measurements of the underwater light field have allowed for the easier calculation of the AOPs such as the diffuse attenuation coefficient for downwelling irradiance K_d , the irradiance reflectance R , and the remote sensing reflectance, R_{rs} .

2.1 SEMIANALYTIC BIO-OPTICAL MODELS

Various models have been developed to relate IOPs to or determine IOPs from AOPs (Gordon et al., 1975; Morel and Prieur, 1977; Gordon and Morel, 1983; Kirk, 1984, 1991; Gordon, 1991; Carder et al., 1999; Ciotti et al., 1999; Stramska et al., 2000). The AOPs commonly used in these models include $K_d(\lambda, z)$, the irradiance reflectance $R(\lambda, z)$ and the remote sensing reflectance R_{rs} . Some of these models are based on numerical simulations of the underwater radiative transfer and involve various types of assumptions (e.g., the spectral behavior of IOPs) or require knowledge of surface illumination or sea state as model inputs. Next we present some basic relationships that have been developed relating AOPs, IOPs and some seawater constituents.

2.1.1 Remote sensing reflectance and IOPs

The AOP that defines the color of the ocean and is of interest to remote sensing is the irradiance reflectance R (just beneath the sea surface) and is given by

$$R(\lambda, 0) = E_u(\lambda, 0)/E_d(\lambda, 0), \quad (1)$$

where E_u is the upwelling irradiance (radiant flux per unit surface area) and E_d is the downwelling irradiance at null depth (denoted by 0).

Many studies have modeled the behavior of the underwater light field based on the absorption and scattering properties of the medium. One approach uses the Monte Carlo method to simulate the light field in waters with specified optical properties and environmental conditions such as the angle of the incident light field and sea conditions (Kirk, 1984). The results of these studies have shown that the reflectance at the sea surface is a function of the backscattering coefficient b_b and the absorption coefficient a (Gordon et al., 1975; Morel and Prieur, 1977; Gordon and Morel, 1983; Gordon et al., 1988), and can be approximated as

$$R(0) = fb_b/(a + b_b), \quad (2)$$

where f is a variable that depends upon the solar zenith angle, the optical properties of seawater, and the wavelength of light (Morel and Gentili, 1991; 1996). These IOPs and AOPs are generally functions of light wavelength λ and depth z and will be used when required for clarity.

However, since there is a directional component to the light observed by the remote sensor, it is common to deal with the term remote sensing reflectance, R_{rs} , which is defined just below the sea surface as

$$R_{rs}(\lambda, 0) = L_u(\lambda, 0)/E_d(\lambda, 0), [\text{sr}^{-1}] \quad (3)$$

where L_u is the upwelling or water leaving radiance (radiant flux per unit surface area per steradian, $\text{Wm}^{-2}\text{nm}^{-1}\text{sr}^{-1}$) and is a function of both zenith and azimuth angles. For most oceanic waters the albedo for single scattering ($\varpi = b/(b+a)$) may not be sufficiently high for the upwelling radiances below the surface or the water-leaving radiances to form an isotropic field (Morel and Gentili, 1993, 1996). A proportionality

factor Q , which relates a given upwelling radiance $L_u(\theta, \phi)$ to the upwelling irradiance E_u , expresses this nonisotropic character of the light field (here θ is the nadir angle, ϕ the azimuth angle, and $Q = E_u/L_u$). Based on the definition of Q and on Eqs. (1) and (3), Q relates R_{rs} to R (just beneath the surface) as

$$Q(\theta, \phi, \lambda) = R(\lambda, 0)/R_{rs}(\theta, \phi, \lambda, 0), [\text{sr}]. \quad (4)$$

From Eqs. (2) and (4), we can express R_{rs} just below the sea surface as

$$R_{rs}(0) = (f/Q) * b_b/(a + b_b), [\text{sr}^{-1}]. \quad (5)$$

The subsurface values of $R_{rs}(\lambda, 0)$ are extrapolated to above water (Mobley 1994) and generally given by the approximation

$$R_{rs} = 0.54 (f/Q) * b_b/(a + b_b), [\text{sr}^{-1}]. \quad (6)$$

From Eq. (6) we observe the remote sensing reflectance as being related to the scattering and absorption properties of the water which are in turn determined by the seawater constituents such as phytoplankton biomass, CDOM and detrital or nonalgal particles. The value of the ratio f/Q has been shown to vary less than f and Q individually for oceanic waters (Morel and Gentili, 1993), and was estimated from a limited data set to have values between 0.09 and 0.12 (determined at the SeaWiFS satellite wavebands) for a river dominated coastal region (D'Sa and Miller 2003). The basic expression (Eq. (6)) is generally applicable to all waters including coastal waters.

The coefficients a and b_b in Eq. (6) are the sum due to contributions from the various individual seawater components including pure water. An example of absorption by phytoplankton, CDOM and pure water (Pope and Fry, 1997) in the spectral range 400 to 750 nm for a coastal location is shown in Fig. 1. The corresponding R_{rs} spectrum (Fig. 1, right panel) for the same location shows low reflectance in the blue wavebands that can be attributed to high absorption by phytoplankton and CDOM, while high reflectance in the green (around 555 nm) may be attributed to scattering by suspended material. A peak in the R_{rs} spectrum observed at around 683 nm can be attributed to phytoplankton chlorophyll fluorescence.

2.1.2 Diffuse attenuation coefficient and IOPs

The diffuse attenuation coefficient for downwelling irradiance $K_d(\lambda, z)$ is calculated from the spectral downwelling irradiance profiles $E_d(\lambda, z)$ and is defined as the slope of natural log transformation of downwelling irradiance as a function of depth. The vertical diffuse attenuation coefficient K_d has been related to IOPs (Gordon et al., 1975; Gordon, 1989) as

$$K_d = (a + b_b)/\mu_d, [\text{m}^{-1}], \quad (7)$$

where μ_d is the cosine of the mean downwelling light field. The value of μ_d has been shown to vary from 0.65 to 0.85 and depends on water depth, solar zenith angle, and the ratio of backscattering to absorption (Bannister, 1992). To a first approximation, K_d has been shown to be directly proportional to the absorption coefficient, and in phytoplankton dominated waters to chlorophyll concentrations. For example, a simple correlation analysis between $K_d(443)$ and absorption at 443 nm indicates that for some surface coastal waters, $K_d(443)$ is directly related to the absorption coefficient at the same waveband (Fig. 2).

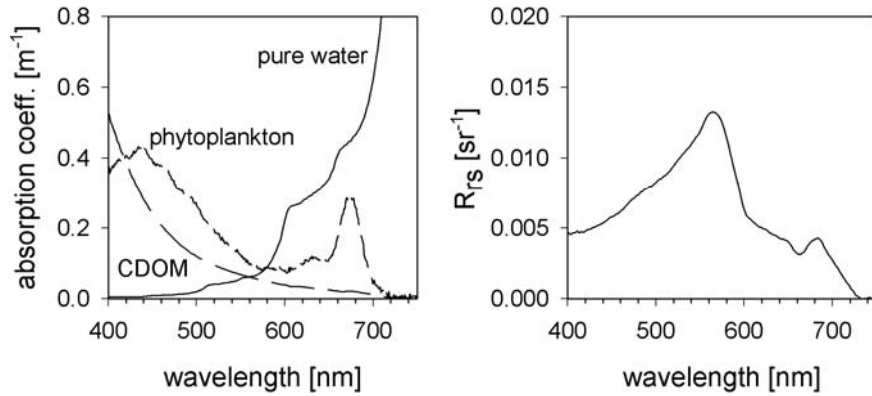


Figure 1. An example of phytoplankton and CDOM absorption spectra for surface water samples at a coastal location along with a pure water absorption spectrum (left panel). Corresponding remote sensing reflectance R_{rs} determined at the same location from above water radiance measurements (right panel).

Determination of the AOPs, K_d and R_{rs} from measurements of the underwater light field have been used to obtain estimates of absorption and backscattering coefficients. Furthermore, knowledge of the spectral characteristics of absorption, scattering and backscattering of the various seawater constituents are used in the parameterization of these IOPs in terms of these constituents. For oceanic waters, parameterization of the IOPs in terms of chlorophyll has enabled the retrieval of chlorophyll and other associated variables from the AOPs such as R_{rs} . However, these parameterizations may not be applicable in some coastal waters where the various seawater constituents do not

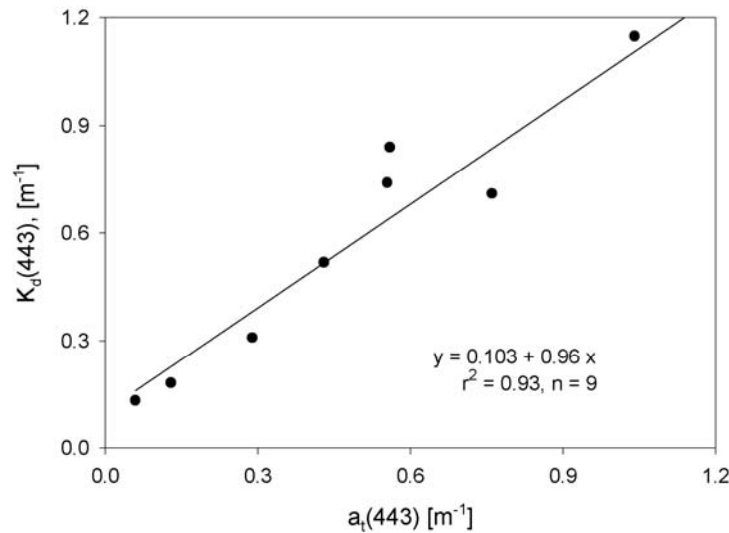


Figure 2. Diffuse attenuation coefficient $K_d(443)$ versus absorption $a_\lambda(443)$ (particulate plus CDOM) for various locations in a coastal environment. co-vary with chlorophyll. Nonetheless, we briefly review some of these absorption and scattering models and examine them in the context of their applicability to coastal waters.

2.1.3 Parameterization of absorption

The major light absorbing constituents in seawater are phytoplankton, detrital or nonalgal particles and CDOM. The total absorption a is the additive sum of contributions by pure water a_w (Pope and Fry, 1997) phytoplankton a_{phy} , detrital or nonalgal particles a_{nap} and CDOM absorption a_{cdom} and can be written as

$$a(\lambda) = a_w(\lambda) + a_{phy}(\lambda) + a_{nap}(\lambda) + a_{cdom}(\lambda), [\text{m}^{-1}] \quad (8)$$

where particle absorption $a_p(\lambda)$ is due to phytoplankton and nonalgal particles and can be written as

$$a_p(\lambda) = a_{phy}(\lambda) + a_{nap}(\lambda). \quad (9)$$

Phytoplankton absorption can account for a large fraction of the total absorption in oceanic waters and is usually defined in terms of its pigment-specific coefficients as

$$a_{phy}(\lambda) = [Chl] a^*_{phy}(\lambda), \quad (10)$$

where $a^*_{phy}(\lambda)$ is the chlorophyll-specific absorption coefficient of phytoplankton ($\text{m}^2 \text{mg Chl}^{-1}$) and is not a constant. The variability in the phytoplankton absorption coefficients per unit chlorophyll concentration or $a^*_{phy}(\lambda)$ can be attributed to various factors such as pigment composition, packaging, light history, cell size, nutrients, and temperature (Mitchell and Kiefer, 1988; Bricaud and Stramski, 1990). Many studies that have documented the variability in absorption properties of phytoplankton in natural populations have been mainly confined to oceanic waters (Mitchell and Kiefer, 1988; Bricaud and Stramski, 1990; Bricaud et al., 1995). Results from a large data set obtained from different regions of the world (covering the chlorophyll concentration range 0.02–25 mg m^{-3}) showed the a^*_{phy} values to decrease rather regularly (0.18 to 0.01 $\text{m}^2 \text{mg}^{-1}$) from oligotrophic to eutrophic waters (Bricaud et al., 1998).

CDOM absorption has been parameterized in the visible range (400 to 700 nm) with the spectrum typically fitting an exponential function (Bricaud et al., 1981) as

$$a_{cdom}(\lambda) = a_{cdom}(\lambda_0) e^{[S(\lambda-\lambda_0)]}, \quad (11)$$

where S (nm^{-1}) is the slope of the exponential decrease with wavelength and $a_{cdom}(\lambda_0)$ is the absorption coefficient for CDOM at a reference wavelength (e.g., 400 nm). While values between -0.017 and -0.014 nm^{-1} have been used in bio-optical models, the value of S can vary over a wider range (e.g., from -0.01 to -0.02) (Kirk, 1994; Carder et al., 1989; Miller et al., 2002), with values generally lower in coastal waters and increasing offshore (Vodacek et al., 1997).

Spectral absorption by detrital or nonalgal particles has been found to be similar to CDOM absorption and a value of 0.01 m^{-1} for the spectral slope S_{nap} has been reported for some inland waters (Roesler et al., 1989). Semianalytic bio-optical models (e.g., Carder et al., 1999; Ciotti et al., 1999) have combined the contributions by these two seawater constituents.

Based on field data and the assumption of CDOM and detrital particle absorption co-varying with chlorophyll, a well known bio-optical model for spectral absorption coefficient of Case 1 waters developed by Prieur and Sathyendranath (1981) and further modified by Morel (1991) is parameterized in terms of chlorophyll concentration and is given by

$$a(\lambda) = [a_w(\lambda) + 0.06a^*_{phy}(\lambda)[Chl]^{0.65}][1 + 0.2 \exp^{(-0.014(\lambda - 440))}]. \quad (12)$$

The applicability of this model in coastal waters will depend on whether absorption by CDOM and nonalgal particles co-vary with chlorophyll, and on whether the other assumptions (e.g., spectral slope value of -0.014) are appropriate.

2.1.4 Parameterization of scattering

The total spectral scattering coefficient $b(\lambda)$ can be separated into contributions by pure water $b_w(\lambda)$ (Morel, 1974) and total particles $b_p(\lambda)$ as

$$b(\lambda) = b_w(\lambda) + b_p(\lambda), \quad (\text{m}^{-1}). \quad (13)$$

Light transmission is also influenced in addition to the scattering coefficient by the angular distribution of scattering, and is defined by the normalized volume scattering function or the scattering phase function. It is obtained by dividing the volume scattering function $\beta(\psi)$ ($\text{m}^{-1}\text{sr}^{-1}$) by the total scattering function b as

$$\bar{\beta}(\psi) = \beta(\psi)/b. \quad (14)$$

Scattering and backscattering coefficients are obtained by integrating the normalized volume scattering function from 0 to 180 and from 90 to 180°, respectively. Although the backscattering coefficient is the important term in bio-optical models (e.g., Eq. (6)), it has, until recently, been a difficult parameter to measure directly. As such, particle scattering b_p has been related to particle backscattering b_{bp} through the backscattering ratio ($B = b_{bp}/b_p$), and the backscattering coefficient expressed as

$$b_b(\lambda) = \frac{1}{2} b_w(\lambda) + B b_p(\lambda), \quad \text{or} \quad (15)$$

$$b_b(\lambda) = b_{bw}(\lambda) + b_{bp}(\lambda). \quad (16)$$

where b_{bw} is the backscattering due to water molecules (Smith and Baker, 1981). In oceanic Case 1 waters with low chlorophyll content, backscattering contribution by water molecules to total backscattering is not negligible (Morel and Loisel, 1998), while in coastal waters scattering by suspended particles dominates. Based on a number of data points collected in oceanic and coastal waters (Petzold, 1972), a constant value (~ 0.0183) has generally been assumed for the backscattering ratio (Gould et al., 1999; Mobley et al., 2002). For oceanic waters, backscattering ratio has also been expressed as a decreasing function of increasing chlorophyll (Morel and Maritorena, 2001). The shapes of scattering and backscattering spectra have been described by functions of the form λ^n , with values between 0 and -2 being often used for the exponent n (Sathyendranath et al., 1989; Morel, 1988; Mobley, 1994). In eutrophic waters, the scattering coefficient was shown not to vary much spectrally (Gordon et al., 1988; Morel, 1988) due to the presence of larger particles.

A commonly used bio-optical model for scattering (Gordon and Morel, 1983) that is parameterized in terms of chlorophyll concentrations ($[\text{Chl}]$, mg m^{-3}) is given by

$$b(\lambda) = 0.30 [\text{Chl}]^{0.62} (550/\lambda). \quad (17)$$

A model for particle backscattering also expressed in terms of chlorophyll (Morel and Maritorena, 2001) is

$$b_{bp} = b_p(550) \{0.002 + 0.02[0.5 - 0.25 \log[\text{Chl}]/(550/\lambda)]\}, \quad (18)$$

where $b_p(550)$ is given in terms of Chl (Loisel and Morel, 1998) and expressed as

$$b_p(550) = 0.416 [\text{Chl}]^{0.76}. \quad (19)$$

These relationships are however based on the assumption that nonalgal particles (e.g., detrital and inorganic) co-vary with chlorophyll concentrations and may need to be evaluated for coastal waters.

2.2 EMPIRICAL REMOTE SENSING ALGORITHMS

Empirical algorithms on the other hand provide direct relationships between ratios of remote sensing reflectance or water leaving radiances and seawater constituents such as chlorophyll. They make use of the differential absorption of phytoplankton in the blue (maximum at 443 or 490 nm) and green (minimum at 555 nm) to obtain estimates of chlorophyll. Using simple linear regression of log-transformed data, the power equation has been widely used to relate water-leaving radiances to chlorophyll concentrations (Gordon et al., 1983; Mitchell and Holm-Hansen, 1991). Based on a large set of field data, empirical algorithms based on cubic polynomials have been developed for the SeaWiFS and MODIS satellite sensor wavebands. The two widely used algorithms are the ocean chlorophyll 2 (OC2) modified cubic polynomial and the ocean chlorophyll 4 (OC4) maximum band ratio algorithms (O'Reilly et al., 1998; O'Reilly et al., 2000). The two-band ratio or OC2 algorithm for example is given by the relation

$$[Chl] = 0.0929 + 10^{(0.2974 - 2.2429X + 0.8358X^2 - 0.0077X^3)}, \quad (20)$$

where $X = \log(R_{rs490}/R_{rs555})$ and the remote sensing reflectance R_{rs} defined as nL_w/F_0 (F_0 is the solar constant), and nL_w is the normalized water leaving radiance. The OC4 is a four-band maximum band ratio formulation and uses a fourth order polynomial (five coefficients) to estimate [Chl] and is given by

$$[Chl] = 10^{(0.366 - 3.067X + 1.930X^2 + 0.649X^3 - 1.532X^4)}, \quad (21)$$

where $X = \log(R_{rs443}/R_{rs555} > R_{rs490}/R_{rs555} > R_{rs510}/R_{rs555})$. It uses one of the band ratios with the maximum value and is based on the shift of the maximum of R_{rs} spectra toward higher wavelengths with increasing chlorophyll. Although, the OC2 and OC4 empirical algorithms have been useful in estimating chlorophyll concentrations in both Case 1 and 2 waters, a few studies have shown some large errors in these estimates in some coastal waters (Darecki and Stramska 2004).

3. Methods and Instruments

Recent developments in optical instrumentation have demonstrated their utility in providing new insights into the bio-optical properties of various coastal waters (Twardowski et al., 1999; Sosik et al., 2001; D'Sa and Miller, 2003; Twardowski et al., Chapter 4). Optically complex coastal regions may include river-dominated coastal margins that are regions of high biogeochemical and physical activity. For example, in a SeaWiFS satellite derived chlorophyll image of the northern Gulf of Mexico (Fig. 3), we observe the Mississippi river plume associated with the brighter regions (high chlorophyll concentrations) and showing a highly variable surface chlorophyll distribution. Studies have revealed this region to be optically complex and mainly influenced by the physical and biogeochemical processes associated with river discharge (Sydor et al., 1998; Lohrenz et al., 1999; Miller and D'Sa, 2002).

Numerous instruments and methods are presently available for carrying out bio-optical measurements in oceanic waters (see Twardowski et al., Chapter 4). Protocols are available (Fargion and Mueller, 2000) for measuring bio-optical and radiometric data for satellite ocean color sensor validation. These include the calibration and characterization of field instruments, field methods and data analyses. Instruments used

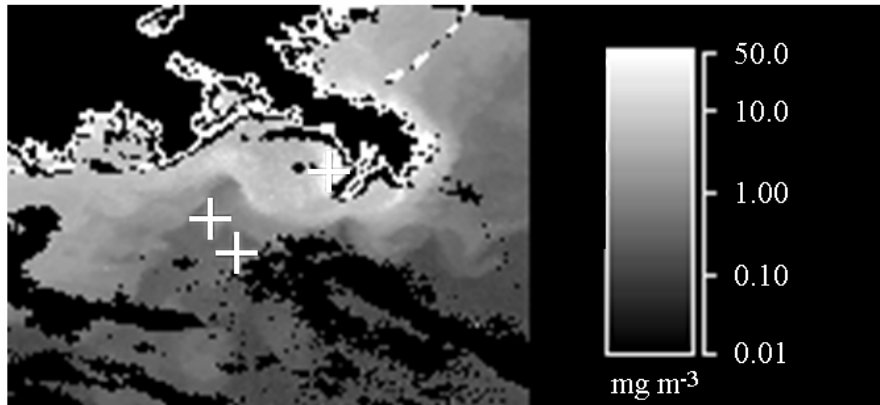


Figure 3. An example of an optically complex coastal region in the northern Gulf of Mexico influenced by the Mississippi River. The SeaWiFS (Sea-viewing Wide Field-of-view Sensor) derived chlorophyll (mg m^{-3}) image was processed using SEADAS software and the OC4 empirical algorithm. Pluses in the figure indicate one nearshore and two offshore locations (based on distance from the coast) as examples of waters with contrasting bio-optical properties. Land and clouds are masked to black.

to characterize the bio-optical properties in oceanic waters include radiometers and absorption and scattering meters. These instruments are often integrated along with a CTD instrument into a single bio-optical package (e.g., Miller and D'Sa, 2002) enabling simultaneous measurements of water column optical and physical variables. Discrete water samples are generally collected to calibrate the optical measurements. For example, spectrophotometric absorption measurements on filtered seawater samples are used to obtain the spectral absorption characteristics of particulate and dissolved components in seawater. Here we describe briefly some instruments that have been used to obtain vertical bio-optical profiles along with methods for discrete sampling and analyses.

3.1 WATER COLUMN MEASUREMENTS

Examples of water column bio-optical measurements include: absorption and attenuation (ac-9, WETLabs), backscattering (Hydroscat-2, HOBILabs; VSF3, WETLabs), spectral downwelling irradiance and upwelling radiance (OCR, OCI-200, Satlantic; PRR-800, Biospherical Instruments) at wavebands corresponding to ocean color satellite sensors, and chlorophyll fluorescence (Wetstar, WETLabs).

3.1.1 IOP measurements

A dual-path absorption and attenuation meter (ac-9, WETLabs) is used for measuring absorption and attenuation coefficients at nine 10-nm spectral bandwidths (412, 440, 488, 510, 532, 555, 650, 676 and 715 nm) in the visible and near infrared over a 25 cm path length (Moore et al., 1992; Zaneveld et al., 1992). Optically clean water (e.g., Barnstead NANOpure) is used as a reference to calibrate the ac-9, and thus the estimated absorption and attenuation coefficients does not include contributions by pure water. Measured absorption and attenuation are corrected for temperature, salinity and scattering to give the corrected absorption coefficients $a_t(\lambda, z)$ (i.e. absorption due to particulate and dissolved components) and the attenuation coefficients $c(\lambda)$ (Zaneveld et al., 1994; Pegau et al., 1997; Twardowski et al., 1999) Particle scattering coefficients

$b_p(\lambda, z)$ at the eight visible wavebands are calculated as the difference between the attenuation and absorption coefficients. Vertical profiles of absorption coefficients due to CDOM $a_{cdom}(\lambda, z)$ are obtained by attaching a 0.2 μm pleated maxicapsule filter (Gelman) to the intake tubing of the ac-9. Particle absorption $a_p(\lambda, z)$ is then computed as

$$a_p(\lambda, z) = a_t(\lambda, z) - a_{cdom}(\lambda, z). \quad (22)$$

Instruments for measuring scattering have been constructed with either the detector or source/projector being able to rotate relative to each other (Petzold, 1972; Kirk, 1994) enabling the calculation of the volume scattering function $\beta(\omega)$ (per meter per steradian) over the instrument measuring range. The backscattering coefficient b_b can be estimated by integrating the measured $\beta(\omega)$ from 90 to 180° in scattering angle. A method based on Mie computations has shown that there exists an approximately constant ratio between the backscattering coefficients and $\beta(\omega)$ at 120° (Oishi, 1990). Two commercial field instruments have been developed based on this concept; the Hydrosat-2 and 6 (HOBi Labs), and the ECO BB (WETLabs). The Hydrosat-2 measures backscattering at two wavebands (442 and 532 nm) while the Hydrosat-6 at six wavebands, and is based on a calibration method to convert the optical backscattering signal to a measurement of $\beta(\omega)$ at a single backscattering angle of 140° (Maffione and Dana, 1997). The 117° angle of scattering measured by the ECO BB meter was based on the determination of this angle as a minimum convergence point for variations in the volume scattering function $\beta(\omega)$ induced by suspended materials and water itself (Boss and Pegau, 2001). Estimated $\beta(\omega)$ at this angle is converted to backscattering and further corrected to account for losses due to attenuation of some backscattered light in the path between the sampling volume and detector. The ECO-VSF (WETLabs) optical backscattering sensor measures the optical scattering at three distinct angles of 100, 125, and 150°, thus allowing the determination of the backscattering coefficient through interpolation and extrapolation from 90 to 180°.

3.1.2 Radiometric measurements

Spectral radiometric measurements of the marine light field are now routinely collected with commercial radiometers. Important in-water radiometric profile measurements of spectral downwelling irradiance $E_d(\lambda, z)$, upwelling irradiance $E_u(\lambda, z)$, and upwelling radiance $L_u(\lambda, z)$ allow the determination of AOPs and are used in the calibration and validation of ocean color sensors, bio-optical modeling and primary production studies (Morel, 1988; Behrenfeld and Falkowski, 1997; Fargion and Mueller, 2000; Hooker and Maritorena, 2000; Stramska et al., 2000).

Radiometric measurements of downward irradiance (E_d) and upward radiance (L_u) at wavebands corresponding to satellite ocean color sensors (e.g., 412, 443, 490, 510, 555, 665, and 683 nm) made using radiometers (e.g., OCI and OCR-200, Satlantic; PRR-800 and PRR-2600, Biospherical Instruments) allow the determination of AOPs such as K_d and R_{rs} . Depth-dependent diffuse attenuation coefficients for downwelling irradiance K_d are computed for each wavelength as $d\{\ln[E_d(z)]\}/dz$. Similarly, the diffuse attenuation coefficients for upwelling radiance K_L are computed using L_u measurements. Values of $K_d(\lambda, z)$ and $K_L(\lambda, z)$ at the shallowest depth are 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 sub-surface values $E_d(\lambda, 0^-)$ and $L_u(\lambda, 0^-)$ are extrapolated to values just above the sea surface (Mueller and Austin, 1995). Remote sensing reflectance $R_{rs}(\lambda, 0^+)$ is then calculated as

$$R_{rs}(\lambda, 0^+) = L_u(\lambda, 0^+)/E_d(\lambda, 0^+), \quad (23)$$

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. Primary sources of uncertainty in the radiometric measurements and the AOP determination include ship perturbation (Voss et al., 1986), instrument shading (Gordon and Ding, 1992) and variability due to sky conditions (e.g., clouds) during the in-water measurements.

3.1.3 Hydrographic and fluorescence measurements

Hydrographic data consisting of temperature and salinity are derived from measurements of conductivity-temperature-depth (CTD) using a profiler (e.g., SBE 49, SeaBird). These measurements are important in determining the properties of water masses associated with different physical processes (e.g., fronts, upwelling, and plumes) that often have characteristic optical properties. Temperature and salinity measurements are also required for correcting the absorption measurements made with the ac-9 absorption and attenuation meter.

Continuous profiles of *in situ* chlorophyll fluorescence intensity are generally obtained in conjunction with CTD measurements using commercial fluorometers (e.g., WETStar, WETLabs; Aquatraka II, Chelsea Instruments). Integration of these instruments with the optical instruments is desirable in coastal waters since it allows for simultaneous measurements of multiple variables that often change at small spatial and temporal scales. Chlorophyll fluorescence profiles are generally calibrated against chlorophyll pigments obtained from discrete samples using either the High Performance Liquid Chromatography (HPLC) or those derived from fluorometric analysis. As observed (Fig. 4) high correlations between chlorophyll fluorescence (volts) and chlorophyll concentrations (mg m^{-3}) enables reliable estimates of chlorophyll profiles to be obtained along with optical measurements.

3.2 ABOVE WATER REMOTE SENSING REFLECTANCE

An alternative to deriving R_{rs} from in-water radiometric measurements described previously is to derive R_{rs} from radiance measurements made above the water (Carder and Steward, 1985; Carder et al., 1993; Mobley, 1999). These measurements are generally made from a ship deck using a radiometer to measure radiance signals that are proportional to that emanating from i) the sea surface L_{sea} at nadir angle θ (usually chosen between 30 and 50°) and azimuth angle ϕ (usually with an orientation of 90°) to the plane of the sun, ii) the sky radiance L_{sky} measured with the radiometer looking upward (at same angles but in the zenith direction), and iii) the radiance reflected from a horizontal plaque (L_{pl}) with a known bi-directional reflectance. Measurements of the radiance reflected from the calibrated plaque is used as a proxy for $E_d(\lambda, 0^+)$ (Eq. (23)). Also, due to skylight reflected off the sea surface contaminating the L_{sea} measurements, L_{sky} values are used to correct for it. Remote sensing reflectance is calculated as (Mueller and Austin, 1995; Toole et al., 2000)

$$R_{rs} = (L_{sea} - \rho(\theta)L_{sky})/(\pi L_{pl}/\rho_{pl}) - \text{residual}(750), \quad (24)$$

where $\rho(\theta)$ is the Fresnel reflectance of the sea surface at a viewing angle θ , and ρ_{pl} is the reflectance of the plaque. Any residual reflected sky radiance is removed by subtracting the signal at 750 nm (Toole et al., 2000).

High spectral resolution radiometers generally used for shipboard determinations of above-water radiance include i) Analytical Spectral Devices (ASD) (Boulder, Colorado)

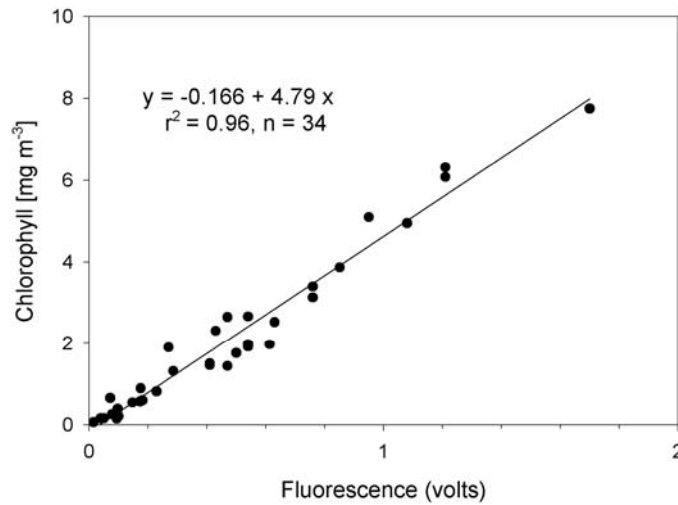


Figure 4. Chlorophyll estimates from discrete samples obtained using the HPLC method plotted as a function of chlorophyll fluorescence from the profiling fluorometer. Fluorescence values correspond to depth of discrete samples.

512-channel, fiber-optic spectrometer, and ii) the GER 1500 (Geophysical and Environmental Research), a 512-channel, 1-nm spectral resolution fiber-optic system. A radiometer (GER 1500) was adapted with optical fibers for shipboard operations and used in the determination of R_{rs} in a river-dominated coastal region (Miller and D'Sa, 2002). A Spectralon plaque (Labsphere) with a nominal reflectance of 98% was used as a reference. Following SeaWiFS protocols (Mueller and Austin, 1995), a typical measurement sequence with the fiber optic radiometer was to measure radiance spectra of the sea surface at 30° nadir viewing angle, followed by the sky radiance at 30° zenith angle, and the radiance reflected off the Spectralon plaque. These measurements are usually repeated three or more times. Following Eq. (24), the data are processed to estimate the above water $R_{rs}(\lambda)$. However, uncertainties in the above-water determination of R_{rs} due to sea-state effects (Toole et al., 2000) such as rough sea conditions and presence of white caps and foam could possibly render some of these measurements impractical (Kirk, 1994).

3.3 DISCRETE MEASUREMENTS

Water samples at discrete depths are generally collected using a CTD rosette multi-bottle array system immediately prior to or following optical profiles for better correlation with optical measurements. These samples are processed at sea or taken to the laboratory for various types of analyses such as pigment concentrations, particulate and CDOM absorption using SeaWiFS protocol (Mueller and Austin, 1995) and will be briefly discussed in the following section.

3.3.1 Phytoplankton pigment concentrations

Phytoplankton pigment concentrations have been determined using the fluorometric measuring technique (Parsons et al., 1984) and in more recent times the application of High-Performance Liquid Chromatography (HPLC) method (Wright et al., 1991) has been recommended (Fargion and Mueller, 2000).

Depending on phytoplankton biomass, a variable volume of water (50-500 ml) is filtered through Whatman GF/F filters for fluorometric analysis of chlorophyll concentration (Parsons et al., 1984). The filters are homogenized and kept refrigerated in the dark while pigments are extracted in 90% acetone for approximately 6 hours or longer. Fluorescence is measured following extraction in a Turner Designs fluorometer previously calibrated with pure chlorophyll *a* (Sigma). The fluorometric method however, has been shown to significantly under- or over-estimate chlorophyll concentrations due to the presence of chlorophyll degradation products and accessory pigments (Trees et al., 1985; Bianchi et al., 1995).

HPLC determination of phytoplankton pigments such as chlorophyll *a* and phaeopigments and other accessory pigments have been recommended for validation of bio-optical algorithms for ocean color sensors (Fargion and Mueller, 2000) and include protocols and standards that closely follow those adopted by the Joint Global Ocean Flux Study (JGOFS) (UNESCO, 1994). Briefly, seawater samples are filtered onto a 25 cm glass fiber filter (Whatman, GF/F) under low vacuum. These are then stored in cryotubes kept in liquid nitrogen and analyzed in the laboratory with high-performance liquid chromatography (HPLC). Frozen sample filters are homogenized in 1.5 ml 90% acetone, centrifuged, and diluted with 0.5 M aqueous ammonium acetate before injection. Peak identifications were made using standards for the various pigments followed by the determination of chlorophyll and other pigments.

3.3.2 Particle absorption

Light absorption of particles suspended in seawater are obtained by filtering the particles following Mitchell and Kiefer (1988). Depending on the particle load, different volumes of seawater samples are filtered onto a 25 mm glass fiber filter (Whatman GF/F) at low vacuum and immediately analyzed or frozen in liquid nitrogen for latter spectroscopic analysis. The optical density of the filters (OD_f) are measured in a dual-beam scanning spectrophotometer (e.g., Lambda-18, Perkin-Elmer) generally between 380 and 750 nm. A filtrate saturated Whatman GF/F filter is used as a blank. Particle absorption $a_p(\lambda)$ is calculated as

$$a_p(\lambda) = 2.3 OD_f(\lambda) A/V\beta, \quad (25)$$

where A is the clearance area of the filter (m^2), V is the volume of seawater filtered (m^3), and multiplication by 2.3 converts base-10 logarithm to natural logarithm. The value for the pathlength amplification factor of the filters β is taken to be either a constant (Roesler, 1998) or to be wavelength dependent (Bricaud and Stramski, 1990). After particle measurements, the sample filters are extracted in methanol (Kishino et al., 1985) or bleached (Tassan and Ferrari, 1995) to remove phytoplankton pigments, and the optical density of the filter is determined again in the spectrophotometer. The absorption coefficient of nonpigmented particulates or $a_{nap}(\lambda)$ is also determined using Eq. (25). Phytoplankton or algal absorption $a_{phy}(\lambda)$ is then calculated as the difference between $a_p(\lambda)$ and $a_{nap}(\lambda)$.

3.3.3 CDOM absorption

Measurements of spectral absorption of the soluble material in seawater or the colored dissolved organic matter (CDOM) have been obtained in diverse oceanic and coastal waters using spectrophotometers with 10 cm pathlength cells (Bricaud et al., 1981; Blough et al., 1993). Seawater samples are filtered through pre-rinsed 0.2 μm membrane filters (e.g., Nuclepore nylon), and the optical density spectra $OD_{cdom}(\lambda)$ of the filtrate relative to purified water are obtained using a spectrophotometer. Necessary

care should be taken during handling of the seawater samples to avoid contamination and photo-degradation. CDOM absorption coefficients $a_{cdom}(\lambda)$ are calculated as

$$a_{cdom}(\lambda) = 2.303 OD_{cdom}(\lambda)/l, [\text{m}^{-1}] \quad (26)$$

where l is the pathlength of the sample cell or cuvette (usually 0.1 m), and OD_{cdom} is the optical density relative to pure water.

An alternate method for determining CDOM absorption is the use of a long pathlength aqueous capillary waveguide based spectrophotometer that effectively increases the sensitivity of measurements (D'Sa et al., 1999; D'Sa and Steward, 2001). This technology was further developed into a multiple pathlength aqueous waveguide system (Fig. 5) that enabled the determination of CDOM absorption spectra in diverse inland, coastal and oceanic waters (Miller et al., 2002).



Figure 5. Multiple pathlength capillary waveguide system used for measuring CDOM absorption at sea.

4. Coastal Bio-optical Properties

Bio-optical properties of optically complex Case 2 waters have been studied in numerous regions that include: coastal, river-dominated, upwelling regions, fronts and estuaries. Here we review some studies that examined the physical influences on optical properties and the distribution of seawater constituents. We also examine light variability in relation to IOPs, AOPs and present examples of bio-optical data in a river-dominated coastal region.

4.1 LINKAGES BETWEEN PHYSICAL AND BIO-OPTICAL PROPERTIES

Physical influences associated with advective currents, tides, resuspension, stratification, mixing and flow of river waters often determine the bio-optical properties and carbon fluxes in coastal waters. In studies conducted on the New England continental shelf, physical processes associated with characteristic seasonal patterns in stratification and mixing contributed to the optical variability mostly through effects on phytoplankton (Sosik et al., 2001). In coastal waters of the Antarctic Peninsula, elevated

values of beam attenuation coefficients were associated with phytoplankton blooms in stratified surface waters and resuspension in bottom waters (Mitchell and Holm-Hansen, 1991). Over longer time scales, variations in chlorophyll fluorescence on the inner shelf off Duck, North Carolina were related to changes in water mass properties that could be attributed to alternating events of upwelling and downwelling (D'Sa et al., 2001). In examining the specific absorption for total particulates, detritus and phytoplankton in the California Current System, the variability in specific absorption due to phytoplankton $a_{ph}^*(\lambda)$ was found to be related to the hydrographic and chemical environment (Sosik and Mitchell, 1995).

Optical properties of the U.S. Middle Atlantic Bight were examined during four cruises along a cruise track extending from Delaware Bay to the Sargasso Sea (DeGrandpre et al., 1996). The overall seasonal and spatial ranges for CDOM and particulate absorption (at 442 nm) and chlorophyll concentrations were 0.02-0.41 m^{-1} , 0.01-0.49 m^{-1} , and 0.07-9.4 mg m^{-3} , respectively. Largest values in these variables were near the coast, with many of the peaks along the transect corresponding to frontal structures. Additionally, CDOM absorption was found to be highest in April, most likely due to increased freshwater inputs from spring runoff. Studies of CDOM absorption in another location in the Mid Atlantic Bight (Boss et al., 2001) revealed that on short time scales, variability in the vertical distribution of CDOM absorption was mostly due to high frequency internal waves, while over longer periods and episodically, CDOM variability was dominated by storms.

In river-dominated coastal regions, CDOM absorption and salinity are often well correlated (Blough et al., 1993). Freshwater input from surrounding watersheds and new CDOM production from *in situ* biologic activity were factors found contributing to the temporal and spatial variability of CDOM absorption in Narragansett Bay and Block Island Sound (Rhode Island) (Keith et al., 2002). The seasonal flow of river discharge by the Mississippi river strongly influenced the spatial and temporal variability in the bio-optical properties in the Northern Gulf of Mexico (Miller and D'Sa, 2002). In the Mississippi River Bight, stratification due to lower salinity surface waters overlying more saline oceanic waters strongly influenced the spatial and vertical structure of the bio-optical field (D'Sa and Miller, 2003).

An example of the large variability in the bio-optical properties associated with changes in the physical properties (e.g., temperature and salinity) in a river dominated coastal system can be observed in Fig. 6. At the nearshore location, surface waters with lower salinity and temperature were associated with high phytoplankton biomass ($\sim 8 \text{ mg m}^{-3}$ of chlorophyll) that decreased with depth and increasing salinity and temperature. Optical properties of absorption ($a_t = a_p + a_{cdom}$) at 440 nm also decreased with depth as the chlorophyll profile. The backscattering profile b_b however showed lower values in surface waters that increased with depth, indicating that phytoplankton was not the main contributor to the backscattering signal. At the offshore location, more oceanic conditions prevailed (~ 35.8 psu) with low chlorophyll concentrations ($\sim 0.5 \text{ mg m}^{-3}$), and the optical properties an order of magnitude lower than the nearshore location. This data clearly indicates the strong linkages between the physical and bio-optical properties and provides the opportunity to evaluate bio-optical models for water with stratified (Gordon and Clark, 1980) or non-uniform pigment profiles (Sathyendranath and Platt, 1989).

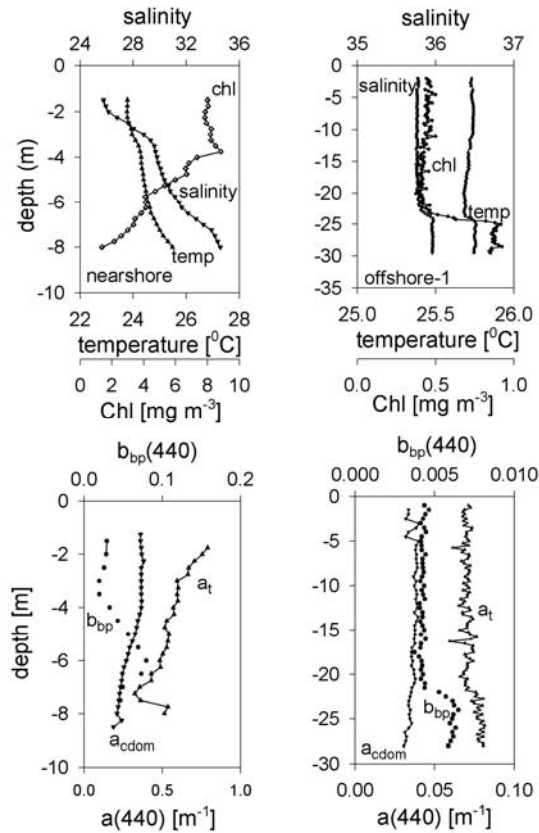


Figure 6. Vertical profiles of temperature, salinity and chlorophyll at two coastal locations (nearshore and offshore) in the northern Gulf of Mexico. Corresponding water column profiles of absorption, scattering and backscattering (440 nm) at the same locations (lower panel).

4.2 ABSORPTION AND SCATTERING CHARACTERISTICS

For any given water body, the total spectral absorption coefficient is the sum of the known absorption coefficients of pure water and that due to dissolved and particulate matter. In the case of scattering and backscattering coefficients, the contributions are from pure water and particulate matter. In oceanic waters, phytoplankton and its derived products are the main contributors to absorption and scattering. In these waters, the various components (except that due to pure water) are often assumed to covary with chlorophyll concentration (Morel and Prieur, 1977). Based on this assumption, and knowledge of the spectral characteristics of these constituents, reflectance models and ocean color algorithms have been developed for estimating seawater constituents from remote sensing (Gordon et al., 1988; Roesler and Perry, 1995; Garver and Siegel, 1997; Bricaud et al. 1998; Carder et al., 1999; Reynolds et al., 2001). The application of these models to coastal waters may require a better understanding of the absorption and

scattering characteristics of the various seawater constituents. Next we review studies that have documented the optical properties in some coastal waters.

4.2.1 Absorption by seawater constituents

In a comprehensive study in coastal waters around Europe (Babin et al., 2003), the relationship between phytoplankton absorption and chlorophyll concentration was found to be generally similar to those for open ocean waters (Bricaud et al., 1995). However, the study found significant departures from the general trend due to unusual cell size and high phaeopigment concentrations.

A few studies on the absorption properties of detrital or nonalgal particles in coastal waters have been described (Roesler et al., 1989; Duarte et al., 1998; Babin et al., 2003). In most cases, the absorption spectra of these particles were well described by an exponential function. Average values for the slope of the exponential function were about 0.011 nm^{-1} in inland marine waters (Roesler et al., 1989) while an average value of 0.0123 nm^{-1} was obtained in coastal waters around Europe (Babin et al., 2003). Light absorption by marine mineral particles in coastal waters, showed a similar behavior as that of nonalgal particles and were shown to have an average spectral slope of about 0.011 nm^{-1} (Bowers et al., 1996).

Optical properties of Case 2 waters can be substantially affected by CDOM absorption and numerous studies have shown their effect on ocean color algorithms. Blough et al. (1993) determined that the discharge of colored organic matter by the Orinoco River strongly influenced the optical quality of the Caribbean waters with major implications for the carbon cycle.

Spectral absorption of seawater constituents (phytoplankton, detrital or nonalgal particles, and CDOM) determined from samples taken at different locations in a river dominated coastal environment (Fig. 7) demonstrates the large variability in particulate (~ 0.08 to 0.6 m^{-1}) and CDOM (~ 0.1 to 0.8 m^{-1}) absorption at 400 nm. For nearshore locations, detrital and CDOM absorption were greater than phytoplankton absorption, while for the offshore location, phytoplankton absorption was dominant. Variability in spectral absorption (particulate plus CDOM absorption) at six spectral bands at a nearshore coastal location (Fig. 8, left panel) shows absorption decreasing with increasing wavelength. Such datasets obtained from various coastal waters would be essential in evaluating or developing new absorption parameterizations (e.g., Eq. (18)) for the seawater constituents.

4.2.2 Scattering and backscattering

Scattering in the marine environment is dependent on the amount and composition of the suspended particles through their size, shapes and refractive indices (Stramski and Kiefer, 1991). Uncertainties remain on the contributions of various particle size fractions to light scattering (Beardsley et al., 1970; Brown and Gordon, 1973), or on the relative importance to scattering by organic or inorganic particles (Brown and Gordon, 1973; Zaneveld et al., 1974). In coastal waters the larger range and size distribution of particles present greater challenges, with backscattering by suspended sediments often contributing significantly to the ocean color signal.

Petzold (1972) determined b and b_b from measurements of volume scattering function obtained at numerous locations in Case 1 and Case 2 waters that included the turbid San Diego Harbor. The values of the backscattering ratios obtained from the above dataset have been widely used in determining backscattering from scattering. While b_b and b was shown to be linearly related for the Petzold data set (Gould et al., 1999), field measurements in the Mississippi River Bight indicated non-linear relation-

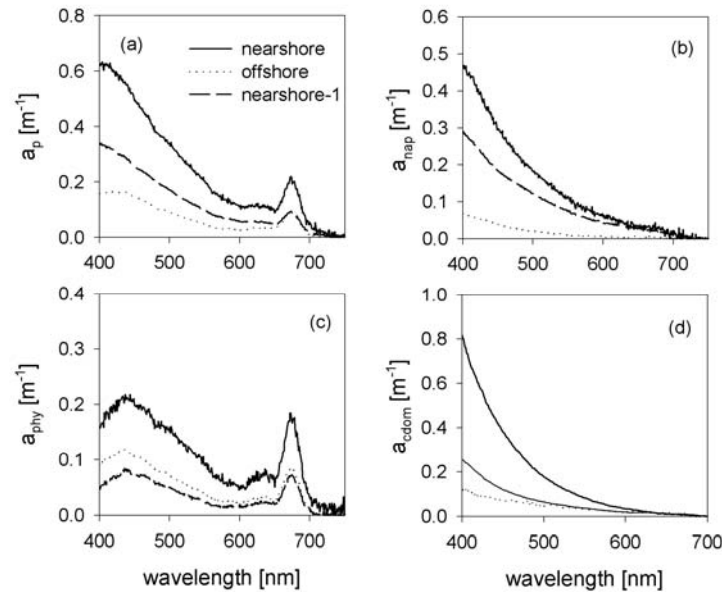


Figure 7. Spectral absorption corresponding to (a) total particulate a_p , (b) nonalgal particles a_{nap} , (c) phytoplankton a_{phy} , and (d) CDOM a_{cdom} for surface waters in a coastal river dominated environment.

ship between the two variables (D'Sa and Miller, 2003). In presenting the results of field measurements in turbid waters, Whitlock et al. (1981) observed the ratio b_b/b to have only small spectral variations, while the magnitude changed with increased water turbidity. Spectrally, the backscattering ratio in coastal waters was found to be only weakly sensitive to changes in wavelength (Risovic, 2002). Bulk refractive index for understanding particle composition in Case 1 and Case 2 waters were described in terms of the backscattering ratio and the hyperbolic slope of the particle size distribution (Twardowski et al., 2001). Estimates of the refractive index agreed with expected values for algal cells and inorganic minerals.

An example of the water-column structure of spectral scattering (412, 440, 488, 510, 555, 650 nm) and backscattering (442 and 589 nm) for a nearshore location (Fig. 8, right panel) shows little correlation with corresponding chlorophyll profile (Fig. 5, left panel). We observe both scattering and backscattering increasing with depth while chlorophyll decreased, indicating the greater influence of suspended sediments on scattering. Spectrally, both scattering and backscattering decreased with increasing wavelength. The data presented here indicates that characterizing scattering and backscattering in terms of chlorophyll may not be appropriate in some coastal waters and more field data may be needed to better understand the relationships (Hamre et al., 2003).

4.3 LIGHT FIELD CHARACTERISTICS AND OPTICAL PROPERTIES

The amount of visible radiant energy and its spectral content emerging from the sea depends on the downwelling incident light, the sun elevation, sky state, sea state, and the optical properties of absorption and backscattering of the seawater itself. Numerous numerical models have been developed to simulate the underwater light field (Mobley et

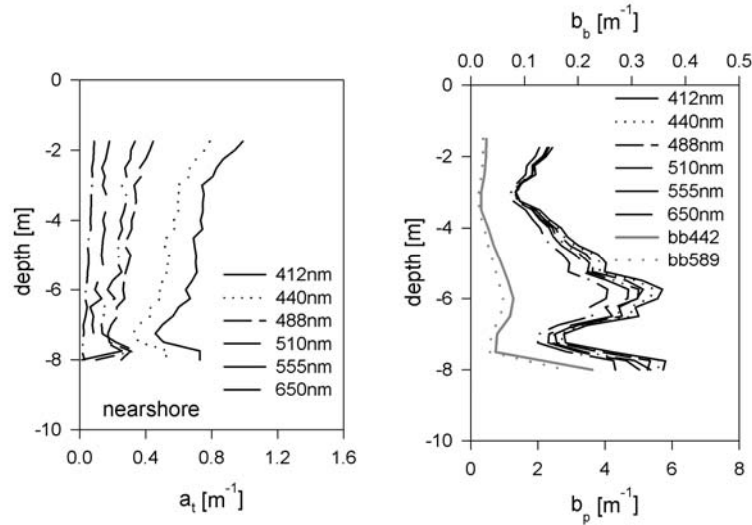


Figure 8. Water column profiles of absorption a_t (left panel) and scattering b_p (right panel) spectra (412, 440, 488, 510, 555, 650 nm) for a coastal nearshore location. Backscattering, $b_b(442)$ and $b_b(589)$ are also shown (— and in the right panel).

al., 1993). The underwater light field is most frequently defined in terms of irradiance (e.g., downwelling irradiance) since it is important in photosynthesis and plays a central role in the theory of radiation transfer in water (Kirk, 1994). The spectral composition and intensity of the downwelling light flux or the downwelling irradiance $E_d(\lambda, z)$ changes progressively with increasing depth z as a result of its interaction with seawater and its constituents through the process of absorption and scattering. $E_d(\lambda, z)$ diminishes in an approximately exponential manner with depth and is given by

$$E_d(\lambda, z) = E_d(\lambda, 0) e^{-K_d(\lambda) z}, \quad (27)$$

where $E_d(\lambda, z)$ and $E_d(\lambda, 0)$ are the values of downward irradiance at depth z meters and just below the surface respectively.

Kirk (1984) determined a relationship between the diffuse attenuation coefficient K_d and absorption a and scattering b using a Monte Carlo model of the propagation of photons underwater. This model was used to extract the IOPs of absorption and scattering in a turbid estuary from *in situ* radiometric measurements (Gallegos et al., 1990). A similar study using modeled derived IOPs (a and b) from radiometric estimates of AOPs (R_{rs} and K_d) (Morel and Gentili, 1993; Gordon, 1989) showed good agreement with field measurements of a and b in the blue-green region of the spectrum (McKee et al., 2003).

The behavior of the light field E_d , K_d and IOPs for two coastal locations is illustrated in Figure 9. The top panel shows the changes in the spectral downwelling light field with depth at a nearshore and offshore locations. The spectra of the attenuation coefficient for downwelling irradiance $K_d(\lambda)$ for surface waters are shown in the mid row, while the corresponding profiles of total absorption (at 440 nm) and chlorophyll are shown in the bottom panel. The light level diminishes rapidly at the nearshore location in the blue waveband ($\sim 1\%$ at 5 m depth) in comparison to the offshore location where the 1% level in the blue is at ~ 30 meters. At the nearshore coastal location, light attenuation in the blue due to absorption by high levels of CDOM and phytoplankton is

comparable to that in the red. In contrast, at the offshore location, the light level diminishes much more slowly in the blue than in the red. Significant differences are observed in the spectral diffuse attenuation coefficients $K_d(\lambda)$ at the two coastal locations that can be attributed primarily to absorption by particulate and dissolved components in seawater (D'Sa et al., 2002b).

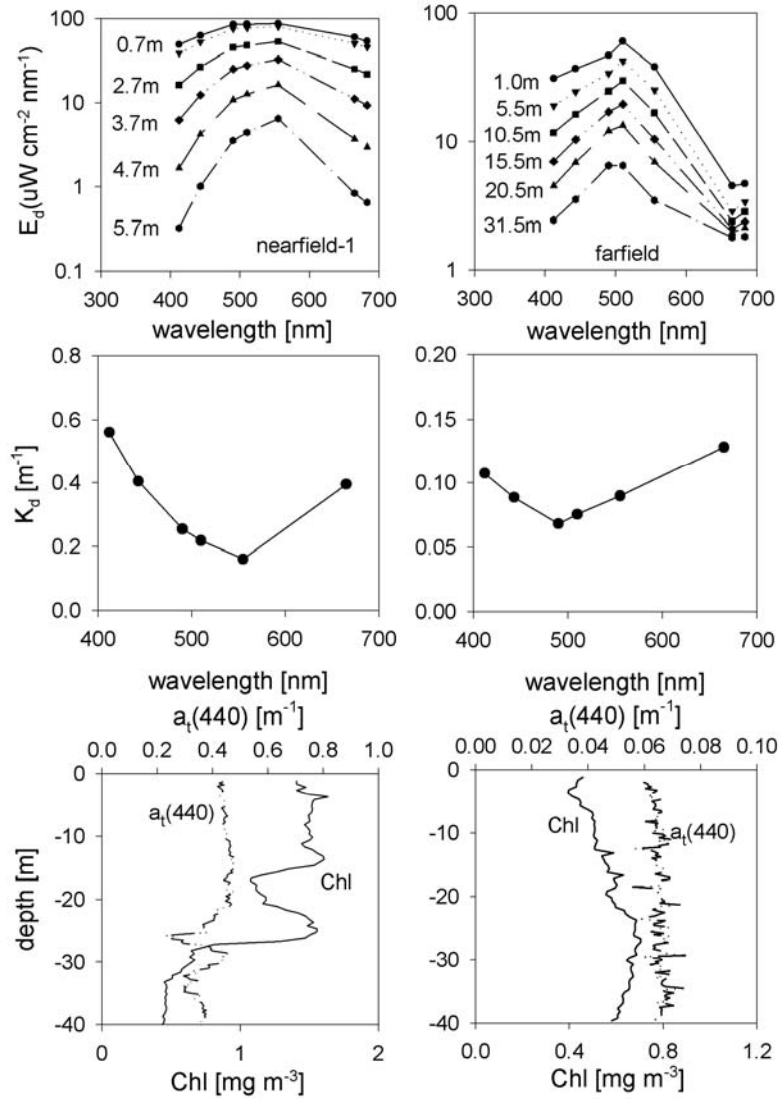


Figure 9. Spectral downwelling light field at various depths at a nearshore (left panel) and an offshore location (right panel). Spectral diffuse attenuation coefficient $K_d(\lambda)$ in surface waters (mid row) and (c) vertical profiles of absorption (particulate plus CDOM) at 440 nm and chlorophyll (bottom row) are shown for the same locations.

Remote sensing reflectance or water-leaving radiance defines the color of the ocean that contains information on the inherent optical properties and the seawater constituents. In analyzing the spectral reflectance curves obtained from Case 1 and 2 waters (Morel and Prieur, 1977), it was observed that the spectra were modified in different ways by the seawater constituents through their effects on absorption and scattering properties. Observations from a 3-year field program in the Santa Barbara Channel, California (Toole and Siegel, 2001) showed that the remote sensing reflectance variability was tightly coupled to biologically and terrestrially derived particles, with the largest variability in the spectra determined by the backscattering processes.

The basic relationship between remote sensing reflectance and the IOPs (e.g., Eq. (6)) or its approximations (Morel and Prieur, 1977; Gordon and Morel, 1983) derived from numerical simulations of the radiative transfer equation has been used to interpret remote sensing reflectance or ocean color data in terms of seawater optical properties and constituents (Carder et al., 1999; Lee et al., 2002). Volume absorption coefficients of turbid coastal waters determined from R_{rs} were in agreement with field observations for a certain absorption range and were based on assumptions related to sea surface roughness, spectral scattering characteristics and absorption in the near-infrared (Sydor et al., 1998). Bio-optical studies have also considered the need to account for the effects of bottom reflectance, CDOM fluorescence, and water Raman scattering on the remote sensing reflectance signals in coastal waters (Maritorena et al., 1994; Lee et al., 1994, 1998; Ackleson, 2003).

Examples of remote sensing reflectance spectra (shown at wavebands corresponding to the SeaWiFS satellite sensor) in a river dominated coastal environment (Fig. 10) are seen to exhibit two general characteristics. At locations with low surface chlorophyll and CDOM concentrations, the reflectance values were higher in the blue spectral region and exhibited high blue to green ratios (Group 2, Fig. 10). At nearshore locations, higher chlorophyll and CDOM concentrations resulted in low reflectance in the blue wavebands and thus low values in the blue to green ratios (Group 1, Fig. 10). Reflectance at 555 nm was also higher due to backscattering contributions by suspended sediments. This example broadly demonstrates the complexity of the R_{rs} spectra observed in coastal waters.

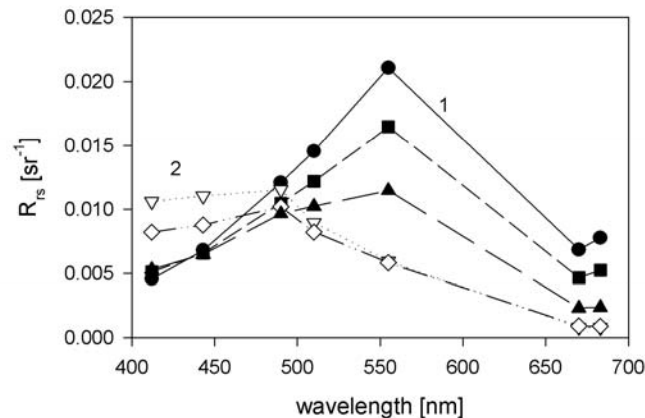


Figure 10. Remote sensing reflectance R_{rs} spectra at various locations in a coastal river dominated region shown at SeaWiFS wavebands. Group 1 (closed symbols) correspond to nearshore locations, while Group 2 (open symbols) correspond to offshore locations.

Empirical algorithms such as the OC2 and OC4 algorithms (O'Reilly et al., 1998) use ratios of remote sensing reflectances (e.g., 412/555, 443/555 or 490/555 nm) to estimate chlorophyll concentrations from atmospherically corrected satellite reflectance signals. Various studies have indicated that the coefficients in the empirical algorithms for chlorophyll may have to be optimized for regional and seasonal conditions (Kahru and Mitchell, 1999; D'Sa and Miller, 2003). Similar empirical algorithms have been developed for CDOM absorption (Kahru and Mitchell, 2001; D'Sa and Miller, 2003). Simple empirical relationships relating water leaving radiance or reflectance and suspended sediments have also been presented for coastal waters (Munday and Alfoldi, 1979; Stumpf, 1988). These studies have demonstrated that empirical algorithms may need to be optimized for regional coastal waters to obtain better estimates of concentrations of seawater constituents.

5. Summary

The application of ocean color remote sensing in coastal waters includes the ability to retrieve various seawater constituents such as chlorophyll, colored dissolved organic matter and suspended sediment concentrations. However, many of the bio-optical and empirical models have been developed mainly for oceanic or the relatively simple Case 1 waters and their application to the optically complex Case 2 waters present many challenges. In this study, we described some of these bio-optical models and assessed their use in coastal waters. A review of bio-optical studies conducted in some coastal waters indicated close linkages between physical and bio-optical properties. As expected, absorption and scattering properties of seawater constituents in coastal waters were observed to be more complex than oceanic Case 1 waters. Scattering and backscattering of particles have been the least studied and new optical instruments provide the potential to obtain a greater understanding of this optical variable and its role in determining ocean color in coastal waters. The spectral composition and intensity of the light field is strongly influenced by the seawater constituents and are reflected in the derived AOPs of diffuse attenuation coefficients and remote sensing reflectance. With increasing number of operational ocean color satellites and improvements in atmospheric correction algorithms, better satellite estimates of water-leaving radiance or remote sensing reflectance are now being obtained. The ability to invert these signals to obtain reliable estimates of the IOPs and seawater constituents is still a major challenge for optically complex coastal waters. While standard empirical ocean color algorithms are being used to obtain estimates of chlorophyll concentrations, a few studies have demonstrated the need for regional empirical algorithms to locally optimize such estimates. Increasing such bio-optical studies is the key to better utilization of ocean color satellite data for coastal waters.

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