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Variability in Ocean Color Observations and
Their Use in the Study of Upper Ocean
Ecosystem Dynamics

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by

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ABSTRACT

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by

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Is there more information in the color of the sea than just a simple measure of the chlorophyll pigment concentration? To answer this question, two basic tools are employed: statistical analysis and mathematical modeling. First, an extensive data set of in situ particulate absorption spectra is analyzed to assess the potential of using ocean color imagers to examine variability in the structure of the near-surface ocean planktonic ecosystem. The important result from this study is that ocean color will reflect only three statistically significant components: the total amount of particulate material, the relative amounts of chlorophyll-containing biomass and detrital materials. Thus, it is unlikely that robust global algorithms for determining particular phytoplankton groups can be developed from remotely sensed ocean color data. These results led the development of a nonlinear ocean color inversion model to maximize the information found in ocean color observations for the analysis of biogeochemical variability. The implementation of this model for the inversion of ocean color spectra results in estimates of concentrations of relevant dissolved and suspended materials found in the ocean including: 1) phytoplankton and phytoplankton pigments, 2) colored dissolved and detrital materials, and 3) inorganic suspended and particulate materials. Accurate estimates of these quantities can then be used in the analysis of biogeochemical variability in the worlds oceans. This inversion approach has been successfully applied to in situ ocean color measurements from the Sargasso Sea. Last, the IOP ocean color inversion model is applied to a global data set of in situ ocean color observations. The results indicate that model performance is strongly dependent upon the IOP shape functions assumed. The simple methods for parameterizing these spectral shapes result in a globally applicable inversion model that can be applied to satellite imagery.
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Chapter 1: Ocean Color From Space

"These different waters may also be sometimes discernible by a difference in their colour, a contrast of shades of blue and green making a line across the sea........ If these marked colour changes can be correctly interpreted we may in the future find aircraft being used to make rapid surveys of the surface conditions in relation to the fisheries."

Sir Alister Hardy, The Open Sea, 1929

The world's oceans cover approximately 70% of the Earth's surface and are central to the continued existence of life on our planet. However, until the recent advent of ocean color remote sensing, knowledge of the oceans was limited to what could be observed and sampled from shipboard or along coastlines. The research presented here is concerned with how the color of the ocean can be used to provide information about the functioning of the ocean's ecosystems. Determinations of the color of the sea have been used previously to provide a single index of the ocean's health, the chlorophyll pigment concentration, which is found in all algae. This follows our intuitive feel for most natural aquatic systems; the more algae in the water, the greener it will appear. This simple fact is the basis of satellite remotely sensed determinations of ocean chlorophyll which was provided from the completed Coastal Zone Color Scanner (CZCS) ocean color satellite mission. The CZCS operated on NASA's Nimbus-7 satellite from 1978-1986, and has caused a revolution in the way oceanographers view the biological, chemical and physical interactions in the world's oceans. Satellite ocean color science will grow dramatically over the next 5 years with as many as 10 satellite ocean color sensors deployed. Hence, it is imperative that detailed ocean color science investigations be conducted now.

The color of the ocean is determined by the absorption and scattering characteristics of water itself, as well as the dissolved and particulate constituents
found in seawater. These include phytoplankton, microscopic plants that float freely in the lighted surface waters, and dissolved and detrital materials of marine and terrigenous origin. For example, productive water with a high concentration of plankton will appear blue-green, while very pure water appears deep-blue. From space, as well as from ships and moorings, these variations in ocean color can now be measured with sensitive optical instruments. These measurements in turn can be used in models to yield information on the variability in the ocean's biogeochemical parameters.

For example, simple, semi-empirical equations can be used to estimate the concentration of chlorophyll-a and its degradation products from optical measurements of backscattered sunlight at three wavebands centered at 443, 520, and 550 nm, covering the blue and green regions of the spectrum. These radiances are not merely reflected from the sea surface, but are derived from sunlight that has entered the ocean, been selectively absorbed, scattered and reflected by the phytoplankton and other suspended materials in the euphotic zone, and then backscattered through the surface. This approach permits quantitative estimates of phytoplankton pigment concentrations within the upper tens of meters of the open ocean, and within somewhat lesser depths in coastal waters.

These estimates in turn have many important applications such as modeling primary production and in turn examining ocean biogeochemistry, particularly with respect to carbon. The magnitude and variability of primary production are poorly known on a global scale, largely because of the high spatial and temporal variability of marine phytoplankton concentrations. Oceanographic vessels move too slowly to map dynamic, large-scale variations in productivity, thus global coverage by shipborne instruments is impossible. Only satellite observations can provide the rapid, global coverage required for studies of ocean productivity worldwide. Phytoplankton and their rate of primary production are an important piece of the global carbon cycle puzzle. The carbon dioxide in the atmosphere is in balance with carbon dioxide in the ocean. During photosynthesis phytoplankton remove carbon dioxide from sea water (and release oxygen as a by-product). This allows the oceans to absorb additional carbon dioxide from the atmosphere. If fewer
phytoplankton existed, atmospheric carbon dioxide would increase. Importantly, dead phytoplankton can sink to the ocean floor and are then covered by other material. In this way, the oceans act as a sink for global carbon.

Important questions regarding the oceans role in the global carbon cycle remain unanswered, such as; 1) What is the rate of carbon flux from surface waters to the deep sea?, and 2) How is the sedimentation rate related to the rate of primary production? To help answer these questions a suite of new ocean color imagers have been or are soon to be launched. In combination with large-scale international programs such as the Joint Global Ocean Flux Study, the World Ocean Circulation Experiment (WOCE), the Tropical Ocean Global Atmosphere Programme (TOGA), and the International Geosphere-Biosphere Programme (IGBP), these observations will greatly advance our knowledge of biological oceanography, global biogeochemical cycles, and the Earth's climate in the years ahead. Potential sources for these new observations include three ocean color scanners scheduled for flight within this decade including; 1) the first United States successor to the CZCS, the Sea-Viewing Wide Field Sensor (SeaWiFS) due to launch in June of 1997 by NASA in conjunction with private industry, 2) The Ocean Color and Temperature Sensor (OCTS) has been recently launched by Japan, and 3) NASA is also planning a Moderate Resolution Imaging Spectrometer (MODIS) and a High Resolution Imaging Spectrometer (HRIIS) for the first Polar Orbiting Platform of the Earth Observing System (EOS), due to launch in the late 1990's.

In this body of work the central question asked is, "Is there more information in the color of the sea than just a simple measure of the chlorophyll pigment concentration?". To answer this question, two basic tools are employed; statistical analysis and mathematical modeling. First, an extensive data set of in situ particulate absorption spectra is analyzed to assess the potential of using ocean color imagers to examine variability in the structure of the near-surface ocean planktonic ecosystem (Chapter 2). Particulate absorption spectra are a measure of the absorption properties of particles found in the water column and are the primary source of variability in ocean color observations. The important result from this study is that ocean color will reflect only three statistically significant components:
the total amount of particulate material, the relative amounts of chlorophyll-containing biomass and detrital materials. Thus, it is unlikely that robust global algorithms for determining particular phytoplankton groups can be developed from remotely sensed ocean color data. This work has been published as Garver, S.A., D.A. Siegel and B.G. Mitchell, 1994, Variability in near-surface particulate absorption spectra: What can a satellite ocean color imager see? *Limnology and Oceanography*, **39**, 1349-1367.

These results led the development of a nonlinear ocean color inversion model to maximize the information found in ocean color observations for the analysis of biogeochemical variability (Chapter 3). The implementation of this model for the inversion of ocean color spectra results in estimates of concentrations of relevant dissolved and suspended materials found in the ocean. Examples of these include: 1) phytoplankton and phytoplankton pigments, the basis of the food web in the ocean, 2) colored dissolved and detrital materials, the breakdown products of organic matter, and 3) inorganic suspended and particulate materials of both marine and terrigenous origin. Accurate estimates of these quantities can then be used in the analysis of biogeochemical variability in the worlds oceans, including phytoplankton distributions, primary production rates, and biogenic gas fluxes. This inversion approach has been successfully applied to in situ ocean color measurements from the Sargasso Sea and is currently in press in the *Journal of Geophysical Research-Oceans* entitled "Inherent optical property inversion of ocean color spectra 1. Time series from the Sargasso Sea", S. A. Garver and D. A. Siegel.

Last, the IOP ocean color inversion model is applied to a global data set of in situ ocean color observations (Chapter 3). The results indicate that model performance is strongly dependent upon the IOP shape functions assumed. The simple methods for parameterizing these spectral shapes result in a globally applicable inversion model that can be applied to satellite imagery. This chapter "Global application of the UCSB non-linear inherent optical property model" is currently in press as part of the SeaWiFS technical memorandum series (Volume 43).
Chapter 2: Variability in Near Surface Particulate Absorption Spectra—What Can a Satellite Ocean Color Imager See?

Abstract

An extensive database of approximately 400 in situ particulate absorption spectra ($a_p(\lambda)$) is analyzed to assess the potential of using ocean color imagers to examine variability in the structure of the near surface ocean planktonic ecosystem. This application of $a_p(\lambda)$ data is appropriate as particulate absorption variations are the dominant source of ocean color variation, and are attributable to changes in the phytoplankton community structure. Empirical orthogonal function analyses are used to estimate the contribution of each statistical mode to the total variance. The EOF analyses showed that >99% of the variance found in the $a_p(\lambda)$ dataset can be simply attributed to the total amount of particulate material. When this source of variability is removed, two significant modes of variability may be identified which comprise 79% and 18% of the normalized variance. These modes are interpreted as representing the relative contribution of chlorophyll containing biomass and detrital materials, verifying the use of two component phytoplankton-detritus models to partition $a_p(\lambda)$. Only a very small amount of the total $a_p(\lambda)$ variability (less than 0.5% of the total) can be attributed to absorption features due to accessory pigment groups. Thus, variability in $a_p(\lambda)$ is almost entirely associated with the quantity of the absorbing materials rather than their spectral quality (or normalized spectral shape). These results suggest that remotely-sensed ocean color spectra will reflect only three statistically significant components: the total amount of particulate material, and the relative amounts of chlorophyll-containing biomass and detrital materials. Our results suggest that for most typical conditions it is unlikely that robust global algorithms for determining particular phytoplankton groups from remotely-sensed ocean color spectra can be developed.

Introduction

Future global ocean observing systems will utilize remotely sensed quantities to monitor the biogeochemical processes of the world’s oceans. Among the
processes scientists wish to investigate are biogenic gas fluxes and primary production rates, as well as variations in phytoplankton distributions. To date, ocean color imagers, such as the Coastal Zone Color Scanner (CZCS), have been used to produce imagery of pigment biomass (chlorophyll $a$ plus pheopigment concentrations; Hovis et al. 1980; Gordon and Morel 1983). The question arises as to the feasibility of using satellite sensors, such as the forthcoming Sea-viewing Wide Field of View Sensor (SeaWiFS), and higher spectral resolution sensors planned for the latter part of this decade, to study the structure of the marine ecosystem beyond simple chlorophyll estimates. Our study is aimed at evaluating this question.

In situ optical quantities, can be linked to ocean color observations using remote sensing reflectance values ($R_{rs}(\lambda)$; where $R_{rs}(\lambda)$ is the subsurface ratio of upwelling radiance, $L_u(\lambda)$, to downwelling irradiance, $E_d(\lambda)$). Values of $R_{rs}(\lambda)$ quantify the water leaving radiance, $L_w(\lambda)$ (when corrected for air-sea interface transmission), that would be sensed by a satellite sensor. Theoretical studies show that $R_{rs}(\lambda)$ may be related to the inherent optical properties of the water column, namely the backscattering and absorption coefficients (e.g., Gordon et al. 1988), and represents the link between in situ ocean optical properties and satellite derivable quantities. The relationship between $R_{rs}(\lambda)$ and inherent optical properties may be approximated by

$$R_{rs}(\lambda) = \frac{L_u(\lambda)}{E_d(\lambda)} = C_1 \frac{b_b(\lambda)}{a(\lambda) + b_b(\lambda)}$$  

where $b_b(\lambda)$ is the backscattering coefficient, $a(\lambda)$ is the absorption coefficient, and $C_1$ is a constant (e.g., Gordon et al. 1988).

Experimental data and theory indicate that under most conditions values of $b_b(\lambda)$ are relatively small compared to values of $a(\lambda)$ and decrease monotonically with respect to wavelength (e.g., Gordon and Morel 1983). Recent modeling studies have concluded that particles less than 1 $\mu$m in size dominate the $b_b(\lambda)$ signal (Morel and Ahn 1991). They suggest that these particles are comprised primarily of heterotrophic bacteria and submicron size detritus. Direct measurements of $b_b(\lambda)$ for phytoplankton cultures support this notion of insignificantly low backscatter coefficients for most algal groups (Ahn et al. 1992). An exception to this are nanoplancton-sized coccolithophores which have a characteristically large backscatter signal (Gordon et al. 1988; Balch et al. 1991). For the purposes of this
study, we will assume that spectral variations in $R_{\text{out}}(\lambda)$ and hence, the water leaving radiance, primarily reflects spectral variations in the absorption coefficient.

The absorption coefficient for natural waters is comprised of the absorption coefficients for pure seawater, $a_w(\lambda)$, particulates, $a_p(\lambda)$, and dissolved materials, $a_d(\lambda)$, or

$$a(\lambda) = a_w(\lambda) + a_p(\lambda) + a_d(\lambda).$$  \hspace{1cm} (2)

Changes in $a(\lambda)$ will be caused by variations in $a_p(\lambda)$ and $a_d(\lambda)$, as $a_w(\lambda)$ is constant (Smith and Baker 1981). In case I waters (where optical properties are regulated by phytoplankton and their degradation products), spectral variations in $a(\lambda)$ are primarily dominated by particulate absorption. Although $a_d(\lambda)$ values can be significant relative to $a_p(\lambda)$, their values decrease monotonically with increasing wavelength, hence their ultimate effect would be to accentuate values in the blue portion of the spectrum as opposed to having a large role in the overall shape of $a(\lambda)$ (Carder et al. 1991). Therefore, particulates should be the major contributor (particularly in case I waters) to both magnitude and shape variations in absorption spectra and thereby, ocean color.

Particulate absorption is comprised of absorption due to viable phytoplankton and detrital materials, or

$$a_p(\lambda) = a_{\text{ph}}(\lambda) + a_{\text{det}}(\lambda).$$  \hspace{1cm} (3)

Phytoplankton absorption can vary with changes in growth rate, cellular pigment concentration and composition (e.g., Bidigare et al. 1987; Mitchell and Kiefer 1988a; Sosik and Mitchell 1991). The spectral shape of phytoplankton absorption results from the combination of chlorophyll $a$ and accessory pigments which absorb light in specific regions of the visible spectrum modified by their packaging within the cell. The package effect describes the decreased specific absorption of algae due to varying cellular content of pigments and varying cell size (Morel and Bricaud 1981; Kirk 1983).

For case I waters, there are three main pigment groups of interest: chlorophylls, carotenoids and phycobilins (e.g., Kirk 1983; Hoepffner and Sathyendranath
The most prominent pigment absorption peaks are for chlorophyll $a$, and are centered at 435 nm and 675 nm. Chlorophyll $a$ is found in all algal groups and plays a central role in photosynthesis. Chlorophyll $b$, found in green algae, absorbs light at wavelengths centered around 470 to 490 nm and at 650 nm. Chlorophyll $c$, contained in diatoms, dinoflagellates, and chrysophytes absorbs light at wavelengths centered around 450 and 630 nm. Carotenoids absorb over a broad band with peak absorption from 475 to 540 nm and are contained in diatoms, chlorophytes, chrysophytes, dinoflagellates, cyanobacteria and prymnesiophytes. The phycobilin pigments include phycocyanin which absorbs in the 580 to 600 nm range, and phycoerytherin, which contains the two chromophores phycoerythrobilin and phycourobilin that absorb in the range 540 to 565 nm and 480 to 500 nm, respectively. These pigments are present in differing proportions in the various species of cyanobacteria, red algae and cryptomonads (Campbell and Iturriaga 1988).

Detrital absorption spectra typically decrease monotonically with increasing wavelength (e.g., Mitchell and Kiefer 1988b; Iturriaga and Siegel 1989; Bricaud and Stramski 1990). Sometimes, absorption peaks due to pheopigment concentrations are observed near 416 and at 685 nm. However, this seems only to occur preferentially deeper in the water column or for coastal environments due to the effects of grazing or photooxidation (Kiefer and SooHoo 1982; Iturriaga and Siegel 1989).

In summary, for case I waters, the spectral variations in $a(\lambda)$, and hence, $R_{\alpha}(\lambda)$, are caused primarily by changes in $a_p(\lambda)$. In order to evaluate the expected spectral signatures in satellite-sensed color spectra, the spectral structure of $a_p(\lambda)$ may be used as a reasonable surrogate. Here, an extensive global data base of in situ $a_p(\lambda)$ is compiled and statistically analyzed using empirical orthogonal function and multidimensional regression analyses to evaluate what ocean ecosystem properties can be determined using ocean color imagery.

**Particulate absorption database**

The database for this study consists of the results of 11 individual cruises from case I waters, totaling 407 $a_p(\lambda)$ spectra, chlorophyll $a$ and pheopigment determinations (Table 1). These data are from a variety of seasons, locations, and depths including open ocean sites in both the Atlantic and Pacific Oceans, and coastal sites within the California Current. While the dataset is not "global" in the sense that it
does not account for all locations and conditions, it does represent many of the major oceanic provinces. The open ocean sites include the Sargasso Sea (Biowatt 85 and Biowatt 87 cruises; Biowatt 87 is a compilation of 4 separate seasonal cruises during 1987), the North Pacific from the Aleutian Islands to Hawaii (RITS-90 cruise), and the South Pacific near Tahiti (Calypso-86 cruise). These open ocean cruises total 68% of the $a_p(\lambda)$ dataset. The coastal sites are all from the California Current off southern California and include the NASA-86 experiment, CLOSURE-90, Watercolors-88 and CalCOFI-90 cruises. The NASA-86 experiment was performed about 1 km off the Scripps pier in La Jolla, California and was the most eutrophic of the cruises; the mean chlorophyll $a$ for this time series was $1.88 \text{ mg m}^{-3}$ compared to the total dataset chlorophyll $a$ mean of $0.72 \text{ mg m}^{-3}$.

All the spectra are from case I waters, where optical properties are regulated by phytoplankton and their degradation products. For this study, the data analyzed are limited to those samples from within the mixed layer or above the 10% PAR depth (photosynthetically available radiation; operationally 30 m). The 10% PAR depth ($z_{90}$) is defined as the depth where the downwelling PAR flux is 10% of its value at the surface. Less than 10% of the contribution to $R_{rs}(\lambda)$ results from photons which have reached beyond this depth (Smith and Baker 1981; Gordon and Morel 1983).

The $a_p(\lambda)$ measurements were determined primarily using the quantitative filter technique (QFT; Yentsch 1957; Mitchell and Kiefer 1988a; Mitchell 1990) with the exception of the Watercolors-88 cruise (Nelson et al. 1993). For the QFT technique, sea water samples are concentrated onto glass fiber filters (generally, Whatman GF/F) and the optical density of the filter ($OD_f$; relative to a wet blank filter) is measured with a spectrophotometer (Truper and Yentsch 1967; Kiefer and SooHoo 1982; Mitchell 1990). The $OD_f$ are transformed into absorption coefficients by accounting for the error due to pathlength amplification, the $\beta$ factor. The $\beta$ factor is the result of multiple scattering by the filter and is defined as the ratio of the optical to geometric pathlength (Butler 1962). Variations in the relationship between $\beta$ and $OD_f$ can influence both the magnitude and steepness of individual $a_p(\lambda)$ spectra (e.g., Mitchell 1990). The $\beta$ algorithms used to convert the $OD_f$ measurements into $a_p(\lambda)$ are tabulated in Table 1. The Watercolors-88 samples were filtered using 0.4 $\mu$m Nuclepore membrane filters and then resuspended (with correction for loss of pigment) in filtrate by 30 seconds of gentle agitation (Nelson et al. 1993). The $OD_s$ (where $OD_s$ is the optical density of the sample in
suspension) of the resulting concentrated suspensions were then measured with a spectrophotometer and transformed into $a_p(\lambda)$. Chlorophyll and pheopigment determinations for all cruises were determined fluorimetrically by standard techniques.

Results

Statistical moment analysis

Mean and standard deviation spectra for the near surface $a_p(\lambda)$ database (Fig. 1) demonstrate a strong similarity between the two shapes. Chlorophyll $a$ absorption peaks are evident at 435 and 675 nm. Suggestions of accessory pigment absorption shoulders can be seen at 470 nm and 540 nm. High levels of absorption between 400 and 440 nm indicates that detrital materials are also important. The standard deviation is larger than the mean spectral signature for all wavelengths, resulting in a spectrally averaged coefficient of variation greater than one (1.3). This illustrates the high degree of variability in the $a_p(\lambda)$ dataset. The similarity between the mean and standard deviation spectral shapes indicates that there is an underlying basic shape for $a_p(\lambda)$ and that $a_p(\lambda)$ variability is primarily due to differing amounts of absorbing material.

The mean spectral signatures for the individual cruises comprising the $a_p(\lambda)$ dataset (Fig. 2a and b) show large inter-cruise differences. The smallest cruise mean $a_p(\lambda)$ are for the Biowatt 87 cruises from the Sargasso Sea whereas the largest mean $a_p(\lambda)$ is found for the NASA-86 experiment. The results of this experiment dominates the statistical moments of our dataset. The NASA-86 spectral and experimental mean $a_p(\lambda)$ is $0.05 \pm 0.03$ m$^{-1}$ which is much larger than the global mean of $0.018 \pm 0.022$ m$^{-1}$. A large degree of intra-cruise variability is also observed (Fig. 2c and d). The coefficients of variation for the individual cruises range from 0.5 to 0.9. Comparisons of the spectral shapes of the means and standard deviations for each cruise show the same marked similarity seen in the global $a_p(\lambda)$ statistics. This similarity between the global and cruise means and standard deviations, as well as the high coefficients of variation, indicates that variations in $a_p(\lambda)$ reflect, to first order, changes in the amount of absorbing material. Thus, to assess the sources of variability in $a_p(\lambda)$ spectra the data must be normalized to
remove this dominant biomass signal.

The \( a_p(\lambda) \) dataset was normalized in two ways. First, the *chlorophyll specific* particulate absorption coefficient, \( a_p^{*_{Chl}}(\lambda) \) (where \( a_p^{*_{Chl}}(\lambda) = a_p(\lambda)/\text{Chl} \ a) \), was calculated. The mean and standard deviation spectral signatures for the *chlorophyll specific* dataset are still similar in shape, with the standard deviation spectra being reduced in comparison to the mean due to the normalization by chlorophyll \( a \) (Fig. 3). This reduction is further indicated by the spectrally averaged coefficient of variation which has decreased to 0.66. Peaks due to absorption by chlorophyll \( a \) remain evident at 440 and 675 nm, as does the high absorption due to detritus from 400 to 440 nm. The mean and standard deviation spectral signatures for the individual \( a_p^{*_{Chl}}(\lambda) \) cruise datasets are still similar in shape and show that *inter*-cruise (Fig. 4a and b), and *intra*-cruise (Fig. 4c and d) variability still remains. The similarity of the mean and standard deviation spectra and the coefficient of variation indicates that chlorophyll is removing only a portion of the variance necessary to act as a sufficient normalizer for examining shape differences in the \( a_p(\lambda) \) database (see Fig. 7).

A second attempt in normalizing the \( a_p(\lambda) \) dataset was made using the spectral mean of each \( a_p(\lambda) \) spectra, \( \langle a_p \rangle \) (Fig. 5; Mitchell and Kiefer 1988b). This results in what we will refer to as the *optical biomass specific* particulate absorption coefficient, \( a_p^{*_{<ap>}}(\lambda) \) (where \( a_p^{*_{<ap>}}(\lambda) = a_p(\lambda)/\langle a_p \rangle \)). The mean and standard deviation spectra for this normalized dataset are no longer similar and the relative magnitude of the standard deviation spectra has been greatly reduced (Fig. 5). The spectrally averaged coefficient of variation for the global \( a_p^{*_{<ap>}}(\lambda) \) database has decreased significantly to 0.12. The mean signature still indicates the presence of chlorophyll \( a \) absorption at 440 and 675 nm, with a slight shoulder at 470 nm (perhaps due to chlorophyll \( b \) absorption). The mean and standard deviation signatures for the individual \( a_p^{*_{<ap>}}(\lambda) \) cruises (Fig. 6) show that the large *inter*-cruise and *intra*-cruise differences have also decreased significantly. The low coefficient of variation and the reduction in the standard deviation spectra indicates that \( \langle a_p \rangle \) values are a more effective normalizer than chlorophyll \( a \) determinations.

Further indication of the effectiveness of using \( \langle a_p \rangle \) values over chlorophyll concentrations for normalization is shown in the percent of spectral variance explained by each normalizer (Fig. 7). Values of \( \langle a_p \rangle \) explain approximately 83% of the variance at each wavelength and exhibit little significant spectral variation.
This is in contrast to the relatively low hindcast skill (69.5%) found using chlorophyll concentrations. Further, the hindcast skill for chlorophyll concentration shows a high degree of spectral variability. In particular, chlorophyll values explain the most variability near 675 nm, the chlorophyll a absorption peak.

**Spectral modes of variability**

Empirical orthogonal function (EOF) analysis was used to examine the contribution of both phytoplankton and detrital materials to the basic scales of variability found in the \( a_p(\lambda) \) dataset. EOF analysis is a useful tool for combining a large number of factors (in this case wavelengths) into a smaller number of uncorrelated components. This analysis has been widely used in meteorology (Lorenz 1956), and physical (Davis 1976) and biological oceanography (Mueller 1976; Eslinger et al. 1989).

The EOF method finds a new coordinate system for a multivariate dataset such that the first coordinate, or EOF mode, contains the highest degree of variance, the second mode has the next highest degree of variance and is orthogonal to the first (their product sums to zero), and so forth. EOF analysis does not operate directly on the data themselves but instead on a summarization of the data, the covariance matrix. This symmetric matrix contains the variances of each wavelength in the leading diagonal and covariance values elsewhere. The EOF analyses used here associate the spectral modes of variability found in the \( a_p(\lambda) \) database with known absorption spectra for specific phytoplankton pigments, detritus or other materials. EOF analyses were performed on the global and individual cruise \( a_p(\lambda) \), \( a_p*_{<sp>}(\lambda) \), and \( a_p*_{Chl}(\lambda) \) datasets.

The spectral covariance plot for the global \( a_p(\lambda) \) dataset (Fig. 8) reflects the general character of the dataset. The wavelengths in the blue and green regions of the spectrum have the highest values of covariance and generally covary with one another and with wavelengths in the red portion of the spectrum (660 to 690 nm).

The first EOF mode for the global \( a_p(\lambda) \) analysis contains more than 99.9% of the variance (Fig. 9) and its shape closely resembles the standard deviation signature for the total dataset (Fig. 1). This indicates that the shapes of particulate absorption spectra are nearly identical, only their amplitudes vary. Hence, this EOF mode is interpreted as reflecting variations in the total particulate or optical biomass mode. The EOF analyses performed on the individual \( a_p(\lambda) \) cruises (not
shown) exhibited similar results. The second EOF mode, though very small (0.01% of \(a_p(\lambda)\) variance), hints at chlorophyll absorption at 675 nm and a broad peak from 440 to 500 nm being inversely correlated with detrital absorption at 400 nm. In order to address the remaining variance in \(a_p(\lambda)\), the dominant variability caused by this optical biomass mode must be removed. Subsequent EOF analyses were then performed on both the global and individual cruise \(a_p * \text{Chl}(\lambda)\) and \(a_p * \text{cap}(\lambda)\) datasets.

The EOF analysis of the global and individual \(a_p * \text{Chl}(\lambda)\) datasets shows similar results (not shown) as the \(a_p(\lambda)\) EOF analysis. Again, more than 99% of the variance is contained in the first mode, and its shape is similar to the spectral standard deviation signature for the \(a_p * \text{Chl}(\lambda)\) dataset (Fig. 3). These results are consistent with the fact that the \(a_p * \text{Chl}(\lambda)\) dataset still contains a relatively high degree of variability (Fig. 3). This again indicates that chlorophyll \(a\) concentrations only account for a portion of the variance in \(a_p(\lambda)\) (see Fig. 7).

EOF analyses performed on the global and individual cruise \(a_p * \text{cap}(\lambda)\) datasets illustrate a different picture (results from the individual cruises are not shown). The covariance matrix of the \(a_p * \text{cap}(\lambda)\) dataset shows that normalization with \(<a_p>\) values has removed a significant amount of the variance due to the optical biomass mode (Fig. 10). A smaller portion of the blue region covaries with itself and with wavelengths in the red portion of the spectrum (675 nm). Regions of inverse correlation are seen between 540 and 440 nm, and between 675 and 410 nm.

The EOF analysis for \(a_p * \text{cap}(\lambda)\) shows two important modes of variability (Fig. 11), comprising 77% and 19% of the variance, respectively. The first mode reflects the presence of particulate absorption at shorter wavelengths (400 to 430 nm region) inversely correlated with the lack of absorption in the 540 to 550 nm region. The spectral shape of this mode still has the characteristic shape of a particulate absorption spectrum except it lacks the chlorophyll \(a\) absorption peak at 675 nm. We interpret this first mode as an indicator for the presence or absence of detrital materials per unit optical biomass. The second mode illustrates an inverse relationship between detrital absorption (400 nm) and chlorophyll absorption bands (440, 470, and 675 nm). The third mode contains only 3% of the \(a_p * \text{cap}(\lambda)\) variance and thus is relatively unimportant. However, its shape is suggestive of the influence of accessory pigments where peaks at 460 and 480 nm are inversely
related with the chlorophyll a absorption peak at 675 nm and detrital absorption at 400 nm. In total, greater than 99% of the variance found in the \( a_p * \text{c} \) \( \lambda \) dataset is contained in the first three modes.

Further EOF analyses were performed to address the question of regional differences. The \( a_p(\lambda) \) spectra were stratified by region into open ocean and coastal datasets (Table 1) and \( a_p(\lambda) \) and \( a_p * \text{c} \) \( \lambda \) EOF analyses were performed. The results of these regional analyses are similar to the results for the global dataset (not shown). EOF analyses for both illustrate a single mode of variability which dominates variability in \( a_p(\lambda) \). When this optical biomass signal is removed through normalization by \( a_p \), two additional modes are found which may be attributed to detrital and chlorophyll absorption. The spectral shapes and percent variance of the EOF analyses varies somewhat between the two regions and in comparison to the total dataset. However, interpretation of the EOF results remain the same.

The fact that the entire global database can be compressed into only one significant mode of variability for \( a_p(\lambda) \) and two modes of variability for \( a_p * \text{c} \) \( \lambda \) illustrates the overriding similarity of \( a_p(\lambda) \) spectra. EOF analyses of geophysical datasets often require ten or more modes of variability to explain most of the variance in a signal. For example, Davis’ (1976) analysis of sea surface temperature and sea level pressure variability in the North Pacific Ocean required at least 15 modes of variability to explain most of the variance. While in a study similar to ours, Mueller (1976) analyzed ocean color spectra off the coast of Oregon and yielded only two significant modes containing 78% and 17% of the total variance. This data compression by EOF decomposition is significant as it illustrates how similar \( a_p(\lambda) \) spectra are to one another.

**Partitioning of phytoplankton and detrital absorption**

The results of the EOF analyses suggest that the constituents that comprise \( a_p(\lambda) \) need further investigation. Here we examine the partitioning of \( a_p(\lambda) \) into phytoplankton and detrital components. This partitioning is important for the study of upper ocean ecosystem dynamics as only the phytoplankton can utilize absorbed radiation. Partitioning the dataset will also allow the examination of the statistical content of the residuals for determining any additional sources of variability that may be attributed to specific algal groups or accessory pigments.
The effects of detrital and algal pigment absorption on $a_p(\lambda)$ may be illustrated by examining the variation in chlorophyll $a$ normalized mean particulate absorption values versus chlorophyll $a$ (Fig. 12). Values of $<a_p>/\text{Chl}$ decrease with increasing chlorophyll $a$ for concentrations less than 1.0 mg m$^{-3}$ (slope = -0.57), indicating that chlorophyll specific absorption is concentration dependent. While above this concentration, values of $<a_p>/\text{Chl}$ show little variation with changes in chlorophyll $a$ concentration (slope = -0.03). Similar observations have been made before (Smith and Baker 1978a; Mitchell and Kiefer 1988b; Carder et al. 1991).

The changes observed in $<a_p>/\text{Chl}$ at low chlorophyll $a$ concentrations can be caused by a variety of processes. For example, pigment packaging would result in a decrease in $<a_p>/\text{Chl}$ for increasing intracellular chlorophyll concentration if particle size remains constant (e.g., Morel and Bricaud 1981; Mitchell and Kiefer 1988a; Nelson et al. 1993). However, this decrease in $<a_p>/\text{Chl}$ should be manifest for relatively large cell sizes which typify waters with high chlorophyll concentrations. The changes shown in $<a_p>/\text{Chl}$ only occur for chlorophyll $a$ values less than 1.0 mg m$^{-3}$ which typically suggests smaller cell sizes and thus smaller package effects (Morel and Bricaud 1981; Kirk, 1983). Hence, packaging may not be responsible for the decrease in $<a_p>/\text{Chl}$ seen at low chlorophyll $a$ concentrations. Also, photoadaptation of cellular pigment concentrations should not be important, as the global database discussed here is constructed using data from the upper water column (above the 10% PAR depth).

More likely, the changes in $<a_p>/\text{Chl}$ at low chlorophyll $a$ concentrations are due to the presence of detrital materials. For example, the global mean value of $<a_p>/\text{Chl}$ for this dataset is 0.04 m$^2$ mg$^{-1}$, this is much larger than typical values for the chlorophyll specific absorption due to phytoplankton from either algal cultures or natural waters (0.016 m$^2$ mg$^{-1}$; Bannister 1974; Smith and Baker 1978a; 0.014 m$^2$ mg$^{-1}$; Morel 1978). This difference suggests that detrital materials are responsible for the higher absorption per unit chlorophyll at low chlorophyll concentrations observed in Fig. 12. Hence, to achieve a better understanding of absorption by phytoplankton, $a_p(\lambda)$ needs to be partitioned into $a_{ph}(\lambda)$ and $a_{det}(\lambda)$ components.

The multidimensional regression analysis of Morrow et al. (1989) is chosen for this partitioning procedure. This model is selected for its ease of
implementation, and because it requires neither chlorophyll data nor measurements of $a_p(380)$ (Bricaud and Stramski 1990) which was unavailable for most of the cruises. In addition, other decomposition methods (e.g., Bidigare et al. 1987; Iturrriaga and Siegel 1989) provide good agreement with the Morrow et al. (1989) model (Bidigare et al. 1990) The model partitions $a_p(\lambda)$ into phytoplankton and detrital components using values of spectral absorption at 675 and 570 nm. The values for 675 nm are used in the model to represent the phytoplankton component because chlorophyll $a$ has a primary absorption peak at this wavelength which is uninfluenced by overlapping absorption from accessory pigments. The choice of 570 nm as the wavelength used to represent the detrital component is determined empirically and represents the region of the spectrum where absorption by phytoplankton pigments is at a minimum (Morrow et al. 1989). Individual spectra are partitioned into phytoplankton and detrital absorption coefficients by minimizing the mean square difference between the original and modeled spectra, using

$$\hat{a}_p(\lambda)_n = A(\lambda) \left[ a_p(675)_n - 0.2 a_p(570)_n \right] + B(\lambda) \left[ a_p(570)_n - 0.07 a_p(675)_n \right] \tag{4}$$

where $\hat{a}_p(\lambda)_n$ is the modeled $n$th $a_p(\lambda)$ spectrum ($n = 407$). $A(\lambda)$ and $B(\lambda)$ are the slopes of the regression analysis, with $A(\lambda)$ representing the phytoplankton component and $B(\lambda)$ representing the detrital component (Morrow et al. 1989).

The regression variables, $a_p(675)$ and $a_p(570)$, are modified by subtracting a fraction of the absorption coefficient from the complementary wavelength because the multiple regression analysis minimizes the interaction between the two factors used in the model. If the analysis were performed with unmodified absorption coefficients the slopes of the regression at the two critical wavelengths would approach zero. To adjust the two spectral regression slopes Morrow et al. (1989) performed a microphotometric analysis of detrital particles and intact cells. For detrital particles the average absorption ratio 675:570 was 0.2, for phytoplankton the average ratio 570:675 was 0.07. These results were then used to offset the discrete absorption coefficients for the phytoplankton and detrital components in Eq. 4.

The results from the model (Fig. 13) show each component's contribution to particulate light absorption (averaged over the global database). Phytoplankton, $\bar{a}_{ph}(\lambda)$, contributes 44% of the total particulate absorption, $\bar{a}_p(\lambda)$, when averaged
over all wavelengths. The absorption by detritus, \( a_{\text{det}}(\lambda) \), contributes 54% of the spectrally averaged total, while the residual component, \( a_{\text{res}}(\lambda) \), is 2%. This model indicates that detrital materials make a slightly larger contribution to \( a_{p}(\lambda) \) than phytoplankton. In total, 98% of the variability is explained by two constant spectral components.

As expected, phytoplankton materials contribute primarily to particulate absorption in spectral regions corresponding to phytoplankton pigment absorption bands (Fig. 14a). The red chlorophyll \( a \) peak is comprised primarily of algal absorption and contributes \( \approx 90\% \) to \( a_{p}(675) \), while the broad peak between 440 nm (Chl \( a \)) and 500 nm (accessory pigments) comprise \( \approx 55\% \) of \( a_{p}(\lambda) \). The unexplained variance (Fig. 14b) comprises only 2% of the dataset and shows weak contributions in the regions of 400 to 500 nm (with peaks at 430 and 455 nm) and at 660 nm. These positive residuals indicate that the Morrow et al. (1989) model underestimates by approximately 5% the contribution to \( a_{p}(\lambda) \) by algal and detrital materials in the spectral region from 400 to 500 nm, and again at 660 nm. While the negative residuals seen in the region from 520 to 575 nm and again at >675 nm indicate that the model is overestimating the contribution to \( a_{p}(\lambda) \) of algal and detrital materials by up to 3% in these regions. When subjected to an EOF analysis, this residual variance yielded no significant information.

The effect of removing the contribution of detrital materials can be seen in the variations in \( \langle a_{\text{ph}} \rangle /\text{Chl} \) versus chlorophyll \( a \) concentration (Fig. 15; where \( \langle a_{\text{ph}} \rangle \) is the spectral mean phytoplankton absorption coefficient for each sample). The slope at low chlorophyll concentrations (< 1.0 mg m\(^{-3}\)) has been reduced to -0.49 (compared to slope = -0.57; Fig. 12) demonstrating the effect that \( a_{\text{det}}(\lambda) \) has on total particulate absorption. Above this threshold, values of \( \langle a_{\text{ph}} \rangle /\text{Chl} \) show little variation with changes in chlorophyll \( a \) concentrations (slope = 0.05), similar to \( \langle a_{p} \rangle /\text{Chl} \) at chlorophyll concentrations above 1.0 mg m\(^{-3}\) (Fig. 12). The database mean value of \( \langle a_{\text{ph}} \rangle /\text{Chl} \) is 0.012 m\(^{2}\) mg\(^{-1}\) which is in good agreement with values from the literature (0.014 to 0.016 m\(^{2}\) mg\(^{-1}\)). There is also some evidence of a weak inverse correlation between \( \langle a_{\text{ph}} \rangle /\text{Chl} \) and chlorophyll \( a \) for values of chlorophyll \( a \) between 0.1 and 1 mg m\(^{-3}\) (e.g. Carder et al. 1991). However, there is a good deal of variability unaccounted for in the \( a_{\text{ph}}(\lambda) \) values. This remaining variance suggests that more sophisticated \( a_{\text{ph}}(\lambda) \) models are required (Bidigare et al. 1987; 1990; Hoepffner and Sathyendranath 1991).
In summary, partitioning \( \tilde{a}_p(\lambda) \) into \( \tilde{a}_{de}(\lambda) \) and \( \tilde{a}_{ph}(\lambda) \) demonstrates the importance of accounting for the contribution of detrital materials. Detrital absorption contributes approximately half of the total particulate absorption, with the greatest contributions for low biomass waters, consistent with previous studies (Mitchell and Kiefer 1988b; Iurriaga and Siegel 1989; Bricaud and Stramski 1990). Detrital absorption masks the photosynthetically relevant absorbed radiation by phytoplankton and its removal is important for the accurate modeling of phytoplankton productivity.

**Discussion**

**Caveats**

Our statistical analysis of a large particulate absorption database makes strong statements concerning the information that can be retrieved from satellite ocean color imagery. Particulate absorption spectra are a useful proxy for ocean color spectra as values of \( a_p(\lambda) \) are responsible for most of the shape variations found in ocean color spectra. However, there are several limitations associated with using these data for this purpose.

Artifacts are associated with both measuring optical densities on glass-fiber filters and converting those measurements into particulate absorption spectra. Unavoidable routine errors from filtration volume estimates and particle distribution on the filters occurs. Also, a significant problem in making \( a_p(\lambda) \) measurements using the QFT technique arises from the large modifications of light transmission when measuring optical densities. These modifications result in a variable \( \beta \) factor which is a non-linear function of the optical density (Mitchell and Kiefer 1988a; Mitchell 1990). Considering all errors, conversion of OD\(_f\) values has an expected overall error of \( \pm 15\% \) (Mitchell 1990).

Additional errors may result from decomposition of cellular pigments during storage, damage to living cells during filtration and postfiltration exposure to air, and imperfect retention of particulate material on the filters (Stramski 1990). These types of errors can bias filter techniques towards an overestimate of detrital materials. The results of this bias will be to distort the resulting spectrum with implications for the partitioning of \( \tilde{a}_p(\lambda) \) into \( \tilde{a}_{de}(\lambda) \) and \( \tilde{a}_{ph}(\lambda) \) and on the results of the present EOF analysis. OD\(_s\) measurements made for the Watercolors-88 data are less likely to be subject to these same errors because they are kept in suspension.
and not exposed to air. However, they do have errors associated with the concentration and resuspension process which are concentration dependent (Nelson et al. 1993).

Errors in fluorimetric chlorophyll a determinations can result in incorrect estimates of chlorophyll a (Trees et al. 1985) due to the presence of chlorophyll b, chlorophyll c, and pheopigments which cannot be isolated from the fluorescence signal. The presence of these pigments can cause chlorophyll a to be both over and underestimated and could potentially affect the $a_p *_{\text{Chl}} (\lambda)$ analyses. Also, the relative contribution of divinyl chlorophyll a to monovinyl chlorophyll a can cause errors up to 10% (Goericke and Repeta 1993; R. Bidigare pers. comm.).

It should also be noted that the present study is confined only to particulate absorption. Contributions by dissolved absorption, which may be significant, further complicate the extraction of phytoplankton properties from $R_{rs}(\lambda)$ values and are not included in this study (Carder et al. 1991). Variability of the particulate backscattering coefficient, the other inherent optical property related to $R_{rs}(\lambda)$ values, is also not incorporated into our analyses. However, with the exception of coccolithophores and Trichodesmium, algal sources of $b_b(\lambda)$ variability will be small. Hence, the interpretations of the present analyses towards an evaluation of algal community structure are reasonable.

Implications for the use of ocean color spectra

The important result shown here is that variability in $a_p(\lambda)$ is almost entirely associated with the quantity of the absorbing materials rather than their spectral quality. The EOF analyses indicate that nearly all of the variance in the global $a_p(\lambda)$ database (> 99.9%) can be accounted for by a single mode of variability (Fig. 9). This mode reflects spectrally the change in the total amount of absorbing material, demonstrating that the basic spectral shapes that comprise $a_p(\lambda)$ are remarkably uniform, only their amplitudes vary.

The EOF analyses of the normalized $a_p(\lambda)$ spectra, $a_p *_{<aP>}(\lambda)$, suggest that only two robust statistical components exist; the relative concentration of detrital materials and a relationship between chlorophyll absorption and detrital materials (Fig. 11). The presence of these two components validates the use of the two component model to partition $a_p(\lambda)$ (e.g., Kiefer and SooHoo 1982). In addition, the EOF analysis shows only hints of the variance associated with phytoplankton
accessory pigmentation (about 0.5% of the total $a_p(\lambda)$ variance). The multidimensional regression analysis, which partitioned $a_p(\lambda)$ into $a_{ph}(\lambda)$ and $a_{det}(\lambda)$, demonstrated that 98% of the total variability may be explained by two constant spectral components.

It should be noted that the statistics on a large dataset will, by its own construction, obscure any rare events that may occur. For example, *Trichodesmium*, a nitrogen-fixing cyanobacterium, blooms episodically at the sea surface in the subtropical and tropical oceans (Carpenter and Romans 1991). This algal species contains phycoerytherin which gives it the unique signature of strong absorption at 495 nm and a shoulder near 550 nm. Algorithms have been developed for the detection of *Trichodesmium* blooms from CZCS imagery (Borstad et al. 1992). However, anomalous spectral signatures of this nature are not observed in this database.

The use of backscatter and fluorescence signals may be the best hope for the determination of algal groups or species. Some algal species, such as coccolithophores, have an unusually large backscatter signal (Balch et al. 1991). This feature could be utilized to develop specific algorithms for this particular algal group (Gordon et al. 1988). Spectral fluorescence signatures may also prove useful in the identification of algal groups. For example, the ubiquitous cyanobacterium, *Synechococcus*, contains phycoerytherin as its primary light harvesting pigment and has a fluorescence emission centered at 575 nm (Campbell and Iturriaga 1988). It may be possible to use this signal in the remote determination of *Synechococcus* populations (Hoge et al. 1987). The role of cyanobacteria and coccolithophores in the global ocean carbon cycle is often significant, therefore algorithms for quantitative estimates of their roles are important.

However, besides these two examples, there remain few other known optical traits for specific algal groups that can be exploited for future algorithm development. Hence, the development of global algorithms for distinguishing phytoplankton taxa with less dramatic optical differences (e.g., diatoms and dinoflagellates) from satellite ocean color remote imagery appears unlikely.

The fundamental conclusion from this study is that spectral shapes for $a_p(\lambda)$ are so similar that it will be exceedingly difficult to retrieve phytoplankton ecosystem structure from ocean color spectra beyond a simple decomposition of algal and detrital properties in near surface waters; accomplishing this on a global scale will indeed be a very significant achievement. Additional information on algal
speciation or accessory pigment concentrations will be masked by these dominant modes of variability, as well as any sources of measurement noise. Thus, these overriding modes of variability will place an inherent limitation on the type of useful information that can be acquired using satellite ocean color imagers.
References


1356-1358.


### Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>(a(\lambda))</td>
<td>Wavelength, nm</td>
</tr>
<tr>
<td>(L_u(\lambda))</td>
<td>Upwelling radiance, W sr(^{-1}) m(^{-2}) nm(^{-1})</td>
</tr>
<tr>
<td>(E_d(\lambda))</td>
<td>Downwelling irradiance, W m(^{-2}) nm(^{-1})</td>
</tr>
<tr>
<td>(R_p(\lambda))</td>
<td>Remote sensing reflectance (= L_u(\lambda)/E_d(\lambda)), sr(^{-1})</td>
</tr>
<tr>
<td>(b_b(\lambda))</td>
<td>Backscattering coefficient, m(^{-1})</td>
</tr>
<tr>
<td>(a(\lambda))</td>
<td>Absorption coefficient, m(^{-1})</td>
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<tr>
<td>(C_1)</td>
<td>Constant = 0.0949</td>
</tr>
<tr>
<td>(a_w(\lambda))</td>
<td>Absorption coefficient for pure seawater, m(^{-1})</td>
</tr>
<tr>
<td>(a_p(\lambda))</td>
<td>Absorption coefficient for particulates, m(^{-1})</td>
</tr>
<tr>
<td>(a_d(\lambda))</td>
<td>Absorption coefficient for dissolved materials, m(^{-1})</td>
</tr>
<tr>
<td>(a_{ph}(\lambda))</td>
<td>Absorption coefficient for phytoplankton, m(^{-1})</td>
</tr>
<tr>
<td>(a_{det}(\lambda))</td>
<td>Absorption coefficient for detrital materials, m(^{-1})</td>
</tr>
<tr>
<td>Chl</td>
<td>Chlorophyll concn, mg m(^{-3})</td>
</tr>
<tr>
<td>OD(_f)</td>
<td>Optical density of sample on filter</td>
</tr>
<tr>
<td>OD(_s)</td>
<td>Optical density of sample in suspension</td>
</tr>
<tr>
<td>d</td>
<td>Cuvette path length, m</td>
</tr>
<tr>
<td>(a_p \ast_{Chl} (\lambda))</td>
<td>(a_p(\lambda)/\text{Chl} a \ (\text{Chlorophyll-specific}), \text{m}^2 \text{mg}^{-1})</td>
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</table>
| \(\langle a_p \rangle\) | \[
\frac{1}{301} \sum_{\lambda=400}^{700} a_p(\lambda), \text{m}^{-1}
\] |
| \(a_p \ast_{ap} (\lambda)\) | \(a_p(\lambda)/\langle a_p \rangle \ (\text{Opt. Biomass-specific})\) |
| A(\(\lambda\)) | Spectral slope of phytoplankton |
| B(\(\lambda\)) | Spectral slope of detrital material |
| \(\bar{a}_p(\lambda)\) | Spectrally averaged absorption due to particulates |
| \(\bar{a}_{ph}(\lambda)\) | Spectrally averaged absorption due to phytoplankton, m\(^{-1}\) |
| \(\bar{a}_{det}(\lambda)\) | Spectrally averaged absorption due to detritus, m\(^{-1}\) |
| \(\bar{a}_{res}(\lambda)\) | Spectrally averaged absorption due to residuals, m\(^{-1}\) |
| \(< a_{ph}> \) | \[
\frac{1}{301} \sum_{\lambda=400}^{700} a_{ph}(\lambda), \text{m}^{-1}
\] |
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<th>Cruise Location</th>
<th>Source*</th>
<th>Beta** Algorithm</th>
<th>Time</th>
<th>N (All Depths)</th>
<th>n (0 to 30 m)</th>
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<td>MK88</td>
<td>Apr-85</td>
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<td>M90</td>
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<td>WSC/DAK</td>
<td>MK88</td>
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<tr>
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<td>M90</td>
<td>Nov-90</td>
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<td>M90</td>
<td>Nov-90</td>
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<td>NP90</td>
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<tr>
<td>Scripps Canyon (NASA-86)</td>
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<td>MK88</td>
<td>Nov-85 to May-86</td>
<td>101</td>
<td>81</td>
</tr>
</tbody>
</table>

Total Spectra = 908 407

Table 1. Cruises comprisirng the global database of particulate absorption spectra.


Figure 1. Mean and standard deviation spectral signatures of the particulate absorption global database.

Figure 2. Mean (a) and standard deviation (c) spectral signatures of open ocean cruises comprising the particulate absorption global database. Mean (b) and standard deviation (d) spectral signatures of coastal cruises comprising the particulate absorption global database.

Figure 3. As Fig. 1, but comprising the chlorophyll-specific particulate absorption database.

Figure 4. As Fig. 2, but comprising the chlorophyll-specific particulate absorption database.

Figure 5. As Fig. 1, but of the optical biomass-specific particulate absorption database.

Figure 6. As Fig. 2, but of the optical biomass-specific particulate absorption database.

Figure 7. Percent variance explained by both $a_p$ and chlorophyll values versus $a_p$ (hindcast skill).

Figure 8. Covariance plot of the particulate absorption global database.

Figure 9. EOF analysis of the particulate absorption global database.

Figure 10. Covariance plot of the optical biomass specific global database.

Figure 11. EOF analysis of the optical biomass specific global database.

Figure 12. Variations in chlorophyll $a$ normalized mean particulate absorption values versus chlorophyll $a$ (plotted as log$_{10}$). slope = -0.40 for all data (A); slope = -0.57 for chl values < 1.0 mg/m$^3$ (B); slope = -0.03 for chl values > 1.0 mg/m$^3$ (C).

Figure 13. Two component spectral decomposition of particulate absorption global database (Morrow et al. 1989 model).

Figure 14. Percent phytoplankton (a) and residual (b) absorption of the total particulate absorption database (from Morrow et al. 1989 model).

Figure 15. Variations in chlorophyll $a$ normalized mean phytoplankton absorption versus chlorophyll $a$ (plotted as log$_{10}$; where $a_{ph}$ is the spectral mean phytoplankton absorption coefficient for each sample modeled from Morrow et al. 1989). Slope = -0.29 for all data (A); slope = -0.49 for chl values < 1.0 mg/m$^3$ (B); slope = 0.05 for chl values > 1.0 mg/m$^3$ (C).
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7

% variance explained using $<ap>$ values

% variance explained using chlorophyll values

wavelength (nm)
Figure 8
Figure 9

Mode 1 = 99.98%

Mode 2 = 0.01%
Figure 11

Mode 1 = 77.4 %

Mode 2 = 19.3 %

Mode 3 = 3.1 %
Figure 13

- Total Particulate Absorption
- Modelled Particulate Absorption
- Detrital Component 54%
- Phytoplankton Component 44%
- Residuals 2%

[Graph showing absorption coefficient vs. wavelength (nm)]
Figure 14

(a) Phytoplankton

(b) Residuals
Figure 15
Chapter 3: Inherent optical property inversion of ocean color spectra and its biogeochemical interpretation 1. Time series from the Sargasso Sea

Abstract. A nonlinear statistical method for the inversion of ocean color spectra is used to determine three inherent optical properties (IOPs), the absorption coefficients for phytoplankton and dissolved and detrital materials, and the backscattering coefficient due to particulates. The inherent optical property inversion model assumes that (1) the relationship between remote-sensing reflectance and backscattering and absorption is well known, (2) the optical coefficients for pure water are known, and (3) the spectral shapes of the specific absorption coefficients for phytoplankton and dissolved and detrital materials and the specific backscattering coefficient for particulates are known. This leaves the magnitudes for the three unknown coefficients to be determined. A sensitivity analysis is conducted to determine the best IOP model configuration for the Sargasso Sea using existing bio-optical models. The optical and biogeochemical measurements used were collected as part of the Bermuda Bio-Optics Project and the U.S. Joint Global Ocean Flux Study Bermuda Atlantic Time Series (BATS). The results demonstrate that the IOP model is most sensitive to changes in the exponential decay constant used to model absorption by dissolved and detrital materials. The retrieved chlorophyll a estimates show excellent correspondence to chlorophyll a determinations ($r^2 = 81\%$), similar to estimates from standard band ratio pigment algorithms, while providing two additional retrievals simultaneously. The temporal signal of retrieved estimates of absorption by colored dissolved and detrital materials is mirrored in ratios of $K_d(410)$ to $K_d(488)$, a qualitative indicator for nonalgal light attenuation coefficients. The backscatter coefficient for particles is nearly constant in time and shows no correspondence with the temporal signal observed for chlorophyll a concentrations. Last, the IOP model is evaluated using only those wavelengths which closely match the Sea Viewing Wide Field of View Sensor wave bands. This results in only a 1 to 6% decrease in hindcast skill with the BATS biogeochemical data set. This is encouraging for the long-range goal of applying the IOP model to data from upcoming ocean color satellite missions.

1. Introduction

The images produced by the coastal zone color scanner (CZCS) provided new insights for biological oceanographers and gave unprecedented information about the marine biosphere [Gordon and Morel, 1983; Mitchell, 1994]. However, this instrument was primarily used to determine only a single index, the chlorophyll pigment concentration, to describe the entire functioning of the ocean's ecosystem. This is clearly not enough information to explain all the important biogeochemical processes in the ocean such as the cycling of carbon and nitrogen and predictions of regional fishery yields.

Ocean color observations can and should yield more information than simply the single chlorophyll pigment concentration. Here we use a nonlinear statistical method for the inversion of ocean color spectra to produce three relevant inherent optical properties (IOPs) for the analysis of biogeochemical variability: the absorption coefficient by phytoplankton, the absorption coefficient by dissolved and detrital materials, and the backscattering coefficient due to particulates. Methods to invert ocean color
observations, such as those employed here, have been extensively explored by Morel and Prieur [1977], Sugihara et al. [1985], Sathyendranath et al. [1989], Gordon et al. [1988], and Roesler and Perry [1995].

The color of the sea will be related to those photons which are backscattered from within the water column and are not absorbed before entering the atmosphere. Hence changes in the total absorption coefficient, $a(\lambda)$ (notation list is provided), and the backscattering coefficient, $b_b(\lambda)$, regulate the variations in ocean color spectra or remotely sensed reflectance [$R_{rs}(\lambda)$], where $R_{rs}(\lambda)$ is defined as the ratio of upwelled radiance to downwelled irradiance ($=L_u(\lambda)/E_d(\lambda)$). Values of $a(\lambda)$ an be effectively partitioned into absorption due to water, phytoplankton, and nonalgal materials [e.g., Kishino et al., 1984; Carder et al., 1989; Garver et al., 1994]. The value of $b_b(\lambda)$ is typically much smaller than $a(\lambda)$ for case I waters [Gordon et al., 1988]. In addition, there are no a priori reasons why absorption and scattering properties should be well correlated [Kitchen and Zaneveld, 1990].

Theoretical studies have shown that remote-sensing reflectance can be related to the IOPs of the water column, which in turn are composed of the individual absorbers and scatterers, including water, particulates, and dissolved materials. Hence IOPs can be used to study upper ocean biological processes, including phytoplankton distributions, primary production rates, and biogenic gas fluxes. Ocean color observations can be either remotely sensed ($R_{rs}(0^+,\lambda)$), as by the upcoming sea viewing wide field of view sensor (SeaWiFS) or ocean color thermal sensor (OCTS) missions, or obtained in situ ($R_{rs}(z,\lambda)$), such as in the Bermuda Bio-Optics Program (BBOP) [Siegel et al., 1995a,b]. Remotely sensed ocean color observations have the advantage of providing basin scale coverage of the upper mixed layer, while in situ observations provide high vertical resolution (ship) and/or high temporal (mooring) coverage [e.g., Smith et al., 1987; Dickey, 1991].

We demonstrate that an IOP inversion approach for the analysis of ocean color spectra can be successfully applied in the blue ocean and that the retrievals provide useful information for the evaluation of the functioning of the biogeochemical system in the Sargasso Sea. This region is an excellent location to investigate biogeochemical processes on monthly to interannual timescales due to the strong seasonal variations in ocean biogeochemical cycles [e.g., Menzel and Ryther, 1960, 1961; Siegel et al., 1995a; Michaels et al., 1994]. To evaluate the IOP inversion model, we assess its capabilities as a chlorophyll a model, examine the temporal changes in nonalgal absorption, assess the modeling and potential sources of the particulate backscatter coefficient, and evaluate the application of the IOP model to upcoming satellite ocean color imagery.

2. Modeling Methodology

The goal of the IOP inversion model is to maximize the information that can be extracted from ocean color observations. For this study, the IOP inversion model is
applied to in situ observations of $R_{rs}(\lambda)$ from the Bermuda Bio-Optics Project [Siegel et al., 1995a,b]. The model is general enough to be applied to other oceanic regions with confidence in its success and has the advantage of providing measures of uncertainty for the modeled inherent optical properties.

The IOP inversion model is based upon the following three assumptions. First, the relationship between $R_{rs}(\lambda)$ and $b_p(\lambda)$ and $a(\lambda)$ is assumed to be well known. Second, the optical coefficients for pure water, $a_w(\lambda)$ and $b_{pw}(\lambda)$, are known [Smith and Baker, 1981]. Last, the spectral shapes of the specific absorption coefficients for phytoplankton and non-algal materials and the specific backscattering coefficient for particulates, $a_{ph}(\lambda)$, $a_{dm}(\lambda)$, and $b_{bp}(\lambda)$, are known functions of their magnitudes (please note that the asterisks are used to indicate these are spectral shapes; see notation list). Knowing these factors, the magnitudes of the unknown absorption and backscattering coefficients may be determined.

The IOP inversion model assumes that the relationship between $R_{rs}(\lambda)$ and the ratio of backscattering to absorption coefficients is known and stable, for example,

$$R_{rs}(\lambda) \equiv \frac{L_u(\lambda)}{E_d(\lambda)} \approx \sum_{i=1}^{2} l_i \left[ \frac{b_p(\lambda)}{b_p(\lambda) + a(\lambda)} \right]$$

(1)

where $L_u(\lambda)$ is upwelling radiance just beneath the sea surface, $E_d(\lambda)$ is downwelling irradiance at the same depth, $l_1 = 0.0949$ sr$^{-1}$, and $l_2 = 0.0794$ sr$^{-1}$ [Gordon et al., 1988]. The quadratic form of (1) should be particularly important for high $R_{rs}(\lambda)$ observations such as those found in the blue Sargasso Sea. A comparison of the linear and quadratic forms of (1) demonstrates that values of $b_p(\lambda)/(a(\lambda) + b_p(\lambda))$ from a measure of $R_{rs}(\lambda)$ could be overestimated if only the linear term in (1) is used and that difference will increase with increasing values of $R_{rs}(\lambda)$ (Figure 1). For example, a value of $R_{rs}(\lambda) = 0.01$ sr$^{-1}$ could result in a 10% difference in the estimate of $b_p(\lambda)/(a(\lambda) + b_p(\lambda))$, while a value of $R_{rs}(\lambda) = 0.03$ sr$^{-1}$ might result in a 25% difference between the two model forms (Figure 1). This difference should be particularly important for clear waters with high $R_{rs}(\lambda)$ values.

The absorption and backscattering coefficients in (1) are the sums of the individual coefficients due to the absorbers and scatterers which are present and can be written as

$$b_p(\lambda) = b_{pw}(\lambda) + b_{bp}(\lambda)$$

(2)

where $b_{pw}(\lambda)$ is the backscatter due to pure seawater and $b_{bp}(\lambda)$ is the backscatter due to particles, and

$$a(\lambda) = a_w(\lambda) + a_{ph}(\lambda) + a_{dm}(\lambda)$$

(3)

where $a_w(\lambda)$ is the absorption due to seawater, $a_{ph}(\lambda)$ is the absorption due to phytoplankton, and $a_{dm}(\lambda)$ is the absorption due to the combined effects of colored dissolved and detrital materials (CDM). For our model, the spectral signatures of CDM will be modeled as a single exponential shape as the signals due to colored dissolved
organic and detrital materials are likely to be inseparable [Carder et al., 1991; Siegel and Michaels, 1996].

The IOP inversion model assumes that values of \( a_{w}(\lambda) \) and \( b_{bw}(\lambda) \) are known (Figure 2a). The absorption and backscattering properties of pure seawater have been tabulated by Smith and Baker [1981]. Using values of the diffuse attenuation coefficient for irradiance in the clearest natural waters, Smith and Baker [1981] deduced proper values for the absorption coefficient of seawater. The coefficient for total scattering by seawater, \( b_{m}^{sw}(\lambda) \), is taken from Morel [1974], who has reviewed in great detail the theory and observations pertaining to scattering by both pure water and pure seawater. Values of the backscattering coefficient for sea water are assumed to be equal to \( 1/2b_{m}^{sw}(\lambda) \).

The IOP model is based upon the assumption that spectral shapes for \( a_{ph}^{*}(\lambda) \), \( a_{dm}^{*}(\lambda) \), and \( b_{bp}^{*}(\lambda) \) are fixed or known functions of a single index. The spectral shape of phytoplankton absorption results from the combination of the light-absorbing properties of chlorophyll \( a \) and other accessory pigments which absorb in specific regions of the visible spectrum (centered at 440 and 675 nm) modified by their packaging within the cell [Kirk, 1994]. Four \( a_{ph}^{*}(\lambda) \) models are explored here [Prieur and Sathyendranath, 1981; Morel, 1988; Garver et al., 1994; Bricaud et al., 1995] (Figure 2b). The Prieur and Sathyendranath [1981] \( a_{ph}^{*}(\lambda) \) model was statistically derived from 90 spectral absorption coefficients which were calculated using upwelling and downwelling irradiance values from various case I marine regions. The Morel [1988] \( a_{ph}^{*}(\lambda) \) model was obtained by averaging values of 14 cultured phytoplankton species. The Garver et al. [1994] \( a_{ph}^{*}(\lambda) \) model was obtained from the partitioning of an extensive database of particulate absorption spectra assembled from 11 cruises in the Atlantic and Pacific, both open ocean and coastal, using the multidimensional regression model of Morrow et al. [1989]. The Bricaud et al. [1995] \( a_{ph}^{*}(\lambda) \) model was developed as a power law fit with respect to chlorophyll \( a \) of 815 \( a_{ph}(\lambda) \) spectra measured using the filter pad and methanol extraction techniques. The shapes of the modeled \( a_{ph}^{*}(\lambda) \) spectra are all constant except for the Bricaud et al. [1995] model which is a function of the chlorophyll \( a \) concentration.

In contrast, the CDM component of absorption is modeled as an exponential function which decreases with increasing wavelength [Carder et al., 1991; Roesler et al., 1989], or

\[
a_{dm}(\lambda) = a_{dm}(\lambda_{o}) \exp[S(\lambda - \lambda_{o})]
\]

where \( a_{dm}(\lambda_{o}) \) is the absorption by CDM at a reference wavelength, \( \lambda_{o} = 440 \) nm, and values of \( S \), the exponential decay constant, were chosen to span values found in the literature (\( S = -0.006, -0.014, \) and \(-0.020 \) nm\(^{-1} \); Figure 2c).

Backscattering in the oceans by marine particulates has only recently been studied in detail, and it is clear that there is a spectral signature and that scattering and backscattering in particular vary greatly for different types of particulates. It appears
that marine particles of the order of 1 \( \mu \text{m} \) in diameter and smaller are the major source of backscattering in the open ocean. Living organisms in this size range include viruses, heterotrophic and photoautotrophic bacteria, and small eucaryotic algal cells, as well as inanimate detrital particles [Stramski and Kiefer, 1991; Morel and Ahn, 1991]. Direct measurements of \( b_p(\lambda) \) for phytoplankton cultures support the notion of insignificantly low values of algal backscatter coefficients for case I waters [Bricaud et al., 1983; Ahn et al., 1992]. An exception to this is the nanoplancton-sized coccolithophores and in particular detached coccoliths, which have a characteristically large backscatter signal [Balch et al., 1991].

Experimental data and theory indicate that under most conditions, values of \( b_{bp}(\lambda) \) decrease monotonically with respect to wavelength. Three power law spectra, going as \( \lambda^{0}, \lambda^{-1}, \text{and } \lambda^{-2} \) are each used individually as the \( b_{bp}(\lambda) \) modeled spectrum (Figure 2d). The spectral signature of particulate backscatter has been commonly modeled as \( \lambda^{-1} \) [Gordon and Morel, 1983; Morel, 1987, 1988; Roessler and Perry, 1995]. However, recent work has shown that 0.2-0.5 \( \mu \text{m} \) size particles make the dominant contribution to particulate backscattering and should be modeled as \( \lambda^{-2} \) [Stramski and Kiefer, 1991]. The backscatter due to phytoplankton cells is both typically smaller and spectrally uniform and is modeled as \( \lambda^{0} \) [Bricaud et al., 1983; Morel and Ahn, 1991].

The IOP inversion model can now be rewritten (see (1)) as the summation of the various components comprising absorption and scattering:

\[
\hat{R}_{r}(\lambda) = \sum_{i=1}^{2} \left[ \frac{b_p(\lambda)}{b_p(\lambda) + a_a(\lambda) + Chl a_{ph}^{*}(\lambda) + a_{dm}(\lambda)\exp(S(\lambda - \lambda_0))} \right]
\]

(5)

where \( b_p(\lambda) = b_a(\lambda) + b_{bp}(\lambda) a_{bp}^{*}(\lambda) \), \( b_{bp}(\lambda) \) is modeled as \( (\lambda/\lambda_0)^n \) (n = 0, 1, 2), \( Chl \) is chlorophyll a (milligrams per cubic meter) for the Bricaud et al. [1995], Morel [1988] and Garver et al. [1993] \( a_{ph}(\lambda) \) models, and \( Chl \) is \( a_{ph}(441) \) for the Prieur and Sathyendranath [1981] \( a_{ph}^{*}(\lambda) \) model. The model is inverted by overconstraining in wavelength and solving for the three unknown parameters, \( b_{bp}(\lambda_0), Chl, \) and \( a_{dm}(\lambda_0) \). By multipying the retrieved magnitudes by the assumed shapes, IOP estimates at each wavelength can be determined.

The difficulty with the inversion procedure is that the final IOP model is nonlinear (equation (5)). A general nonlinear least squares model can be written as [Bates and Watts, 1988]

\[
Y_n = f(x_n, \theta_p) + Z_n
\]

(6)

where \( Y_n \) are the measured responses (=\( R_{rg}(\lambda_n) \)), \( f(x_n, \theta_p) \) is the expectation function (= \( \hat{R}_{r}(\lambda_n) \)), \( n \) is the index of realization per observation (a total of 8 wavelengths), \( x_n \) is the matrix of independent variables (\( b_{bp}^{*}(\lambda_n), a_{ph}^{*}(\lambda_n) \) and \( a_{dm}^{*}(\lambda_n) \)), \( \theta_p \) is the array of unknown parameters (\( b_{bp}(\lambda_0), Chl, \) and \( a_{dm}(\lambda_0); p = 3 \)), and \( Z_n \) are the model residuals. This model is of the same form as the general linear regression model, where \( Z_n \) is assumed to have a normal distribution, with the exception that the expected responses are nonlinear functions of the parameters. It is the squared sum of the
residuals which is minimized by selecting the optimal array, $\theta_p$. When analyzing a particular set of data, the matrix $x_n$ is fixed, and it is the dependence of the expected responses, $Y_n$, on the parameters, $\theta_p$, that is of interest. For our application, a Gauss-Newton algorithm is employed which uses a linear approximation to the expectation function to iteratively improve an initial parameter guess. This iterative process continues until convergence is obtained, meaning that there is no useful change in the elements of the parameter vector [Bates and Watts, 1988]. The parameter estimates from the IOP model, $b_{yp}(\lambda_\gamma)$, Chl, and $a_{dm}(\lambda_\beta)$, are then multiplied by the value of their shape spectra at 441 nm to obtain estimates of the three IOPs, $a_{ph}(441)$, $a_{dm}(441)$, and $b_{yp}(441)$. For example, $a_{ph}(441) = Chl \cdot a_{ph}(441)$. Standard errors for the parameter estimates are determined by evaluating the derivative matrix at the least squares parameter estimates. Using the standard errors associated with these estimates, an interval of values that is likely to contain the true value of the IOPs can then be obtained. These $1-\alpha$ confidence intervals are calculated for each of the modeled IOPs at the 0.95 level:

$$\hat{\theta}_p \pm \sigma_e(\hat{\theta}_p) \cdot t(n - p; \alpha/2)$$

(7)

where $\sigma_e(\hat{\theta}_p)$ are the standard errors from the nonlinear regression and $t(n - p; \alpha/2)$ is the upper quantile for the Student's t distribution with $n - p$ degrees of freedom [Bates and Watts, 1988].

To validate the IOP model, a sensitivity analysis is performed which examines the effects of varying the different modeled components composing the IOP model. This involves using the different modeled spectra for particulate and dissolved substances found in the literature ($a_{ph}^*(\lambda), a_{dm}^*(\lambda), b_{yp}^*(\lambda)$) in a series of model runs. The retrieved IOPs from each of these model runs are then used in linear regressions with the BATS biogeochemical data set for empirical comparison and temporal scale interpretation.

3. Data Sources

In situ optical and biogeochemical measurements from the U.S. Joint Global Ocean Flux Study (JGOFS) Bermuda Atlantic Time Series (BATS) are used in this study. Methods for these data have been presented in detail several times [Knap et al., 1993; Michaels et al., 1994; Siegel et al., 1995b]. The BATS site is located 75 km southeast of Bermuda 31°50' N, 64°10' W in the Sargasso Sea. Cruises are biweekly to monthly with an average of 16 per year beginning in October 1988. Optical profiles were taken as part of the Bermuda Bio-Optics Project (BBOP), which shares both ship time and water samples with BATS. Optical profiling commenced in January 1992.

Determinations of downwelling spectral irradiance and upwelling radiance are made as part of the BBOP program using a multichannel profiling spectroradiometer (BioSpherical Instruments, Inc., MER-2040 [Smith et al., 1984]). This study analyzes $R_{rs}(\lambda)$ spectra from near noontime casts for 1992 and 1993. The optics casts composing the data set are taken from 37 separate dates over the 24 month period. To maximize the size of the data set, $R_{rs}(\lambda)$ are calculated for both 0° m and 5 m depths,
resulting in a total of 72 spectra; no significant differences in IOP inversion results were found between the 0° and 5 m $R_{rs}(\lambda)$ spectra. For the data presented, the BBOP spectroradiometer measures downwelling irradiance in eight spectral bands (410, 441, 465, 488, 520, 565, 589, and 665 nm) and upwelled radiance in nine wave bands (410, 441, 465, 488, 520, 565, 589, 665, and 683 nm). Extrapolated values of downwelling irradiance and upwelling radiance just beneath the surface, $E_d(0°,\lambda)$ and $L_u(0°,\lambda)$, are calculated using a robust least squares formulation. In addition, values of the diffuse attenuation coefficient $K_d(\lambda)$, are calculated using measurements of $E_d(z,\lambda)$ in a least squares regression over 10 m intervals [Siegel et al., 1995b].

The BBOP package is deployed ~3 m off the stern of the R/V Weatherbird II, which is oriented toward the Sun to most effectively reduce ship shadowing [Mueller and Austin, 1992]. Direct examination has shown that the effects of ship shadows are not appreciable with this deployment procedure [Weir et al., 1994]. Self-shading by the spectroradiometer has also been shown to not be a problem unless $a(\lambda) \cdot R \geq 0.01$ [Gordon and Ding, 1992], where $R$ is the radius of the instrument (10 cm). Thus instrument self-shading will occur only if values of $a(\lambda)$ are $>0.1$ m$^{-1}$, which at this site is only observed for wavelengths greater than 600 nm. For the analyses presented here, this source of error may be effectively ignored (see discussion section). Optical calibrations were performed every 4 to 6 months at the University of California, Santa Barbara (UCSB) ocean optics calibration facility which participates in the SeaWiFS optical calibration laboratory round robin exercises [Mueller et al., 1993, 1994]. Thus the lamp radiance plaque and integrating sphere standards used to calibrate the BBOP spectroradiometer are directly traceable to the National Institute of Standards and Technology. An intercomparison between calibration facilities shows differences in calibration constants of less than 1% for $E_d(\lambda)$ and 1 to 2% for $L_u(\lambda)$ (D. Menzies, personal communication, 1995). Immersion coefficients for the BBOP irradiance collector were recently determined [Mueller, 1996].

The biogeochemical observations from the BATS program that will be used as a model validation data set for this study include phytoplankton pigments measured by high pressure liquid chromatography (HPLC; milligrams per cubic meter) and fluorometry (milligrams per cubic meter), mixed layer depths (meters), nutrients (nitrate and nitrite; micromoles per kilogram), particulate organic carbon (POC; micrograms per kilogram), particulate organic nitrogen (PON; micrograms per kilogram), bacterial abundance (numbers per cubic meter), and the diffuse attenuation coefficient ($K_d(\lambda)$; m$^{-1}$). The ratio of $K_d(410)$ to $K_d(488)$ has been shown to be a good quantitative indicator of CDM concentration [Siegel et al., 1995a; Siegel and Michaels, 1996]. Model retrievals of $a_{ph}(441)$ and $a_{dm}(441)$ show some level of correspondence to the BATS pigment determinations, nutrient concentrations, mixed layer depths, and the ratio of $K_d(410)$ to $K_d(488)$, while model retrievals of $b_{pp}(441)$ should correspond to the particulate fields of POC, PON, and bacteria. All the variables in the validation data set are measured within 5 m of the surface, with the exception of the $K_d(\lambda)$ data which were taken from a depth of 20 m. When possible, $R_{rs}(\lambda)$ spectra and BATS biogeochemical data are taken from the same day. For five of the spectra
used, BATS pigment data are not available for that day, and data either 1 day before or after the date of the optics cast are used.

4. Results

4.1. Temporal Variation in Optical and Biogeochemical Parameters

Seasonal variations in both optical and biogeochemical observations from the BATS site are caused primarily by short-lived springtime phytoplankton blooms and periods of deep mixing. The magnitude of these blooms appears to be correlated with the intensity of winter storms, suggesting that the ventilation of 18° water and its vertical transport of new nutrients into the euphotic zone controls primary production off Bermuda. This seasonal cycle of the 18° water ventilation is an important aspect of the temporal changes in the biological properties of the Sargasso Sea [Menzel and Ryther, 1960, 1961; Michaels et al., 1994; Siegel et al., 1990, 1995a].

The BATS pigment determinations (fluorometric chlorophyll a, fluorometric chlorophyll a plus pheopigments, and HPLC chlorophyll a) are all extremely similar to one another and show strong seasonal variability with elevated concentrations (>0.2 mg m^-3) in the winter-spring months (Table 1a; Figure 3a). This is coincident with the changes in nutrient concentrations which are above detectability in the winter-spring months when mixed layer depths are at their deepest (Table 1a; Figure 4a). An annual cycle is also observed for ratios of K_d(410) to K_d(488), the qualitative indicator of CDM absorption, with the highest values again observed during the winter-spring months (Figure 3b) [Siegel et al., 1995a; Siegel and Michaels, 1996]. This ratio is positively and significantly correlated with the various pigment determinations (Table 1a); however, the timing of the seasonal cycles differs somewhat in duration (Figure 3).

Weak or nonexistent seasonal cycles are observed for the POC, PON, and bacterial abundance data (Figure 4b), with positive correlations observed among these particulate fields (Table 1a).

The temporal pattern observed for Rrs(λ) also shows a strong seasonal cycle (Plate 1). Values of Rrs(λ) are highest in the late spring, summer, and fall (April-November) and lowest in the winter (December-March). Thus the Sargasso Sea will be "bluer" in summer and "greener" in the winter. The Rrs(410-488) values for April to November are typically in the 0.015-0.025 sr^-1 range. Therefore using a linear Rrs(λ) to IOP ratio model (equation (1)) during these time periods could lead to overestimates of roughly 15 to 20% for these wavelengths (Figure 1). The Rrs(410-488) wavelengths are the most highly correlated to the BATS variables, and demonstrate the greatest seasonal variability (Table 1b; Plate 1). Conversely, the green-red wave bands (≥520 nm) show little correlation with any of the BATS variables. The blue-green Rrs(λ) distribution has strong inverse relationships with all three pigment determinations and the ratios of K_d(410) to K_d(488) (Table 1b). This relationship between Rrs(λ) and both pigments and ratios of K_d(410) to K_d(488) suggests that changes in a(λ) are primarily responsible for the temporal changes in Rrs(λ). It appears that bλ(λ) is not a significant
factor in driving \( R_{rs}(\lambda) \) temporally, as is demonstrated by the weak correlation's between \( R_{rs}(\lambda) \) observations and particulates fields such as POC and bacteria.

\[ \text{4.2. IOP Model Evaluation} \]

The sensitivity analyses performed on the IOP inversion model assess the effects of varying the spectral shape components \( (a_{ph}^*(\lambda), a_{dm}^*(\lambda), b_{bp}^*(\lambda)) \) of the model. The first set of model runs begins with a base state of the particulate specific backscatter coefficient modeled as \( \lambda^{-1} \) and the phytoplankton specific absorption coefficient modeled using the Morel [1988] \( a_{ph}^*(\lambda) \) spectrum. Three \( a_{dm}^*(\lambda) \) spectra \( (S = -0.006, -0.014, -0.02 \text{ nm}^{-1}) \) are then applied to the entire data set while holding the \( a_{ph}^*(\lambda) \) and \( b_{bp}^*(\lambda) \) spectra constant (Figure 5a). The \( S = -0.006 \text{ nm}^{-1} \) case gives the poorest results. This is evidenced by the percent variance explained in the linear regressions between the retrieved \( a_{ph}(441) \) from this model run and the BATS pigment determinations \( (r^2 = 12-18\%); \text{Table 2}) \). The other two modeled \( a_{dm}^*(\lambda) \) spectra result in a significantly higher percent variance explained for the same regressions, with the \( S = -0.02 \text{ nm}^{-1} \) case being slightly better than the \( S = -0.014 \text{ nm}^{-1} \) case (77 to 84% versus 63 to 73%). As is shown in Figure 5a, changes in the value of the exponential decay constant, \( S \), have a significant effect on the magnitude of the \( a_{ph}(441) \) and \( a_{dm}(441) \) retrievals and less of an effect on the \( b_{bp}(441) \) retrievals. The \( a_{dm}(\lambda) \) spectrum calculated using \( S = -0.02 \text{ nm}^{-1} \) is chosen to continue with the sensitivity analysis. This value of the exponential decay constant is consistent with CDM absorption spectra obtained by both Green and Blough [1994], who found a range of \( S \) values from -0.018 to -0.02 \text{ nm}^{-1}, and Nelson et al. [1997] who determined an average value of \( S = -0.025 \text{ nm}^{-1} \) (standard deviation = 0.004) in the Sargasso Sea.

For the second set of model runs, three \( b_{bp}^*(\lambda) \) spectra \( (\lambda^0, \lambda^{-1}, \lambda^{-2}) \) are each used in individual model runs, while holding the \( a_{dm}^*(\lambda) \) and \( a_{ph}^*(\lambda) \) spectra constant with \( S \) equal to -0.02 \text{ nm}^{-1} \) and Morel [1988], respectively. The results of the linear regressions for this set of model runs are virtually identical (Table 3), as are the retrieved values of the three IOPs (Figure 5b). The retrieved \( a_{ph}(441) \) and \( a_{dm}(441) \) values show a strong seasonal cycle with highest values in the winter months. Retrievals of \( b_{bp}(441) \) are nonseasonal with the largest \( b_{bp}(441) \) retrievals occurring for the \( \lambda^{-1} \) model. The choice of the \( b_{bp}^*(\lambda) \) model used has little effect on the results of the IOP inversion for this particular data set. The \( \lambda^{-1} \) spectra, a common representation from the literature for particulate backscatter [e.g., Morel, 1987], are chosen. It is recognized that this conclusion may not hold for other oceanographic regions, in particular for case II waters.

The third model sensitivity analysis compares the four \( a_{ph}^*(\lambda) \) spectra. The results of the linear regressions are again quite similar (Table 4). The Garver et al. [1994] and the Bricaud et al. [1995] \( a_{ph}^*(\lambda) \) spectra result in the least number of negative \( a_{dm}(441) \) retrievals for the summer-fall 1993 season (3% versus 15 to 19% for Prieur and Sathyendranath [1981] and Morel [1988], although statistically none of these retrieved negative values are significantly different than zero; Figure 5c). Varying the \( a_{ph}^*(\lambda) \) spectra used as input to the IOP model results in only minor changes in
retrievals of either \( a_{ph}(441) \) or \( a_{dm}(441) \) and even less of a change in retrievals of \( b_{bp}(441) \). As with the second model set, retrievals of \( a_{ph}(441) \) are approximately equal to or greater than the value of \( a_{w}(441) \) during the winter and early spring, while the retrievals of \( a_{dm}(441) \) are approximately equal to the value of \( a_{w}(441) \) during the winter and early spring. The \( b_{bp}(441) \) retrievals are less than or equal to the value of \( b_{bw}(441) \) throughout the time series. The Bricaud et al. [1995] model is chosen to continue with the sensitivity analysis as it results in very few negative retrievals of \( a_{dm}(\lambda) \) and it allows for variations in the \( a_{ph}^*(\lambda) \) spectra due to changes in pigment composition and packaging.

### 4.3. Final IOP Model

The IOP model is found to be most sensitive to changes in the \( a_{dm}^*(\lambda) \) spectra, with some variability in model results seen when varying the \( a_{ph}^*(\lambda) \) spectra and minimal variability observed using the different \( b_{bp}^*(\lambda) \) spectra. The final version of the IOP inversion model is composed of the CDM specific absorption coefficient, modeled with \( S = -0.02 \text{ nm}^{-1} \), the modeled phytoplankton specific absorption coefficient of Bricaud et al. [1995], and the particulate specific backscattering coefficient modeled as \( \lambda^{-1} \).

The point estimates of the retrieved IOPs from this final model are shown in figure 5d, along with their 95% confidence intervals. The linear regressions between the final model IOPs and the BATS biogeochemical variables are shown in the last three columns of Table 4.

The average seasonal changes in the \( a_{ph}(441) \) and \( a_{dm}(441) \) retrievals are greater than their respective confidence intervals, indicating the significance of the temporal changes observed. The confidence intervals also demonstrate that the majority of the \( a_{ph}(441) \) and many of the \( a_{dm}(441) \) retrievals for the winter to late spring (December-March) are greater than or equal to \( a_{w}(441) \) and that the two negative \( a_{dm}(441) \) retrievals from summer 1993 are not significantly different than zero. There are no significant temporal changes observed in the \( b_{bp}(441) \) retrievals, and the values for this IOP are consistently smaller than or equal to \( b_{bw}(441) \) throughout the entire time series.

The retrieved \( a_{ph}(441) \) values from the final model show a strong seasonal cycle and explain \( \sim 77\% \) of the total variance in the BATS fluorometric pigment determinations and 84% of the HPLC chlorophyll \( a \) (last three columns of Table 4). The magnitude of the spring bloom shown for 1992 is stronger than that seen in 1993 (Figure 5d). This is consistent with the changes in the nitrate+nitrite concentrations seen for this time period, suggesting a higher convective flux of nutrients into the euphotic zone for 1992 than for 1993 (Figure 4a). The retrieved \( a_{dm}(441) \) values also show a strong seasonal cycle and explain \( \sim 77\% \) of the variance in the pigment determinations and 70% of the variance in the ratios of \( K_d(410) \) to \( K_d(488) \). Time periods of high \( a_{dm}(441) \) retrievals correspond to periods of deep mixing, causing dissolved and detrital materials to be brought to the surface. Time periods of low \( a_{dm}(441) \) correspond to shallow mixing, perhaps resulting in photobleaching of colored dissolved and detrital material trapped at shallower depths. This pattern is also
illustrated in the seasonal variability of $K_d(410)$ to $K_d(488)$ (Figure 3b). The nonseasonality observed in the retrieved $b_{bp}(441)$ values from the final model is reflected in the lack of coincidence between this parameter and any of the BATS biogeochemical variables.

To evaluate model performance, the residuals from the final model are examined to determine constant variance and a normal distribution. Small departures from normality do not affect the model greatly, but gross nonnormality is potentially serious as calculated model statistics and confidence intervals depend on the normality assumption. A normal probability plot of the IOP model residuals indicates they are normally distributed, while a plot of the fitted values versus the individual residuals shows near-constant variance with no unusual outliers (figures not shown). A plot of the spectrally summed root mean squared error ($RMSE$) versus time shows an annual cycle, with larger $RMSE$ in the summer than in the winter months (Figure 6). This demonstrates that for this data set, the IOP model fits the in situ $R_{pq}(\lambda)$ spectra better in the winter, during conditions of higher pigment and CDM concentrations, than during the "blue" water conditions of the summer months. This suggests that our knowledge of "pure" seawater optical properties or our blue water optical parameterizations may still need improvement.

5. Discussion

We have shown that a statistically based ocean color inversion approach can be successfully applied in the blue ocean. These results give insights into what can be determined from space using ocean color spectra and how they relate to biogeochemical processes. To further evaluate the final IOP inversion model we (1) assess its capabilities as a chlorophyll $a$ model, (2) examine the temporal changes in the retrieved estimates of CDM absorption, (3) assess the modeling and potential sources of the particulate backscatter coefficient, and (4) evaluate the application of the IOP model to satellite ocean color imagery, such as from the upcoming SeaWiFS and OCTS missions.

5.1. The IOP Model as a Chlorophyll Model

One of the primary goals of the SeaWiFS mission is to provide global coverage of chlorophyll $a$ concentrations to within an accuracy of 35% [Hooker et al., 1992]. As the final IOP model is developed using only existing globally applicable bio-optical models, it can potentially provide global estimates of chlorophyll $a$ concentrations. The retrieved chlorophyll $a$ estimates from the final IOP model show excellent correspondence in a linear regression with the BATS HPLC chlorophyll $a$ determinations ($r^2 = 81\%$; Figure 7a). This result can be compared with chlorophyll estimates obtained from a band ratio or CZCS-type pigment algorithm of the form [Gordon and Morel, 1983]

$$
CZCS_{chl} = A \frac{L_y(\lambda_2)\theta}{L_y(\lambda_1)}
$$

(8)
where $CZCS_{chl}$ is the band ratio estimated chlorophyll concentration (milligrams per cubic meter), $L_u(\lambda)$ is the upwelled radiance, $\lambda_1 = 441$ nm, $\lambda_2 = 565$ nm, $A = 1.92$ mg m$^{-3}$, and $B = -1.80$.

The results of the two models are quite similar, with the CZCS chlorophyll estimates explaining 86% of the variance in the BATS HPLC chlorophyll $a$ determinations. Other CZCS band ratio models yielded similar results [Gordon and Morel, 1983]. When evaluated by season, the two models perform markedly better in the winter ($r^2 = 73$ to 94%), when chlorophyll $a$ values are highest, than during the summer season ($r^2 = 1$ to 15%). Importantly, the IOP model chlorophyll $a$ estimates have a clearer 1:1 relationship with the BATS HPLC chlorophyll $a$ values, as is indicated by a slope of 0.97 (intercept = 0.033 mg m$^{-3}$). In contrast, the CZCS regression has a slope of 1.75 (intercept = -0.005 mg m$^{-3}$). This underestimate of the BATS HPLC chlorophyll $a$ values by the CZCS algorithm is particularly apparent in the winter-spring months (Figure 7b), whereas the IOP model chlorophyll $a$ estimates more closely approximate the magnitudes of the BATS HPLC chlorophyll $a$ values. This is perhaps due to the IOP models ability to separate phytoplankton absorption from CDOM absorption [Sierd C. van den Berg, 1989; Siegel and Michaels, 1996]. The seasonal underestimate of chlorophyll $a$ by the CZCS algorithm may be consistent with this idea. It should also be noted that the CZCS algorithm was not developed using very much blue water data [Gordon and Morel, 1983]. Hence this comparison with the "global" CZCS band ratio algorithm may not be fair using the present blue water data set. Another explanation for the difference in model results is that the empirical CZCS algorithm was developed with pigment data (fluorometric techniques) measured on GF/C filters, as opposed to the Briceaud et al. [1995] model used here which was developed with pigment data (HPLC techniques) on GF/F filters. GF/C filters have a higher porosity than GF/F filters, with a 15% underestimate of chlorophyll $a$ using GF/C filters shown by Chavez et al. [1995].

### 5.2. Temporal Changes in CDM Versus Total Absorption

As discussed previously, absorption by CDM appears to play an important role in affecting retrievals of chlorophyll $a$ concentrations. The fraction of total absorption attributed to CDM is evaluated by examining the ratio of $a_{dm}(441)$ to $a_{tot}(441)$ retrievals from the final model (where $a_{tot}(441) = a_w(441) + a_p(441) + a_{dm}(441)$). Seasonally, CDM absorption is shown to range from 0 to 35% at 441 nm and from 0 to 50% at 410 nm (Figure 8a). Higher CDM absorption is observed in the winter-spring months when deep mixed layer depths bringing colored dissolved and detrital materials to the surface, while CDM absorption is at a minimum in the summer-fall months when the mixed layer is shallowest and the water column is stratified [Siegel et al., 1995a]. The temporal signal of absorption due to CDM is mirrored in the ratios of $K_d(410)$ to $K_d(488)$ (Figures 4b and 8b), which explain 86% of the variance in the ratios of $a_{dm}(441)$ to $a_{tot}(441)$. Accurate estimates of CDM absorption are important as its presence can confound estimates of chlorophyll $a$ from ocean color spectra [e.g., Siegel and Michaels, 1996]. Further, the robust detection of CDM absorption gives a
remotely sensed parameter which describes the concentration of colored decomposition products in the sea. It is yet unclear how this parameter may be used to make better predictions of ecosystem functions. However, it should be clear that seasonal changes in the rates of photochemistry should be affected by CDM absorption values [Siegel and Michaels, 1996].

5.3. Modeling of Particulate Backscatter

The modeled values of particulate backscatter for this data set have been shown to be smaller than or equal to values of backscatter by pure seawater and lacking any temporal signal, despite the significant seasonal chlorophyll $a$ signal observed. This is inconsistent with several previous bio-optical models of particulate backscatter. For example, Morel [1988] models particulate backscatter as a weak function of the chlorophyll $a$ concentration, or

$$b_{bp}(\lambda) = 0.30\text{Chl}^{0.62}\left[0.002 + 0.02(1/2-1/4\log \text{Chl})\left[\frac{550}{\lambda}\right]\right]$$  (9)

where Chl is the chlorophyll $a$ concentration (milligrams per cubic meter). This empirically derived model was developed for case I waters only with a $\lambda^{-1}$ wavelength dependence for $b_{bp}(\lambda)$. For the range of BATS chlorophyll $a$ concentrations observed (0.02 to 0.31 mg m$^{-3}$; Figure 3a) the average $b_{bp}(441)$ value calculated using this model is 0.0018 m$^{-1}$. This is in agreement with the average IOP model $b_{bp}(441)$ retrieval, which is also 0.0018 m$^{-1}$. A second estimate of $b_{bp}(441)$ uses the approximation of Gordon et al. [1988],

$$b_{s}(\lambda) = K_{a}(\lambda) / 0.11R_{s}(\lambda)$$  (10)

where $K_{a}(\lambda)$ is averaged over the upper 20 m of the water column. Using this approximation, the average $b_{bp}(441)$ estimate is again consistent with the average IOP model $b_{bp}(441)$ retrieval at 0.0017 m$^{-1}$. Though all three $b_{bp}(441)$ estimates are quite similar in magnitude, the Morel [1988] backscatter model demonstrates a seasonal cycle as a function of chlorophyll $a$, while the other two models show no seasonal signal (figure not shown). In addition, none of the three particulate backscatter estimates are significantly correlated with one another. These varied results in estimates of $b_{bp}(\lambda)$ demonstrate how divergent the various current backscatter models are and the difficulty in accurately estimating this parameter.

While these roughly consistent retrievals of $b_{bp}(\lambda)$ demonstrate they are not related to changes in chlorophyll $a$ concentration, they make no statement as to the other possible sources of the $b_{bp}(\lambda)$ signal. For example, bacterial abundance’s have recently been implicated as a significant component of the particulate backscatter signal [Stramski and Kiefer, 1990, 1991; Morel and Ahn, 1991]. Values for backscatter due to bacteria, $b_{bbac}(\lambda)$, can be calculated using

$$b_{bbac}(\lambda) = N\pi \frac{D^2}{4} Q_{bb}(\lambda, m, D)$$  (11)
where \( N \) is the numerical abundance of bacteria observed at the BATS site (cells per cubic meter; Figure 4b), \( \bar{D} \) is an average diameter of bacterial cells (micrometers), \( Q_{bb}(\lambda, m, \bar{D}) \) is the efficiency factor for backscattering, and \( m \) is the real part of the refractive index. Values of \( \bar{D} \) observed at the BATS site range from 0.42 to 0.49 \( \mu \text{m} \) [Carlson et al., 1996], and a typical range of \( Q_{bb}(441) \) for bacteria from Mie calculations is \( 5 \times 10^{-4} \) to \( 2 \times 10^{-5} \) for refractive indices of \( m = 1.042 \) and 1.068 [Stramski and Kiefer, 1990]. The results of these calculations indicate that values of \( b_{bbac}(441) \) could compose from 2 to 12\% of the modeled \( b_{bp}(441) \) retrievals.

A second estimate of the role of bacteria in particulate backscatter can be made based on the laboratory experiments of Stramski and Kiefer [1990], who measured a bacteria specific backscattering coefficient of \( 2.7 \times 10^{-16} \text{ m}^2 \text{ cell}^{-1} \). Using the observed bacterial abundance's (Figure 4b), bacteria could contribute up to 9\% of the IOP modeled particulate backscatter. These calculations are in general agreement with Stramski and Kiefer [1991] and Morel and Ahn [1991], who estimate that heterotrophic bacteria typically account for 5-20\% of backscattering in oligotrophic waters. This suggests that other constituents besides heterotrophic bacteria must contribute the remainder of the \( b_{bp}(\lambda) \) signal. These particles are likely to be inanimate particulates such as submicron size detrital particles as suggested by Stramski and Kiefer [1991]. This question remains unresolved at this time.

5.4. Application to Upcoming Satellite Ocean Color Missions

The final phase in the assessment of the IOP inversion model is its application to the next generation of ocean color satellite imagers such as the SeaWiFS mission. Importantly, only six visible wave bands will be available for SeaWiFS (412, 443, 490, 510, 555, and 670 nm [Hooker et al., 1992]). In order to evaluate the application of the IOP model to SeaWiFS imagery, we use only the wave bands nearest those planned for SeaWiFS. Further, as the \( R_{rs}(670) \) channel may be used for atmospheric correction [Ding and Gordon, 1995], it has been omitted from the analysis. The results of the SeaWiFS model are nearly identical to the final IOP model (Figure 9) with a change of only 1 to 6\% in the linear regressions between the retrieved SeaWiFS IOPs and the BATS data set (Table 5 versus final model results in Table 4). In addition, the retrieved SeaWiFS IOPs and confidence intervals are virtually identical to the final IOP model results, which use all eight available wave bands (Figure 9 versus Figure 5d). This demonstrates the potential usefulness of applying the IOP model to future SeaWiFS imagery as a global case I algorithm. A more comprehensive evaluation of its suitability as a global model is presently underway.

6. Conclusions and Summary

An inherent optical property inversion model for ocean color spectra has been successfully applied to data from the Sargasso Sea. Specifically, the IOP model retrieves estimates of absorption by phytoplankton, absorption by CDM, and backscatter by particulates, as opposed to the single chlorophyll \( a \) parameter so often
retrieved using CZCS-type algorithms. The strong seasonal variations in ocean biogeochemistry observed in the Sargasso Sea, coupled with the suite of optical and biogeochemical data available through the BBOP and BATS programs, have afforded an excellent opportunity to develop and test the IOP inversion model.

The results of this study show that changes in the constituents that compose total absorption are primarily responsible for the temporal changes observed in \( R_{rs}(\lambda) \). Most importantly, changes in the dissolved and detrital absorption properties are a more significant source of ocean color variability in the Sargasso Sea than changes in phytoplankton absorption. The retrieved \( a_{ph}(441) \) and \( a_{dm}(441) \) estimates show strong seasonal cycles and good correspondence with BATS pigment determinations and indicators of CDM concentration such as the ratio of \( K_{d}(410) \) to \( K_{d}(488) \). IOP model estimates of chlorophyll \( a \) concentrations compare well with those derived from standard band ratio algorithms, demonstrating its value as a chlorophyll \( a \) algorithm. Retrieved estimates of \( a_{dm}(441) \) compose approximately 35% of the total absorption coefficient during the winter-spring season and 0 to 10% during the summer season. This illustrates the importance of estimating CDM absorption in conjunction with chlorophyll \( a \) concentrations, as the presence of CDM will obscure the chlorophyll \( a \) induced ocean color signal.

In contrast, retrieved estimates of particulate backscatter show no significant temporal variations. The retrieved \( b_{bp}(441) \) values are typically smaller than \( b_{bw}(441) \) for the entire time series and demonstrate no correspondence with any of the BATS variables. This indicates that \( b_{bp}(\lambda) \) is, at best, weakly affected by chlorophyll containing particles. Bacteria are shown to contribute up to 10% to estimates of particulate backscatter, in agreement with both Stramski and Kiefer [1991] and Morel and Ahn [1991]. This illustrates that other constituents besides bacteria must contribute to \( b_{bp}(\lambda) \).

The long-range goal of this work is to apply the IOP inversion model to remotely sensed ocean color imagery, such as from the upcoming SeaWiFS and OCTS satellite missions. It is recognized here that while modeling CDM absorption using an exponential decay constant of 0.02 nm\(^{-1}\) may hold for the blue Sargasso Sea, it is by no means a global constant. The fact that the exponential decay constant is the greatest source of variability in the IOP model and that it varies both spatially and temporally will necessitate the reconfiguration of the IOP model to retrieve the exponential decay constant, \( S \), as a parameter. This is something that we are presently investigating. The ability to successfully retrieve accurate estimates of \( a_{ph}(441) \), \( a_{dm}(441) \), \( b_{bp}(441) \) (and in the future \( S \)) from ocean color imagery will provide new parameters so that basin scale estimates of biological processes, such as phytoplankton distributions, primary production rates, and biogenic gas fluxes, can be successfully modeled from space.
Notation

\( \lambda \)  wavelength, nm.

\( \lambda_w \)  reference wavelength (= 440), nm.

\( a(\lambda) \)  total absorption coefficient, m\(^{-1}\).

\( b(\lambda) \)  total scattering coefficient, m\(^{-1}\).

\( b_p(\lambda) \)  total backscattering coefficient, m\(^{-1}\).

\( R_{rs}(\lambda) \)  remote sensing reflectance (= \( E_s(\lambda)/E_d(\lambda) \)), sr\(^{-1}\).

\( E_d(\lambda) \)  downwelling irradiance, W m\(^{-2}\) nm\(^{-1}\).

\( E_s(\lambda) \)  upwelling radiance, W m\(^{-2}\) nm\(^{-1}\).

\( a_s(\lambda) \)  absorption coefficient for pure seawater, m\(^{-1}\).

\( b_s(\lambda) \)  backscattering coefficient for pure seawater, m\(^{-1}\).

\( a_p(\lambda) \)  absorption coefficient for phytoplankton, m\(^{-1}\).

\( a_{ds}(\lambda) \)  absorption coefficient for dissolved/detrital materials, m\(^{-1}\).

\( b_p(\lambda) \)  backscattering coefficient for particulates, m\(^{-1}\).

\( Chl \)  chlorophyll concentration, mg m\(^{-3}\).

\( a_{p}^* (\lambda) \)  \( a_p(\lambda) / Chl \), m\(^2\) mg\(^{-1}\).

\( a_{ds} (\lambda) \)  \( a_{ds}(\lambda) / a_p(\lambda_w) \).

\( b_{p}^* (\lambda) \)  \( b_p(\lambda) / b_d(\lambda_w) \).

\( l_1 \)  constant = 0.0949, sr\(^{-1}\).

\( l_2 \)  constant = 0.0794, sr\(^{-1}\).

\( b_{se}^m (\lambda) \)  total scattering by seawater, m\(^{-1}\).

\( S \)  exponential decay constant, nm\(^{-1}\).

\( Y_n \)  responses (equal to \( R_{rs}(\lambda_w) \)) from nonlinear model, sr\(^{-1}\).

\( f(x_n, \theta_p) \)  nonlinear model expectation function (equal to \( \hat{R}_{rs}(\lambda_w) \)), sr\(^{-1}\).

\( n \)  index of realization per observation (total of eight wavelengths).

\( x_n \)  matrix of independent variables from nonlinear model.

\( \theta_p \)  array of unknown parameters from nonlinear model.

\( Z_n \)  residuals from nonlinear model, sr\(^{-1}\).

\( a_{p}^*(441) \)  modeled absorption coefficient for phytoplankton (equal to \( Chl \cdot a_{p}^*(441) \)), m\(^{-1}\).

\( a_{ds}^*(441) \)  modeled absorption coefficient for CDM (equal to \( a_{ds}(\lambda_w) \cdot a_{ds}^*(441) \)), m\(^{-1}\).

\( b_{p}^*(441) \)  modeled backscattering coefficient for particulates (equal to \( b_p(\lambda_w) \cdot b_{p}^*(441) \)), m\(^{-1}\).

\( \sigma_r \)  standard errors from nonlinear model.

\( k_d(\lambda) \)  diffuse attenuation coefficient, m\(^{-1}\).

\( CZCS_{chl} \)  chlorophyll estimates from CZCS pigment algorithm.
$A$ constant = 1.92, mg m$^{-3}$.

$B$ constant = -1.80.

$a_{am(441)} = a_{am(441)} + a_{pm(441)} + a_{pm(441)}$, m$^{-1}$.

$b_{bact}(\lambda)$ backscattering coefficient due to bacteria, m$^{-1}$.

$N$ numerical abundance of bacteria observed at BATS site, cells m$^{-3}$.

$\bar{D}$ average diameter of bacterial cells, mm.

$Q_{ab}$ efficiency factor for backscattering.

$m$ real part of the refractive index (= 1.042 and 1.068).
References


Figure List

Figure 1. A comparison of the linear and quadratic forms of (1), demonstrating that values of $b_2/(a + b_2)$ from a measure of $R_{ss}(\lambda)$ will differ depending on the model form used. These differences will increase with increasing values of $R_{ss}(\lambda)$; thus the quadratic form of (1) will be particularly important for high $R_{ss}(\lambda)$ observations such as those found in the blue Sargasso Sea.

Figure 2. Known and assumed spectral shapes composing the IOP inversion model: (a) Absorption and backscattering by pure seawater ($a_{wp}(\lambda)$ and $b_{wp}(\lambda)$). (b) Four $a_{wp}^*(\lambda)$ modeled spectra [Prieur and Sathyendranath, 1981; Morel, 1988; Garver et al., 1994; Bricaud et al. 1995] (P&S81, M88, G94, and B95). (c) Three $a_{pm}^*(\lambda)$ modeled spectra, line A.: $S = -0.006$, line B.: $S = -0.014$ and line C.: $S = -0.020$ nm⁻¹. (d) Three $b_{pm}^*(\lambda)$ modeled spectra, line A.: $\lambda_0^0$, line B.: $\lambda_1^1$, and line C.: $\lambda_2^2$.

Figure 3. U.S. JGOFS Bermuda Atlantic Time Series (BATS & BBOP) data: (a) Pigment determinations (fluorometric chlorophyll $a$, fluorometric chlorophyll $a$ plus pheopigments, and HPLC chlorophyll $a$; milligrams per cubic meter) and (b) Wavelength ratios of the diffuse attenuation coefficient ($K_d(410)$ to $K_d(488)$).

Figure 4. U.S. JGOFS Bermuda Atlantic Time Series (BATS) data: (a) Nutrient concentrations (nitrate and nitrite; micromoles per kilogram) and mixed layer depths (meters) and (b) Particulate organic carbon (POC; micrograms per kilogram), particulate organic nitrogen (PON; micrograms per kilogram), and bacterial abundance (number per cubic meter).

Plate 1. Bermuda Bio-Optics Project (BBOP) data; time series of remote-sensing reflectance spectra ($R_{rs}^*(\theta, \lambda)$) used as input to IOP inversion model ($n=8$ wavelengths). Units are in sr⁻¹.

Figure 5. Results of sensitivity analyses performed on the IOP inversion model to assess the effects of varying the assumed spectral shape components. The three retrieved IOPs are the absorption coefficient due to phytoplankton ($a_{ph}(441)$), the absorption coefficient due to colored dissolved and detrital material ($a_{dm}(441)$), and the backscattering coefficient due to particulates ($b_{pg}(441)$). (a) Model set 1: three $a_{dm}^*(\lambda)$ spectra ($S = -0.006, -0.014, -0.02$ nm⁻¹) are each applied to the entire data set while holding the $a_{ph}^*(\lambda)$ and $b_{pg}^*(\lambda)$ spectra constant as Morel [1988] and $\lambda^{-1}$, respectively. (b) Model set 2: three $b_{pg}^*(\lambda)$ spectra ($\lambda_0^0, \lambda_1^1, \lambda_2^2$) are each applied to entire data set while holding the $a_{dm}^*(\lambda)$ and $a_{ph}^*(\lambda)$ spectra constant as $S$ equal to -0.02 nm⁻¹ and Morel [1988], respectively. (c) Model set 3: four $a_{ph}^*(\lambda)$ spectra [Prieur and Sathyendranath, 1981; Morel, 1988; Garver et al., 1994; Bricaud et al., 1995] (P&S81, M88, G94, and B95) are each applied to entire data set while holding the $a_{dm}^*(\lambda)$ and $b_{pg}^*(\lambda)$ spectra constant as $S$ equal to -0.02 nm⁻¹ and $\lambda^{-1}$, respectively. (d) Final Sargasso Sea version of the IOP inversion model composed of the CDM specific absorption coefficient, modeled with $S = 0.02$ nm⁻¹, the modeled phytoplankton specific absorption coefficient of Bricaud et al. [1995], and the particulate specific backscattering coefficient modeled as $\lambda^{-1}$. Point estimates of the retrieved IOPs are shown along with 95% confidence intervals.

Figure 6. Time series of spectrally summed root mean squared error ($RMS_E$) from final Sargasso Sea IOP inversion model.

Figure 7. (a) Results of linear regressions between BATS HPLC chlorophyll $a$ determinations and the estimated chlorophyll $a$ concentrations from the IOP inversion model ($r^2 = 81\%$) and a CZCS band ratio chlorophyll algorithm ($r^2 = 86\%$). Units are
milligrams per cubic meter. (b) Time series of BATS HPLC chlorophyll a determinations and estimated chlorophyll a concentrations from the IOP inversion model and a CZCS band ratio chlorophyll algorithm. Units are milligrams per cubic meter.

**Figure 8.** (a) Time series of ratios of $a_{dm}(410)$ to $a_{tot}(410)$ and $a_{dm}(441)$ to $a_{tot}(441)$. (b) Results of linear regression between $a_{dm}(441)$ to $a_{tot}(441)$ and $K_d(410)$ to $K_d(488)$ ($r^2 = 86\%$).

**Figure 9.** Results of the final version of the IOP inversion model using the six wavelengths that most closely match the sea viewing wide field of view sensor (SeaWiFS) wave bands minus the 670 nm atmospheric correction channel ($n=5$). Point estimates of the retrieved IOPs are shown along with 95% confidence intervals.
### Table 1a. Pearson's Correlation Coefficient of BATS Validation Data Set

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<th>$F_{\text{tot}}$</th>
<th>$F_{\text{chl-a}}$</th>
<th>HPLC$_{\text{chl-a}}$</th>
<th>Nutrients</th>
<th>MLD</th>
<th>Bacteria</th>
<th>POC</th>
<th>PON</th>
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BATS validation data set includes pigments measured by fluorometry and high pressure liquid chromatography ($F_{\text{chl-a}}$, $F_{\text{chla-a}}$, HPLC$_{\text{chl-a}}$; milligrams per cubic meter), nutrients (nitrate and nitrite; micromoles per kilogram), mixed layer depth (MLD; meters), bacterial abundances (numbers per cubic meter), particulate organic carbon and nitrogen (POC and PON; micromoles per kilogram), and ratios of $K_{s}(410)$ to $K_{s}(488)$.

*These correlation coefficients are significant at a level of 0.95.

### Table 1b. Pearson's Correlation Coefficient of $R_{n}(\lambda)$ Data Set

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<td>0.50*</td>
<td>-0.14</td>
<td>-0.14</td>
<td>-0.41*</td>
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</tr>
<tr>
<td>$R_{n}(520)$</td>
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<td>-0.33</td>
<td>-0.37*</td>
<td>-0.35*</td>
<td>0.12</td>
<td>-0.18</td>
<td>-0.07</td>
<td>-0.14</td>
<td>-0.41*</td>
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<tr>
<td>$R_{n}(565)$</td>
<td>0.13</td>
<td>0.13</td>
<td>0.10</td>
<td>0.09</td>
<td>-0.13</td>
<td>-0.12</td>
<td>-0.07</td>
<td>0.00</td>
<td>-0.09</td>
</tr>
<tr>
<td>$R_{n}(589)$</td>
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<td>0.17</td>
<td>0.14</td>
<td>0.03</td>
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<td>$R_{n}(665)$</td>
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<td>0.17</td>
<td>0.00</td>
<td>-0.23</td>
<td>-0.03</td>
<td>-0.02</td>
<td>0.17</td>
<td>0.19</td>
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</table>

$R_{n}(\lambda)$ data are remote-sensing reflectance at eight wave bands (nanometers).

*These correlation coefficients are significant at a level of 0.95.
Table 2. Results of Linear Regressions (Percent Variance Explained; r²) Between Retrieved IOPs (αₚ(641), αₚ(441), and bₚ(641)) and BATS Biogeochemical Variables for Sensitivity Analysis Varying αₚ(53)

Spectra (Here, λₙ and Movel [1988] are held as constant)

<table>
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<tr>
<th></th>
<th>S = 0.008 nm⁻¹</th>
<th>S = 0.014 nm⁻¹</th>
<th>S = 0.020 nm⁻¹</th>
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<td></td>
<td>αₚ(641)</td>
<td>αₚ(441)</td>
<td>bₚ(641)</td>
</tr>
<tr>
<td>Pi</td>
<td>18</td>
<td>71</td>
<td>32</td>
</tr>
<tr>
<td>Piₚ</td>
<td>18</td>
<td>71</td>
<td>37</td>
</tr>
<tr>
<td>HPLCₚ</td>
<td>12</td>
<td>68</td>
<td>37</td>
</tr>
<tr>
<td>Eₚ(410-488)</td>
<td>46</td>
<td>75</td>
<td>37</td>
</tr>
<tr>
<td>POC</td>
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<td>6</td>
<td>5</td>
</tr>
<tr>
<td>PON</td>
<td>33</td>
<td>32</td>
<td>22</td>
</tr>
<tr>
<td>Nutrients</td>
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<td>42</td>
<td>6</td>
</tr>
<tr>
<td>MLD</td>
<td>3</td>
<td>25</td>
<td>14</td>
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<tr>
<td>Bacteria</td>
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</table>
Table 3. Results of Linear Regressions (Percent Variance Explained: $r^2$) Between Retrieved IOPs ($a_{i,j}(441)$, $a_{i,j}(441)$, and $b_{i,j}(441)$) and BATS Biogeochemical Variables for Sensitivity Analysis Varying $b_{ij}(\lambda)$ Spectra (Here $S = 0.020$ and Morel [1988] are held as constant)

<table>
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<tr>
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<th>$\lambda^3$ Spectra</th>
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<tr>
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<td>71.0</td>
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<tr>
<td>HPLC</td>
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<td>3.0</td>
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<tr>
<td>$E_{410:488}$</td>
<td>39.0</td>
<td>8.0</td>
<td>39.0</td>
</tr>
<tr>
<td>POC</td>
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<td>0.0</td>
</tr>
<tr>
<td>PON</td>
<td>12.0</td>
<td>0.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Nutrients</td>
<td>39.0</td>
<td>7.0</td>
<td>38.0</td>
</tr>
<tr>
<td>MLD</td>
<td>39.0</td>
<td>2.0</td>
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</tr>
<tr>
<td>Bacteria</td>
<td>0.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Table 4: Results of Linear Regressions (Percent Variance Explained: $r^2$) Between Retrieved IOPs ($a_{441}$, $a_{441}$, and $b_{441}$) and BATS Biogeochemical Variables for Sensitivity Analysis Varying $a_{441}(A)$

Spectra (Here $S = 0.02$ and $L^2$ are held as constant)

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<tbody>
<tr>
<td>$a_{441}$</td>
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<td>$a_{441}$</td>
<td>$a_{441}$</td>
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<td>Fl</td>
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<td>Bacteria</td>
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</table>
Table 5. Results of Linear Regressions (Percent Variance Explained: $r^2$) Between Retrieved IOPs ($a_{111}(6441)$, $a_{111}(6441)$, and $b_{111}(6441)$) and BATS Biogeochemical Variables for Final IOP Model Using SeaWiFS Wavebands minus 670 nm atmospheric correction channel ($n = 5$)

<table>
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<tr>
<th>Variable</th>
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<th>$a_{111}(6441)$</th>
<th>$b_{111}(6441)$</th>
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<tbody>
<tr>
<td>$F_{	ext{chl}}$</td>
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<td>76</td>
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<td>$F_{	ext{m-c}}$</td>
<td>75</td>
<td>73</td>
<td>5</td>
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<tr>
<td>HPLC$_{111}$</td>
<td>86</td>
<td>76</td>
<td>6</td>
</tr>
<tr>
<td>$K_{11(0.485)}$</td>
<td>34</td>
<td>69</td>
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</tr>
<tr>
<td>POC</td>
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<tr>
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<tr>
<td>Bacteria</td>
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</tbody>
</table>
Figure 2
Figure 3
Plate 1: $R_{rs}(\lambda, 0-5\text{m, time})$ (sr$^{-1}$)
Figure 5c
Figure 5d
Figure 7
CHAPTER 4: GLOBAL APPLICATION OF THE GS97 NON-LINEAR INHERENT OPTICAL PROPERTY INVERSION MODEL

Abstract

Inherent optical properties (IOPs) are the essential bi-optical link between ocean color data and biogeochemical parameters. Here, a well tested non-linear inherent optical property inversion model (the GS97 IOP model) is applied to a global data set of ~900 ocean color spectra from a wide variety of primarily Case I waters (chlorophyll a range 0.02 to 33.0 mg m\(^{-3}\)). The goal of the model is to maximize the amount of information retrieved from ocean color observations. To accomplish this three parameters are selected; 1) absorption by phytoplankton, 2) absorption by dissolved and detrital materials, and 3) backscatter by particulates. The parameter estimates are improved upon via a sensitivity analysis of the spectral shapes selected for use as components of the GS97 IOP model. Importantly, there is no model “tuning” beyond this simple shape selection process. Sensitivity analysis results indicate that the choice of the GS97 spectral shape components vary with environment. Specifically, in oligotrophic waters (<1.0 mg m\(^{-3}\) chl a), the IOP model is most sensitive to the choice of the exponential decay constant, S, used to model spectral absorption by dissolved and detrital materials. In mesotrophic waters (>1.0 mg m\(^{-3}\) chl a), it is most sensitive to changes in the spectral structure of the phytoplankton absorption coefficient. The choice of the spectral shape used to model particulate backscatter does not appear to be significant for either of these oceanic regimes.

Retrieved estimates of chlorophyll a concentration explain 87% of the variance in measured chlorophyll a concentrations. This demonstrates that the GS97 IOP model is useful as a chlorophyll measurement tool, though a bias does exist, causing the model to overestimate at low chlorophyll a concentrations and underestimate at high chlorophyll a concentrations. In agreement with Morel (1987), a weak
power-law relationship is observed between modeled estimates of particulate backscatter and measured chlorophyll a concentrations ($r^2 = 50\%$; power-law exponent = 0.72). Most of the particulate backscatter retrievals are less than or equal to the value of backscatter for pure seawater, with the exception of most of the Case II observations. The retrieved estimates of percent dissolved and detrital absorption comprise from 0% to as much as 90% of total non-seawater absorption at 440 nm, and a trend of decreasing CDM (colored dissolved and/or detrital organic materials) absorption fraction with increasing chlorophyll a concentration is observed. However, this relationship shows little quantitative correspondence to measured chlorophyll a concentrations ($r^2 = 15\%$). This contradicts previous bio-optical assumptions that chlorophyll a is the single index for Case I waters. Importantly, this study demonstrates that semi-analytical bio-optical algorithms produce consistent results and are capable of providing more information than simply chlorophyll a.

1. INTRODUCTION

Remotely sensed observations of near surface ocean color can be used to study ocean biogeochemistry by determining such parameters and processes as pigment concentration, sediment concentration and primary production. Ocean color imagery (OCI) is a valuable tool in that it provides a global view of daily biological and algal processes. Because the biogeochemical parameters of interest must be modeled from OCI data, it is necessary to develop algorithms that will maximize the amount and quality of information.

The GS97 IOP model is evaluated here for use as a global algorithm for the many new OCI missions that have launched or will launch shortly. The model employs non-linear statistical methods for the inversion of ocean color spectra to produce three IOPs for the analysis of biogeochemical variability; 1) the absorption coefficient by phytoplankton, 2) the absorption coefficient by dissolved and detrital materials, and 3) the backscattering coefficient due to
particulates (Garver and Siegel 1997). Methods to invert ocean color observations, such as those employed here, have been explored by Morel and Prieur (1977), Sugihara et al. (1985), Sathyendranath et al. (1989), Gordon et al. (1988), Roessler and Perry (1995), and Hoge and Lyon (1996). The IOP model attempts to maximize the information contained OCI data without any specific “tuning” of model coefficients beyond a sensitivity analysis to chose the spectral shapes used in the model.

2. Data Sets

The two data sets used in this study are the GS97-Global (Garver-Siegel 1997 Global data set) selection data set and the SeaBAM (SeaWiFS Bio-Optical Algorithm Mini- Workshop) validation data set. Both are comprised of remote sensing reflectance spectra \( R_r(0^\circ,\lambda) \); defined as the ratio of upwelling radiance, \( L_u(0^\circ,\lambda) \), to downwelling irradiance, \( E_d(0^\circ,\lambda) \), just above the sea surface) and concurrent measurements of chlorophyll \( a \) from a variety of primarily Case I sites, with some Case 2 data (~20%). The SeaBAM data set is presented in Table 1, it contains 876 \( R_r(0^\circ,\lambda) \) spectra and chlorophyll \( a \) determinations. The GS97-Global (\( n = 927 \)) was compiled originally to perform a global sensitivity analysis of the GS97 IOP model. It differs somewhat from the SeaBAM data set in that it does not include the AMT (Atlantic meridional transect program) data set or the data set assembled by S. Maritorena (see Table 1), it also includes some BBOP (Bermuda bio-optics program), CALCOFI (California cooperative fisheries investigation) and WOCE (World ocean circulation experiment) observations that are not a part of the SeaBAM data set. This difference in selection and validation data sets is not thought to be important as the two data sets exceedingly similar.

The SeaBAM data set was developed for use by the participants of the SeaWiFS Bio-Optical Algorithm Mini- Workshop (SeaBAM) held at the Institute for Computational Earth System Science (ICESS) on the University of California Santa Barbara (UCSB) campus January 22-24, 1997. The
The purpose of the workshop was to evaluate both semi analytical and empirical algorithms for use as the operational SeaWiFS chlorophyll-\(a\) and CZCS-pigment algorithms. This data set is an updated version of the GS97-Global data set with the changes made described in the above paragraph above. The remainder of this section will refer to the SeaBAM data set (Table 1) only.

The data comprising the SeaBAM data set can be found at the following web sites:
2) WOCE Bio-Optics: http://ldeo.columbia.edu/bio_info/HTMLe/opt_WOCE.html
3) U.S. JGOFS Home Page: http://www1.whoi.edu/jgofs.html
4) BBOP Data Archive: http://www.ices.uccsb.edu/bbop/bbop_archive.html

The CARDER and North Sea data sets are both originally above water measurements (i.e., \(R_{r_s}(0^+,\lambda)\)), while the remainder of the data sets are originally below water measurements \((R_{r_s}(0^-,\lambda)); \text{ Table 1}\) which have been extrapolated through the sea surface to keep the data sets consistent. The BBOP, WOCE, EQPAC (Equatorial Pacific) and NABE (North Atlantic bloom experiment) data are comprised of below water measurements that range from 0\(^-\) to ~5m depths. This was done to maximize the size of these data sets. No significant differences in the GS97 IOP inversion results were found between the 0\(^-\) spectra and the spectra taken at depths to 5m.

The \(R_{r_s}(0^+,\lambda)\) spectra can be related to measurements of remote sensing reflectance from just beneath the sea surface \((R_{s}(0^-,\lambda))\) as

\[
R_{s}(0^-,\lambda) \equiv \frac{t}{n^2} \cdot R_{s}(0^+,\lambda)
\]

(1)

where \(t\) is the transmittance term for light across the sea surface \((\equiv 0.98)\), and \(n\) is the index of refraction from air to water \((\equiv 1.341; \text{ Austin and Halikas 1976})\).

The data sets used here are all assumed to be composed of quality measurements of optical profiles and pigment
concentrations (i.e., the optical instruments are correctly calibrated and the profiles correctly processed, the pigment data are analyzed using standard methods). There is a mixture of both fluorometric and HPLC pigment data which may be the source of some undetermined amount of error.

The chlorophyll \( a \) range of the SeaBAM data set is 0.02 to 33.0 mg m\(^{-3}\), spanning three orders of magnitude, with a mean of 0.940 and a standard deviation of 2.887 (mg m\(^{-3}\); Table 1). The data is also highly skewed towards the low end of the distribution (Figure 1a) and a log transformation yields a more normal distribution which is necessary for subsequent regression analyses (Campbell 1995; Figure 1b).

The \( R_{rr}(0^+,\lambda) \) spectra are comprised of the 6 wavelengths for each subdata set that most closely match the Sea Viewing Wide Field of View Sensor (SeaWiFS) and Ocean Color Thermal Sensor (OCTS) wavebands (412, 443, 490, 510, 550, 665 nm). However, the GS97 IOP algorithm uses the exact center wavelength only, and the 665 nm wavelength is not available for the AMT data and a portion of the NABE data (Table 1). These data are used with the five available wavelengths only. A test of the significance in using the 665 nm channel have shown its omission to have a negligible effect on the model retrievals (Garver and Siegel 1997). Data points were considered outliers and removed from the SeaBAM data set if the ratio of modeled to in situ chlorophyll \( a \) was greater than 5:1 or less than 1:5, two or more times for eight different chlorophyll \( a \) prediction models used in the SeaBAM workshop (pers. comm. Stephane Maritorena, 1997).

Sample \( R_{rr}(0^+,\lambda) \) spectra are created by sorting the SeaBAM data set by chlorophyll \( a \) concentration and calculating three mean \( R_{rr}(0^+,\lambda) \) spectra for chlorophyll \( a \) concentrations, <0.1 mg m\(^{-3}\), 0.1-1.0 mg m\(^{-3}\), and >1.0 mg m\(^{-3}\) (Figure 2). These sample spectra demonstrate 1) how the spectra "flatten" as a function of increasing chlorophyll \( a \) concentration, 2) that the variance in these measurements as a function of chlorophyll \( a \) is contained almost exclusively in the blue-green portion of the spectrum, and 3) that using or
omitting the 665 nm channel is not significant due to the minimal variance observed at this wavelength.

The three most oligotrophic open ocean experiments are the BBOP, EQPAC and WOCE experiments (Table 1). These are typified by chlorophyll a means of approximately 0.1 (mg m\(^{-3}\)), compared to the global SeaBAM data set chlorophyll a mean of approximately 1.0 (mg m\(^{-3}\)). The BBOP data set is from the Bermuda Bio-Optics Program (BBOP) and the Bermuda Atlantic Time Series (BATS). This time series was started in 1988 to investigate the seasonal and interannual variability in the biological and chemical processes of the Sargasso Sea and is a part of the U.S. Joint Global Ocean Flux Study (JGOFS). The data set consists of a time series of 139 \(R_{\text{m}}(0^\circ, \lambda)\) spectra from January, 1992 through December, 1995 from this open ocean site located 75 km southeast of Bermuda (31° 50' N; 64°10' W; Knap et al. 1993; Sorenson et al. 1994; Michaels et al. 1994; Siegel et al. 1995ab; Siegel et al. 1997). The 1992-1993 optical data consist of 8 wavebands (412, 441, 465, 488, 520, 565, 589 and 665 nm) while the 1994-1995 data set has 12 spectral bands (410, 441, 465, 488, 510, 520, 565, 589, 625, 665 and 683 nm). The phytoplankton pigments used here are measured by high performance liquid chromatography (HPLC chl \(a\); mg m\(^{-3}\)). This data set has the lowest mean chlorophyll \(a\) (0.093 mg m\(^{-3}\)) concentration of the SeaBAM subdata sets (Table 1).

The WOCE data set is comprised of data taken during the World Ocean Circulation Experiment in both the equatorial Pacific and equatorial Atlantic (legs P19 and A15; Marra et al. 1992; Marra 1992). This global survey of pigments and optics was supported by the U. S. Joint Global Ocean Flux Study. The data set is comprised of 70 \(R_{\text{m}}(0^\circ, \lambda)\) spectra (410, 441, 488, 520, 565 and 665 nm). The concurrent pigment determinations are fluorometric chl \(a\) (mg m\(^{-3}\)).

The EQPAC data set is from the U.S. JGOFS Equatorial Pacific Project which focused its efforts in 1992 at open ocean sites along 140°W between 12° N and 12° S (Murray et al. 1995). The purpose of this project was to study the carbon cycle in a region that is a major contributor to the global carbon cycle. The data come from a spring and fall
survey cruise (tt008 and tt012) and consists of 136 $R_n(0^+,\lambda)$ spectra and concurrent pigment determinations (HPLC chl $a$; mg m$^{-3}$). The $R_n(0^+,\lambda)$ spectra are measured at 410, 441, 488, 520, 550, 633, 656, and 683 nm.

The AMT, CARDER, CALCOFI and NABE data sets have chlorophyll $a$ means closer to the SeaBAM mean, ranging from $\sim$0.5-1.5 (mg m$^{-3}$), with high degrees of variability and some large individual data points observed in the AMT and CALCOFI data sets (Table 1). The AMT data are from the Atlantic Meridional Transect program who's primary objective was to investigate the basic biological processes in the open Atlantic Ocean on very broad spatial scales (funded by the Natural Environmental Research Council (NERC) and the National Aeronautics and Space Administration (NASA)). The data set consists of 42 spectra and pigment determinations (fluorometric chl $a$; mg m$^{-3}$; Robins et al. 1996) from the AMT-1 transect which was approximately 50°N to 50°S from Grimsby (England) to Stanley (Falkland Islands) in September and October, 1995. The $R_n(0^+,\lambda)$ data are measured at 412, 443, 490, 510, 555, 665 and 683 nm.

The CARDER data set is composed of 87 $R_n(0^+,\lambda)$ spectra collected on several different cruises at four subtropical sites including the Arabian Sea, Gulf of Mexico, N. Atlantic and the Pacific. These data are used as the development data set for the Carder semi-analytical algorithm. The $R_n(0^+,\lambda)$ data are measured at 6 wavelengths (412, 443, 490, 510, 555, and 670 nm), the chlorophyll $a$ determinations are fluorometric chl $a$ (mg m$^{-3}$).

The NABE data set is from the North Atlantic Bloom Experiment (legs 4 and 5), a multinational, multidisciplinary pilot study of JGOFS investigating the spring phytoplankton bloom in the North Atlantic and its associated biogeochemical processes (Ducklow et al. 1993, Livingston et al. 1992). The data were collected during 1989 at approximately 20°W between 46°N and 59°N. The 112 $R_n(0^+,\lambda)$ spectra are calculated from measurements at 6 and 8 wavelengths (leg 4/leg 5; 410/412, 441/441, 488/488, 520/521, 550/550, na/589, 633/na, 656/na, 683/na). The pigment determinations are HPLC chl $a$ (mg m$^{-3}$).
The CALCOFI data set comprises almost one third of the global \( R_r(0^+,\lambda) \) data set with 259 \( R_r(0^+,\lambda) \) spectra and pigment determinations (fluorometric chl \( a \); mg m\(^{-3}\); Mitchell et al. 1996). This coastal ocean experiment samples a grid in the Southern California Bight at approximately 30-35°N and 117-124°W at three month intervals commencing in August, 1993. This area encompasses the full dynamic range of temperate coastal and open ocean trophic structure.

A compilation data set containing Case 1 and Case 2 stations under clear and stable sky conditions was assembled by S. Maritorena for use in the SeaBAM workshop algorithm comparisons. The data come from a variety of sites including Monterey Bay and the Gulf of California (Case 1, \( n = 13 \)), the North Sea (Case 2, \( n = 10 \)), Chesapeake Bay (Case 2, \( n = 10 \)), and the Canadian Arctic Ocean (Case 1, \( n = 8 \)). The pigment data are a mixture of both high performance liquid chromatography and fluorometric techniques (mg m\(^{-3}\)). It is the most mesotrophic of all the data sets with a chlorophyll \( a \) mean of 8.137 (mg m\(^{-3}\)).

3. GS97 IOP Model Methodology

The goal of the GS97 IOP inversion model is to maximize the information that can be extracted from ocean color observations. The model is general enough to be applied to a variety of oceanic regions with confidence in its success, and has the advantage of providing measures of uncertainty for the modeled inherent optical properties. A detailed description of the model is found in chapter 3 of this dissertation and in Garver and Siegel (1997).

The GS97 IOP model is based upon the following three assumptions. First, the relationship between \( R_r(\lambda) \) and the total backscattering \( (b_b(\lambda)) \) and absorption \( (a(\lambda)) \) coefficients are assumed to be well known. Second, the optical coefficients for pure water, \( a_w(\lambda) \) and \( b_w(\lambda) \), are known (Smith and Baker 1981; Pope 1993; Morel 1974). Last, the spectral shapes of the specific absorption coefficients for phytoplankton and nonalgal materials and the specific
backscattering coefficient for particulates, \( a_{ph}^*(\lambda) \), \( a_{cdm}^*(\lambda) \) and \( b_{bp}^*(\lambda) \), are known functions of their magnitudes (the asterisks are used to indicate that these are spectral shapes, see also eqn (4)). Assuming these shapes, the magnitudes of the unknown absorption and backscattering coefficients may be determined.

The functional relationship among \( R_{rs}(0^*, \lambda) \), \( a(\lambda) \) and \( b_{b}(\lambda) \) is (Gordon et al. 1988; Waters 1994):

\[
R_{rs}(0^*, \lambda) = \sum_{i=1}^{2} c_i \left( \frac{b_{b}(\lambda)}{b_{b}(\lambda) + a(\lambda)} \right)^i
\]

where the constants \( c_1 \) and \( c_2 \) are taken to be 0.0949 sr\(^{-1}\) and 0.0794 sr\(^{-1}\), respectively (Gordon et al. 1988). The absorption and backscattering coefficients are further partitioned into water, particulate and dissolved components, or

\[
b_{b}(\lambda) = b_{bw}(\lambda) + b_{bp}(\lambda)
\]

\[
a(\lambda) = a_{w}(\lambda) + a_{p}(\lambda) + a_{a}(\lambda)
\]

where \( b_{bp}(\lambda) \) and \( a_{p}(\lambda) \) are the particulate backscattering and absorption coefficients and \( a_{a}(\lambda) \) is the absorption spectrum due to dissolved materials.

Values for \( b_{bw}(\lambda) \) and \( a_{w}(\lambda) \) are assumed to be known (Table 2; Morel 1974; Pope 1993), although some controversy remains over their exact values (e.g., Kirk 1994; Siegel and Michaels 1996). The coefficient for total scattering by seawater, \( b_{m}^{sw}(\lambda) \), is taken from Morel (1974), who has reviewed in great detail the theory and observations pertaining to scattering by both pure water and pure seawater. Values of the backscattering coefficient for seawater are assumed to be equal to 1/2 \( b_{m}^{sw}(\lambda) \). The Pope (1993) and Smith and Baker (1981) \( a_{w}(\lambda) \) values are both used for the absorption by coefficient. The Pope (1993) \( a_{w}(\lambda) \) values were calculated using an integrating cavity absorption meter which resolves absorption coefficients as low as 0.004 m\(^{-1}\). Smith and Baker (1981) deduced values for the absorption coefficient of seawater using values of the diffuse attenuation coefficient for irradiance in the clearest natural waters. The Smith and Baker (1981) values are 1.5 to 2.5 times larger than the Pope (1993) values in the violet and
blue region of the spectrum (Figure 3). This may be result of the Smith and Baker (1981) data being contaminated by the presence of CDM. The implications of using the Pope (1993) \( a_w(\lambda) \) values in place of the Smith and Baker (1981) values is that the modeled retrievals of \( a_{cdm}(\lambda) \) will increase. The Pope (1993) values for \( a_w(\lambda) \) have been recently adopted for use by the SeaWiFS bio-optical algorithm committee.

The particulate absorption spectrum is further divided into phytoplankton (\( a_{ph}(\lambda) \)) and detrital material (\( a_d(\lambda) \)) or

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

In many ocean color inversion models, the contributions to total absorption by detrital particulates (\( a_d(\lambda) \)) and dissolved organic materials (\( a_g(\lambda) \)) are lumped together into a single term that includes both colored dissolved and detrital organic materials (\( a_{cdm}(\lambda) \)) as it is thought that these factors are indistinguishable (e.g., Carder et al. 1989; Roesler and Perry 1995; Garver and Siegel 1997). Thus, the absorption coefficient can be expressed as

\[
a(\lambda) = a_w(\lambda) + a_{ph}(\lambda) + a_{cdm}(\lambda)
\]

The GS97 IOP inversion model parameterizes \( a_{ph}(\lambda) \), \( a_{cdm}(\lambda) \), and \( b_{bp}(\lambda) \) (Garver and Siegel 1997) as,

\[
a_{ph}(\lambda) = C \ a_{ph}^*(\lambda, C)
\]

\[
a_{cdm}(\lambda) = a_{cdm}(\lambda_0) \ \exp(S(\lambda-\lambda_0))
\]

\[
b_{bp}(\lambda) = b_{bp}(\lambda_0) \ (\lambda/\lambda_0)^n
\]

where \( a_{ph}^*(\lambda, C) \) is the chlorophyll specific phytoplankton absorption coefficient (which may be a function of \( C \)), \( S \) is the spectral decay constant for CDM absorption (typically \(-0.014\) to \(-0.02 \) nm\(^{-1}\); e.g., Garver and Siegel 1997; Carder et al. 1989; Roesler and Perry 1995), \( n \) is power law exponent for particulate backscattering coefficient \( (n \equiv 1) \) and \( \lambda_0 \) is a scaling wavelength. The complete IOP inversion model can be expressed as
\[ R_{\text{rs}}(0; \lambda) = \sum_{i=1}^{2} c_i \left\{ \frac{b_{m}(\lambda) + b_{s}(\lambda_n)(\lambda / \lambda_n)^{n}}{b_{m}(\lambda) + b_{s}(\lambda_n)(\lambda / \lambda_n)^{n} + a_{w} + a_{w}(\lambda, C) + a_{w}(\lambda, n) \exp(S(\lambda - \lambda_n))} \right\} (5) \]

By determining \( R_{\text{rs}}(0; \lambda) \) in more than 3 wavelengths, non-linear least-squares techniques can be used to solve equation (5) for the unknown IOP factors (\( C, a_{\text{cdm}}(\lambda_0) \) and \( b_{bp}(\lambda_0) \)) once the IOP shape factors (\( a_{ph}(\lambda, C), S \) and \( n \)) are decided upon. The values of \( S \) and \( n \) may also be determined in this manner if \( R_{\text{rs}}(0; \lambda) \) is provided in enough wavebands.

A Levenberg-Marquardt algorithm is employed which uses a linear approximation to the expectation function to iteratively improve an initial parameter guess (Press et al. 1992). This iterative process continues until convergence is obtained. The specific numerical methods for solving equation (5) and determining the magnitudes of the three IOPs are discussed in Garver and Siegel (1997) (also in chapter 3 of this document) with an excellent broader description of nonlinear techniques being found in Bates and Watts (1988).

Standard errors for the parameter estimates are determined by evaluating the derivative matrix at the least squares parameter estimates. Using the standard errors associated with these estimates, an interval of values that is likely to contain the true value of the IOPs can then be obtained (Garver and Siegel 1997).

To choose the most globally applicable configuration of the GS97 IOP model, a sensitivity analysis was performed which examines the effects of varying the modeled components comprising the model. This involves using the different modeled spectra for particulate and dissolved substances found in the literature in a series of model runs. The GS97-Global data set is used for this selection process.

The retrieved chlorophyll \( a \) estimates from the model configuration that is chosen as the optimal global GS97 IOP model are then compared, via a type II reduced major axis regression (rma), to the measured pigment concentrations for the SeaBAM data set. This type of regression model is preferred when attempting to fit a straight line to data with errors in both coordinates (Press and Teukolsky 1992). In
addition, both the in situ and modeled chlorophyll a data are log transformed due to the log normal distribution inherent in these data (Figure 1). This maintains the assumption of constant variance and keeps the largest chlorophyll a data points from being weighted more heavily in the rma regression (Campbell 1995).

4. RESULTS

4.1. Sensitivity Analysis

The GS97 IOP model optimizes the information retrieved from ocean color observations via a sensitivity analysis of the spectral shapes selected as the individual model components (Garver and Siegel 1997). The model configuration chosen via this analysis differs depending on the chlorophyll a concentration of the ocean color spectra used as input to the IOP model (Table 3).

For chlorophyll concentrations <1.0 mg m⁻³, a model configuration using Bricaud et al. (1995) for phytoplankton absorption, a value of -0.02 nm⁻¹ for the dissolved and detrital absorption slope parameter, and particulate backscatter modeled as $\lambda^{-1}$ results in the highest percent variance explained in an rma regression between the modeled and measured chlorophyll a concentrations (Table 3bc). The greatest improvement in the IOP model chlorophyll a estimates is due to the choice of the exponential slope parameter, $S$. The choice of using the Bricaud et al. (1995) $a_{ph}^*(\lambda)$ over the Morel (1988) $a_{ph}^*(\lambda)$ also improves the model results somewhat, while the choice of $n$ for the $b_{bp}(\lambda)$ model does not cause any significant change in the model results (not shown).

In contrast, at chlorophyll concentrations above 1.0 mg m⁻³ the best model configuration is Morel (1988) for phytoplankton absorption, a value of -0.02 nm⁻¹ for $S$, and particulate backscatter modeled as $\lambda^{-1}$. The use of the Morel (1988) $a_{ph}^*(\lambda)$ model results in the greatest improvement in the IOP model chlorophyll a estimates, while the choice of using -0.02 versus -0.14 nm⁻¹ for the spectral slope.
parameter. This results in only a small and probably insignificant increase in the percent variance explained between the modeled and measured chlorophyll concentrations (Table 3ad). The choice of the $b_p(\lambda)$ model still does not significantly affect the model results.

The Morel (1998) model is found to perform more consistently over the range of chlorophyll concentrations present in the global data set. The Brincaud et al. (1995) model underestimates greatly at chlorophyll $a$ concentrations $>2.0$ mg m$^{-3}$. The divergence between these two models with increasing chlorophyll $a$ concentration is shown in figure 4. The Brincaud et al. (1995) model was originally used as a component in the IOP model for the bluer waters of the Sargasso Sea and was chosen because it allows for variations in the $a_{ph}(\lambda)$ spectra caused by pigment composition and packaging (Garver and Siegel 1997).

The Pope (1993) $a_{w}(\lambda)$ values and the Smith and Baker (1981) $a_{w}(\lambda)$ values are both used in the GS97 IOP model. The results demonstrate that the Pope (1993) values improve the modeled chlorophyll $a$ estimates at concentrations $<0.1$ mg m$^{-3}$ ($r^2 = 38\%$ vs. $47\%$; Table 4).

4.2. Final Global GS97 IOP Model Applied to SeaBAM Data Set

The final global GS97 IOP model chosen for use with the wide range of ocean color observations contained in the SeaBAM data set consists of the Morel (1988) $a_{ph}(\lambda)$ model for phytoplankton absorption, an $S$ of -0.02 nm$^{-1}$ for the dissolved and detrital materials absorption parameterization, particulate backscatter modeled as $\lambda^{-1}$, absorption by water using the values of Pope (1993), and backscatter by water from Morel (1974). This final form of the GS97 IOP model is applied to the entire SeaBAM data set.

The modeled chlorophyll $a$ estimates explain 87% of the variance in the measured chlorophyll $a$ concentrations (Figure 5; Table 5). A bias is noted, along with a slope of less than one, thus the model overestimates at lower chlorophyll
a concentrations and underestimates at higher chlorophyll a concentrations.

The modeled estimates of percent dissolved and detrital absorption have a high degree of variability and are shown to range from 0% to as high as 90% of total non-seawater absorption at 440 nm (Figure 6; Table 5). A general trend of decreasing CDM absorption with increasing chlorophyll a concentration is observed, though no quantitative correspondence to the measured chlorophyll a data exists (log-linear variables; r² = 15). An exception to this trend is the Case II Chesapeake Bay observations which exhibit high CDM absorption estimates at high chlorophyll a concentrations. Two other high CDM/high chlorophyll points observed are in the CARDER data set, both these points are Gulf of Mexico observations.

The particulate backscatter retrievals show a weak relationship to chlorophyll a (r² = 50%; Figure 7a; Table 5). This is roughly in agreement with the Morel (1987) particulate backscatter model. The slope for the Morel (1987) model is 0.45 versus 0.72 for the GS97 IOP model. Importantly, the majority of the bₚ(410) retrievals are at or below the value for backscatter by water at 410 nm (Figure 7b). The data points above bₚ(410) are primarily the Case II observations from the North Sea and Chesapeake Bay data sets.

5. CONCLUSIONS

The GS97 IOP model is a theoretically driven model which retrieves three parameters globally using SeaWIFS and OCTS wavelengths. The model is general enough to be applied to a variety of oceanic regions and has the advantage of providing measures of uncertainty for the modeled inherent optical properties (Garver and Siegel 1997). Importantly, there is no "model tuning" beyond a simple spectral shape analysis procedure that selects the best overall model configuration to optimize the information retrieved from OCI data.
The results of the sensitivity analysis demonstrate that the choice of the spectral shape parameters used in the model varies as a function of chlorophyll a concentration. At low concentrations (<1.0 mg m\(^{-3}\) chl a), the choice of the slope parameter, S, used to model absorption by dissolved and detrital materials is responsible for explaining the highest degree of variability in the modeled parameters. While at concentrations >1.0 mg m\(^{-3}\) chl a, the model is most sensitive to changes in the spectral structure of the chlorophyll specific absorption coefficient. For the majority of the SeaBAM data set, which is predominantly Case I, the choice of the spectral shape used to model particulate backscatter does not change the results of the IOP model parameter estimates.

The GS97 IOP model has been shown to be a useful chlorophyll prediction tool, though a bias is found. Thus, it will be necessary to investigate means to more effectively optimize the model coefficients in order improve model performance. The retrieved estimates of percent dissolved and detrital absorption 1) have a very high degree of variability, 2) do not co-vary with measured chlorophyll a concentrations, and 3) are quite high for some of the open ocean data sets (i.e., BBOP). These results are important as they contradict the previous bio-optical assumptions that these quantities do co-vary in the open ocean. This also indicates that there is much more CDM in the open ocean than originally thought, the presence of which may effect band ratio estimates of chlorophyll a. Therefore, a single index of chlorophyll a alone is not going to be a sufficient to explain all the variability in the properties of the water column. This confirms the necessity of developing bio-optical algorithms, such as the GS97 IOP model, that are capable of retrieving multiple parameters simultaneously.

The particulate backscatter estimates for the SeaBAM data set are all equal to or below the value of backscatter by water, with the exception of the North Sea and Chesapeake Bay Case II observations. This suggests that while a \(\lambda^{-1}\) model for particulate backscatter is sufficient for the open ocean, as is evidenced by the lack of change in the sensitivity analysis, it may not be adequate for coastal
waters with high amounts of total suspended materials. The application of the GS97 IOP model for use in coastal waters will necessitate the reconfiguration of the particulate backscatter model component. Finally, to validate either of these two model parameters, in situ measurements of both colored dissolved and detrital materials and particulate backscatter are badly needed.

Glossary

IOP Inherent optical property
GS97 Garver-Siegel 1997 IOP inversion model
CDM Colored dissolved and/or detrital organic material
OCI Ocean color imager(y)
BBOP Bermuda bio-optics program
WOCE World ocean circulation experiment
EQPAC Equatorial Pacific
NABE North Atlantic bloom experiment
AMT Atlantic meridional transect program
CALCOFI California cooperative fisheries investigation
UCSB University of California Santa Barbara
ICESS Institute for computational earth system science (UCSB)
SeaBAM SeaWiFS Bio-optical algorithm mini-workshop

Table Captions

Table 1: Locations, dates and providers of the subdata sets of remote sensing reflectance spectra and chlorophyll a determinations comprising the SeaBAM data set.

Table 2: Absorption and backscattering coefficients for pure sea water (m^-1: Smith and Baker, 1981; Pope, 1993; Morel, 1974).
Table 3: Sensitivity analysis examining the effects of varying the components comprising the GS97 IOP model. This involves using the different modeled spectra for particulate and dissolved substances found in the literature in a series of model runs applied to the GS97-Global data set. The various model configurations are compared via a linear regression of measured versus modeled chlorophyll $a$ concentrations (shown as $r^2$). Results are shown for a.) the entire data set, b.) $R_n(\lambda)$ spectra who's concurrent chlorophyll determinations is < 0.1 mg m$^{-3}$, c.) $R_n(\lambda)$ spectra who's concurrent chlorophyll determinations is 0.1-1.0 mg m$^{-3}$, d.) $R_n(\lambda)$ spectra who's concurrent chlorophyll determinations is > 0.1 mg m$^{-3}$.

Table 4: Sensitivity analysis examining the effects of varying the values for absorption by pure sea water ($a_w(\lambda)$; Smith and Baker 1981; Pope 1993). The model configurations are compared via a linear regression of measured versus modeled chlorophyll $a$ concentrations (shown as $r^2$). Results are shown for a.) the entire data set, b.) $R_n(\lambda)$ spectra who's concurrent chlorophyll determinations is < 0.1 mg m$^{-3}$, c.) $R_n(\lambda)$ spectra who's concurrent chlorophyll determinations is 0.1-1.0 mg m$^{-3}$, d.) $R_n(\lambda)$ spectra who's concurrent chlorophyll determinations is > 0.1 mg m$^{-3}$.

Table 5: Results of Type II reduced major axis regressions comparing the retrieved GS97 IOP model parameter estimates to measured chlorophyll $a$ determinations from the SeaBAM data set.

Figure List

Figure 1: a) Histogram of measured chlorophyll $a$ determinations from the SeaBAM data set; b) ) Histogram of log transformed measured chlorophyll $a$ determinations from the SeaBAM data set.

Figure 2: Averaged $R_n(0^*,\lambda)$ spectra from the SeaBAM data set spectra representing chlorophyll $a$ concentrations of a) <0.1 mg m$^{-3}$; b) 0.1-1.0 mg m$^{-3}$; and c) >1.0 mg m$^{-3}$.

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Figure 3: Ratio of the Smith and Baker (1981) $a_w(\lambda)$ to the Pope (1993) $a_w(\lambda)$ values.

Figure 4: Ratio of the Bricaud et al. (1995) $a_{ph}(\lambda)$ model to the Morel (1998) $a_{ph}(\lambda)$ model.

Figure 5: Results of a Type II reduced major axis regression comparing the retrieved GS97 IOP model chlorophyll $a$ versus measured chlorophyll $a$ determinations from the SeaBAM data set.

Figure 6: Results of a Type II reduced major axis regression comparing the retrieved GS97 IOP model percent dissolved and detrital absorption versus measured chlorophyll $a$ determinations from the SeaBAM data set.

Figure 7: Results of a Type II reduced major axis regression comparing the retrieved GS97 IOP particulate backscatter versus measured chlorophyll $a$ determinations from the SeaBAM data set.

Notation

$\lambda$ wavelength, nm.
$\lambda_0$ reference wavelength (=440), nm.
$0^-$ just below the sea surface, m.
$0^+$ just above the sea surface, m.
$t$ transmittance term for light across the sea surface (=0.98).
$n^2$ index of refraction from air to water (=1.341).
$R_{rs}(\lambda,z)$ remote sensing reflectance (= $L_u(\lambda,z)/E_d(\lambda,z)$), sr$^{-1}$.
$L_u(\lambda,z)$ upwelling radiance, W sr$^{-1}$ m$^{-2}$ nm$^{-1}$.
$E_d(\lambda,z)$ downwelling irradiance, W m$^{-2}$ nm$^{-1}$.
$a(\lambda)$ total absorption coefficient, m$^{-1}$.
$b(\lambda)$ total scattering coefficient, m$^{-1}$.
$b_b(\lambda)$ total backscattering coefficient, m$^{-1}$.
$a_w(\lambda)$ absorption coefficient for pure seawater, m$^{-1}$.
$b_{bw}(\lambda)$ backscattering coefficient for pure seawater, m$^{-1}$.
$b_{msw}(\lambda)$ total scattering by seawater, m$^{-1}$.
$c_1$ constant = 0.0949, sr$^{-1}$
$c_2$ constant = 0.0794, sr$^{-1}$

$a_p(\lambda)$ absorption coefficient for particulates, m$^{-1}$.

$a_g(\lambda)$ absorption coefficient for dissolved materials, m$^{-1}$.

$a_{ph}(\lambda)$ absorption coefficient for phytoplankton, m$^{-1}$.

$a_d(\lambda)$ absorption coefficient for detrital materials, m$^{-1}$.

$a_{cdm}(\lambda)$ absorption coefficient for dissolved/detrital materials, m$^{-1}$.

$b_{bp}(\lambda)$ backscattering coefficient for particulates, m$^{-1}$.

$C$ chlorophyll concentration, mg m$^{-3}$.

$n$ power law exponent for particulate backscatter ($n \approx 1$).

$S$ exponential decay constant, nm$^{-1}$.

$a_{ph}^*(\lambda) = a_{ph}(\lambda)/C$, m$^2$ mg$^{-1}$.

$a_{cdm}^*(\lambda) = a_{cdm}(\lambda)/a_{cdm}(\lambda_0)$.

$b_{bp}^*(\lambda) = b_{bp}(\lambda)/b_{bp}(\lambda_0)$.

$a_{ph}(\lambda) = C a_{ph}^*(\lambda)$, m$^{-1}$.

$a_{cdm}(\lambda) = a_{cdm}(\lambda_0) \exp(S(\lambda-\lambda_0))$, m$^{-1}$.

$b_{bp}(\lambda) = b_{bp}(\lambda_0) (\lambda/\lambda_0)^{-n}$, m$^{-1}$.

References


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Pope R. M., Optical absorption of pure water and sea water using the integrating cavity absorption meter, Master's Thesis, Department of Physics, Texas A & M University, 1993.


Sathyendranath, S., L. Prieur, A. Morel, A three-component model of ocean colour and its application to remote sensing of phytoplankton


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**Table 1: Global SeaBAM Data Set**

* Denotes pigment determinations made using HPLC techniques.
** Denotes pigments determinations made using fluorometric techniques.
*** Denotes both techniques.
Table 2: Absorption and Scattering Coefficients

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For Pure Sea Water (m²/t)

Table 2: Absorption and Scattering Coefficients
Table 3

a. Global Data Set (n = 927)

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b. Chl Conc. <0.1 chl mg m⁻³ (n = 329)

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<thead>
<tr>
<th>iop model form</th>
<th>iop chl vs. measured chl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morel aph*, S= 0.014, λ-1</td>
<td>22%</td>
</tr>
<tr>
<td>Morel aph*, S= 0.02, λ-1</td>
<td>38%</td>
</tr>
<tr>
<td>Bricaud aph*, S= 0.02, λ-1</td>
<td>49%</td>
</tr>
</tbody>
</table>

c. Chl Conc. 0.1-1.0 chl mg m⁻³ (n = 434)

<table>
<thead>
<tr>
<th>iop model form</th>
<th>iop chl vs. measured chl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morel aph*, S= 0.014, λ-1</td>
<td>37%</td>
</tr>
<tr>
<td>Morel aph*, S= 0.02, λ-1</td>
<td>54%</td>
</tr>
<tr>
<td>Bricaud aph*, S= 0.02, λ-1</td>
<td>62%</td>
</tr>
</tbody>
</table>

d. Chl Conc. >1.0 chl mg m⁻³ (n = 164)

<table>
<thead>
<tr>
<th>iop chl</th>
<th>measured chl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morel aph*, S= 0.014, λ-1</td>
<td>70%</td>
</tr>
<tr>
<td>Morel aph*, S= 0.02, λ-1</td>
<td>75%</td>
</tr>
<tr>
<td>Bricaud aph*, S= 0.02, λ-1</td>
<td>0%</td>
</tr>
</tbody>
</table>
Table 4


<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Global data set</td>
<td>84%</td>
<td>84%</td>
</tr>
<tr>
<td>Chl conc. &lt;0.1 mg m⁻³</td>
<td>38%</td>
<td>47%</td>
</tr>
<tr>
<td>Chl conc. 0.1-1.0 mg m⁻³</td>
<td>54%</td>
<td>53%</td>
</tr>
<tr>
<td>Chl conc. &gt;1.0 mg m⁻³</td>
<td>75%</td>
<td>75%</td>
</tr>
</tbody>
</table>
Table 5

Results of Type II Reduced Major Axis Regression (N = 876)

<table>
<thead>
<tr>
<th>measured chl a (log) versus:</th>
<th>intercept</th>
<th>slope</th>
<th>$r^2$</th>
<th>rmse</th>
<th>bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>modeled chl a (log)</td>
<td>0.244</td>
<td>0.77</td>
<td>87%</td>
<td>0.44</td>
<td>0.38</td>
</tr>
<tr>
<td>modeled %cdom (linear)</td>
<td>26.0</td>
<td>-28.0</td>
<td>15%</td>
<td>46.0</td>
<td>43.0</td>
</tr>
<tr>
<td>modeled bbp (log)</td>
<td>-2.66</td>
<td>0.72</td>
<td>52%</td>
<td>2.55</td>
<td>-2.50</td>
</tr>
</tbody>
</table>
Figure 1a: SeaBAM Data Set

Figure 1b: SeaBAM Data Set
Figure 3: Ratio of SB (1981) aw to Pope (1993) aw

[Graph showing the ratio of SB (1981) aw to Pope (1993) aw over a range of wavelengths (nm).]
Figure 4: Ratio of Brécaud et al. (1995) aph* to Morel (1988) aph*

[Diagram showing spectral attenuation with wavelength (nm) on the x-axis and intensity on the y-axis, with different lines representing different concentrations of chlorophyll (10 mg/m^3, 1 mg/m^3, 0.1 mg/m^3, and 0.01 mg/m^3).]