Deriving in situ phytoplankton absorption for bio-optical productivity models in turbid waters

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[1] As part of Hyperspectral Coupled Ocean Dynamics Experiment, a high-resolution hydrographic and bio-optical data set was collected from two cabled profilers at the Long-Term Ecosystem Observatory (LEO). Upwelling- and downwelling-favorable winds and a buoyant plume from the Hudson River induced large changes in hydrographic and optical structure of the water column. An absorption inversion model estimated the relative abundance of phytoplankton, colored dissolved organic matter (CDOM) and detritus, as well as the spectral exponential slopes of CDOM and detritus from in situ WET Labs nine-wavelength absorption/attenuation meter (ac-9) absorption data. Derived optical weights were proportional to the parameter concentrations and allowed for their absorptions to be calculated. Spectrally weighted phytoplankton absorption was estimated using modeled spectral irradiances and the phytoplankton absorption spectra inverted from an ac-9. Derived mean spectral absorption of phytoplankton was used in a bio-optical model estimating photosynthetic rates. Measured radiocarbon uptake productivity rates extrapolated with water mass analysis and the bio-optical modeled results agreed within 20%. This approach is impacted by variability in the maximum quantum yield ($\phi_{\text{max}}$) and the irradiance light-saturation parameter ($E_{\text{PAR}}(\text{PAR})$). An analysis of available data shows that $\phi_{\text{max}}$ variability is relatively constrained in temperate waters. The variability of $E_{\text{PAR}}(\text{PAR})$ is greater in temperate waters, but based on a sensitivity analysis, has an overall smaller impact on water-column-integrated productivity rates because of the exponential decay of light. This inversion approach illustrates the utility of bio-optical models in turbid coastal waters given the measurements of the bulk inherent optical properties.

INDEX TERMS: 4853 Oceanography: Biological and Chemical: Photosynthesis; 4847 Oceanography: Biological and Chemical: Modeling; 4894 Oceanography: Biological and Chemical: Instruments and techniques; KEYWORDS: coastal, productivity, optics


1. Introduction

[2] There is growing evidence that anthropogenic-induced changes to the coastal ocean are increasing and will continue to do so as coastal regions are developed worldwide [Hallegraeff, 1993]. This is significant as the coastal ocean represents a significant fraction of the total ocean productivity [Field et al., 1998; Biemans and Ziemann, 1992], produces 90% of the global fish catch [Holligan and Reiners, 1992], and acts as a nutrient buffer between the terrestrial ecosystems and the open ocean [Biscaye et al., 1994; Falkowski et al., 1994]. Despite the functional importance of the coastal ocean, our understanding of physical and biological processes in nearshore coastal waters (<30 m deep) is severely limited due to its highly turbulent nature [Brink, 1997]. Therefore there is a need to develop effective means to map biological and chemical processes in coastal ecosystems.

[3] Optical techniques are more commonly being used to assess spatial and temporal phytoplankton dynamics of offshore waters [cf. Advances in Ocean Optics, Journal of Geophysical Research, 100(C7), 13,133–13,372, 1995]; however, these approaches are often compromised because of the optical complexity of coastal waters. For example, ocean color satellite chlorophyll algorithms are based on ratios of remote sensing reflectance ($R_{\text{rs}}$) at different wave lengths. Most satellite algorithms assume that $R_{\text{rs}}$ patterns are based on case 1 waters where the in situ absorption and water-leaving radiance ($L_w$) signal in the blue wave lengths are dominated by chlorophyll absorption while $L_w$ in the green wavelengths is relatively insensitive to chloro-
phyll concentrations [Gordon and Morel, 1983]. Inaccuracies in this approach arise in coastal waters that contain significant amounts of other absorbing/scattering compounds such as dissolved organics, detritus, and even variable phytoplankton communities [Morel and Prieur, 1977; T. Bergmann et al., The impacts of a recurrent resuspension event and variable phytoplankton community composition on remote sensing reflectance, submitted to Journal of Geophysical Research, 2002]. These errors directly impact the utility of optical techniques for estimating primary production and in turn impacts our understanding of carbon flux and nutrient recycling in nearshore ecosystems and their relation to ecosystem function [Jickells, 1998; Cloern, 2001].

[4] Resolving the impact of primary production on any oceanic system is ultimately a question of scale [Bidigare et al., 1992], which has been recently addressed with comparisons of local, regional, and global productivity models in ocean observatories. Comparisons of modeled and measured primary production in these observatories showed mixed results. For example, satellite-based depth-integrated models [see Behrenfeld and Falkowski, 1997 for review] performed well when integrated over long time periods (~200 days) but failed to resolve episodic production events on the order of days to months [Siegel et al., 2001]. Failures in these satellite approaches on regional scales are probably related to the degree to which particular algorithms are “tuned” to a specific region and the resolution of the time step in which satellites sample regions because of orbital trajectories and the occurrence of cloudy weather. Ondrusek et al. [2001] also reported that satellite-based depth-integrated models also did not perform well, however, estimates were improved using a wavelength-resolved model. This model was dependent on chlorophyll specific mean spectrally weighted absorption of phytoplankton (a* ph), which explained 82% of the variance and was able to resolve small-timescale phytoplankton blooms. Productivity models that incorporate a* ph performed well in many different waters [Smith et al., 1989; Bidigare et al., 1992; Waters et al., 1994; Morel et al., 1996] because they describe the fraction of photosynthetically available radiation (PAR) that is absorbed, which is a function of phytoplankton abundance, distribution, community structure, and physiology. Most often studies using these models use chemical extraction [Kishino et al., 1983] or high-performance liquid chromatography (HPLC) to measure a ph, which limits the amount of data that is available thus making comparisons to satellite data difficult [Siegel et al., 2001]. Secondly, the presence of other compounds that absorb light in coastal waters can complicate these approaches.

[5] Between the depth-integrated productivity models and the laboratory-dependent wavelength-resolved models there exists a gap in our ability to resolve and assess the episodic productivity events such as upwelling and river plumes in coastal systems that potentially account for a significant portion of the seasonal productivity signal [Walsh, 1978]. Depth-integrated approaches are limited not only in algorithm development but also in the resolution of temporal coverage due to clouds, while the use of wavelength-resolved models derived from discrete water samples are limited to relatively short space and timescales because of sampling logistics. While there is progress being made in developing satellite productivity algorithms for coastal turbid waters, the issues of cloud cover persist. Therefore if we are to understand the episodic nature of coastal systems on seasonal scales, there is a need to collect parameters for wavelength-resolved models on high-resolution space and timescales over broad regions to improve productivity estimates in turbid coastal regions.

[6] Here we present a high-resolution time series of in-water physical and optical data collected by two cabled profilers as part of the Long-term Ecosystem Observatory (LEO) [see Schofield et al., 2002] to demonstrate an approach which can potentially “fill the gap” between satellite-based depth-integrated productivity models and productivity models dependent on discrete water samples such as wavelength-resolved models. From this time series we directly derive the spectral absorption of phytoplankton in coastal waters from bulk optical parameters measured with “off the shelf” technology and quantify its utility in bio-optically estimating primary productivity in coastal waters. We discuss assumptions and errors associated with our approach. These absorption-based bio-optical model estimates compared well with a physiology-based model rooted in measured photosynthetic-irradiance (P-E) parameters. This technique represents a high-resolution approach to calculating spectrally weighted phytoplankton absorption independent of laboratory extractions. While the scope of our study does not and cannot address the scope of the variability in primary production in the coastal ocean, we feel that automated optical approaches such as the one presented here provide a link for wavelength-resolved models to be applied on broad spatial scales through the use of autonomous platforms.

2. Methods

[7] The 2000 Hyperspectral Coupled Ocean Dynamics Experiment (HyCODE) conducted at LEO represents an integrated coastal-ocean-observing network [Glenn et al., 2000; Schofield et al., 2002]. As part of this experiment, in-water physical and bio-optical time series data were collected from two profiling instrument nodes linked to shore via an electrooptical cable. These nodes were deployed approximately 4 km offshore in 13 m of water at 39°27.41'N, 74°14.75'W (node B and the optical profiler, Figure 1). This study represents data collected from calender days 202-215. Node B provided hydrographic data, and the optical profiler provided optical data. These nodes were separated by about 100 m.

2.1. Profiler Data Sets

[8] As opposed to traditional methods of water-column profiling using lowered instrument packages from ships, both the optical profiler and node B had frames anchored to the seafloor with instrument packages attached to floating drogues that were depth controlled by an underwater winch. Data measured by these profilers streamed directly to the Rutgers University Marine Field Station (RUMFS) in real time via an electrooptical cable, where it was processed and visualized. Node B included a Sea-Bird conductivity-temperature-depth (CTD) mounted with a WET Labs chlorophyll fluorometer, which was sampled at 2 Hz and was profiled at a vertical rate of 2 cm s⁻¹ at regular
intervals. The optical profiler included a WET Labs nine-wavelength absorption/attenuation meter (ac-9) (412, 440, 488, 510, 532, 555, 650, 676, and 715 nm), which sampled at 8 Hz, and a two-wavelength backscatter/fluorometer that sampled at 2 Hz. The optical profiler also profiled at a rate of 2 cm \(s^{-1}\). The ac-9 was factory and clean-water calibrated prior to the experiment, and absorption values were corrected for scattering by subtracting absorption at 715 nm. Absorption, attenuation, backscatter, and chlorophyll fluorescence data were averaged into 0.25-m bins. Because of the abundance of gelatinous zooplankton in the water column and their impact on the data when in the ac-9 tubes, a data filter was applied to eliminate spikes of data of greater than 300% change in signal for any 0.25-m bin. While this would eliminate the potential to document any microlayer [Dekshenieks et al., 2001], we believe that the highly turbulent nature of these waters would minimize their presence. These “spikes” were rare and represented less than 2% of the total data. Additionally, discrete measurements at the profiler were taken by ship over a series of days at the profilers and analyzed for chlorophyll concentration using high-performance liquid chromatography to validate the fluorometer measurements. Node B logged a total of 255 downward profiles while 565 downward profiles were logged from the optical profiler during this experiment. Both node B and optical profiler profiling times were evenly distributed over the course of the experiment, with two exceptions when node B required servicing for about 4 hours.

Absorption, attenuation, and backscatter data were used as input into a radiative transfer model (Hydrolight v. 4.2) to model the spectral scalar irradiance from 400 to 700 nm. Hydrolight model runs applied [Pope and Fry, 1997] pure water absorption values. The Hydrolight model computed a new spectral scattering phase function when the backscatter to total scatter ratio changed by more than 0.005. These model runs also incorporated wind velocity measurements from the RUMFS meteorological tower to estimate surface roughness. The sky spectral radiance distribution is calculated within Hydrolight via RADTRAN based on user-supplied date, time, location, and cloud cover. This modeled spectral irradiance was scaled to wavelength-integrated photosynthetically active radiation values measured at the RUMFS field station. The derived spectral diffuse attenuation coefficients from Hydrolight were then used to propagate the scaled spectral irradiance to all depths.

### 2.2. Optical Inversion Model and Mean Spectral Phytoplankton Absorption

Figure 1. Location of node B and optical profiler connected via electro-optical cable (dashed line) to the Rutgers Marine Field Station located in the Mullica River estuary. Bottom contours are the 5-m isobaths.

![Figure 1](image1.png)

Data were inverted using the optical signature inversion (OSI) model [O. Schofield et al., submitted manuscript, 2003] to estimate the relative abundance weights of phytoplankton, colored dissolved organic matter (CDOM), and detritus. This was based on inverting the bulk ac-9 absorption using a series of spectral absorption curves that represent the major absorbing constituents in the water column. Phytoplankton curves represented the means of high-light- and low-light-adapted phytoplankton from three major phytoplankton taxa: chlorophyll\(_a\)-, chlorophyll\(_b\)-, and phycobilin-containing phytoplankton [Johnsen et al., 1994]. CDOM and detritus absorption curves were treated as idealized exponential functions with a variable amplitude and spectral exponential decay slope (Figure 2). The OSI model varied the amplitudes of all these curves, as well as the exponential slopes of the CDOM and detritus curves within the boundaries of known constraints to minimize the difference between the calculated and measured diffuse attenuation coefficients.

![Figure 2](image2.png)

Figure 2. Input spectra used to invert the in situ absorption values measured by the ac-9 using the OSI model. Phytoplankton spectra are averages of high-light- and low-light-adapted phytoplankton from Johnsen et al. [1994]. Phytoplankton group one represents chlorophyll\(_a\)-containing classes of Bacillariophyceae, Dinophyceae, and Prymnesiophyceae. Phytoplankton group 2 represents the phycobilin-containing class Cryptophyceae. Phytoplankton group 3 represents the chlorophyll\(_a\)-containing classes of Chlorophyceae, Prasinophyceae, and Euglenophyceae. CDOM and detritus spectra are idealized exponential functions.
Figure 3. Paired $E_{\text{PAR}}$ and $\phi_{\text{max}}$ reported water column means and standard deviations from various studies: 1–3, Sathyendranath et al. [1999]; 4–7, Figueiras et al. [1999]; 8–10, Lorenzo et al. [2002]; 11, Moline and Prêzelin [1996]; 13–21, Kvytayanga et al. [1998]; 22, Schofield et al. [1993]; and 23 New Jersey Coastal Region (LEO). Antarctic studies are characterized by low $E_{\text{PAR}}$ and high $\phi_{\text{max}}$, while the opposite trend is evident for tropical and temperate waters. The mean values for this study for $E_{\text{PAR}}$ and $\phi_{\text{max}}$ were calculated from all the literature studies in temperate and tropical waters except those estimated at the study site using $^{14}$C incubations (all values not labeled “Antarctic” or “New Jersey Coastal Region (LEO)”).

difference between the total modeled absorption (sum of all phytoplankton, CDOM, and detritus curves) and total absorption measured by the ac-9. The OSI model returns the estimated weights of each phytoplankton group, and CDOM and detritus, as well as the spectral exponential slopes (or decay) of CDOM and detritus. These weights are analogous to the amplitude or abundance of their respective absorbing constituent.

Spectral absorption of phytoplankton ($\sigma_{ph}(\lambda, z, t)$) was calculated by

$$\sigma_{ph}(\lambda, z, t) = \sum_{n=1}^{3} w_{n}(\lambda, z, t) a_{n}(\lambda),$$

where $n$ is the phytoplankton group number, $w_{n}(\lambda, z, t)$ is the calibrated inverted scalar weight calculated by the OSI model of a specific group of phytoplankton ($m^{-1}$), which is not spectrally dependent, and $a_{n}(\lambda)$ is the relative absorption of the input spectra of specific group of phytoplankton at a given wavelength. OSI calibration data showed that the amplitude of the phytoplankton spectra was generally underestimated due to the package effect of natural populations compared to the laboratory cultures from which the input spectra are derived. Although there was an underestimation, this underestimation was well quantified so that a calibration factor of 1.393 was applied to the relative weights of phytoplankton derived by the OSI (Schofield et al., submitted manuscript, 2003). Modeled spectral scalar irradiance values were combined with $\sigma_{ph}(\lambda, z, t)$ to calculate the mean spectral absorption of phytoplankton $\bar{a}_{ph}(\lambda, z, t)$ (m$^{-1}$) using:

$$\bar{a}_{ph}(\lambda, z, t) = \frac{1}{400} \int E_{\text{PAR}}(\lambda, z, t) a_{ph}(\lambda, z, t) d\lambda,$$

where $E_{\text{PAR}}(\lambda, z, t)$ is spectral scalar irradiance from 400 to 700 nm (W m$^{-2}$) modeled by Hydrolight v. 4.2.

2.3. Bio-Optical Modeling of Primary Production
From an ac-9

The bio-optical model used in this study to calculate primary production was

$$PP(z, t) = \bar{a}_{ph}(z, t) \phi_{\text{max}} E_{\text{PAR}} \tanh \left( \frac{E_{\text{PAR}}(z, t)}{E_{\text{PAR}}(z, t)} \right),$$

where PP(z, t) is primary production (mg C m$^{-3}$ h$^{-1}$), $\bar{a}_{ph}$ 292 (z, t) is calculated from equation (2) and was based solely on the optical inversion of ac-9 data, $\phi_{\text{max}}$ is the maximum quantum yield of carbon fixation (mol C mol photons$^{-1}$ absorbed$^{-1}$), $E_{\text{PAR}}$ is the irradiant flux at which photosynthesis becomes light saturated (mol photons m$^{-2}$ s$^{-1}$), and $E_{\text{PAR}}(z, t)$ is the PAR-integrated scalar irradiant flux on the phytoplankton cells (mol photons m$^{-2}$ s$^{-1}$) modeled by Hydrolight v. 4.2. $E_{\text{PAR}}(z, t)$ was used for this calculation because phytoplankton absorbs light from all 301 directions. Because our in situ optical data set did not 302 include measurements of $\phi_{\text{max}}$ and $E_{\text{PAR}}$, we conducted a 303 literature survey to determine a mean for these waters 304 (Figure 3, see figure legend for references). The data in 305 Figure 3 represent the mean and standard deviation of the 306 water column measured in each study. The mean $\phi_{\text{max}}$ 307 and $E_{\text{PAR}}$ value used in this study were calculated from all the 308 literature studies in temperate and tropical waters except 309 from those labeled “Antarctic” or “New Jersey Coastal 310 Region (LEO)” in Figure 3. We did not include values of 311 $\phi_{\text{max}}$ and $E_{\text{PAR}}$ estimated by $^{14}$C incubations from the 312 LEO site in this mean because we wished to keep the bio- 313 optical method of estimating primary productivity and the 314 physiological method of estimating productivity as inde- 315 pendent as possible. The mean values used for $\phi_{\text{max}}$ and $E_{\text{PAR}}$ for this study were 0.025 mol C mol photons$^{-1}$ absorbed$^{-1}$ and 124.85 mol photons m$^{-2}$ s$^{-1}$, respectively. 318 In this manuscript, this productivity model will be simply 319 referred to as the bio-optical model.

2.4. Productivity Measurements of Phytoplankton

[11] Discrete water samples were collected at the profilers 322 with Niskin bottles from the R/V Waterford on calendar days 323 203, 208, and 212 at both the surface and at a depth of 8 m 324 (Table 1). These days coincided with major changes in 325 water-column structure that were observed from real-time 326 observation of profiler data, which allowed for adaptive 327 sampling. These samples were collected at approximately 328 1000 LT on these days and kept dark for 30 min while 329
Table 1. Phytoplankton Physiological Parameters Measured During Experiment

<table>
<thead>
<tr>
<th>Day (Depth)</th>
<th>(P_{\text{max}}, \text{mol C m}^{-3} \text{h}^{-1})</th>
<th>(E_{\text{o}}, \text{mmol photons m}^{-2} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>203 (surface)</td>
<td>1.21</td>
<td>146.44</td>
</tr>
<tr>
<td>203 (8 m)</td>
<td>1.07</td>
<td>55.66</td>
</tr>
<tr>
<td>208 (surface)</td>
<td>1.38</td>
<td>62.08</td>
</tr>
<tr>
<td>208 (8 m)</td>
<td>3.05</td>
<td>140.88</td>
</tr>
<tr>
<td>212 (surface)</td>
<td>1.76</td>
<td>96.09</td>
</tr>
<tr>
<td>212 (8 m)</td>
<td>3.64</td>
<td>71.23</td>
</tr>
</tbody>
</table>

returning to the field station. Aliquots were then filtered onto 47-mm GF/F filters and stored in an −80°C freezer for phytoplankton pigment determination using HPLC analysis using the methods of Wright et al. [1991]. Photosynthetic-irradiance curves were measured using the methods of Prézelin et al. [1989]. Measured carbon uptake values for each of the \(P-E\) curves were curve fitted as a hyperbolic tangent function using the Simplex method of Cacchi and Cacheris [1984] to estimate the chlorophyll-specific maximum photosynthetic rate (\(P_{\text{max}}, \text{mol C m}^{-3} \text{h}^{-1}\)), the light-limited slope of photosynthesis (\(E_{\text{l}}\)), and the photosynthetic light-saturation parameter (\(E_{\text{s}(\text{PAR})}\)). Error estimates were calculated using the methods of Zimmerman et al. [1987].

The general model used in this study to calculate physiology-based primary production is based on the work of Jassby and Platt [1976]:

\[
PP(z, t) = P_{\text{max}}(z, t) \tanh \left( \frac{E_{\text{o}(\text{PAR})}(z, t)}{E_{\text{s}(\text{PAR})}(z, t)} \right)
\]

where \(PP, P_{\text{max}}, E_{\text{o}(\text{PAR})},\) and \(E_{\text{s}(\text{PAR})}\) are as described previously. To extrapolate physiological parameters (\(P_{\text{max}}\) and \(E_{\text{s}(\text{PAR})}\)) measured at the profilers over the same depth-time area that the profilers were deployed (gives them similar \(z\) and \(t\) distribution as equation (3)), multivariate cluster analysis of paired salinity and temperature observations from node B was used to define statistical boundaries on water masses. Salinity and temperature values were standardized by subtracting the mean of the data set and dividing by the standard deviation of the data set. On the basis of Euclidian distance, a distance matrix was calculated for the data set and then hierarchically clustered according to Ward’s linkage [Ward, 1963]. The generated similarity index was used in conjunction with a multivariate analysis of variance (MANOVA) to define the major groupings of temperature and salinity observations (i.e., water masses).

Physiological parameters were measured within each of the statistically distinct water masses except a water mass in the lower portion of the water column on days 213–215. This restricted physiology-based depth-integrated productivity calculations to days 202–212. In the case where a specific water mass was continuous throughout the depth of the water column, the water mass was subdivided at the 8-m mark, below the climatological depth of the thermocline in this area (7 m), so that the physiological parameters measured at the surface and at 8-m depth in the water mass were separated. On the basis of this extrapolation method, the depth-integrated productivity was calculated.

The assumptions of this approach do not incorporate diel variation of physiological parameters, which have been shown to be important in calculating short-timescale productivity [Sournia, 1974; Prézelin et al., 1987; Prézelin, 1991]. To mediate these effects, measurements were made at approximately the same time of day. However, these diel cycles introduce errors into our comparison of physiology-based and bio-optical calculations of primary production, although not just our errors. In this manuscript, this productivity model will be referred to as the physiology-based model.

3. Results

3.1. Hydrographic and Optical Variability at the LEO

Profilers

[16] The winds, surface currents, and hydrographic structure of the water column were highly variable with several major events occurring during the experiment (Figures 4 and 5). These events directly impacted the distribution of phytoplankton biomass and other absorbing constituents such as CDOM and detritus that modulate the in-water spectral light field, therefore affecting what phytoplankton can absorb for photosynthesis. On calendar days 202–203, strong northeasterly winds were in phase with the surface currents measured using a SeaSonde Radar system, showing a strong southward alongshore flow (Figure 4). The density structure was stratified during this time period (Figure 5a). On days 203–205, the winds shift abruptly, blowing from the southwest, and surface currents progressively rotated toward the northeast. This is coincident with the appearance of comparatively denser water at the bottom, which resulted in strong stratification. The presence of this cold bottom water was reflected in the optical properties. Associated with the bottom water were smaller particles as indicated by the backscatter to total scatter ratio (Figure 5b) [Stramski and Morel, 1990]. During these times of strong stratification the majority of the phytoplankton biomass was present in the upper water column (Figures 5c and 5d). The exponential slopes and relative abundance of the CDOM and detritus also reflected the physical hydrography with low concentrations and large exponential slopes associated with the dense bottom water (Figure 6 and Table 2). Large

![Figure 4](image-url)
exponential slopes are often associated with marine-derived 
waters in this region, reflecting the degradation and break- 
ing of double bonds of the CDOM [Vodacek et al., 1997]. 

On day 206, winds became northeasterly, and the 
surface currents turned to the southwest; however, the 
bottom water intrusion of dense seawater persisted until 
day 207 when it was eventually dissipated during a period 
of strong winds and increasing current velocities. When the 
stratification eroded, phytoplankton concentrations in- 
creased throughout the water column (Figures 5c and 5d). 
Interestingly, the concentration of the CDOM and detritus 
decreased dramatically throughout the water column during 
these mixing events (Figures 6a and 6c). The northeasterly 
winds persisted until approximately day 208. Despite this, 
surface currents continued to flow southward with increasing 
velocity. This trend continued until day 210, when 
winds were from the north, and surface currents were 
flowing >60 cm s\(^{-1}\) to the south. The entire water column 
during this time was well mixed, with decreased density and 
salinities as low as 28.5 practical salinity unit (Figure 5a).

Cross-shore transects of salinity and temperature to 
the north of the profiler and measured currents surface 
current radars (Figure 4) indicated a large volume of 
southward flowing low-salinity water. Given the large 
volume of relatively fresh water at the profilers, the water 
was likely from the Hudson River [Johnson et al., 2003; 
R. J. Chant and S. M. Glenn, Secondary circulation and 
mixing in a buoyant coastal current, submitted to 
Journal of Geophysical Research, 2003, hereinafter referred to as 
Chant and Glenn, submitted manuscript, 2003]. The pres- 
ence of the Hudson River water was clearly delineated in 
the optical properties reflecting high concentrations of large 
particles (Figure 5b), phytoplankton (Figures 5c and 5d), 
CDOM, and detritus (Figures 6a and 6c). The phytoplank- 
ton community during this experiment was primarily diatom 
based determined by the abundance of fucoxanthin in the 
HPLC samples. Concurrent with the high concentrations of 
CDOM and detritus was a decrease in their respective 
spectral exponential slopes. Low exponential slopes often 
indicate that the CDOM and detrital material are young.

Figure 5. Time series of in situ data taken by the profilers during the experiment. (a) Density structure 
with water mass boundaries (white) defined by cluster analysis (see text). (b) The ratio of scattered and 
backward scattered light. (c) Chlorophyll fluorescence measured by the optical profiler. (d) The OSI-
derived calibrated relative phytoplankton abundance. Optical and biological parameters have similar 
patterns as the hydrographic structure. Relationships between these bulk optical and derived optical 
parameters and the density structure are found in Table 2.
Local winds did not heavily influence the plume (Chant and Glenn, submitted manuscript, 2003) suggesting southward flow resulted from a buoyancy-derived pressure gradient. Alternating southeast and southwest winds blew from days 211 to 215 while the surface currents weakened and eventually the currents veered offshore (Figure 4). Associated with this was a restratification and intrusion of dense bottom waters. As before, the dense bottom waters were characterized by low concentrations of phytoplankton, CDOM, detritus, and small particles (Figures 5 and 6). [19] The clustering scheme applied to the hydrographic data suggests that at least three water masses were advected past and sampled by the profilers. A MANOVA showed that the three water masses defined by this clustering scheme were significantly different (Pillai Trace approximately $F = 2988.747, p = 0.000$). The major features defined by cluster analysis as specific water mass types were the deep intrusions on calendar days 202–207 and 212–215, intermediate mixed regime on calendar days 206–210, and the Hudson River Plume on calendar days 210–214 (Figure 5a). This clustering was also consistent with the major changes observed in the in situ optical properties and derived optical constituents (Figures 5 and 6). While the time series shown has multiple forcing events, in general, as the water column becomes less dense, absorption and attenuation increased as well as the derived loads of phytoplankton biomass, CDOM, and detritus. This suggests that the high optical loads during this time period may be terrestrial in origin.

![Figure 6. Time series of inverted in situ absorption data taken by the optical profiler during the experiment. (a) The relative abundance of CDOM and (b) the exponential slope of the CDOM curve. (c) The relative abundance of detritus and (d) the exponential slope of the detritus curve. Derived optical properties show distinct characteristics of the hydrographic structure during the experiment. Relationships between these derived optical parameters and the density structure are found in Table 2.](image)

| Table 2. Correlation of Inherent and Derived Optical Properties With Density$^a$ |
|----------------------------------|-----|-----|
| Variable                        | $R^2$ | Slope |
| $A_{440}$, m$^{-1}$             | 0.58 | -    |
| $C_{555}$, m$^{-1}$             | 0.27 | -    |
| $B_{547}$, m$^{-1}$             | 0.06 | +    |
| $B_{547}/B_{440}$               | 0.27 | +    |
| Chlorophyll fluorescence         | 0.22 | -    |
| $W_{\text{phyto}}$              | 0.46 | -    |
| $W_{\text{CDOM}}$               | 0.59 | -    |
| $W_{\text{detritus}}$           | 0.60 | -    |
| $S_{\text{CDOM}}$               | 0.03 | +    |
| $S_{\text{detritus}}$           | 0.02 | +    |

$^a$Although not all correlations are strong, they are significant ($p = 0.000$). In general, high optical loads are associated with less dense water. This suggests that optical loads during this time period are terrestrial in nature.
Conversely, the particle size index (ratio of backscatter to total scatter), and the spectral exponential slopes of CDOM and detritus were positively correlated. This suggests that steeper slopes and smaller particles are coincident with marine waters during this time period (Table 2).

3.2. Spectrally Weighted Phytoplankton Absorption

Surface irradiance during the course of the experiment was highly variable due to passing storms and patchy cloud cover. Peak $E_{a(PAR)}$ values during the clearest atmospheric days approached 2000 μmol photons m$^{-2}$ s$^{-1}$ while surface irradiance values during stormy days were four times lower (Figure 7a). In general, PAR attenuated rapidly, with its first attenuation length usually 0.5–1.5 m deep (Figure 7c). Modeled hyperspectral profiles of $E_a(\lambda)$ indicated that attenuation was largest in the wavelengths associated with maximal absorption peaks of chlorophyll, illustrating the importance of phytoplankton to bulk optical properties. Similar to chlorophyll biomass, values of $a_{ph}$ calculated from equation (2) showed the largest values in the Hudson River water mass and the lowest values in the deep water intrusions. However, $a_{ph}$ decreased and smeared with depth due to the decreased availability of red and blue wavelengths of light at depth. The $a_{ph}$ thus did not reflect the same vertical and temporal structure as chlorophyll fluorescence because the wavelengths at which chlorophyll absorbs maximally were differentially attenuated more rapidly in the water column due to the spectral optical structure of the water column (Figures 7b and 7d).

3.3. Physiology and ac-9-Derived Bio-Optically Based Primary Production

To extrapolate discrete $^{14}$C measurements over time, measured physiological variables associated with $^{14}$C incubations were assigned to specific water masses defined by multivariate cluster analysis of temperature and salinity as described in section 2.4. These physiological measurements extrapolated into depth and time space using water mass analysis were then combined with the continuous light fields based on the in situ optical profiler measurements and the Hydrolight calculations (Figure 7c). Values were integrated over depth and will be herein referred to as the productivity calculated through the physiology-based model. This time series of depth-integrated primary production was compared
to the bio-optical model estimates using the ac-9-derived weighted phytoplankton absorption and equation (3). To convert $\alpha_{ph}$ into a productivity rate, we required estimates of $f_{max}$ and $E_k$(PAR) which were taken from the literature (Figure 3). Using the mean values for $f_{max}$ (0.025 mol C mol photons$^{-1}$) and $E_k$(PAR) (124.85 mol photons m$^{-2}$ s$^{-1}$) for temperate marine waters, the depth-integrated bio-optical model showed good agreement with depth–integrated physiology–based model ($r^2 = 0.91$, $p < 0.001$). The total productivity predicted by the two models was different by 20%.

4. Discussion

4.1. Physical and Optical Properties of the Study Site

Southwesterly wind-driven coastal upwelling is an annual event at LEO and has been observed every summer over the last decade (Glenn et al., submitted manuscript, 2003). These upwelling-favorable events result in phytoplankton blooms [Schofield et al., 2002] and represent one of the dominant biogeochemical signals in nearshore (<30 m depth) New Jersey coastal waters (Glenn et al., submitted manuscript, 2003). However, the optical properties in the region are complex due to the proximity of the Mullica River estuary (Figure 1) and the presence of coastally trapped freshwater plumes from the Hudson River, which introduce significant amounts of CDOM and detritus. Therefore the waters at LEO are often classified as “case 2” [Morel and Prieur, 1977]. The T-S relationships in this study indicated the presence of significantly different water masses; however, their boundaries were difficult to resolve from a T-S diagram alone. Measured and derived optical properties were also highly variable and showed significant correlations to hydrographic structure (Table 2).

4.2. Bio-Optical Modeling of Photosynthesis in Coastal Waters

Implicit in many primary production models is some parameterization of $\alpha_{ph}$ [cf. Bidigare et al., 1992], which has general inverse relationship between $f_{max}$ and $E_k$(PAR). The purpose of time-integrating water-column productivity over these three scales is that they address the short- to medium-timescale events which characterize physical forcing and biological responses in the LEO-15 research area (S. M. Glenn et al., Studying the biogeochemical impact of summertime upwelling using a coastal ocean observatory, submitted to Journal of Geophysical Research, 2003, hereinafter referred to as Glenn et al., submitted manuscript, 2003). Interestingly, the mean-paired $f_{max}$ and $E_k$(PAR) observations from our literature survey (Figure 3) were generally coincident with the error minima (Figure 9).

Figure 8. Using mean-paired $E_k$(PAR) and $f_{max}$ from temperate and tropical oceans excluding this study, bio-optically modeled (dashed) and physiology-based productivity that was extrapolated on the basis of the water mass analysis (solid) was in good agreement across all days ($r^2 = 0.91$, $p < 0.001$). The total productivity predicted by the two models was different by 20%.

Figure 9. (a)–(c) Relative percent error isoclines between the $^{14}$C extrapolated to the ac-9-based water-column-integrated productivity estimates over instantaneous, daily, and 11-day timescales, respectively. The shape of these contours shows the effect of $f_{max}$ and $E_k$(PAR) covariance on modeled productivity estimates. Data points represent literature means from Figure 3 and are coincident with the error isoclines.
traditionally been measured using discrete water samples or estimated empirically [Bricaud et al., 1995; Cleveland, 1995]. Often \( a_{ph} \) is derived from the product of biomass and biomass-normalized phytoplankton absorption \( (a_{ph}^*) \) [Sakshaug et al., 1997]. The utility of this approach is limited given the laboratory requirements for deriving \( a_{ph}^* \), and the well-documented variability in \( a_{ph}^* \) seasonally [Sathyendranath et al., 1999], regionally [Bricaud and Stramski, 1990; Hoepffner and Sathyendranath, 1992; Sosik, 1996; Arbones et al., 2000], and physiologically [Prézelin and Bozdar, 1986; Lewis et al., 1988; Bricaud et al., 1995]. Ideally, the parameterization of \( a_{ph}^* \) is not needed if \( a_{ph} \) could easily be derived from in situ bulk optical measurements. Currently, off-the-shelf technology offers the potential to measure bulk optical properties [Dickey, 1991; Chang and Dickey, 1999].

[25] High-resolution maps of \( a_{ph} \) can be derived from an ac-9 (Figure 7d) allowing wavelength dependency of phytoplankton absorption and spectral light quality to be estimated. To first order \( a_{ph} \) is described by chlorophyll biomass \(( r^2 = 0.71, p = 0.000) \); however, \( a_{ph} \) is a consistently decreasing function with depth. This decrease, a second-order effect, reflects the spectral skewing of light with depth. This spectral skewing of \( a_{ph} \) is sensitive to the relative concentrations of the other in-water constituents. For example, when CDOM and detritus signals were large (day 210) blue wavelengths (400–450 nm) of light were attenuated 30% faster than when CDOM and detritus signals were low (day 202). In contrast, the difference in red wavelength (650–700 nm) attenuation was approximately 7%. The result of this variable skewing of the in situ light field accounts for the scatter between the phytoplankton fluorescence estimates and \( a_{ph} \). Given in situ \( a_{ph} \) and \( E_{k(PAR)} \), the remaining difficulty for estimating photosynthesis is defining the magnitude of \( \phi_{max} \) and \( E_{k(PAR)} \); as these terms cannot currently be derived optically. While \( \phi_{max} \) has been related to fluorescence transients via fast repetition rate fluorometry [Köber et al., 1988; Falkowski, 1992; Kolber and Falkowski, 1993], conversion of the electrons generated by photosystem II to carbon fixation is difficult [Kroon and Dijkman, 1996]. This conversion requires a thorough understanding of the environmental and physiological regulation of the photosynthetic quotient [Laws, 1991]. In nature, both \( \phi_{max} \) and \( E_{k(PAR)} \) are variable in time and space ranging from hours to seasons [Sournia, 1974; Prézelin, 1991; Kyewalyanga et al., 1998; Gong et al., 1999; Sathyendranath et al., 1999; Marra et al., 2000] and meters to kilometers [Schofield et al., 1993; Lindley et al., 1995; Sosik, 1996; Kyewalyanga et al., 1998].

Over these scales, \( \phi_{max} \) and \( E_{k(PAR)} \) can vary by a factor of 10 and 5, respectively. To compensate for this effect, \( E_{k(PAR)} \) has been empirically or theoretically parameterized from underwater irradiance fields [Waters et al., 1994; Moline et al., 1998]. Parameterizations of \( \phi_{max} \) have proven difficult, and so is often assumed to be constant or is measured using radiolabel incubations [Marra, 1993; Waters et al., 1994; Ondrusek et al., 2001]. It was a pleasant surprise then that using temperate and tropical ocean means of \( \phi_{max} \) and \( E_{k(PAR)} \) from the literature resulted in such a good agreement of physiology-based productivity. Therefore we felt this serendipitous result merited further analysis.

[26] The relationship between \( a_{ph}, E_{k(PAR)}, \) and \( \phi_{max} \) is coupled via

\[
E_{k(PAR)} = \frac{P_{max}}{\phi_{max} a_{ph}},
\]

which implies a general inverse, covariant relationship between the product of \( \phi_{max} \) and \( a_{ph} \) and \( E_{k(PAR)} \). However, sensitivity analyses of these terms in bio-optical productivity models [Sosik, 1996] suggest that \( a_{ph} \) is not strongly coupled to either \( E_{k(PAR)} \) or \( \phi_{max} \). This effect is probably a function of photoprotective pigments [Bidigare et al., 1989; Schofield et al., 1996]. In contrast, \( E_{k(PAR)} \) and \( \phi_{max} \) appear to be strongly coupled with each other [see Figure 6 in the work of Sosik, 1996]. This is supported by the nonnormal natural distribution of \( \phi_{max} \) and \( E_{k(PAR)} \), which shows an inverse distribution suggesting that \( \phi_{max} \) and \( E_{k(PAR)} \) covary in a nonlinear fashion (Figures 3 and 9). This implies that their errors are not additive. Therefore determining the sensitivity of an absorption-based bio-optical model without considering this covariance would overestimate the importance of the variability of \( \phi_{max} \) and \( E_{k(PAR)} \) to a productivity estimate. Because of this we varied \( \phi_{max} \) and \( E_{k(PAR)} \) over their natural ranges independent of other water column properties to quantify their impact on water-column productivity. In addition, this error analysis assumed that errors in the model related to the production of photo-protective pigments were low because they were found in negligible amounts in the HPLC analysis (zeaxanthin 0.1–0.2 µg L\(^{-1}\)) during the experiment and because of the highly turbid nature of the water column.

[27] The net result of this analysis is that the variation in \( \phi_{max} \) dominates the error in the productivity estimates over hourly, daily, and 11-day timescales in temperate waters (Figure 9). This is not surprising given past field results in which \( \phi_{max} \) varied by a factor of 10 [Bannister and Weidemann, 1984; Cleveland et al., 1989; Schofield et al., 1993; Babin et al., 1996]. While the bio-optical model was very sensitive to \( \phi_{max} \), when considering literature values, the variability in \( \phi_{max} \) is markedly constrained temperate and tropical waters ranging from ~0.015 to 0.04 mol C mol\(^{-1}\) photons absorbed\(^{-1}\). Generally, the highest values are found at depth, often near nutriclines [Cleveland et al., 1989], where photosynthesis is light limited. Therefore the impact on integrated water-column productivity is relatively small. In these temperate waters, \( E_{k(PAR)} \) varies by a factor of 7 (50–350 µmol photons m\(^{-2}\) s\(^{-1}\)), reflecting photoacclimation processes [Falkowski and LaRoche, 1991; Escoubas et al., 1995]. However, the impact of \( E_{k(PAR)} \) variability is relatively small in our analysis, as is evidenced by the elongation of the error contours along the \( E_{k(PAR)} \) axis (Figure 9). This reflects that a change in \( E_{k(PAR)} \) (especially when \( E_{k(PAR)} > 100 \)) does not dramatically impact the proportion of the total water-column photosynthesis that is light-saturated as this is largely determined by the exponential decay of light. It is the combined effect of naturally constrained \( \phi_{max} \) values and the rapid exponential decay of light in our system that allow for our approach of bio-optically estimating productivity to reasonably approximate the physiology-based model.

[28] While these general paradigms apply to temperate and tropical waters, caution should be used, as this is not a global phenomenon. In the Southern Ocean, discrete and
water-column-averaged $\phi_{\text{max}}$ values (Figures 3 and 9) are on average two times higher than that measured in tropical and temperate waters. The variance in $\phi_{\text{max}}$ is also high. In these polar waters the $E_{\text{PAR}}(\phi)$ magnitude (<100 $\mu$mol photons m$^{-2}$ s$^{-1}$) and variability (factor of 4) is low. Given equation (3) and that mean and variability of $E_{\text{PAR}}(\phi)$ are relatively low, the light-saturated photosynthetic term is dominated by the product of $\phi_{\text{max}}$ and $a_{\phi}$. [29] In contrast, the tropical and temperate oceans are generally stratified much of the year and have high incident irradiance during the phytoplankton growing season. Because of these factors, the euphotic zone is generally nutrient limited. The combination of low nutrient with high-light conditions can reduce the average water column, $\phi_{\text{max}}$. This decrease reflects the production of photoprotective pigments [Bidigare et al., 1989; Schofield et al., 1996; Fujita et al., 1994; Babin et al., 1996] and a decrease in functional photosynthetic reaction centers [Falkowski et al., 1989].

The phytoplankton response to the high-light environment is an increase in $E_{\text{PAR}}(\phi)$ given a sufficiently stable environment [Ryther and Menzel, 1959; Côté and Platt, 1983].

5. Conclusions

[30] Bio-optical measurements show promise for mapping phytoplankton; however, these techniques have often been compromised in turbid coastal waters. The bulk and derived optical parameters mimicked the hydrographic structure that was dominated by three distinct water masses advected through the study area. The correlations of density with bulk-derived optical properties suggest that much of the optical load is from terrestrial sources. Calculated $a_{\phi}$, from the relative phytoplankton weight and spectral irradiance showed that $a_{\phi}$ was to first order a function of biomass but was modulated based on the spectral absorbing characteristics of in-water biotic and nonbiotic constituents. In addition, $a_{\phi}$ could be used to initialize a bio-optical productivity model and calculate productivity within 20% given reasonable estimates of $\phi_{\text{max}}$ and $E_{\text{PAR}}(\phi)$. Sensitivity analysis of the bio-optical model indicated that most of the error is potentially associated with $\phi_{\text{max}}$; however, the natural range of water-column-averaged $\phi_{\text{max}}$ is constrained. The bio-optical model was not as sensitive to $E_{\text{PAR}}(\phi)$ when estimating water-column productivity because of the exponential decay of light in these turbid waters.

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