DATA REPORT FOR CALIBRATION
OF A BIO-OPTICAL MODEL
FOR NARRAGANSETT BAY

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NOTICE

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ABSTRACT

Bio-optical models describe the quality and quantity of the light field at various depths in the water column. The absorption and scattering of light within the water column are wavelength dependent. The behavior of light also varies depending on the specific dissolved and particulate constituents in the water column, making local (or at least regional) calibration of such models necessary. This report provides the calibration data specific for Narragansett Bay, Rhode Island, relative to absorption by colored dissolved organic matter (CDOM), non-algal particles (NAP) and phytoplankton, and total backscattering. With the calibration in place, information on the concentration of CDOM, total suspended solids and chlorophyll $a$ is all that is needed in order to calculate the light for any depth for sites those parameters represent.

Keywords: bio-optical model, Narragansett Bay, diffuse attenuation coefficient, light absorption, light scattering

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INTRODUCTION

The data contained in this report supports the development of calibration curves for the use of a bio-optical model for Narragansett Bay, RI. The calibration will support research evaluating the applicability of a bio-optical model for light quantity in establishing depth limits for seagrass (*Zostera marina*) in Narragansett Bay, RI. To accomplish this, a site specific calibration of the model was necessary. The model provides estimates of changes in light quantity and quality with depth which can be used, to predict the maximum depth likely for seagrass. In the case of Narragansett Bay, the seagrass is *Zostera marina*. As light travels through the water column it interacts with water molecules, dissolved materials, suspended inorganic and organic particulates and phytoplankton, resulting in a variety of absorption and scattering phenomena. Because these phenomena (especially absorption) are wavelength dependent and vary with the particular constituents of a given waterbody, it is necessary to calibrate the bio-optical model’s parameters for each region of the country—and maybe for each body of water of interest within those regions. With calibrations completed, measures of colored dissolved organic matter (CDOM), total suspended solids (TSS) and chlorophyll *a* (Chl *a*) for any given location allows estimates of light penetration to be calculated.

The model used is based on Lee et al. (2005), as described by Kenworthy et al. (2014).

\[
K_d(\lambda) = (1 + 0.005\theta_0) a_t(\lambda) + 4.18[1 - 0.52\exp(-10.8 a_t)]b_b(\lambda) \tag{EQ 1}
\]

Where:
- \(\lambda\) = wavelength of light (nm)—Equation 1 is wavelength dependent,
- \(K_d(\lambda)\) = spectral diffuse attenuation coefficient (m\(^{-1}\)),
- \(\theta_0\) = above-water solar angle of incidence (degrees)—zenith angle,
- \(a_t(\lambda)\) = total absorption coefficient (m\(^{-1}\))—note, \(\lambda\) omitted when this is in the exponent for simplicity,
- \(b_b(\lambda)\) = backscattering coefficient (m\(^{-1}\)).

By integrating over the visible wavelengths, the diffuse attenuation coefficient for photosynthetically active radiation (PAR) can be calculated,

\[
K_d(PAR) = \frac{1}{z} \ln\left(\frac{PAR_z}{PAR_0}\right) \tag{EQ 2}
\]

Where:
- \(K_d(PAR)\) = diffuse attenuation coefficient, integrated over 400 to 700 nm,
- \(z\) = depth in meters,
- \(PAR_z\) = light spectrum at depth \(z\), and
- \(PAR_0\) = light spectrum at surface.

The Equation 1 requires two site specific pieces of information, the absorption and back scattering coefficients. The absorption coefficient (m\(^{-1}\)) is an additive equation:

\[
a_{total}(\lambda) = a_{water}(\lambda) + a_{CDOM}(\lambda) + a_{particles}(\lambda) + a_{pigments}(\lambda) \tag{EQ 3}
\]
Where total absorption is a function of four primary components, absorption by water itself, by colored dissolved organic matter (CDOM), by particles (total suspended solids—TSS) and by pigments (i.e., phytoplankton—usually related to chlorophyll \(a\)). Absorption by pure water is a fixed function (wavelength dependent), and the relationship between wavelength and absorption from Pope and Fry (1997) is usually used. The difference in the absorption of light between pure water and seawater is minimal and often ignored. The other three components have predictable relationships between absorption and wavelength of light; however, these relationships need to be calibrated for each body of water.

Since we are interested ultimately in how much light makes it down to a given depth for seagrass, absorption only gives a portion of the story. Light also is scattered within the water column. While most of this light is scattered in the forward direction (e.g., continues downward), a significant portion of the light entering the water column is scattered back out of the system. The percentage of light backscattered is empirically derived for each area of interest. Total scattering (m\(^{-1}\)) is calculated as:

\[
b(\lambda) = b_p(\lambda) + b_w(\lambda) \tag{EQ 4}
\]

Where \(b_w(\lambda)\) is the total scattering associated with pure water (also referred to as molecular scattering), and, light absorption, is considered a constant, wavelength dependent factor. The other parameter, \(b_p(\lambda)\), is total particulate scattering (in all directions). Unlike absorption, there is no easy method to distinguish between pigmented and non-pigmented particle scattering.

The methods to calibrate each of the parameters associated with the bio-optical model are presented below. All of the data represented by the calibration figures are presented in Appendices.

**METHODS**

This calibration establishes the relationship between several easily measured water column properties (Chl \(a\), TSS and CDOM) and the components of absorption and scattering that contribute to Equation 1. Samples from Narragansett Bay were collected from the upper, middle and lower Bay (see Figure 1) from different times of the year, representing Zostera’s predominant growing season. The purpose of the sampling scheme was to establish how variable the calibration parameters are with respect to time and space. One calibration has been established for the entire Bay for all months within which the seagrass *Zostera marina* grows.
Figure 1. Map of Narragansett Bay showing location of sampling stations
Absorption by water

There is no calibration associated with the absorption by pure water. It is considered a standard relationship, and is plotted in Figure 2. In general, the additional absorption at seawater salinities due to the salts is minimal in the 400 to 680 nm range (Kirk 2011), and is usually ignored in coastal applications.

![Figure 2. The relationship between wavelength and absorption coefficient in pure water. Data from Pope and Fry, 1997](image)

Absorption by CDOM—The relationship between absorption coefficient due to Colored Dissolved Organic Matter (CDOM) and wavelength of light follows an exponential decay function (Bricaud et al. 1981, Kirk 2011). The slope for the decay function (designated as $S_{CDOM}$) is generally consistent for a given body of water. Because the relationship between absorbance and wavelength is assumed consistent, the curve can be normalized to a single reference wavelength—usually 440 nm.

$$a_{CDOM}(\lambda)_{norm} = e^{-S_{CDOM}(\lambda-440)}$$

EQ 5

The actual absorbance of light at a given wavelength will be governed entirely by the concentration of CDOM at the reference wavelength. Therefore, all that is needed is the absorbance at 440 on a filtered sample in order to “reconstitute” the entire absorbance vs wavelength curve. That is:

$$a_{CDOM}(\lambda) = a_{CDOM}(440) * a_{CDOM}(\lambda)_{norm}$$

EQ 6

Note: $a(440)$ vs CDOM concentration is generally considered to be a linear relationship.
Calibration method: water samples were processed as described in Keith et al. (2002). CDOM measurements were made using a Perkin-Elmer Lambda 35 spectrophotometer using a 10 cm path length cell with deionized water as the reference. Measured absorbance was recorded at 1 nm intervals from 400 to 750 nm. Final data scans were averaged\(^1\) every 5 nm.

Generally, when using a spectrometer to measure the concentration of a dissolved compound or compounds the only interaction of the beam of light with the substance in the cuvette is either absorption or transmission. However, even under the best of conditions some light will be scattered out of the pathway (scattering due to water is accounted for with the blank, but not scattering due to CDOM). Since this is neither absorbed nor transmitted, it is a source of error—it did not get measured as part of the transmitted light. To correct for this, measured absorbance recorded at 750 nm was subtracted from values measured at all of the other wavelengths. Absorbance at 750 nm is usually assumed to be zero, therefore any recorded non-transmittance at 750 nm was assumed to be a loss of light due to scattering rather than true absorbance. These corrected measurements are in absorbance, which is the \(\log_{10}\) of the ratio of transmitted to incident light. Because we are interested in the absorption coefficient (which is related to exponential decay), we actually need the natural log of that ratio—which is the same as multiplying the original Perkin-Elmer absorbance by 2.303 (the natural log of 10). Finally, the absorption coefficient was divided by the path length in meters (0.1 m) to convert the units to \(\text{m}^{-1}\).

Absorption by non-pigmented particles (or non-algal particles (NAP)—As with CDOM, the relationship between absorbance due to non-pigmented particulates and wavelength of light follows an exponential decay function (Gallegos 2001, Roesler et al. 1989). This decay coefficient \(S_{\text{NAP}}\) is fairly consistent for a given body of water. As with CDOM, the NAP curves also were normalized to a reference wavelength—440 nm.

\[
a_{\text{NAP}}(\lambda)_{\text{norm}} = e^{-S_{\text{NAP}}(\lambda-440)} \quad \text{EQ 7}
\]

The actual absorbance of light at a given wavelength will be governed largely by the concentration of TSS at the reference wavelength. Once that relationship is established the entire absorption curve can be recreated. That is:

\[
a_{\text{NAP}}(\lambda) = a_{\text{NAP}}(440) * a_{\text{NAP}}(\lambda)_{\text{norm}} \quad \text{EQ 8}
\]

Note: unlike CDOM, \(a_{\text{NAP}}(440)\) vs TSS concentration is not necessarily a linear relationship. Therefore, the calibration step needs to include establishing the site-specific relationship between the absorbance at a reference wavelength (usually 440 nm) and TSS. Our data for \(a_{\text{NAP}}\) vs TSS was very scattered. However, the range of TSS values in Narragansett Bay was narrow compared to other locations (e.g., Chesapeake Bay—Gallegos et al. 2006). Our data appeared to be consistent with that presented by Babin et al. (2003), therefore in our final model we used their relationship between \(a_{\text{NAP}}\) and TSS.

\(^1\) For example, data for 400 nm is the average of 400 through 404 nm, for 405 the average of 405 through 409, and so forth.
Calibration method: Calibration was performed in two parts. We followed the procedure outlined in Gallegos and Neale (2002) and Mitchell et al. (2003), except we used a 50 mm integrating sphere coupled to the Perkin-Elmer Lambda 35. Sample water (200 mL) was filtered using a glass fiber filter (GF/F, nominal pore size of 0.7 µm), and absorption on the filter (from 350 to 750 nm) was measured before and after extraction with methanol (to remove algal pigments—see below). The second measurement is the one needed for non-pigmented particles. The difference between the two spectra is the absorption by phytoplankton pigments (see next section). Just as with CDOM, the decay slope for absorption coefficient plotted against wavelength was calculated by fitting the exponential equation to the data. The second calibration step was to establish the relationship between TSS and absorption at 440 nm. TSS was determined by filtering a volume of water (e.g., 500 mL) onto a pre-weighed glass fiber filter. Just as with CDOM, we multiplied the absorbance data from the spectrophotometer by 2.303 to convert to absorption coefficients (see Kishino et al. 1985, Tassan and Ferrari 1995). In addition, correction for volume filtered and area of the filter was included (see below). The 750 nm correction listed above for CDOM is even more important with the quantitative filter technique. Scattering of the light away from the entrance of the integrating sphere may be appreciable, and will be recorded as absorption. Generally, absorption at 750 nm is considered to be negligible, so any values recorded at this wavelength were likely due to scattering.

In addition to the above scattering error, photons have a high probability of experiencing multiple scattering events on their way through the filter. This increases the effective path length of the light for which correction is also needed. Fortunately, Cleveland and Weidemann (1993) have done this correction empirically:

$$OD_{susp}(\lambda) = 0.378 \ OD_{filt}(\lambda) + 0.523 \ OD_{filt}(\lambda)^2$$  \hspace{1cm} EQ 9

Where $OD_{susp}$ is the optical density of the suspended particles for a given wavelength, and $OD_{filt}$ is the optical density of the particles on the filters. Remember, optical density is the ratio of the log10 of the absorbance of the sample to the log10 of a reference. To adjust this to an absorption coefficient—which accounts for the exponential decrease in light with depth—we have to convert to natural logarithms (multiply by 2.303). Finally, we have to account for the volume filtered ($V$) and the clearance area ($A$) of the filter. If we express the former in m$^3$ and the latter in m$^2$, then the unit for the absorption coefficient will be in m$^{-1}$:

$$a_{NAP}(\lambda) = \frac{2.303 \ OD_{susp}(\lambda)}{V/A}$$  \hspace{1cm} EQ 10

Methanol treatment—After each filter was measured for total particle absorption, each was placed into a separate polystyrene petri dish (60 x 15 mm) and 10 mL of room temperature methanol was gently added. Extraction in the methanol lasted a minimum of 1 hr. Filters were then removed from the petri dish, replaced into the filter apparatus, and the methanol within the petri dish run through the filter to remove any particulates that might have been dislodged during the filtration process.

2 Because the degree of wetness of the filter can affect the scan results, after filtering each sample, 100uL of 0.22 um filtered seawater was added back to each filter just prior to measurements.
the extraction process. Afterwards, 10 mL of 0.22 um filtered seawater was used to rinse the methanol from the filter.

**Absorption by phytoplankton**—The relationship between absorbance due to phytoplankton and wavelength does not follow a set function (e.g., exponential) as did CDOM and non-algal particulates. Therefore, an empirically derived absorption spectrum is used in the modeling effort. We used two procedures to establish this average spectrum. The first is derived from the most recent research on seagrass bio-optical models. (Biber et al. 2008, Gallegos 2005, Gallegos and Neale 2003, Gallegos et al. 2006). Here the empirically derived spectra were normalized to absorption at 675 nm and then averaged by wavelength.

\[ a_{\phi}(\lambda)_{\text{norm}} = \frac{a_{\phi}(\lambda)}{a_{\phi}(675)} \]  

**EQ 11**

Where:

- \( a_{\phi}(\lambda)_{\text{norm}} \) = the normalized absorption of pigmented particles for a given wavelength,
- \( a_{\phi}(\lambda) \) = the absorption of pigmented particles for a given wavelength, and
- \( a_{\phi}(675) \) = the absorption of pigmented particles at 675 nm.

A relationship between chlorophyll \( a \) (Chl \( a \)) concentration and \( a_{\phi}(675) \) was used to establish a specific pigment absorption spectra for a given location. As with \( a_{\text{NAP}}(440) \) vs TSS concentration, the relationship between absorption at 675 nm and chl \( a \) concentration is not necessarily linear. Therefore, the calibration step included establishing the site specific relationship between the absorbance at 675 nm and chl \( a \) concentration.

\[ a_{\phi}(675) = A[\text{Chl } a]^B \]  

**EQ 12**

The coefficients \( A \) and \( B \) are empirically derived. The actual absorbance of light at a given wavelength now can be estimated entirely by the concentration of chlorophyll \( a \) using the reference wavelength. That is:

\[ a_{\phi}(\lambda) = a_{\phi}(675) \ast a_{\phi}(\lambda)_{\text{norm}} \]  

**EQ 13**

In a second approach, we established relationships between Chl \( a \) and every wavelength between 400 and 700 nm in 5 nm steps. This is the approach used by Bricaud et al. (1995) and Matsuoka, et al. (2007). This latter approach accounts for the fact that phytoplankton light absorption in the blue region of light is much more variable than that in the red region. This is largely due to packaging effect (the amount of pigment per unit cell and its arrangement within the cell), photo-acclimation, or both. Photo-acclimation can result in a significant change in the concentration of accessory photosynthetic pigments, as well as non-photosynthetic, photo-protective pigments. Both of these types of pigments have their greatest absorption in the blue region.

**Calibration method:** As with absorption by non-pigmented particles, absorption by phytoplankton pigments requires two steps. However, the first step—establishing the absorption spectrum—was accomplished during the calibration of the non-pigmented particles by subtracting from the total absorption spectrum of the filter the absorption spectrum of the
particulates alone. The second calibration step needed was to establish the relationship between the concentration of Chl \( a \) and absorption (from the particle filter method) at wavelengths of interest. In general, the procedure for collecting and processing water samples followed those used by NASA (Mitchell, et al. 2003)—which were consistent with the procedure used by Gallegos and Neale (2002) for their work in Case 2 waters. Chlorophyll \( a \) analyses were similar to those described in Keith et al. (2002). Samples (100 mL) were filtered onto 47 mm Whatman GF/F filters using a hand vacuum pump. Filters were placed into 15 mL screw-capped polystyrene tubes containing 10 mL of 90% acetone, and extracted in a freezer overnight (approximately 18 hr) in the dark. Fluorescence was measured using a Turner Designs Model AU-10 fluorometer equipped with the Non-Acidification Optical Kit (P/N 10-040R).

**Scattering**

Unlike absorption, whose parameters can be measured with typical instrumentation available in most laboratories, scattering requires specialized equipment. We used an ac-s in situ spectrophotometer from WET Labs to measure total scattering. This instrument simultaneously measures total light attenuation and total absorbance in approximately 4nm increments between the wavelengths of 400 and 730 nm. Scattering is calculated by the difference between total attenuation and total absorption. Absorption was corrected for scattering using 739 nm as the reference wavelength according to the procedure described by Slade et al. (2010). The ac-s measurements were made in the laboratory using a gravity fed system (Slade et al. 2010).

The actual scattering of light at a given wavelength is governed largely by the concentration of TSS. Scattering is assumed to be minimally influenced by CDOM (if at all) and Chl \( a \) has no direct influence. Its influence on scattering is through the “particles” (phytoplankton) with which it is associated. The relationship between scattering at a reference wavelength (555 nm) and total suspended solids (TSS) is described by the equation (Kenworthy et al. 2014):

\[
b_p(555) = \alpha TSS^\beta
\]

EQ 14

Where:

- \( b_p(555) \) = total particle scattering at 555 nm,
- \( TSS \) = total suspended solids (mg/L), and
- \( \alpha \) and \( \beta \) are empirically derived coefficients.

In 2014 backscattering was measured directly in situ Narragansett Bay using a Satlantic Profiler II Ocean Profiler (Satlantic LP Canada), equipped with a backscattering sensor (a 470 and 700 nm). We also made some direct backscattering measurements in 2013 using a HydroScat (Hydro-Optics, Biology and Instrumentation Laboratories) (at 420 nm). The data from both were combined\(^3\) to establish the relationship between TSS (mg/L) and backscattering

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\(^3\) Backscattering data from the HydroScat at 420nm was adjusted downward using the relationship between wavelength and particle backscattering established using the Satlantic profiler.
coefficient (m$^{-1}$). Wavelength specific backscattering was calculated assuming a linear relationship between backscattering at 470 and 700 nm.

As with absorption, there is no calibration associated for scattering by pure water, it is considered a standard relationship with wavelength of light (Buiteveld et al. 1994). Backscattering is assumed to be half of the total scattering. The backscattering absorption coefficients are plotted in Figure 3.

\[
\text{Backscattering} = \frac{1}{2}\text{bw}
\]

![Figure 3. Plot of standard backscattering coefficient for pure water (Buiteveld et al. 1994)](image)

**RESULTS**

**CDOM Calibration**

Figure 4 shows the CDOM scans for samples collected during the summer 2013 and spring 2014. Figure 5 is a summary of all of the data in Figure 4 normalized at 440 nm. The overall average spectral slope ($S_{\text{CDOM}}$) was 0.0159 nm$^{-1}$ with a standard deviation of 0.0011 nm$^{-1}$ ($n = 51$). This is similar to the spring/summer average for data reported by Keith et al. (2002) from the years 1999 and 2000 (0.0166 nm$^{-1}$). It is also similar to the overall average (0.0176 nm$^{-1}$) presented in Babin et al. (2003) for 346 CDOM samples for coastal waters around Europe. It appears that, at least for coastal waters, the calibration curve for CDOM is fairly consistent.
**Figure 4.** CDOM absorption scans for samples from Narragansett Bay—summer 2013 and spring 2014. Data for these curves are presented in Appendix A.

**Figure 5.** Summary of CDOM calibration data for Narragansett Bay—normalized at 440 nm. Solid black line is the mean of all 51 curves. Red dashed lines are plus and minus one standard deviation. Solid yellow line is the best fit trend line (Equation 5). The open and closed markers are data from Gallegos and Neale (2002) for the Rhode River, Maryland and the St. Johns River, Florida, respectively.
NAP Calibration

Figure 6 shows the Non-algal particle (NAP) absorption scans for samples collected during the summer of 2013. Figure 7 is a summary the data presented in Figure 6 normalized to 440 nm. The overall average spectral slope ($S_{\text{NAP}}$) was 0.0136 nm$^{-1}$ ($n = 37$). As with CDOM, this also is similar to the overall average (0.0123 nm$^{-1}$) presented in Babin et al. (2003) for 348 NAP samples for coastal waters around Europe. Although, it is greater than the average reported (0.0088 nm$^{-1}$) for recent work in the Chesapeake Bay (Gallows et al. 2006). Figure 7 also shows a slight depression in the absorption coefficient for wavelengths less than 425 nm. It is not clear why this happened; however, a similar effect is shown in samples from the Baltic Sea in Babin et al. (2003). For the purposes of the bio-optical model for Narragansett Bay, this slight shift in absorption coefficient was ignored.

The absorption curves for NAP occasionally were not smooth, especially in the 400 to 450 and 650 to 700 nm ranges. This is not uncommon. We followed the procedure as presented by Babin et al. (2003) and Matsuoka et al. (2011), whereby the non-linear regression was conducted on each curve without the data in these ranges. This was done to “avoid any residual pigment absorption that might still have been present.”

![NAP Absorption](image)

Figure 6. Non-algal particle (NAP) absorption scans from Narragansett Bay—summer 2013 (July, August and September). Data for these curves are presented in Appendix B
Typically, a correlation between absorption by non-pigmented particles and TSS is used to adjust the normalized calibration curve to in situ absorption coefficients (Gallegos et al. 2006, and others—including Kenworthy et al. 2014). Figure 8 (top left) shows the relationship between $a_{\text{NAP}}(440)$ and TSS for samples collected in Narragansett Bay. There does not appear to be a relationship. However, the range of TSS values in our data set is narrow compared to those in other data sets. Gallegos et al. (2006) show what appears to be a similar amount of scatter within their Figure 9a. Our Figure 8 (top right) shows the Narragansett Bay data re-plotted with the range on the axes the same as the range used in Gallegos et al. (2006). The degree of vertical scatter is similar to that displayed in Gallegos et al. (2006) Figure 9c—although the absorption coefficient in Narragansett Bay for a give TSS value is slightly less than that in their Figure 9c. Similarly, we re-plotted the data along with the regression for $a_{\text{NAP}}$ vs TSS (SPM$^4$ in their paper) published in Babin et al. (2003), see Figure 8 (bottom). The degree of scatter within the range of TSS for Narragansett Bay is similar to that depicted in Figure 15 of Babin et al. (2003). The central tendency of our absorption coefficient data appears to line up fairly well with the regression from Babin et al. (2003), so for the purpose of using TSS to establish NAP absorption (m$^{-1}$) within Narragansett Bay, we used their equation ($0.31 \times$ TSS in mg/L).

Figure 7. Summary of NAP calibration data for Narragansett Bay—normalized at 440 nm. Blue markers represent the mean of all 37 curves. Red dashed lines are plus and minus one standard deviation. Solid black line is the best fit trend line (Equation 7)
Phytoplankton Calibration

Figure 9 shows the phytoplankton (pigmented particles) absorption scans for samples collected during the summer of 2013 (July, August and September). Each curve is normalized to the absorption at 675 nm. Figure 10 shows the average of all 31 normalized curves. This is the empirical calibration curve for the bio-optical model. The final absorption curve is created based on the chlorophyll $a$ concentration for a given site (see Equation 3). Figure 11 shows the relationship between chl $a$ and phytoplankton particle absorption at 675 nm. A similar plot is shown in Figure 12 for chl $a$ and absorption at 440 nm. Table 1 contains all of the coefficients for absorption at wavelengths ranging from 400 to 700 nm in 5 nm increments relative to chl $a$ concentration. These data can be used to establish a calibration curve whose shape will vary depending on the concentration of chl $a$. This is the process used by Matsuoka et al. (2007) and others to create their absorption curves. Figure 13 compares calculated absorption curves using

Figure 8. The relationship between non-algal particle absorption and total suspended solids for Narragansett Bay. The data in the plot at the top left are re-plotted in the top right plot using the axes ranges from Gallegos et al. (2006). The data are re-plotted again in final panel using the axes from Babin et al. (2003). Data are in Appendix C.
both procedures. The “normalize” curves use Figure 10 and the relationship in Figure 11 to create the five phytoplankton absorption curves for chl $a$ ranging from 0.5 to 20 ug/L. The “A-B” curves used the data presented in Table 1 to create an additional five absorption curves. The difference between the two calibration techniques is chl $a$ concentration dependent and confined largely to the blue end of the spectrum. This region of the curves is influenced by photo-acclimation. During photo-acclimation cells growing in higher light (e.g., low concentrations of Chl $a$ in the water) create additional pigments (mostly non-photosynthetic pigments) for protection against the higher energy wavelengths (the blue region). The clearer the water (i.e., the lower the concentration of Chl $a$), the greater the expected concentration of photo-protective pigments—which have their primary absorption in the higher energy (short wavelengths) end of the spectrum.

**Figure 9.** Phytoplankton particle absorption scans from Narragansett Bay—summer 2013 (July, August and September). Each curve is normalized to its absorption at 675 nm. Original, non-normalized data are in Appendix D
Figure 10. Average of the normalized pigmented particle (phytoplankton) absorption scans from Figure 9

Figure 11. The relationship between chl $a$ concentration and particle absorption at 675 nm. Data are in Appendix E
Figure 12. The relationship between chl $a$ concentration and particle absorption at 440 nm. Data are in Appendix E.

Figure 13. A comparison of phytoplankton particle absorption spectra using two different methods of calibration. See text for explanation. Top 2 plots are for 20 ug/L, next 2 are for 10 ug/L, and so on.
Table 1. Parameters for power regression expressed as \( \text{Abs}(\lambda) = A \times \text{Chl} \ a^B \). Units of absorption are \( m^{-1} \), units for \( \text{chl} \ a \) are \( \mu g/L \). These data are used to create absorption curves for phytoplankton particles—the shape of which is \( \text{chl} \ a \) concentration dependent.

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<th>B</th>
<th>( r^2 )</th>
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**Backscattering Calibration**

Scattering is the most variable of the parameters measured for water clarity estimates using a bio-optical model. Scattering data also are not as prevalent in the literature as are absorption data, since scattering measurements require specialized instrumentation that has only recently become more available. Calibration for scattering coefficients typically involves establishing a correlation between TSS and total scattering for a reference wavelength (usually 555 nm). Although relationships between a combination of parameters (e.g., TSS, Chl a and CDOM) have
been used occasionally (Gallegos 2005). No matter what parameter or combination of parameters, the variability of scattering coefficients is usually fairly high, especially when compared with that for absorption coefficients. One plausible explanation is that scattering is highly dependent on not only the concentration of suspended matter, but also the specific make up of that material with respect to size, shape and composition (especially inorganic versus organic). And, unlike absorption measurements, there is not an easy method to segregate measurements on the different components.

Figure 14 shows the relationship between total scattering at 555 nm and the concentration of TSS for samples collected in Narragansett Bay. Clearly there is not a good relationship. There also was no relationship between location or time of year, with respect to the relationship. Gallegos (2005) explains some of the variation observed in scattering coefficient for water samples collected in the lower St. Johns River, Florida by segregating his samples by salinity. He was able to show better relationships among TSS and total scattering than we were; however, the ranges of values for both TSS and measured scattering were greater for his measurements. When our data are plotted with these expanded ranges (Figure 15), the degree of variability is very similar to that presented in Figure 9c of Gallegos (2005). This is also true when we compare our data using observation from Figure 11a in Gallegos et al. (2006) for Chesapeake Bay. Figure 16 is our data re-plotted again, this time using the axes ranges from Gallegos et al. (2006).

![Figure 14](image_url)

**Figure 14.** Relationship between total scattering at 555 nm and total suspended solids for Narragansett Bay. Data are in Appendix F
Figure 15. The same data as presented in Figure 14 except the axes are expanded to coincide with those from Gallegos (2005)

Figure 16. The same data as presented in Figure 14 except the axes are expanded to coincide with those from Gallegos et al. (2006)
Our highly variable relationship between total scattering and TSS is consistent with what others have experienced. We were able, however, to establish a better relationship between TSS and particle backscattering. Data showing this are presented in Figure 17. Gallegos et al. (2006) also had a relationship between backscattering and TSS. The range of their data was estimated from their Figure 12c. The backscattering data from Gallegos et al. (2006) was measured at 532 nm. We adjusted these data upward by about 10% to account for the slight influence of wavelength on backscattering (see below). Even though backscattering is a better relationship to TSS, it still is not great, but it is likely the best that can be done for now. The regression line is a non-linear fit to a power function. The equation for the line is:

\[
b_{bp}(470) = 0.0095 * TSS^{0.379}
\]

EQ 15

Where:

- \( b_{bp}(470) \) = particle backscattering at 470 nm (m\(^{-1}\)), and
- \( TSS \) = total suspended solids (mg/L).

A calibration curve for backscattering versus wavelength was established using the data we have for backscattering at 470 nm and 700 nm from the Satlantic profiles. By necessity we assumed that the relationship between wavelength and backscattering was linear. This line is:

\[
b_{bp}(\lambda) = -0.041 \left( \frac{\lambda}{1000} \right) + 0.0477
\]

EQ 16

We then took these data and normalized them to \( b_{bp}(470) \). This relationship is multiplied by the \( b_{bp}(470) \) calculated from the relationship in Figure 17 to achieve the final backscattering coefficients for a given site.

![Figure 17](image-url)

**Figure 17.** Relationship between backscattering at 470 nm and total suspended solids for Narragansett Bay. The red markers are data collected using a HydroScat in 2013. The blue markers are data from the Satlantic Profiler in 2014. The blue solid line is the regression (Equation 15) fit to the red and blue markers. The vertical dashed lines are ranges estimated from Gallegos et al. (2006) for comparison. Data are in Appendix F.
PUTTING IT ALL TOGETHER

Referring back to Equation 1, we need three pieces of information in order to calculate the
diffuse extinction coefficient ($K_d$): the solar zenith angle of incidence in degrees, total absorption
by wavelength, and total backscattering, also by wavelength. The zenith angle is easily
calculated using NOAA’s solar calculator, which can be used directly on their webpage, or
spreadsheets can be downloaded (http://www.esrl.noaa.gov/gmd/grad/solcalc/calcdetails.html).
All that is needed is the latitude and longitude for a site, date, time zone and time of day. For
total absorption and backscattering all that is needed are measurements or modeled values for
CDOM, TSS and Chl a.

Total absorption (Equation 3) is wavelength dependent. We have chosen to make the calculation
in 5 nm increments from 400 to 700 nm. Absorption by water ($a_{water}$) has a fixed relationship
with wavelength (see Figure 2). Absorption by CDOM for Narragansett Bay is calculated from:

$$a_{CDOM}(\lambda) = a_{CDOM}(440) * e^{-0.0159(\lambda-440)}$$

Where: $a_{CDOM}(440)$ is the directly measured (or modeled) value of CDOM absorption at 440 nm.
Absorption by non-algal particles is calculated by first deriving the absorption at 440 nm:

$$a_{NAP}(440) = 0.31 * TSS$$

Where: TSS is total suspended solids in mg/L. Absorption for each wavelength of interest is
then calculated using:

$$a_{NAP}(\lambda) = a_{NAP}(440) * e^{-0.0136(\lambda-440)}$$

Finally, absorption by phytoplankton, $a_{\phi}(\lambda)$, is estimated by first deriving the absorption at
675 nm, using:

$$a_{\phi}(675) = 0.0282[Chl a]^{0.855}$$

Where: [Chl a] is the concentration of chlorophyll a in µg/L. This value is then used to establish
the absorption at all of the wavelengths of interest, using:

$$a_{\phi}(\lambda) = a_{\phi}(675) * a_{\phi}(\lambda)_{norm}$$

Where: $a_{\phi}(\lambda)_{norm}$ is the wavelength dependent absorption curve, normalized to 675 nm
(see Figure 10). Alternately, we could derive the phytoplankton absorption curve by calculating
absorption for each wavelength as an independent relationship with the concentration of Chl a
(see Table 1).

Total backscattering is calculated as the sum of backscattering from pure water and
backscattering due to everything else. Backscattering from water is considered a fixed
relationship with wavelength (see Figure 3). Backscattering by the constituents within
Narragansett Bay water is calculated based on spectral backscattering coefficients normalized to 470 nm. Backscattering at 470 nm is calculated using:

\[ b_{bp}(470) = 0.0095 * TSS^{0.379} \]

Where: TSS is total suspended solids in mg/L. Final spectral backscattering coefficients are calculated using:

\[ b_{bp}(\lambda) = b_{bp}(470) * (1.678 - 0.00144 * \lambda) \]

The latter portion of the right side of the above equation is the Equation 16 normalized at 470 nm (dividing Equation 16 by Equation 16 solved using \( \lambda = 470 \)).

The total spectral absorption and spectral backscattering coefficients are then plugged into Equation 1 to calculate the spectral diffuse attenuation coefficients. These are used, in turn, in Equation 2 to calculate the total diffuse attenuation coefficient for photosynthetically active radiation (PAR). To do this you need the spectrum of light at the surface of the water. This information can be calculated using readily available free software from the National Renewable Energy Laboratory (http://www.nrel.gov/rredc/smarts/). What is needed is the global horizontal irradiance (the irradiance hitting a horizontal surface). This is a combination of direct, beam and diffuse irradiance. The units used are not important (Wm\(^{-2}\) or photon flux are often used), the attenuation coefficient is a ratio—the units cancel out.
REFERENCES


Appendices

Appendices A through F are in the attached Microsoft Excel file, Bio-optical model appendices—data for Narragansett Bay.xlsx. To access the file, select the attachments icon within Adobe Acrobat. It contains the data used to create the figures associated with the calibration for absorption and scattering.