Spectral attenuation and backscattering as indicators of average particle size

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1. INTRODUCTION

The particle size distribution (PSD) is a fundamental property of particle assemblages in natural waters and is important in a variety of marine sciences. For example, the PSD can aid in the comprehension of phytoplankton community dynamics [1] and sediment transport [2]. Measurements of PSD for particles in the approximate size range of 1 to 100 μm are typically made on discrete water samples (e.g., a Coulter counter), are time-consuming, and have the additional problem of disturbing the in situ size distribution, such as by breaking aggregates. More recently, in-water instruments for particle sizing using near-forward laser diffraction have been used in a variety of applications [1,3–12].

To better understand natural processes at a broad range of time and space scales, a great deal of effort within the oceanographic community is being spent adapting sensors for platforms such as gliders, profiling floats, and moorings [13,14]. In situ optical sensors possess a number of characteristics that make them ideal for autonomous platforms. Most notable is their high sampling rate and low power consumption. Furthermore, measurements of inherent optical properties (IOPs), such as the particulate beam attenuation coefficient, $c_p(\lambda)$ (m$^{-1}$), and the backscattering coefficient, $b_{bs}(\lambda)$ (m$^{-1}$), have been proposed as proxies for a number of environmental water properties, ranging from phytoplankton biomass [15,16] to underwater visibility [17,18]. This paper investigates the use of these IOP measurements to yield information about the PSD.

Oceanic PSDs, expressed as number size distributions, $N(D)$ (number of particles per unit volume per unit particle size; common units of L$^{-1}$μm$^{-1}$, m$^{-3}$μm$^{-1}$, or m$^{-4}$), are often approximated as a number PSD power law function of diameter, $D$ (μm),

$$N(D) \sim D^{-J},$$

where $J$ is the (dimensionless) PSD power law slope [19]. PSD slopes usually range from around 2.5 to 5, with 4 being a typical oceanic value [20–24]. Other more realistic PSD models have been used that include multiple power law slopes for different size ranges [25], roll-off of particles above or below a specified size [26], and a superposition of two generalized gamma functions combining biologically and terrestrially derived material [27]. However, many (especially energetic coastal) environments are poorly described by these simple models, leading to significant errors in modeling optical properties from the PSD [24]. Rather than pursuing an exact
description of the PSD, in many cases it is sufficient and informative to quantify the PSD and its changes by focusing on parameters such as median particle size or other nonparametric descriptors of the PSD [28].

Measurements of the particulate beam attenuation coefficient in the ocean typically exhibit an inverse power law dependence on wavelength, $\lambda$ (nm), as

$$c_p(\lambda) \sim \lambda^{-\gamma}.$$  \hfill (2)

Based on theoretical derivation (assuming nonabsorbing spheres), the spectral slope, $\gamma$ (dimensionless), has been shown to be linearly related to the power law slope of the PSD, i.e., $\gamma \approx J - 3$ [29–31]. Boss et al. [32] presented a dataset of $\gamma$ measurements from an optical profiling package and a limited number of PSD slopes from Coulter counter analysis of collocated (but not coincident) rosette bottle samples. Their finding that both the spectral slope and PSD slope were strongly correlated supports the theoretically derived link between $\gamma$ and PSD slope, $J$. With appropriate consideration for absorption and extremes of particle size distribution [31], the relation appears applicable to a wide range of oceanic particles.

Availability of particulate backscattering measurements as remotely sensed ocean color products, as well as from multispectral backscattering sensors deployed in situ and on autonomous platforms, has raised the question of whether or not the spectral shape of backscattering, $\gamma_{bb}$ (dimensionless) in $b_{bb}(\lambda) \sim \lambda^{-bb_{\gamma}}$ (e.g., [33–35]), is an indicator of particle size in a similar manner to $\gamma$. While spectral beam attenuation typically exhibits smooth power law dependence on wavelength, absorption by natural particles is expected to cause deviation from the power law spectral shape of scattering and backscattering due to a combination of effects: (1) incident photons absorbed by particles will not be elastically scattered, and (2) anomalous dispersion in strong absorption bands [36–38]. We expect the effects of anomalous dispersion to play little role in the present study due to the lack of pronounced absorption peaks in our measurements and because they will tend to be averaged out due to the wide spectral bandwidths (approximately 10–20 nm FWHM) of currently available backscattering sensors [38].

To the best of our knowledge, no direct comparison of in situ spectral backscattering and PSD exists in the literature. However, using an inversion model to retrieve $b_{bb}(\lambda)$ from satellite ocean color data, Loisel et al. [39] computed global maps of $\gamma_{bb}$ and found them to compare well with expectations of the domination by small particles (e.g., picoplankton and colloids) in the subtropical gyres and by larger particles in coastal, upwelling, and high latitude regions. Kostadinov et al. [40] used a similar approach, with a Mie-based model linking the PSD slope and $\gamma_{bb}$. In a follow-on study, Kostadinov et al. [41] used this approach to examine particle (i.e., phytoplankton) size distribution in the open ocean (i.e., pico-, nano-, and micro-plankton stocks) and also found seasonal and gyre-scale spatial trends in line with the most probable size distributions.

2. METHODS

A. Field Deployments

Field measurements of spectral backscattering, spectral particulate attenuation, and particle size were made as part of the Optics Acoustics and Stress In Situ (OASIS) project at the Woods Hole Oceanographic Institution Martha’s Vineyard Coastal Observatory (MVCO) during September–October of 2004, 2005, 2007, 2009, and 2011.

The MVCO subsea node [42] is located south of Edgartown, Martha’s Vineyard (Massachusetts, http://www.whoi.edu/mvco) on the 12 m isobar. The seafloor in this region consists of shore-perpendicular swaths of alternating course and fine sand. There is strong tidal forcing (~1.5 m spring tidal range) that leads to east–west advection along the south shore of Martha’s Vineyard. Wave forcing is dominated by southerly waves, with wave heights typically highest from late summer to spring, especially during large wave events associated with the passage of tropical storms and hurricanes in the Atlantic. Our selection of the months of September and October for the OASIS experiment was rooted in capturing these “fall transition” storms [43–45]. Significant wave heights and near-bottom currents were inferred by a 1200 kHz Workhorse Monitor (Teledyne RD Instruments, Inc., Poway, California, http://www.rdinstruments.com) acoustic Doppler current profiler deployed as part of the core MVCO instrumentation at the node.
Here we used data from the 2007 and 2009 deployments as detailed below. These years were chosen because they comprised a core set of instrumentation including a LISST-100X particle sizer, a 10 cm pathlength ac-9 spectral absorption and attenuation meter (WET Labs), and an ECO BB9 spectral backscattering meter (WET Labs). Each year we deployed the instrumentation on a tripod, with sampling volumes at 1.2 m above bottom. The instrumentation was powered, and data were delivered to, onshore computing facilities via the MVCO subsea node. All measured data were merged and binned into 5 min intervals for analysis.

The OASIS 2007 deployment ran from 2 to 24 September (yearday 245 to 267). To minimize possible effects of biofouling, diver operations were conducted for the cleaning of optical surfaces and changing of the ac-9 cartridge filter [46] on yearday 253. The OASIS 2007 dataset used in this study consists of measurements made between yearday 255 and 261 (Fig. 1), during which there were two storm-induced resuspension events associated with the remains of Tropical Storm Gabrielle. The BB9 ran on a 2:3 minute on:off duty cycle to reduce attraction of phototactic organisms. The BB9 gain was changed at the factory to reduce severe saturation issues observed during OASIS 2005. Absorption data during this deployment were not available due to an improperly fitted ac-9 a-tube.

The OASIS 2009 campaign consisted of two separate deployments, 25 September to 2 October (yearday 268 to 275) and 16 to 22 October (yearday 289 to 295), with each deployment characterized by the passage of a storm system resulting in a significant dynamic range in physical forcing. The tripod was recovered and serviced between deployments, and diver operations for cleaning optical surfaces and replacing ac-9 filter cartridge were conducted on yearday 292. Data from the ac-9 were not available during the first deployment due to power supply issues that were resolved before the redeployment; in this analysis we focused on the second deployment between yearday 289 to 295 (Fig. 2). Similar to the 2007 deployment, the BB9 was run on a 1:4 minute on:off duty cycle.

B. LISST-100X Particle Size Distribution Measurements

The LISST-100X in situ particle sizing instruments operate on the principle of laser diffraction [3]. In short, a collimated laser beam (670 nm) illuminates a sample volume where it is scattered through a Fourier lens toward receiving optics consisting of a pinhole and photodiode transmission detector (for the estimation of beam attenuation) surrounded by a set of 32 coplanar and concentric ring-shaped detectors. Because particle scattering is highly peaked in the near forward, the ring edge radii increase logarithmically. This covers an angle range of approximately 0.08–15° or 0.04–7.5° (in water), for the LISST-100X Type-B and -C instruments, respectively. Particles that are small compared with the illuminating wavelength tend more toward isotropic scattering, while larger particles tend toward scattering in the near forward (i.e., diffraction). This basic physical premise is used in an inversion algorithm to estimate the PSD from the pattern of scattered light [47].

The laser diffraction particle sizing method is widely used and covered by ISO standards in industry [48] and has been evaluated (compared with other sizing methods such as Coulter, microscopy, and sieving) with natural suspensions, sorted sediment, phytoplankton cultures, as well as traceable size standards in both lab and in situ studies [1,9,24,49]. In general, several artifacts in the LISST-100X PSD can be considered. First, measurements of highly modal size distributions such as microsphere standards are able to accurately resolve the peak of the distribution but will be wider due to the nature of the inversion algorithm. Similarly, the peaks of multimodal particle size distributions are accurately resolved as long as the peaks are sufficiently separated and the particle aspect ratios are near one; for size distribution modes that are very close (usually less than a few size bins, depending on the algorithm
and particle matrix used), the inverted PSD will appear smeared. Second, for highly nonspherical particles, the inverted PSD can indicate modes corresponding to features of the nonspherical particles (for example, the PSD for algal cultures of Ceratium longipes with modes corresponding to a spheroid enclosing the entire body of the cell, the central body without horns, and the width of the horns [1]). Third, particles outside of the designed measurement range can cause rising tails in the inverted PSD.

LISST-100X data were processed in MATLAB (The MathWorks, Inc., Natick, Massachusetts, http://www.mathworks.com) using the manufacturer-provided protocols and inversion routine, yielding an estimate of volumetric sectional area size distribution, \( V(D) \) (\( \mu \text{L}^{-1} \)). Empirical inversion matrices based on nonspherical sediment particles were used [50], yielding particle size distribution having 32 bins with medians spanning 1.09–184 \( \mu \text{m} \) (Type-B) and 2.06–357 \( \mu \text{m} \) (Type-C). The nonspherical sediment inversion matrices are typically found to be less affected by particles outside of the measurement range [50,51].

Optical properties in the geometric optics regime and the laser diffraction method are more related to areal size distribution (total cross sectional area for a given size bin per volume), so we convert \( V(D) \) to area distribution, \( A(D) \) (\( \text{m}^2 \text{m}^{-3} \)), based on the assumption of spherical geometry. Our observed PSDs were generally not well represented as power law functions of size (Fig. 3), similar to recent observations by Reynolds et al. in coastal waters [24]. Therefore, we used the PSD data to calculate an average particle size [31,52], based on the particle cross-sectional area size distribution,

\[
D_{\text{avg}} = \frac{\sum_i A(D_i) D_i}{\sum_i A(D_i)}.
\]  

Type-B and Type-C instruments were deployed in 2007 and 2009, respectively. Due to the difference in size ranges between the two instruments, the set of bins used in calculating \( D_{\text{avg}} \) was reduced to the size range common between the two instruments, \( \sim 2–184 \mu \text{m} \) (solid red line in Fig. 3). In addition, beam attenuation due to particles and dissolve material at 670 nm, \( c_{\text{pg}}(670) \), was derived from the LISST-100X measurements (acceptance angles in water of 0.026\(^\circ\) and 0.013\(^\circ\) for the Type-B and -C instruments).

C. ac-9 Absorption and Attenuation Measurements
Measurements of attenuation and absorption were made using a WET Labs ac-9 combination spectral beam transmissometer and reflecting tube absorption meter, measuring attenuation and absorption at nine wavelengths, \( \lambda = [412, 440, 488, 510, 532, 555, 650, 676, \text{ and } 715] \) nm, at 6 Hz [53]. The same 10 cm pathlength ac-9 was used during all field campaigns, in each case deployed with an automated valve system to make periodic measurements on samples drawn through a large surface area 0.2 \( \mu \text{m} \) filter cartridge (GE Osmonics Memtrex Nylon, 0.64 \( \text{m}^2 \) filtration area), and contained in a diver-replacable fixture. The automated valve system was powered via the MVCO node and programmed to take filtered measurements for five minutes each hour, allowing for the
calculation of calibration- and drift-independent particulate attenuation and absorption measurements [46].

For each measured particulate attenuation spectra $c_p(\lambda)$, a power law fit Eq. (2) was made using an unconstrained nonlinear optimization procedure (MATLAB fminsearch, the Nelder—Mead method).

Particulate absorption spectra $a_p(\lambda)$ were calculated from the measured absorption $a_{p,m}(\lambda)$ using the “proportional” scattering correction presented in Röttgers et al. [54]:

$$a_p(\lambda) = a_{p,m}(\lambda) - (a_{p,m}(715) - a_{715}^L) \left( \frac{c_p^{e_1}(\lambda) - a_{p,m}(\lambda)}{c_p^{e_1}(715) - a_{715}^L} \right),$$

where $a_{715}^L = 0.212a_{p,m}(715)^{1.135}$ and $e_1 = 0.56$.

D. BB9 Backscattering Measurements

The WET Labs ECO BB9 measures the volume scattering function $\beta(\lambda, \theta)$ at a single angle in the backward direction, $\theta \approx 124^\circ$, at nine illumination wavelengths, $\lambda = [400, 440, 488, 510, 532, 595, 660, 715, \text{and} 880]$ nm, at a 6 Hz sampling rate. Raw instrument data, $raw(\lambda)$, were processed according to standard protocols as follows. The total volume scattering for each wavelength channel was calculated as

$$\beta(\lambda, 124^\circ^c) = s(\lambda)[raw(\lambda) - d(\lambda)]K(\lambda),$$

where $s(\lambda)$ and $d(\lambda)$ are manufacturer-supplied scaling factors and dark offsets, respectively. BB9 calibration was performed by the manufacturer before each OASIS campaign (20 June 2007 and 26 Aug 2009) using a concentration series of 2 pm beads (uncertainties in the calibration are examined in Appendix A).

The attenuation correction factor, $K(\lambda)$, in Eq. (5) corrects for the loss of photons within the instrument pathlength [55,56]:

$$K(\lambda) = \exp(L_{pg}(\lambda)),\hspace{1cm}(6)$$

where $a_{pg}(\lambda)$ is the combined absorption due to particles and dissolved materials [$a_{pg}(\lambda) = a_p(\lambda) + a_c(\lambda)$], and $L$ is the effective pathlength. The correction includes only $a_p(\lambda)$, assuming that losses due to water absorption and particle scattering are accounted for in the calibration procedure. For an ECO BB sensor with a centroid angle of $\theta \approx 124^\circ$, $L \approx 0.015$ m [56].

Dissolved absorption, $a_c(\lambda)$, measurements were not available during the 2009 OASIS campaign (due to the use of the calibration and bio fouling independent differencing technique). Previous ac-9 measurements during OASIS 2005 indicated that dissolved absorption was nearly constant: $a_c(440) \approx 0.012$ m$^{-1}$ and $S_g \approx 0.014$, and neither $a_c(440) \approx S_c$ covarying with $a_p(\lambda)$ during resuspension events of $a_p(440) \approx 2$ m$^{-1}$. Additionally, uncalibrated dissolved absorption (440 nm) from 2009 also appeared constant ($<1\%$ MAD) and uncorrelated with particulate absorption. Thus, we assumed a constant dissolved absorption background to calculate $a_{pg}(\lambda)$ for the purpose of BB9 correction, for both the 2007 and 2009 deployments.

No absorption data (particulate or dissolved) were available in 2007. Therefore, we used a linear model vicariously estimating the correction factor using measured LISST-100X attenuation data, where the regression parameters $\rho_0(\lambda)$ and $\rho_1(\lambda)$ were determined from 2009 data (where absorption data and LISST-100X attenuation data were both available) using type-2 major axis regression [57],

$$K(\lambda) = \rho_1(\lambda)c_{pg,LISST}(670) + \rho_0(\lambda).\hspace{1cm}(7)$$

Based on 2009 data used for the regressions, the model was able to estimate the correction factor to within $<1\%$ RMSE for all wavelengths. Given the relative consistency in relationships between the absorption and scattering observed during the 2005 and 2009 datasets, uncertainty in the application of the model to 2007 data is expected to be similar.

The correction factors, $K(\lambda)$, applied to the data used in the analysis (i.e., no bad or saturated channels) were at most $\sim1.05$ and $\sim1.04$ at 400 nm, for 2007 and 2009 data, respectively, and decreased approximately exponentially with increasing wavelength, approaching unity in the red-NIR. In reality, the scattering phase functions of field measurements and calibration microspheres also differs substantially. This leads to additional uncertainty in the attenuation correction of $\beta(\lambda, 124^\circ)$ not explicitly considered here. However, total uncertainty in the attenuation correction is expected to be minor compared to the observed variability in $\gamma_{ch}$. For correction of the BB9 data which had some different wavelength channels than the ac-9, $a_p(\lambda)$ and $c_p(\lambda)$ were linearly interpolated to the BB9 wavelengths at $\lambda = 595$ and 660 nm; and the 400 and 880 nm channels were extrapolated by linear fit to $\log a_p(\lambda)$ for $\lambda = 412$ and 440 nm and $\lambda = 555, 650,$ and 715 nm, respectively. Note that $a_p(676)$ was not used for interpolation or extrapolation due to the chlorophyll absorption peak.

The particulate backscattering coefficient, $bb_p(\lambda)$ (m$^{-1}$), was estimated from $\beta(\lambda, 124^\circ)$ as

$$bb_p(\lambda) = 2\pi\chi_p(124^\circ)[\beta(\lambda, 124^\circ) - \beta_{ch}(\lambda, 124^\circ)].\hspace{1cm}(8)$$

where $\chi_p(124^\circ)$ is a spectrally independent nondimensional factor relating the particulate backscattering coefficient to volume scattering at 124° in the backward direction [58–60] and $\beta_{ch}(\lambda, 124^\circ)$ is the volume scattering coefficient of seawater [61,62]. Based on Sullivan et al. [56], we assumed $\chi_p(124^\circ) = 1.08$.

Spectra typically exhibited a broad maximum in the blue-green (450–550 nm, see Fig. 7), similar to observations by McKee et al. [63] in inorganic-dominated UK coastal waters, also using a BB9 instrument. In the OASIS 2007 and 2009 datasets considered here, saturation of instrument channels was problematic during resuspension events, even after having instrument gains adjusted before field campaigns in 2007 and 2009. Typically, saturation progressed from the NIR to the green as the particle load increased, but saturation was also sometimes problematic in the blue channels. Power law functions of the form of Eq. (2), i.e., $bb_p(\lambda) \sim \lambda^{\gamma_{bb}}$, were fit to measured backscattering spectra, using all wavelength channels and the same unconstrained nonlinear optimization code used for spectral beam attenuation. Uncertainty in the backscattering spectral slope was estimated using a Monte Carlo model (see Appendix A).
E. Optical Proxies for Particle Composition

Several optical proxies for particle composition were calculated in order to show the range of particle types included in our examination of spectral IOPs and particle size:

(i) The particulate single scattering albedo, \( \bar{\omega}_p(\lambda) \), defined by

\[
\bar{\omega}_p(\lambda) = \frac{b_p(\lambda)}{c_p(\lambda)} = \frac{b_p(\lambda)}{a_p(\lambda) + b_p(\lambda)},
\]

is the probability that a photon will be scattered rather than absorbed in a random interaction. When attenuation is mostly due to scattering, \( \bar{\omega}_p(\lambda) \) is near one, and when it is dominated by absorption, \( \bar{\omega}_p(\lambda) \) is near zero. Spectra of \( \bar{\omega}_p(\lambda) \) are lowest in the blue wavelengths due to absorption by phytoplankton and nonalgal particles—even highly scattering minerals have characteristic absorption highest in the blue and decreasing toward the red [64]. Second-order spectral variation in \( \bar{\omega}_p(\lambda) \) is due to absorption by algal pigments, typified by chlorophyll which causes a decrease at \( \bar{\omega}_p(676) \), as well as a shoulder at \( \bar{\omega}_p(440) \).

(ii) Chlorophyll concentration was calculated based on the absorption line height [65] as

\[
CHL_{1H} = \frac{1}{0.0104}(a_p(676) - a_{BL}(676))[\text{mg m}^{-3}]
\]

where the baseline absorption at 676 nm, \( a_{BL}(676) \), is calculated by linear interpolation of \( a_p(\lambda) \) between \( a_p(650) \) and \( a_p(715) \).

(iii) The particle backscattering ratio, \( \tilde{B}_p = b_p(\lambda)/c_p(\lambda) \), was calculated for all BB9 wavelengths, using the extrapolated and corrected ac-9 scattering measurements. This ratio provides a proxy for the bulk index of refraction and thus the organic versus inorganic composition of the suspended particles [66]. It has also been shown to be correlated with the ratio of chlorophyll to beam attenuation, indicating dominance of phytoplankton (\( \tilde{B} \sim 0.005 \)) versus inorganic particles (\( \tilde{B} \sim 0.02 \)) [55]. Due to the lack of absorption measurements in the OASIS 2007 dataset, we also calculated the particulate backscattering to attenuation ratio \( b_p(\lambda)/c_p(\lambda) \). This ratio is a similar proxy for composition as the backscattering ratio [67].

3. RESULTS AND DISCUSSION

A. Particle Size Distributions

Sample PSD for both OASIS 2007 and 2009 are shown in Fig. 3. OASIS 2007 areal PSDs were characterized most prominently by a population of 5–10 \( \mu \)m particles, falling off sharply for smaller particle sizes. It is likely that the 5–10 \( \mu \)m particles were tightly bound micro-aggregates composed of resuspended fine sediments, pico/nano-plankton, and detritus [28]. A second, more varying, population with a mode of 100–200 \( \mu \)m (likely larger aggregates) was superimposed on the 5–10 \( \mu \)m population. This second population ranged from essentially not present, suggesting a unimodal particle population, to similar concentration (in terms of suspended cross sectional area) as the 5–10 \( \mu \)m modal population. The dynamics of this aggregate population could have been due to particle processes (aggregation, disaggregation, resuspension, and settling) acting within the water column to transfer mass between the two modes; or these larger particles could have been mobilized from a “fluff” layer on the seabed [68].

Most of the OASIS 2009 size spectra did not exhibit the strong bimodality as in 2007. There did appear to be a similar, strong 5–10 \( \mu \)m mode, as well as weaker modes at \( \sim 20 \mu \)m and \( \sim 100 \mu \)m. These weaker modes apparently covaried in such a way that the overall behavior appeared roughly as a power law of 5–10 \( \mu \)m (linear in log space), with strong variation of the slope through the deployment. In the largest size bins, some spectra had very steep rising tails for sizes \( > 200 \mu \)m, consistent with a particle population outside of the size range of the LISST-100X. Based on merged particle size spectra from a digital floc camera and LISST-100X covering maximum particle sizes \( > 1 \text{ mm} \) [7], the OASIS 2009 data from yearday 289.5 to 290.5 were characterized by high floc fractions approaching 100% of the volume concentration [69].

B. Variation of Optical Proxies for Particle Composition

Time series of optical proxies for composition during the OASIS 2009 deployment are shown in Fig. 4. The first half of the deployment was characterized by strong resuspension (Fig. 2), with high values of particulate backscattering ratio \( \tilde{B}_p \) indicating that inorganic or mineral composition dominated. However, the chlorophyll concentration was also very high during this period, and our observations spanning approximately 4–8 mgm\(^{-3}\) were similar to the extracted chlorophyll measurements made at the MVCO site by Sosik [70].

The full range of spectral variability of \( \bar{\omega}_p(\lambda) \) is shown in Fig. 5 in gray. We selected three characteristic compositional cases denoted by symbols in the figure: (i) strong resuspension with high scattering as well as nonalgal particle absorption (yearday 289.7, red circles), and two less energetic cases during the second half of the deployment; (ii) low chlorophyll, dominated by nonalgal particles (yearday 293.0, yellow squares); and (iii) higher chlorophyll (yearday 294.9, blue diamonds). In all cases there was a characteristic chlorophyll absorption dip

![Fig. 4](image-url)
visible at 676 nm, and in case (iii) there was also a noticeable shoulder at 440 nm due to relatively higher algal absorption.

The time series of \( b_{bp}(532)/c_p(532) \) for OASIS 2007 is shown in Fig. 6(a), with highest values of the ratio during resuspension events, similar to our observations of \( b_{bp}(532)/b_p(532) \) during OASIS 2009 [Fig. 4(b)]. The distribution of the ratio \( b_{bp}(532)/c_p(532) \) was similar in both the OASIS 2007 and 2009 datasets [Fig. 6(b)], exhibiting similar log-normal-like distributions, with median values of 0.0196 and 0.0194, 5th percentiles of 0.0138 and 0.0162, and 95th percentiles values of 0.0326 and 0.0305 for the OASIS 2007 and 2009 datasets, respectively. The lower values of \( b_{bp}(532)/c_p(532) \) during OASIS 2007 suggested a more organic composition during the less energetic period between resuspension events compared to OASIS 2009. As an example of the similarity between \( b_{bp}(532)/c_p(532) \) and \( b_p(532)/b_p(532) \), both distributions are plotted in Fig. 6(b).

C. Spectral Slopes and Relationship to Particle Size

Measured particulate attenuation spectra, \( c_p(\lambda) \), are typically well approximated by power law functions [30,32]. For our data, the percent error for each wavelength was calculated as

\[
\%Err(\lambda) = \frac{|\hat{c}_p(\lambda) - c_p(\lambda)|}{c_p(\lambda)},
\]

where \( \hat{c}_p(\lambda) \) is the power-law-modeled particulate beam attenuation spectra. Agreement between the power law model and measured attenuation spectra was very good, with 95th percentile of \( \%Err(\lambda) \) for each channel in the range of 0.5%–1.9% for the OASIS 2007 data and 0.1%–0.9% for the OASIS 2009 data.

Backscattering did not appear to be as smooth of a power law function of wavelength as beam attenuation, as shown in Fig. 7. Despite the shape of backscattering spectra, power law fits were reasonable, with 95th percentile of \( \%Err(\lambda) \) for each channel in the range of 4.6%–24% (max 17% excluding the 400 nm channel) for the OASIS 2007 data and 4.3%–15% for the OASIS 2009 data. Residuals for the fit are shown in Figs. 8(a) and 8(b). Since particulate absorption is expected to cause a dip in the backscattering toward the blue, residuals from a power law fit are expected to have a broad maximum with dips toward the blue and red. In general, the residuals from the field data had this expected shape. However, the sharpness of the residuals may also have been due to an improper BB9 calibration scale factor. Additionally, for the 2009 dataset [where \( a_p(\lambda) \) was available], the sum of the absolute residuals was found to be correlated with the shape of \( a_p(\lambda) \) in the blue, in terms of the slope (\( m \)) of the linear fit to \( a_p(\lambda) = m\lambda + b \) for \( \lambda = [412, 440, 488, 510, 532, 555] \) nm (more negative
indicates steeper absorption in the blue). This correlation [Fig. 8(c), \( R^2 = 0.89 \)] was consistent with the hypothesis that nonpower law variability in the spectral backscattering shape is driven by the shape of particulate absorption. The sum of absolute residuals was used due to the observation that as overall goodness of fit decreases, the tendency is for negative residual in the lower blue channels and positive residual in the blue–green hump.

The spectral slope, \( \gamma \), of the particulate beam attenuation appeared linearly related to \( D_{avg} \) derived from LISST-100X PSD data (Fig. 9) and was consistent for both 2007 and 2009 deployments. Linear fits to \( \gamma \) versus \( D_{avg} \) were performed using a type-2 major axis regression and were evaluated based on the coefficient of determination (\( R^2 \)) and normalized root mean square deviation (NRMSD), defined as

\[
\text{NRMSD} = \frac{1}{N} \left( \frac{\sum_{k=1}^{N} (y_k - \hat{y}_k)^2}{\max(y) - \min(y)} \right)^{1/2},
\]

where \( y_k \), \( \hat{y}_k \), and \( N \) are the data, regression estimate, and the number of data, respectively.

Departure from the linear model in 2009 [Fig. 9(a)] coincided with a period where particles larger than \( \sim 80 \mu m \) dropped off sharply causing a decrease in \( D_{avg} \) while the PSD slope for particles <50 \( \mu m \) roughly followed a power law. This is significant in that the large particles >50 \( \mu m \) have reduced influence on \( \gamma \) due to the acceptance angle of the ac-9 (the acceptance angle of a transmissometer effectively serves as a "filter" on size) but do affect \( D_{avg} \) from the LISST-100X. Boss et al. [71] calculated the effect of acceptance angle on measured beam attenuation and found that for the ac-9 instrument that less than half of true scattering is measured for particles >50 \( \mu m \) (their Fig. 2), suggesting an approximate cutoff for the maximum particle size that affects \( \gamma \). We saw an improvement in the relationship (\( R^2 = 0.83 \), NRMSD = 11\%) between \( D_{avg} \) and \( \gamma \) when the average size was calculated for particles less than 50 \( \mu m \) [\( D_{avg,50} \), Fig. 9(b)].
The strength of the proxy relationship between $\gamma_{bb}$ and $D_{avg}$ was also strong ($R^2 = 0.83$, NRMSD = 10%) and not affected by the acceptance angle issue as was attenuation (Fig. 10). Results of a Monte Carlo analysis (described in Appendix A) on a subset ($N = 64$) of the OASIS 2009 data is overlaid on the plot as an indication of the uncertainty in $\gamma_{bb}$ across the range of observations.

Comparison of the power law fit of scattering to attenuation is shown in Fig. 11(a) and is very tight (NRMSD = 1.9%) with a slope of 1.1 and an offset of $-0.3$ which compares well with the relationship found in Boss et al. [72]. The slope of power law fit to backscattering, $\gamma_{bb}$, also compares well with the slope of attenuation $\gamma$ ($\gamma_{bb} = 1.5\gamma - 0.44$, $R^2 = 0.77$, NRMSD = 13%; not shown) and to the slope of scattering, $\gamma_b$ ($R^2 = 0.82$, NRMSD = 12%; Fig. 11(b)]. A nonunity slope of the $\gamma_{bb}$ versus $\gamma_b$ relationship could indicate a spectrally varying particulate backscattering ratio. However, caution should be used in the interpretation of the slope and offset of this relationship due to instrumental artifacts such as the effect of acceptance angle on the scattering coefficient derived from beam attenuation [71] and the small sample volume of the backscattering measurements [21]. Both artifacts effectively limit the upper size limit of particles observed, each with their own size cutoff.

D. Expected and Observed Spectral Variability

Two frameworks for considering theoretical or modeling nonpower law spectral variability in backscattering can be considered: (1) direct simulation of optical properties, and (2) semi-analytical formulation in terms of customary component IOP models.
However, Mie theory has also been shown to have limited applicability in studies of nonspherical, nonhomogenous particles [73–77]. Furthermore, all of these methods calculate single particle optical properties as a function of size, shape, composition, etc., which then must be weighted by the PSD to calculate the optical properties of the bulk suspension. This represents an additional complication in that some model for PSD must be assumed. Furthermore, particle type across the size spectrum is also expected to vary significantly, and different models or model parameterizations must likely be used for the various particle types. This presents a tremendous challenge in terms of computation and development of realistic models.

A semi-analytical framework can also be used to explore the expected variation in spectral backscattering in terms of a set of measured, typical optical properties. A simple estimate of the spectral backscattering coefficient can be expressed as the product of the particulate backscattering ratio, $\tilde{B}_p$ (assumed wavelength-independent [78]), and the particulate scattering coefficient, $\hat{b}_p(\lambda)$, or in terms of beam attenuation, $c_p(\lambda)$, as

$$\hat{b}_{bp}(\lambda) = \tilde{B}_p b_p(\lambda) = \tilde{B}_p \hat{b}_p(\lambda) c_p(\lambda).$$

In each case, the expected backscattering was calculated per Eq. (13), using a spectrally flat $\tilde{B}_p$ determined from the mean of the measured $b_{bp}(\lambda)$ and $b_p(\lambda)$ spectra. The expected spectra are shown in Figs. 12(i)–12(iii), with the higher absorption resuspension-dominated case [Fig. 12(i)] exhibiting a roll-off into the blue, and the less energetic cases [Figs. 12(ii) and 12(iii)] nearly linear with wavelength. A significant source of uncertainty in these estimates was due to the uncertainty in the scattering correction of particulate absorption. BB9 backscattering spectra measured at the times corresponding to each case are also shown in Figs. 12(ii)–12(iii) with uncertainties calculated using the same Monte Carlo code discussed previously. Qualitative agreement between measured and expected spectral characteristics was reasonable, with the same characteristic blue roll-off and linear behaviors. Measurements agreed with expected values well within levels of uncertainty, except for disagreement in the 715 and 880 nm channels for the resuspension-dominated case, where BB9 measurements underestimate.

In general, we have less confidence in these measurements at 715 and 880 nm: (1) BB9 calibration is more difficult for these channels due to the low scattering signals of the 2 μm microspheres, (2) a higher error in scattering correction at 715 nm due to the approximately ±30% uncertainty in the empirical correction used to estimate true absorption at 715 nm from ac-9 measured $a_{p,m}$(715) [54], and (3) extrapolation of absorption data from 715 to 880 nm.

Spectral disagreement in these two comparisons could point to possible spectral variability in the particulate backscattering ratio, $\tilde{B}_p$. The spectral nature of $\tilde{B}_p$ remains an item of debate within the ocean optics community, largely due to the lack of multispectral volume scattering function measurements, leaving most comparisons to be made on backscattering estimated from scattering at a single angle in the backward direction. This ratio is predicted by Mie theory to be spectrally flat for power law size populations of homogenous spheres [78], which is supported by some studies [79,80]. However, other studies have suggested spectral variability of the backscattering ratio, especially in more turbid coastal waters [63,81]. The particulate backscattering ratio calculated from the measured $b_{bp}(\lambda)$ and $b_p(\lambda)$ for the characteristic cases is shown in Fig. 13. Spectral dependence in all three cases is weak and mostly within the uncertainty estimates for each channel. The most significant spectral variability within the visible wavelengths occurs in the less-energetic high-chlorophyll case (iii).

![Fig. 12. Comparison of estimated (colored symbols, solid line) and measured (white symbols, dashed line) backscattering spectra for each of the characteristic compositional cases described in Section 3.B: (i) resuspension dominated, (ii) less energetic with low chlorophyll, and (iii) less energetic with higher chlorophyll. Error bars for each represent the propagated uncertainty of ±σ in $b_{bp}(\lambda)$ from the Monte Carlo model.](image)

![Fig. 13. Spectral backscattering ratio, $\tilde{B}_p(\lambda)$, calculated using ac-9 and BB9 measurements for the three characteristic compositions described in Section 3.B: red circles, resuspension-dominated; yellow squares, less energetic with low chlorophyll; blue diamonds, less energetic with higher chlorophyll. The error bars represent uncertainty of ±σ in both $b_{bp}(\lambda)$ and $\tilde{B}_p(\lambda)$ from the Monte Carlo model.](image)
4. CONCLUSION

Theoretical tools have been an indispensable foundation of ocean optics for decades but are usually limited by assumptions about particle size, shape, and composition (e.g., power law size distribution of homogenous spheres characterized by an index of refraction for the entire population). Such models for power law distributions of homogenous nonabsorbing spheres predict that the spectral slopes of backscattering and attenuation should be a proxy for the power law slope of the particle size distribution. To avoid the assumptions of theoretical methods, we empirically examined the relationship between particle size distribution and spectral shape of attenuation and backscattering directly with co-located and co-incident attenuation, backscattering, and particle sizing instrumentation.

Our results suggest that spectral slopes of attenuation and backscattering can be used to infer changes in particle size, at least for non-algal particle dominated cases such as coastal, river-plume, and bottom boundary layer waters. Future work should include a similar investigation of a wider range of conditions, especially algal-dominated waters.

The observed relationship was further validated using a Monte Carlo analysis including uncertainties due to instrument calibration and ac-9 scattering correction. As a test of closure, the measured backscattering and scattering spectra for end-member cases were found to be in agreement well within the level of propagated uncertainty, except for the high absorption case NIR channels, where instrumental and methodological uncertainties are more significant and not accounted for in the Monte Carlo model. Our measurements may indicate significant spectral variability of the particulate backscattering ratio. However, conclusive determination is difficult given instrumental and methodological uncertainties.

APPENDIX A: UNCERTAINTY IN BACKSCATTERING MEASUREMENTS

Sources of uncertainty in spectral backscattering measurements derived from Eqs. (5), (6), and (8) include: (i) calibration uncertainty in the scale factor, $\alpha(\lambda)$, and dark counts, $d(\lambda)$; (ii) path length attenuation correction, $K(\lambda)$, uncertainty due to the scattering correction of ac-9 absorption measurements; (iii) uncertainty in the relationship between the backscattering coefficient and the measurement of the scattering at a single angle, $\chi_p(124^\circ)$; and (iv) uncertainty in the seawater volume scattering function, $\beta_{sw}(\lambda, 124^\circ)$. Propagated uncertainties in spectral scattering, $b_s(\lambda)$, backscattering, $b_{bb}(\lambda)$, and spectral slope, $\gamma_{bb}$, were estimated using a Monte Carlo approach with inputs summarized in Table 1. Details on the scale factor and scattering correction uncertainties and the Monte Carlo approach are described below.

Uncertainties in the calibration scale factors arise primarily from ignorance of the angular weighting functions, $W(\theta)$, for an individual instrument, choice of microsphere diameter for calibration, traceability of microsphere size distribution, and unknown exact LED wavelength to be used in Mie calculations [56]. Estimated uncertainty in the scale factor due to the angular weighting function and microsphere standard selection is $\sim 5\%$–$10\%$ and for nonnominal LED wavelengths is $\sim 5\%$. This $\sim 7\%$–$11\%$ combined (additive) uncertainty in the scale factor is not expected to be spectrally dependent, due to the highly variable structure in the weighting functions for $2 \, \mu m$ microspheres and the random nature of LED nominal wavelength inaccuracies ($\Delta \lambda$ varies and for each channel independently). Uncertainty in the NIR (880 nm) channel on our ECO BB9 instrument may have been higher due to low scattering by microspheres at that wavelength. Drift in the scale factor is typically $\sim 2\%$–$10\%$ per year for ECO BB-style sensors, due to dimming of the LEDs over time. More severe drift in the blue channels has been attributed to “yellowing” of the optical epoxy in these sensors, and temperature has also been shown to significantly affect instrument response for the red LED channels. Dark offsets were not measured in the field before the deployments, but typical differences observed between factory and field dark offsets are small ($\sim 2$ counts) and not spectrally dependent. These details of WET Labs ECO BB uncertainty are from the review by Sullivan et al. [56] (and via a personal communication [82]) and have also been discussed by Dall’Olmo et al. [83] and Twardowski et al. [84]. Drift was not considered in this uncertainty analysis due to instrument recalibration prior to each OASIS deployment.

In most environments, the pathlength correction described by Eq. (6) is negligible. For example, an absorption of $a_{bb}(412) \sim 0.5 \, m^{-1}$ (typical of coastal waters) would result in an $\sim 1.0\%$ underestimation of particulate backscattering at that wavelength. However, strong non-algal particle absorption present in the OASIS dataset [$a_{bb}(412) \sim 0.4$–$2.6 \, m^{-1}$] for OASIS 2009, as a result of corrections approaching $5\%$ has the potential of contributing a spectral bias that would affect $\gamma_{bb}$. To first order, particle resuspension increases the mean particle size and total amount of material in suspension. This could have hypothetically led to the correlation of the spectral shape of backscattering with particle size due to the pathlength correction, rather than true spectral variability in particulate backscattering, warranting close consideration of uncertainty in the scattering correction. The “proportional” scattering correction presented in Röttgers et al. [54] has uncertainties of $\sim 10\%$ in most visible channels across a wide range of conditions and approximately $20\%$–$30\%$ in channels where absorption tends to be low, such as 715 nm. The relative error presented in their Fig. 8 does not show a strong spectral dependence. However, for our analysis we assumed a worst case scenario where the error in scattering correction results in a spectrally dependent particulate absorption $d_p(\lambda) = \alpha_p(\lambda)e_p(\lambda)$, where $e_p(\lambda) \sim \lambda^\beta$.

The Monte Carlo distribution of the scattering correction error, $e_p(\lambda)$, was defined using a normal distribution of the relative error in absorption $e_p(440) = a_p(440)/\alpha_p(440)$, $\mu = 0$, and $\sigma = 0.1$.

### Table 1. Parameters and Uncertainties Used in the Monte Carlo Analysis of Backscattering Uncertainty

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncertainty, $\sigma$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d(\lambda)$</td>
<td>2 counts</td>
<td>Estimated</td>
</tr>
<tr>
<td>$\alpha(\lambda)$</td>
<td>11%</td>
<td>[56]</td>
</tr>
<tr>
<td>$e_p(440)$</td>
<td>20%</td>
<td>Described in text</td>
</tr>
<tr>
<td>$\chi_p(124^\circ)$</td>
<td>4%</td>
<td>[56,60]</td>
</tr>
<tr>
<td>$\beta_{sw}(\lambda, 124^\circ)$</td>
<td>2.5%</td>
<td>[61,62]</td>
</tr>
</tbody>
</table>

*All uncertainties except scattering correction error, $e_p(\lambda)$, are spectrally independent.*
Monte Carlo realization so that this paper.

We sincerely thank the WHOI engineers, support staff, and divers that worked closely with us at the MVCO to make the OASIS project possible. To name a few: Janet Fredericks, Jay Sisson, Steve Falutico, and Andy Girard; the captains and crews of the R/V Tioga and R/V Connecticut; and the MVCO Data Management Office for making core instrument, including ADCP, data publicly available. Grace Chang and Tommy Dickey (UCSB) loaned us the LISST-100X used in 2009. Jim Loftin from the University of Maine provided countless hours of assistance in experimental design and logistics for the OASIS project. We thank our colleagues Paul Hill, Kristian Curran, John Newgard (Dalhousie University), Tim Milligan, Brent Law (Bedford Institute of Oceanography), and John Trowbridge (WHOI) for a productive collaboration during the OASIS project. Early versions of this manuscript benefited in particular from discussions with Paul Hill and comments from Curtis Mobley and Iwona Cetinić. We also thank Mike Twardowski, James Sullivan, and one anonymous reviewer for thoughtful reviews that have improved the quality of this paper.

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