Comparison of optically derived particle size
distributions: scattering over the full
angular range versus diffraction at
near forward angles

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The volume scattering function (VSF) of particles in water depends on the particles’ size distribution and composition as well as their shape and internal structure. Inversion of the VSF thus provides information about the particle population. The commercially available LISST instrument measures the scattering at near forward angles to estimate the bulk size distribution of particles larger than about 1 μm. By using scattering over the full angular range (0°–180°), the recently improved VSF-inversion method [X. Zhang, M. Twardowski, and M. Lewis, Appl. Opt. 50, 1240 (2011).] can characterize particles in terms of particle subpopulations, which are described by their unique size distribution and composition. Concurrent deployments of the Multispectral Volume Scattering Meter and the LISST in three coastal waters (i.e., Chesapeake Bay, Mobile Bay, and Monterey Bay) allowed us to compare the size distributions derived from these two different methods. We also obtained indirect validation of the results for submicrometer particles and for the composition of particles provided by the VSF-inversion method. For particle sizes ranging from 1 to 100 μm, the concentration was shown to vary over 10 orders of magnitude, and excellent agreement was found between the two methods with a mean relative difference less than 10% for the total size distributions. The inversion results also reproduced spectral variations in the shape of the VSF, although these spectral variations were not frequently observed in our study. The increased backscattering towards the shorter wavelengths was explained by the stronger influence of submicrometer particles affecting the backscattering. Based on published measurements of cell sizes and intracellular chlorophyll-a [Chl] concentrations over a wide range of phytoplankton species and strains, [Chl] was estimated for the inverted subpopulations that were identified as phytoplankton based on their refractive index and mean sizes. The estimated [Chl] agreed well with the fluorescence-based estimates in both magnitude and trend, thus reproducing a bloom event observed at a time series station. © 2012 Optical Society of America

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1. Introduction

Oceanographers often describe matter in water as “dissolved” or “particulate” based on whether or not it passes through the pores of a filter (typically
between 0.2 and 0.7 μm) used to partition it. However, no real boundary exists between these two categories and, indeed, seawater contains a continuum of discrete units [1] ranging from molecules and submicrometer colloidal suspensions to flocs several millimeters in length and fish measuring up to a few meters. Particle size distributions control and are controlled by many physical and chemical processes [2–6] and thus contain information about these processes. Particles also vary in composition from mineral grains to live phytoplankton cells to bubbles to heterogeneous flocs. These diverse groups of particles play different roles in various biogeochemical cycles. For example, the oceanic export of particulate organic carbon (POC) and other nutrients (P, N, Si) from surface waters to the deep ocean is correlated with mineral particle concentrations [7]. Bubbles play significant roles in air-sea gas transfer [8], the scavenging and transformation of dissolved organic carbon into particulate organic carbon [9], and the formation of marine aerosols [10]. Because the size and composition of particles along with their structure and shape modify the radiative transfer of light in the ocean, optical measurements can be used to examine particle properties.

For a given incident illumination upon a medium, the light field within it is determined (neglecting the inelastic processes of Raman scattering and fluorescence) by two inherent optical properties: the absorption coefficient (m⁻¹) and the volume scattering function (VSF, m⁻¹sr⁻¹) [11]. While the former describes how photons are removed within the medium, the second describes how photons are dispersed (redirected). The dispersion of light arises from two sources: molecular scattering by pure water and associated dissolved salts, and scattering by suspended particles. The VSF of pure water with salts is known with observations and theory agreeing to within 2% [12–15]. The observed variation of VSFs in natural waters, after accounting for molecular scattering by seawater, is entirely due to particles. Figure 1 illustrates how the optical and geometrical properties of particles affect the VSF. Following Fig. 1, the mean phase difference \( \Delta \varphi \) of scattered light at angle \( \theta \) by all dipoles at far field would be proportional to \([16]\)

\[
\Delta \varphi(\theta) \sim \sin \frac{\theta}{2}.
\]  

At near forward angles, where \( \sin \frac{\theta}{2} \ll 1 \), \( \Delta \varphi \) is generally small (equal to 0 when \( \theta = 0 \)), which means that the scattering by dipoles is approximately in phase and hence the intensity measured is proportional to the number of dipoles (i.e., the size of particles). Using this theoretical simplification, many sizing techniques have been developed. Simultaneous measurements of the attenuation coefficient at the immediate forward angle (\( \theta = 0 \)) and its fluctuation have been used to estimate the average size and the concentration of particles [17]. The spectral slope of the beam attenuation coefficient has been used to estimate the slope of the Junge (power-law) distribution [18–20], which is often used to represent the mean state of the bulk particle size distribution (PSD) in the ocean [21]. The angular distribution of scattered light in the near forward directions is related to the size distribution of particles [17]. This is the basis for laser diffraction-based sizing technology. Theoretical [22] and experimental [23–25] studies of this technique have led to its commercialization (e.g., LISST-100, Sequoia Scientific, Inc., WA, USA) [26], which have allowed reasonable estimates of PSDs to be made for particles of sizes from approximately 1 to 100 μm in laboratory phytoplankton cultures [27], lakes and rivers [28,29], the marine bottom boundary layer [30,31], and coastal [32,33] and oceanic [34] surface waters. The theoretical advantage of dealing with scattered light in the near forward angles, however, also places limits on the information about particles that can be obtained. Because near forward scattering is not very sensitive to the composition of particles or to smaller particles (i.e., particles smaller than the incident wavelength), only the bulk size distribution for large particles (i.e., particles larger than about three times the incident wavelength) can be obtained.

For scattering at larger angles, the phase difference can no longer be ignored. In this case, the angular distribution of scattering reflects co-variations in the size, the refractive index, the shape, and the internal structure of particles. Thus, the possibility arises of obtaining additional information about particles beyond their bulk size if the full VSF is used. Attempts have been made to characterize particles in the ocean from VSFs (e.g., [35–37]) despite the scarcity of their measurement. After reviewing these earlier studies, Zhang et al. [38] present an inversion method to retrieve both the size and the composition (represented by the refractive index) of particles from VSFs. By carefully constructing a library of candidate particle populations based on a sensitivity analysis of the angular scattering as a function of the size and composition of particles, the proposed method is stable and robust [39]. Compared to other
optical sizing techniques, such as that used for laser diffraction approaches, the Zhang et al. [38] method represents an advancement in two respects: (1) instead of an aggregated size distribution for the bulk particle population, each individual particle subpopulation can be identified and characterized in terms of its size distribution and refractive index; and (2) the size distribution can be resolved over the entire optically sensitive range from the order of approximately $10^{-2}$ to $10^2 \mu m$.

The Zhang et al. [38] method (hereafter referred to as the VSF inversion) was evaluated using a prototype VSF sensor, called MASCOT (WET Labs, Inc.), in relatively clear waters. Czerski et al. [40] found that the bubble populations identified using the VSF inversion agreed well with the concurrent acoustical measurements in waters near Hawaii. Twardowski et al. [39] inverted the wave-injected bubble and suspended sediment populations from the measured VSFs in the surf zone off Scripps Pier; they obtained results consistent with the acoustical measurements of bubbles and the video observations of mineral particles. They also evaluated the effect of particle shape on the inversion and found that with the library of nonspherical particles the inverted mineral particles were more consistent, particularly for mineral groups with large sizes (larger than approximately 20 $\mu m$) because the spherical assumption would show an unrealistic rainbow effect in the phase function for large particles. The VSF inversion was also tested in a more complex environment in the coastal waters off New Jersey [38] using another prototype VSF sensor called the volume scattering meter (VSM) [41]. Even though no independent validation was available, the results seemed reasonable. The particle population was found to be dominated by particles of higher water content and hence lower refractive index, which was in agreement with the results [42] based on the Twardowski et al. method [43]. The aggregated particle size distribution from all of the subpopulations derived from the VSF inversion showed a bimodal distribution [44]. The distribution of the larger particles (greater than $\sim2 \mu m$) resembled the Junge (power-law) distribution, and the average slope was $-4.0 \pm 0.2$, which is in close agreement with the well-known mean value of $-4.0$ for the global ocean.

We conducted field experiments in Mobile Bay, Chesapeake Bay, and Monterey Bay that provided an excellent opportunity to evaluate and compare the two methods used in this study. The diverse particle types in these locations provided a challenging test to evaluate the closure between the Multispectral Volume Scattering Meter (MVSM) and the LISST method. In each of these experiments, VSFs were measured with an improved version of the VSM and a LISST-100X (Sequoia Scientific, Inc.). Particle types in these areas varied widely. Mobile Bay is dominated by minerogenic particles from terrestrial input and resuspension. Monterey Bay typically exhibits large concentrations of organic particles, and during this deployment there were multiple blooms of diatoms and dinoflagellates. Chesapeake Bay contains combinations of mineral, organic, and detrital particles that vary widely by location. The

2. Experiments and Data

A. Multispectral Volume Scattering Meter (MVSM)

Compared to an earlier version of the VSM operating at one wavelength [41], the MVSM measures the VSF with an improved resolution of 0.25° (versus 0.3°) and at eight wavelengths (i.e., 443, 490, 510, 532, 555, 565, 590, and 620 nm) with a spectral bandwidth of 9 nm. Even though the designed angular range was from 0.5° to 179°, the measurements at the near forward angles (<10°) were found to be problematic (more on this in Subsection 2.D). A new halogen bulb was used for each deployment and allowed approximately 5 h “burn-in” time to stabilize its output. Once stabilized, a series of measurements was made with nanopure water at several different temperatures. Dark current values were recorded for each of these measurements and for each in situ measurement, which were then processed with the nanopure water values corresponding to the field temperature.

Because the MVSM uses a rotating detector prism, data acquisition is relatively slow (approximately 10 min for one run for all eight wavelengths). Measurements were thus limited to surface and near-surface locations. With the instrument held at a constant depth, ambient water was pumped through the sample chamber using a SeaBird 5T pump at 2 to 3 l/min. For each measurement, we collected two complete sets of data. Unless there was a large difference between these, these two sets were averaged, and the average was then processed following Berthon et al. [45] to obtain the particulate VSF.

B. LISST

A LISST-100X uses a series of 32 annular detectors to measure light scattered at angles from 0.07° to 13.9° in water. Our particular LISST uses a 532 nm laser for which particle sizes (in diameter) are measured over a range from 1.04 to 199 $\mu m$. Data were collected at a frequency of 1 Hz and processed using the standard LISST software (LISST SOP v4.65) to produce the particle volume concentrations for each size class, which were then postprocessed to produce PSD distributions and VSFs as described below.

Before and after each deployment, a nanopure water sample was measured as a background reference. Each measurement was made after letting the laser warm up for 20 min, thus allowing its temperature and output to stabilize. In the field, the instrument was turned on and immersed in the water for 10 min before beginning a measurement. A typical cast takes approximately 10 to 20 min depending on the depth.

The LISST does show sensitivity to ambient light, of which Reynolds et al. [33] gives an excellent
discussion and suggests a mitigation measure by baffling the optics head of the instrument. We have had a similar experience. Instead of baffling the optics head, we deployed the instrument vertically with the sensor looking down rather than horizontally. This configuration avoided direct sunlight, which is by far the largest source of ambient light contamination. In this setup, only measurements in the upper few meters of the water column showed any significant ambient light contamination, and it only occurred in the outer two annular detector rings. When deployed in the horizontal position, ambient light contamination occurs to much greater depths and over a larger number of detector rings.

After data collection and processing using the manufacturer’s software, the particle volume concentrations \(V(D)\) were averaged and binned into 0.5 m depth intervals. The PSD was then calculated as \(\frac{6V(D)}{\pi D^3 \Delta D}\) for each binned \(V(D)\) by assuming all particles were spheres, where \(D\) is the particle diameter and \(\Delta D\) is the width of each size bin of the LISST.

The VSF is calculated using the log file from the LISST, which contains the digital numbers (DNs) recorded directly from the analog-to-digital converter from each sensor on the instrument. Data were averaged and binned by depth in the same way as the PSD data. Our method for calculating the VSF was similar to that of Slade and Boss [46] and Agrawal and Mikkelsen [47], except that we did not use the small-angle approximation to calculate angles. We instead calculated the angles based on the instrument and detector geometry. The angles in water corresponding to the 33 edges of the 32 detector rings are \(\theta_i = \arcsin\left(\frac{1}{n_w} \sin\left[\arctan\left(\frac{r_i}{f}\right)\right]\right)\), where \(n_w\) is the index of refraction of water at 532 nm and \(f\) is the focal length of the receiver lens, which is 6 cm for the LISST-100X Type B [47] and \(r_i = r_o(200)^{0.8}\) for \(i = 0, 1, \ldots, 32\), where \(r_o = 102 \mu m\) [26]. The LISST was calibrated with solutions of latex microspheres to give absolute VSF measurements. Solutions of spheres (Duke Scientific, now Thermo Scientific) with diameters of 1, 4, 20, 40, and 80 \(\mu m\) were each measured at three concentrations. A Mie light-scattering code and the manufacturer-supplied dispersion curve for the index of refraction [48] were used to calculate calibration coefficients for each detector ring.

C. Field Experiments

Field experiments took place in Mobile Bay (17–26 February 2009), Chesapeake Bay (12–22 October 2009), and Monterey Bay (12–19 October 2010) (Fig. 2). Mobile Bay is a relatively shallow estuary system which contains large concentrations of chlorophyll, terrigenous particles, and colored dissolved organic matter. Chesapeake Bay is a large estuary bay with considerable and variable freshwater inputs. Particles in the water represent a nearly complete spectrum: terrigenous particles, resuspended sediment, phytoplankton, detritus, and CDOM. During 15–18 October 2009, the entire Chesapeake watershed received around 9 cm of rain (estimate based on radar measurements), which interrupted the experiment. This was followed by relatively clear skies. Immediately after the rain, we found higher terrigenous particle and lower chlorophyll concentrations at locations in the middle of the bay. The chlorophyll concentrations then began to increase over the next three days and reached a full bloom by 22 October. Monterey Bay is a highly productive coastal region that has become well known for its fall dinoflagellate blooms, which were present at the time of sampling.

For each measurement, the MVSM was deployed in the water just below the surface usually at a depth of 1 to 2 m. The LISST was deployed separately from the MVSM either by itself or as part of a package with other instruments, and it was used to measure particle profiles of the water column. Data from each instrument were processed separately, and then the combined VSF (at 532 nm) was calculated using the depth-binned LISST data that matched that of the MVSM. When using this deployment protocol,
measurements were not guaranteed to occur at exactly the same time or place. We only found this to be a problem in two of the casts in the highly variable dinoflagellate bloom conditions in Monterey Bay. These casts were not included in the analysis.

D. Combined LISST-MVSM VSF

The scattering coefficients obtained by integrating the MVSM VSFs (after suitable angular extrapolation to zero) were consistently and significantly higher than those of the WET Labs ac-9 or ac-s. While this is not entirely unexpected because of the difference in acceptance angles between the two instruments [49], the MVSM scattering coefficient was often larger than the attenuation coefficient measured by the LISST. Tests with polystyrene spheres revealed problematic measurements from the VSF at near forward angles, particularly for larger spheres. The problems with the MVSM occurred at angles less than 10°.

Because both the LISST and MVSM have a 532 nm wavelength and the LISST measures the VSF up to an angle of 12.96° (using the mean of the detector angles), the two VSF measurements were combined to produce a single VSF. As the MVSM was placed near the surface in the field, the ambient light contamination with LISST data became an issue when forming the combined VSFs. Figure 3(a) shows the LISST VSFs measured in the upper 4 m at a station in Chesapeake Bay. The ambient light contamination is easily seen at the two largest angles for the data where the VSFs take a sharp upwards turn. This effect decreased with increasing depth. This particular example represents an extreme case. However, rather than examine each measurement, we chose to simply remove the last two angles from the LISST VSF data set for all field measurements and to use the MVSM data instead. Thus, the largest LISST angle in the combined VSF is 9.48°, and the first MVSM angle is 9.50° [an example of a combined LISST-MVSM VSF is shown in Fig. 3(b)]. No other fitting or scaling was applied. The results of this procedure for two solutions of polystyrene spheres are shown in Fig. 4, where the theoretical curves were calculated from Mie theory using the refractive index and size distribution values supplied by the manufacturer.

The combined LISST and MVSM VSFs, which were relatively free from ambient light contamination, were used in the inversion. However, because no correction was applied to the LISST data itself, the PSDs directly calculated from the LISST data might be affected by the ambient light contamination, particularly at small sizes.

3. Inversion

A. General Theory

The theoretical background for general inversion techniques can be found in Twomey [50]. The technical details for the VSF-inversion method were provided in Zhang et al. [38] and in Agrawal and Pottsmith [26] for the LISST approach. Here, only a brief review is provided with a focus on highlighting the similarities and differences between near forward diffraction inversion (e.g., LISST) and full angle VSF inversion (see Table 1 for a summary). Assuming there are M particle groups in a sample, the measured VSF $\beta(\theta, \lambda)$ can be modeled as

$$\beta(\theta, \lambda) = \sum_{i=1}^{M} b_i(n(r), F(r), S(r), T(r), \lambda) \tilde{f}_i(n(r), F(r), S(r), T(r), \theta, \lambda),$$  

(2)
where the total scattering coefficient $b_i$, in m$^{-1}$, and the phase function $\tilde{\beta}_i$, in sr$^{-1}$, for each group are determined by the refractive index $n(r)$; number density $P(r)$, in m$^{-1}$; shape $S(r)$, and structure $T(r)$; each of which, in turn, is a function of the particle size $r$, (radius, m$^{-1}$). The optical parameters of $b$, $\beta$, $\tilde{\beta}$, and $n$ are also a function of the wavelength $\lambda$. Equation (2) and its inversion are the guiding principles for both methods. With the objective of deriving $b_i$ from measured $\beta$, the inversion starts with constructing a set of $\tilde{\beta}_i$ (also called a kernel function).

As the phase difference of light scattered by dipoles increases with the scattering angle [Eq. (1)], there is a change in the primary information contained in the VSFs concerning the particles. The near forward angles mostly provide information on the sizes of particles larger than the measurement wavelength, while larger angles are affected by a combination of the sizes, refractive index, shape, and internal structure of particles. Therefore, the kernel functions are built differently (Table 1).

For the LISST, the kernel function is built as $\tilde{\beta}(r, \theta)$ using Mie theory for spherical particles of different sizes (the LISST uses 32 sizes) because the effect of shape is not significant in the near forward angles even though a kernel function based on randomly shaped particles is also provided to correct for the residual shape effect at larger scattering angles [47]. Because scattering in the LISST angular range is not sensitive to the refractive index, only the bulk particle size distribution can be obtained by inversion. However, there are residual effects due to the refractive index. To minimize these effects, the kernel function that we used takes the mean of the Mie calculations with different refractive indices. In practice, the LISST kernel function is further normalized by the volume because the volume concentration of particles is preferred. But, the inversion principle remains the same.

For the VSF inversion, the kernel function is built as $\tilde{\beta}(\text{subpopu}, \theta)$. In this study, there were 126 subpopulations, each of which was identified as a single-species particle population with one representative refractive index $n$ following a lognormal distribution of a mode size $r_{Mo}$ and a standard deviation $\sigma$. Zhang et al. [38] discussed in depth the rationale behind

Table 1. Comparison of the Inversion Schemes and the Particle Information That Can Be Potentially Retrieved from the LISST-100X and MVSM Instruments

<table>
<thead>
<tr>
<th>Inversion</th>
<th>Wavelength (nm)$^a$</th>
<th>Angles (°)$^b$</th>
<th>Kernel Function$^c$</th>
<th>Particle Radius ($\mu$m)$^d$</th>
<th>Particle Shape</th>
<th>Refractive Index ($n$)$^e$</th>
<th>Subpopulation$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LISST-100X</td>
<td>532</td>
<td>0.07–13.9</td>
<td>$\tilde{\beta}(r, \theta)$</td>
<td>0.5–100</td>
<td>sphere</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>LISST-MVSM</td>
<td>532</td>
<td>0.5–179</td>
<td>$\tilde{\beta}(\text{subpopu}, \theta)$</td>
<td>0.02–200</td>
<td>Asym. hexahedra</td>
<td>0.75, 1.02–1.20</td>
<td>$F(n, r_{Mo}, \sigma)$</td>
</tr>
</tbody>
</table>

$^a$The MVSM measures at eight wavelengths (443, 490, 510, 532, 555, 565, 590, and 620 nm), but only the 532 nm data was used during the LISST-MVSM inversion.

$^b$The LISST has 32 angles; the MVSM has 715 angles with a 0.25° increment; the combined LISST-MVSM used LISST measurements up to 9.48° and MVSM for the rest starting at 9.5°.

$^c$For the LISST, it was built for 32 sizes; for the MVSM, it was built for 126 subpopulations.

$^d$For asymmetrical hexahedral particles, the radius is the mean cross-sectional area equivalent.

$^e$Except for bubbles, a constant imaginary index of 0.002 is assumed for particles.

$^f$Each subpopulation was defined by a single-species particle population with one representative refractive index $n$ (= 1.02–1.20, and 0.75 for bubbles) and following a lognormal distribution with a mode size $r_{Mo}$ (= 0.02–10 μm) and a standard deviation $\sigma$ (= 0.1–1.1). The range of these parameters covered the majority of oceanic particles, and their exact values were determined though a sensitivity analysis as described in Zhang et al. [38].
adopting lognormally distributed subpopulations. In essence, theoretically, the natural processes of breakage [51], coagulation [52], or cell division [53] would render a population of particles following the lognormal distribution. Observationally, living or nonliving particle species in the ocean, such as phytoplankton [54], microbes [55], detritus [56–59], and mineral particles [60,61], do follow a lognormal distribution in their number-size spectra.

Because particle shape also affects VSFs, particles are assumed to be of an asymmetric hexahedral shape. We acknowledge that oceanic particles, while not spherical, cannot be represented by a single shape; however the asymmetric hexahedral shape was shown to appropriately simulate the optical properties and polarization states of mineral aerosol particles, which do not possess a particular shape [62]. Morphologically, the asymmetric hexahedral shape, with sharp edges and corners and sides that are not exactly parallel, is believed to be a more realistic representation than spherical or spheroid shapes for marine particles. Optically, the differences in the phase functions between two nonspherical particles are much less than the differences between a spherical and a nonspherical particle [63]. For example, the rainbow peak often associated with spherical particles disappears as the shape departs from sphericity [64]. Note that the shape effect on scattering at visible wavelengths becomes insignificant for particles of sizes less than about 0.2 \(\mu\)m (i.e., in the Rayleigh scattering regime) [65]. Phase functions for randomly oriented asymmetric hexahedra previously computed for the atmosphere [62] were computed for the aquatic medium. A combination of the discrete dipole approximation method [66,67] and an improved geometric optics method [68] were employed to compute the kernel function. For these particles, the radius was represented as a surface area equivalent sphere. The only exception was the bubble populations, which were modeled as spheres coated [69] with a protein-type monolayer film that was 2 nm thick [70].

With the kernel function built, the next step was to solve Eq. (2) for \(b_i\) from measured \(\beta(\theta)\). For the LISST, the number of angles (i.e., 32) was the same as the number of sizes to be resolved. Among the various inversion algorithms, the Chahine algorithm was found to give the best results [25]. For the VSF inversion, the number of angles is often much greater than the number of subpopulations (e.g., the MVSM measures scattering at 715 angles versus 126 subpopulation candidates). The VSF inversion was implemented using the least-squares method with a nonnegativity constraint [71]. In addition, an angularly adjusted weighting was applied such that the peaked forward scattering, which is normally observed in the natural environment, would not skew the convergence and the scattering at all angles was weighted approximately equally. For each \(b_i\) solved, its value was zero, then the corresponding subpopulation was assumed to not be present in the sample. If a subpopulation was present, its number concentration \(N_i\) (m\(^{-3}\)) was calculated as

\[
N_i = \frac{b_i}{C_{\text{sca,i}}},
\]

where \(C_{\text{sca,i}}\) (m\(^2\)) is the scattering cross-sectional area for this particular subpopulation. For the LISST, the total PSD \(F_{\text{LISST}}\) was simply

\[
F_{\text{LISST}} = N_i,
\]

for \(i\) representing one of 32 size bins.

For the VSF inversion, the size distribution for each subpopulation was \(N_iF_i(r_{Mo,i}, \sigma_i)\), where \(F_i\) represents the lognormal function with the mode size \(r_{Mo,i}\) and standard deviation \(\sigma_i\), and the total PSD \(F_{\text{VSF-inversion}}\) was

\[
F_{\text{VSF-inversion}} = \sum_{i=1}^{M} N_iF_i(r_{Mo,i}, \sigma_i)
\]

for \(i\) representing each subpopulation.

Both the sizes and the refractive indices influence the optical properties of particles, and therefore it is possible that particle subpopulations of different sizes and indices could produce similar VSFs within the uncertainty of the measurements. In these cases, the inversion would not be able to differentiate between these “optically equivalent” subpopulations.

As summarized in Table 1, both methods fall into the category of inversion. But the fundamental difference is that information about the subpopulations is obtained from the VSF inversion, while only the total particle size distribution (~1 \(\mu\)m or larger) can be retrieved from the LISST. This is because scattering at the near forward angles is mainly due to larger particles whereas the full VSF is determined by particles of all sizes (small and large relative to the measurement wavelength) as well as by the particle composition. In addition, the inversion techniques are also different.

### B. Forward Modeling

The results for particle subpopulations, either measured or simulated, are often used to model the inherent optical properties [e.g., 72], which in turn are used to predict the under- and above-water light field [e.g., 73]. In this study, we model the spectral variation of the VSFs. Because the MVSM measures the VSF at eight wavelengths, of which the data at 532 nm was used for the inversion, the comparison of modeled and measured spectral VSFs can also serve as an additional validation. The spectral \(\beta_i(\lambda)\) for the subpopulation \(i\) with a size distribution \(F_i\) and a refractive index of \(n_i\) was estimated as
\[ \beta_i(\theta, \lambda) = \int_{r_{\text{min}}}^{r_{\text{max}}} N_i F_i(r_{\text{Mo},i}, \sigma_i) C_{\text{ang}}(\theta, n_i, r, \lambda) \, dr, \]  

(6)

where \( N_i \) and \( F_i(r) \) were derived from the VSF inversion and \( C_{\text{ang}} \) (m\(^2\) sr\(^{-1}\)) was the angular scattering cross section at wavelength \( \lambda \) calculated for particles with a refractive index of \( n_i \) and a radius of \( r \) varying between the minimum (\( r_{\text{min}} \)) and the maximum (\( r_{\text{max}} \)) sizes. Because the size distribution for every subpopulation was lognormal, the exact values of \( r_{\text{min}} \) and \( r_{\text{max}} \), if set significantly lesser and greater than the mode value, would barely affect the outcome of Eq. (6). In our study, they were set at 0.001 \( \mu \)m and 1000 \( \mu \)m, respectively. In forward modeling, the normal dispersion of the refractive index \( n_i \) for a particular subpopulation \( i \) was ignored, which effectively means the spectral variation, if any, is entirely due to the relative shift between the sizes and the wavelength. The error due to this assumption is expected to be limited for nonabsorbing or weakly absorbing particles [18] but could be large for subpopulations, such as phytoplankton species, with significant variation in spectral absorption. With the VSFs for each subpopulation estimated, the bulk spectral VSF was simply

\[ \beta(\theta, \lambda) = \sum_{i=1}^{M} \beta_i(\theta, \lambda). \]  

(7)

C. Estimates of Biogeochemical Quantities

Compared to the LISST method, the VSF inversion provides additional information on the particle composition, which when combined with the sizes allows for a more complete characterization of the particles. While we did not have access to information about individual particles such as from a flow cytometer, a preliminary attempt was made to demonstrate its potential. As shown in Fig. 5 for phytoplankton, the chlorophyll-a concentration [Chl] per cell scales approximately with the volume of the cell. Based on Fig. 5, we estimated [Chl] as

\[ [\text{Chl}] = N_i \times (0.030 \pm 0.006) \times r_{\text{mean},j}^{2.876 \pm 0.115}, \]  

(8)

where \( N_i \) and \( r_{\text{mean},j} \) are the concentration and the mean size of a subpopulation \( i \) whose refractive index is within the range of 1.03 to 1.07 and mean size is within 0.2 to 100 \( \mu \)m. Even though Eq. (8) was developed based on laboratory measurements of a wide range of phytoplankton species as reported in [72,74,75], its use implies an underlying assumption, namely, that any particle population whose refractive index and mean size fall within the ranges shown in Fig. 5 was assumed to be chlorophyll-bearing. This is certainly not always true. On the other hand, most phytoplankton species do have their refractive index and size bounded within the ranges consistent with Fig. 5 [76].

4. Results and Discussion

A. PSD Closure with LISST

The total PSDs derived from the VSF inversion were compared with the LISST estimates in Fig. 6, where one example is shown for each experiment conducted in Monterey Bay (27 sets of data), Chesapeake Bay (37), and Mobile Bay (17). The range of PSDs formed by optically equivalent particles but with different size distributions, if detected, is also shown (upper and lower boundaries). While LISST-derived PSDs are typically reported in diameter, here the sizes of particles are reported in radius to be consistent with the VSF-inversion results. Total PSDs estimated by Eq. (6) from the VSF inversion corresponded well with the LISST estimates with a mean relative difference of 6%, 7%, and 9%, respectively, for the three experiments over the size range from 1 to 100 \( \mu \)m [Fig. 6(d)] over which the PSD varied about 10 orders of magnitude. The agreement of the total PSD between the two methods, while excellent overall, seems to gradually degrade for smaller particles (i.e., \(~\)20–40% for \( r > 10 \mu \)m versus \(~\)80% for \( r < 10 \mu \)m). There are several possible factors. While the combined LISST-MVSM data have eliminated the possible ambient light contamination at the two largest angles for the LISST measurements (Subsection 2.D), the PSDs derived from the LISST alone were still subject to this effect, which affects the retrieval of smaller particles [33]. At larger LISST angles, both the shape [27,77] and the refractive index [78] of particles, while still secondary, start to affect the scattering and hence the estimates of smaller particles. Lastly, the finer particles, outside...
the detection range of the LISST, also affect the retrieval of smaller particles [26,78].

An advantage of the LISST method was that no assumption was made about the particle size distributions, which was in contrast to the VSF-inversion method that assumed that each subpopulation was lognormally distributed, even though this assumption has been corroborated theoretically [51,53] and experimentally for various particle populations [54,60,79,80]. Jonasz and Fournier [81] have shown that the size distribution of marine particles could be approximated by a sum of lognormal functions. The comparisons shown in Fig. 6 further confirm these earlier results, thus supporting the lognormally distributed assumption for particle subpopulations. Other functions (e.g., gamma or Weibull) with shapes similar to a lognormal distribution have also been proposed, but the effect of these subtle differences on the inversion results is minimal [38].

It is remarkable to note that the Junge distribution [21], which was not assumed or involved in either method, still applied to these complex coastal water environments, or at least as a mean state approximation for particles of sizes greater than 2 to 5 μm. The Junge slopes estimated for particles of sizes greater than 3 μm, shown in Fig. 7, are similar between the two methods and range between −3.3 and −4.2 with mean values of −3.7, −4.1, and −3.9 for Monterey Bay, Chesapeake Bay, and Mobile Bay, respectively, which is consistent with the mean values reported for other coastal waters [33,34]. However, it should be recognized that the presence of significant peaks in the distribution often caused a departure from this idealized shape for the PSD.

It is interesting to note some common features in the PSDs that consistently showed up in both results. For example, at the experimental sites of Chesapeake Bay and Mobile Bay, the concentration of particles seemed to reach a local maximum at around 1.5 to 2 μm followed by a local minimum before continuing to rise as the size decreased (only one example for each site is shown in Fig. 6, but this feature was common in the data not shown for Chesapeake Bay and Mobile Bay). A similar pattern can be found in Reynolds et al. (33), e.g., their Figs. 4 and 5 for LISST measurements in Californian coastal water environments.

Fig. 6. Comparison of the PSD derived from the full VSF inversion and the LISST inversion. An example was chosen from each experiment in (a) Monterey Bay, (b) Chesapeake Bay, and (c) Mobile Bay. The upper and lower boundaries denote the range of optically equivalent particles. Relative differences in the PSD between the VSF inversion and LISST for each data set are shown in (d). The vertical bars indicate the upper and lower boundaries estimated for optically equivalent subpopulations. The curves are shifted slightly in the x direction to avoid overlap of the error bars.
waters. The optical properties at visible wavelengths for particles of sizes around a micrometer show dramatic changes as they transition from Rayleigh and Rayleigh–Gans scattering for smaller particles to the geometric approximation for larger particles [e.g., 55]. As both results were optically based with a measurement light at 532 nm, whether or not the local maximum or minimum of PSDs observed for sizes of 1 to 2 μm were an optical artifact should be further verified. However, the continued rise of PSDs at submicrometer sizes, we believe, was a real feature that was probably due to colloidal particles [82,83].

B. Submicrometer Particles

While diffraction patterns observed in the forward angles are mainly affected by particles that are larger than about three times the incident wavelength, submicrometer particles contribute to the angular scattering mainly at backward angles because of their high backscattering efficiency [e.g., 55]. One advantage of the VSF inversion is that it retrieves submicrometer particles. Because we did not have independent estimates of submicrometer particles, we carried out an indirect verification.

The VSFs measured on 13 October 2009, at station CB3 in Chesapeake Bay [the circled symbol in Fig. 2(b)] showed spectral variations, which were consistently observed in subsequent visits to the same station from 19 to 22 October 2009. Rain interrupted the experiment from 14 to 18 October with a total precipitation of nearly 9 cm. Figures 8(a) through 8(e) partition the VSFs measured at 532 nm into contributions by the subpopulations grouped by their refractive indices. Because most of the spectral variations observed in the VSFs occurred at angles greater than 60° to 70°, Fig. 8(f) compares the spectral backscattering coefficient estimated using Eqs. (6) and (7). The measured and calculated backscattering coefficients agree well with each other for both the spectral shape and magnitude, thus indicating that the derived subpopulations using data at only one wavelength were able to reproduce the observed backscattering spectra.

In general, the backscattering at station CB3 increased toward shorter wavelengths because the backscattering was dominated by very small particles (VSPs, \( r_{Mo} < 0.1 \) μm). Because the phase function for VSPs is not very sensitive to the refractive index, the VSF inversion cannot differentiate their composition [38]. Both the magnitude and the spectral shape of backscattering by the VSP population varied in response to the rain-induced runoff even though its contribution to the total backscattering remained relatively constant at about 60%. For example, for 13 October, Fig. 8(a) shows that about 63% of backscattering was due to VSPs, and the contribution only slightly increased to \( \sim 66\% \) on 19 October [Fig. 8(b)] after the rain stopped. During the same time period, the spectral backscattering, however, more than doubled [Fig. 8(f)] in magnitude with a relaxing of the spectral shape from $-2.2$ to $-1.7$, which was an indication that relatively more larger particles in the VSP group were added by the runoff. During the following three days, the total spectral backscattering by the VSPs gradually returned to the prerainfall level in regards to both the magnitude and the shape. We do not know the biogeochemical cause for the dominance of VSPs in the backscattering at this particular station, but similar spectral behavior was observed in Crimean coastal waters in the Black Sea [84] and in a mineral-rich coastal water of the United Kingdom [85]. Interestingly, for the latter study, the observed spectral backscattering could be explained if a lognormally distributed submicrometer particle population is added against a Junge-distributed background [85].

While it has long been postulated as being insignificant to total scattering but a potentially significant contributor to backscattering [83,86], the VSPs, or colloidal particles, have been difficult to identify and quantify directly in the field [82]. The VSPs were found consistently throughout the study areas as well as in other coastal waters [38,39]. Given the assumption of our inversion regarding the angular scattering of particles, the optical behavior of VSPs as shown (Fig. 8) in this study seems to support the earlier theoretical predictions.

C. Overall Particle Dynamics

The results shown above gave us sufficient confidence to further examine the dynamics of different particle subpopulations. An example shown in Fig. 9 illustrates how the PSDs of different particle subpopulations varied at the CB3 station between 13 and 22 October, which experienced enhanced fluvial runoff due to a precipitation event between 14 and 18 October and an algal bloom that was observed on 22 October, including a five-fold increase in the chlorophyll concentration (based on fluorescence) within four days (Fig. 10, solid curve). By grouping different

![Fig. 7. Comparison of Junge slopes estimated from the VSF inversion and the LISST for sizes from 3 to 100 μm. The vertical bars indicate the upper and lower boundaries estimated for optically equivalent subpopulations.](image-url)
subpopulations by their refractive indices, Fig. 9 indicates five persistent subpopulations including VSPs and particle populations with \( n = 1.02, 1.04 \) (except on 19 October), 1.06, and 1.1 respectively. Recall that the MVSM was only deployed at a depth of 1.5 m. The particle population with \( n = 1.2 \), probably representing minerals, only appeared in the surface layer three days immediately after the rain stopped and probably arrived in the bay due to runoff. The VSPs also appear to have responded to fluvial runoff after the rain event because their concentration (proportional to the scattering coefficient) increased by a factor of four. Both of their concentrations dropped in the following days, which is an indication of subsequent settling or flushing of these particles. The influence of mineral particles on scattering was not observed on 22 October, probably due to their settling out of the surface layer four days after the rain stopped. It is also interesting to note that the PSD for VSPs was broadened on 19 October [Fig. 9(b) versus 9(a)], which suggests an influx of relatively larger VSPs due to runoff and that the PSD for mineral particles decreased on 19 and 20 October [Figs. 9(c) and 9(d) versus 9(b)], which is an indication of the settling of larger mineral particles out of the surface water. The change in the size distribution for the VSPs also explains the observed relaxing of the backscattering spectra shown in Fig. 8(f).

The subpopulation with \( n = 1.02 \), probably representing detrital particles of higher water content, seemed to dominate the PSD for sizes greater than 1 \( \mu \)m [Figs. 9(a) through 9(e)] and the total scattering [Fig. 9(f)]. The subpopulations with \( n = 1.04 \) and 1.06 had mean sizes varying between 1 and 4 \( \mu \)m, and the scattering coefficient ranged between 0.1 and 0.5 \( \text{m}^{-1} \). In terms of the refractive index, they are likely representative of phytoplankton cells [76,87]. It is interesting to note that the subpopulation \( n = 1.04 \), which was significant on 13 October...
before the rain started, became dominant again [Fig. 9(e)] on 22 October when an algal bloom was observed; in the meantime, subpopulations with $n = 1.06$ seemed to be present as a background. The subpopulation $n = 1.04$ “disappeared” from the surface water on 19 October after the rain stopped and coincided with the observed drop in the measured [Chl] (Fig. 10, solid curve). The subpopulation $n = 1.06$ has a similar refractive index as diatoms (1.06–1.07) [76,87], which is also a dominant species in Chesapeake Bay [88]. Because Eq. (8) was developed based on laboratory measurements of phytoplankton species with indices between 1.03 and 1.07 (Fig. 5), we estimated the [Chl] for subpopulations $n = 1.04$ and 1.06 (Fig. 10, dotted curve). The estimated [Chl] agreed with the measurements within 10% and was able to reproduce the observed algal bloom. The [Chl] were measured with an in situ fluorometer (Wetstar by WETLabs Inc., Oregon) using the factory calibration, which could have significant biases due to quenching mechanisms and species
composition (see [89] and references therein). This example, however, allowed us to illustrate a potential link between the retrieved PSDs and phytoplankton cells in this environment. More work will be required to test the robustness of such an approach.

The subpopulation \( n = 1.1 \) dominated the PSD for sizes around 1 \( \mu m \) throughout this period. The silicate shell found on diatoms or quartz has an estimated index of 1.06 to 1.10 [76]. Assuming that this subpopulation was a living phytoplankton species, [Chl] would have been significantly overestimated (Fig. 10, dashed curve) compared to the measurements even though the overall trend would still be valid. On the other hand, we do not know whether they represented nonliving particles.

5. Conclusions

The concurrent deployment of a commercial particle sizing device (LISST) and the MVSM in three coastal waters (i.e., Mobile Bay, Chesapeake Bay, and Monterey Bay) offered the opportunity to evaluate two optical inversion techniques based on near forward diffraction and the full angular scattering, respectively. While both methods are an application of inversion of the VSFs, there is a fundamental difference between the diffraction-based inversion and the VSF inversion. The former can only resolve the bulk particle size distributions from the measurement of near forward angular scattering where the scattered light beams are mostly in phase with each other. On the other hand, the latter method uses the full angular scattering where light of different phases interacts with each other and thus can characterize particles in terms of both size and composition. This allows the inversion to retrieve subpopulations representing unique combinations of the refractive index and size distribution. The other differences include the following: (1) the kernel function was constructed assuming spherical particles for the LISST inversion and nonspherical (asymmetrical hexahedra) particles for the VSF inversion, and (2) the inversion was executed using the Chahine algorithm for the LISST and the least-squares method with a nonnegativity constraint for the VSF inversion.

Despite these differences in methodology, excellent agreement was found for the total particle size distributions between the LISST measurements and the VSF-inversion results. For particles of sizes 1 to 100 \( \mu m \), where the particle concentrations varied over 10 orders of magnitude in these three dynamic coastal waters, the mean difference in the total PSDs between these two methods was only 7% (Fig. 6) with the maximum difference being less that 80%, which was found for particles less than 10 \( \mu m \) in size. We believe that the relatively larger differences at smaller sizes were at least partly due to ambient light contamination, which affected the LISST estimates for small particles (Fig. 3). Other small differences may result from the assumptions of a uniform refractive index [78] and spherical particles [27,77] for the LISST inversion. Because the LISST method retrieves the PSD directly while the VSF inversion found the total PSD by aggregating each subpopulation, the agreement for the total PSD indicated a closure between these two methods. Both the Junge function [19,20,55,72] and the lognormal function [51,53,54,60,79–81] have been used to approximate the particle size distribution and to simulate optical properties. Our results also confirmed a closure between these two paradigms, namely, the Junge distribution represents a mean state of aggregation of individual particle populations, each of which is distributed lognormally. However, more often than not, the mean state is violated.

We indirectly evaluated the retrieval from the VSF inversion for particles of smaller size because we did not have independent measurements. The inversion results at CB3 station in Chesapeake Bay from 13 to 22 October were able to reproduce changes in both the magnitude and the shape of the observed VSF spectra (Fig. 9) even though such spectral behavior was observed infrequently during these experiments. The increased backscattering towards the shorter wavelengths was explained by the dominance of VSPs in the backscattering (~60%) even though they contributed less than 3% to the total scattering.

Possible phytoplankton subpopulations were identified based on the refractive index and mean sizes. The corresponding chlorophyll-a [Chl] concentration was estimated using an empirical relationship between [Chl] and the size of cells (Fig. 5), which was based on laboratory measurements of phytoplankton species [72,74,75]. The estimates of [Chl] at station CB3 in Chesapeake Bay agreed with the fluorescence-based estimates within 10% when using the subpopulations with \( n = 1.04 \) and 1.06, thus replicating the algal bloom event observed three days after a precipitation event in the watershed.

While the VSF inversion needs to be further validated by the scientific community, the results of this study and of earlier reports [38–40] do give us confidence that this approach will allow us to look further at individual subpopulations and submicrometer particles for which few field observations are available.

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