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Invited feature

New insight into particulate mineral and organic matter in coastal ocean waters through optical inversion

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ABSTRACT

Suspended particulate inorganic matter (*PIM*) and particulate organic matter (*POM*) often exhibit significant variation both spatially and temporally in coastal oceans. The size distributions and optical properties of these particles are poorly known. Utilizing a newly developed inversion technique from the measured angular scattering pattern, we were able to examine *POM* and *PIM* in terms of detailed particle size distributions (PSD) and optical volume scattering functions (VSF), gaining further insights and knowledge of particles that will greatly improve biogeochemical investigations and remote-sensing algorithms. We report the results on two extremes or end-members of possible coastal environments, sediment-laden, turbid Mobile Bay, Alabama, USA and biologically productive, clear water Monterey Bay, California, USA. The optically inferred mass concentrations of *PIM* and *POM*, when accounting for the fractal nature of suspended particles, agreed well with the respective gravimetric determinations within the analysis and inversion uncertainty. Despite intra- and inter-site variability, the inferred PSDs in both coastal regions commonly showed an apparent background population of *PIM* at radii <0.6–1 μm overlaid by *POM* of radii between 2 and 20 μm. The PSDs also saw increased contribution by *PIM* at radii >50 μm. The clearly distinctive PSDs between *PIM* and *POM* provide evidence to support the Risović two-component model for suspended particulates. The shape of the VSFs, i.e., the scattering phase functions, for *POM* are similar between the two sites (backscattering ratio ≈ 0.0015), but the *PIM* in Monterey Bay exhibited a higher backscattering ratio than in Mobile Bay (backscattering ratios 0.012 vs. 0.008, respectively). At both sites, the mass-specific scattering cross section values for *PIM* ($\sigma_{[PIM]}$) are about 70–80% lower than $\sigma_{[POM]}$, while the mass-specific backscattering cross section values for *PIM* ($\sigma_{b[PIM]}$) are 10–25% greater than $\sigma_{b[POM]}$.

1. Introduction

The biogeochemical influences of particles are closely linked to their mass concentration, size distributions, state of aggregation, and composition. Indeed, these particle characteristics are both controlled by, and, in turn, controlling factors of most biogeochemical processes. Particles, through optical absorption and scattering, alter profoundly the light field penetrating through aquatic habitats. This leads to application of the absorption and scattering properties of the altered optical field, observed both *in situ* and remotely, to invert other properties of the suspended particulates (Marañón et al., 2000; Zhang et al., 2013).

Inferring the concentration of suspended matter in the surface waters from their scattering and backscattering properties requires mass-specific scattering (σ) and backscattering (σ_b) cross sections (in units of m^2 g^{-1}, Bukata et al., 1995). Optical inversion is particularly challenging in the coastal environment with a mixture of significant and varying amounts of mineral and other types of detritus in addition to biogenic particles, because the mass-specific cross sections vary significantly between different particles. To better facilitate optical inversion in coastal waters, particles are often partitioned into two general groups, particulate inorganic

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matter (*PIM*) and particulate organic matter (*POM*), and each group is treated differently (Bukata et al., 1995; Gould et al., 2001; Bowers and Binding, 2006; Stavn and Richter, 2008; Martinez-Vicente et al., 2010). However, the difficulty in determining mass-specific scattering cross sections even for these two broadly defined particle groups has forced researchers to utilize empirical ratios of the total scattering coefficient to the mass concentration of mineral (*PIM*) or organic matter (*POM*) or the sum of both, total suspended solids (*TSS*), to yield an empirical "specific scattering coefficient" (Babin et al., 2003). This can be done for both the total scattering coefficient (b^* in $m^2\ g^{-1}$) and the backscattering coefficient (b_b^* in $m^2\ g^{-1}$). Although the dimensions of the two types of parameters (i.e., σ vs. b^*) are similar, the empirical coefficients are not properly defined optically (utilizing the total scattering coefficient rather than the scattering coefficient attributable to the scattering material in question) and cannot be directly analyzed by optical theory. While these empirical scattering coefficients are easy to measure, they contain so many unknown factors that their interpretations are often regional- and/or temporal-specific and tend to vary with any change in the nature of the suspended matter throughout the year. The total scattering coefficient has been shown to be a significant predictor of *PIM* mass (Binding et al., 2005), *POM* (Stavn and Richter, 2008), *TSS* (McKee and Cunningham, 2006), or biomass (Martinez-Vicente et al., 2010). New methods of analysis, however, have been proposed to derive mass-specific scattering cross sections for the two major particle groups (Stavn and Richter, 2008; Bowers et al., 2009), i.e., $\sigma_{[M]}$ and $\sigma_{b[M]}$, where *M* is either *PIM* or *POM*. The use of properly defined scattering/backscattering cross sections also allows other properties of the suspended matter besides concentration to be determined (Stavn, 2012). However, $\sigma_{[M]}$ and $\sigma_{b[M]}$ thus derived are sometimes assumed to be constant within a coastal area, which may not always be the case.

In addition to mass concentration, the surface area of suspended particles is of critical importance. The biogeochemical study of the sorption-desorption of critical nutrients for phytoplankton, trace elements, organic detrital matter, and pollutants is a function of the surface area of the suspended particles. The particle size distribution (PSD) is required to determine the surface area of the suspended particles. A widely used PSD model in oceanography assumes that the particle concentration decreases with particle sizes following a power law with a constant slope (Bader, 1970), also known as the Junge distribution. This power law PSD represents only an approximate mean state of a mixture of all particles (Sheldon et al., 1972; Jonasz and Fournier, 1996), from which, however, the PSDs of individual particle species may deviate significantly. For example, observations of living or non-living particles in the ocean, such as phytoplankton (Campbell, 1995), bacteria (Morel and Ahn, 1990, 1991), microbes (Stramski and Kiefer, 1991), detritus (Longhurst et al., 1992; Wells and Goldberg, 1992; Yamasaki et al., 1998; Vaillancourt and Balch, 2000), and mineral particles (Lambert et al., 1981; Jonasz, 1987), all show a log-normal distribution in their number-size spectra. Theoretically, the log-normal distribution arises from the natural processes of breakage (Epstein, 1947), coagulation (Lai et al., 1972), or cell division (Campbell and Yentsch, 1989). Despite continual advancement in sizing technology, e.g., the commercially available Laser *In situ* Scattering and Transmissometer (LISST, Sequoia Inc., Agrawal and Pottsmith, 2000), it is still difficult to resolve PSDs of *PIM* and *POM*, particularly in their natural habitat. This has greatly limited our understanding of particle dynamics and their optical and biogeochemical significance in coastal waters (Gallegos and Menzel, 1987; Risović and Martinis, 1994; Atteia et al., 1998; Risović, 2002; Davies et al., 2014).

Recent advances in the measurement of the angular scattering or volume scattering function (VSF) (Lee and Lewis, 2003; Sullivan and Twardowski, 2009) are allowing further improved inversion approaches to the problem of optically inverting the major types of suspended matter (Zhang et al., 2002; Czerski et al., 2011; Zhang et al., 2011; Twardowski et al., 2012; Zhang et al., 2012, 2013). Because the angular pattern of the scattered light carries detailed information of composition, mass, and size distribution of particles (Bohren and Huffman, 1983), analyzing the VSFs yields not only the concentrations of virtually all types of suspended particulates, based on refractive index, but also the particle size distribution (PSD) of each constituent.

Thus, in this study, we applied the VSF inversion method to retrieve the characteristics of the major suspended particle types in two contrasting coastal systems, Mobile Bay, Alabama, USA and Monterey Bay, California, USA that can be considered end members of the possible variations in coastal waters. We further subdivided particle populations into mineral particles and organic particles based on their refractive indices and examined the PSDs and VSFs of each group. We validated this method by comparing the optical inversions with the gravimetric determinations of *PIM* and *POM* in the Mobile Bay and Monterey Bay coastal systems.

2. Materials and methods

2.1. Field experiments

Field experiments were conducted in Mobile Bay, Alabama (17–26 February 2009) and Monterey Bay, California (12–19 October 2010) (Fig. 1). The two sites contrast diametrically in terms of particulate matter composition. Mobile Bay, a relatively shallow estuary system containing large concentrations of chlorophyll, terrigenous particles, and colored dissolved organic matter, is dominated by minerogenic particles, probably from terrestrial input and resuspension. Monterey Bay is a highly productive coastal region with a large concentration of organic particles; during the experiment, there were multiple blooms of diatoms (predominantely *Pseudo-nitzschia* sp.) and dinoflagellates (predominantely *Prorocentrum nicans*).

At each sampling station, the volume scattering function (VSF, $m^{-1}\ sr^{-1}$) of water was measured by two instruments, a prototype Multi-spectral Volume Scattering Meter (MVSM) and a commercial LISST-100X (Type B; Sequoia, Inc., WA.). In addition, the water samples were collected for laboratory analysis of particulate inorganic matter (*PIM*) and particulate organic matter (*POM*).

2.2. PIM and POM measurements

The gravimetric technique for *PIM* and *POM* concentrations is based on standard Loss-On-Ignition (LOI) of the APHA Manual (Pearlman et al., 1995). This involves filtering water samples through 0.7 μm Whatman GF/F glass fiber filters, ashed and preweighed. Water sample volumes varied from 400 to 1025 mL in Mobile Bay and from 1250 to 3000 mL in Monterey Bay. The differences in volume filtered were due to the suspended clay load in Mobile Bay while there was no evidence of suspended clay minerals in Monterey Bay during sample collection. After filtration, the sample filters were dried at 103° C for two hours. The sample was dried and weighed again and the procedure stopped if the weights agreed to within two standard deviations of the weight scale. The samples were then ashed at 550° C for 15 min. The procedure was repeated until constant weight was achieved. The APHA technique was extended to account for and correct sea salt and water of hydration retention effects on Whatman GF/F glass fiber filters (Stavn et al., 2009). These corrections were applied to both suspended particulate measurements of Mobile Bay and Monterey Bay.