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Effect of particulate aggregation in aquatic environments on the beam attenuation and its utility as a proxy for particulate mass

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Abstract: Marine aggregates, agglomerations of particles and dissolved materials, are an important particulate pool in aquatic environments, but their optical properties are not well understood. To improve understanding of the optical properties of aggregates, two related studies are presented. In the first, an in situ manipulation experiment is described, in which beam attenuation of undisturbed and sheared suspensions are compared. Results show that in the sheared treatment bulk particle size decreases and beam attenuation increases, consistent with the hypothesis that a significant fraction of mass in suspension is contained in fragile aggregates. Interestingly, the magnitude of increase in beam attenuation is less than expected if the aggregates are modeled as solid spheres. Motivated by this result, a second study is presented, in which marine aggregates are modeled to assess how the beam attenuation of aggregates differs from that of their constituent particles and from solid particles of the same mass. The model used is based on that of Latimer [Appl. Opt. **24**, 3231 (1985)] and mass specific attenuation is compared with that based on homogeneous and solid particles, the standard model for aquatic particles. In the modeling we use recent research relating size and solid fraction of aquatic aggregates. In contrast with Mie theory, this model provides a rather size-insensitive mass specific attenuation for most relevant sizes. This insensitivity is consistent with the observations that mass specific beam-attenuation of marine particles is in the range 0.2-0.6m²/gr despite large variability in size distribution and composition across varied aquatic environments.

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References and links

1. K. L. Carder, and D. K. Costello, "Optical effects of large particles," in *Ocean Optics*, R. W. Spinrad, K. L. Carder, and M. J. Perry, eds. (Oxford University Press, 1994), pp. 243–257.
2. D. K. Costello, K. L. Carder, and W. Hou, "Aggregation of diatom bloom in a mesocosm: Bulk and individual particle optical measurements," *Deep Sea Res. Part II Top. Stud. Oceanogr.* **42**(1), 29–45 (1995).
3. W. Hou, K. L. Carder, and D. K. Costello, "Scattering phase function of very large particles in the ocean," *Proc. SPIE* **2963**, 579–584 (1997).
4. A. Hatcher, P. Hill, and J. Grant, "Optical backscatter of marine flocs," *J. Sea Res.* **46**(1), 1–12 (2001).
5. E. N. Flory, P. S. Hill, T. G. Milligan, and J. Grant, "The relationship between floc area and backscatter during a spring phytoplankton bloom," *Deep Sea Res. Part I Oceanogr. Res. Pap.* **51**(2), 213–223 (2004).
6. H. C. van de Hulst, *Light Scattering by Small Particles* (Dover, 1981).
7. M. V. Berry, and I. C. Percival, "Optics of fractal clusters such as smoke," *Opt. Acta (Lond.)* **33**, 577–591 (1986).
8. C. M. Sorensen, "Light scattering by fractal aggregates: A review," *Aerosol Sci. Technol.* **35**, 648–687 (2001).
9. P. Latimer, "Experimental tests of a theoretical method for predicting light scattering by aggregates," *Appl. Opt.* **24**(19), 3231–3239 (1985).

10. D. Stramski, A. Bricaud, and A. Morel, "Modeling the inherent optical properties of the ocean based on the detailed composition of the planktonic community," *Appl. Opt.* **40**(18), 2929–2945 (2001).
11. A. Morel, "Diffusion de la lumière par les eaux de mer. Résultats expérimentaux et approche théorique," in *Optics of the Sea* (AGARD Lectures Series, 1973), pp. 3.1–3.1–76.
12. E. Boss, M. S. Twardowski, and S. Herring, "Shape of the particulate beam attenuation spectrum and its inversion to obtain the shape of the particulate size distribution," *Appl. Opt.* **40**(27), 4885–4893 (2001).
13. M. Babin, A. Morel, V. Fournier-Sicre, F. Fell, and D. Stramski, "Light scattering properties of marine particles in coastal and open ocean waters as related to the particle mass concentration," *Limnol. Oceanogr.* **48**, 843–859 (2003).
14. M. Jonasz, and G. Fournier, *Light Scattering by Particles in Water: Theoretical and Experimental Foundations* (Academic Press, 2007).
15. W. R. Clavano, E. Boss, and L. Karp-Boss, "Inherent optical properties of non-spherical marine-like particles – from theory to observations," *Oceanogr. Mar. Biol. Annu. Rev.* **45**, 1–38 (2007).
16. E. T. Baker, and J. W. Lavelle, "The effect of particle size on the light attenuation coefficient of natural suspensions," *J. Geophys. Res.* **89**(C5), 8197–8203 (1984).
17. Y. C. Agrawal, and H. C. Pottsmith, "Instruments for particle size and settling velocity observations in sediment transport," *Mar. Geol.* **168**(1–4), 89–114 (2000).
18. P. Traykovski, R. J. Latter, and J. D. Irish, "A laboratory evaluation of the laser in situ scattering and transmissometry instrument using natural sediments," *Mar. Geol.* **159**, 355–367 (1999).
19. W. H. Slade, and E. Boss, "Calibrated near-forward volume scattering function obtained from the LISST particle sizer," *Opt. Express* **14**(8), 3602–3615 (2006).
20. A. Khelifa, and P. S. Hill, "Models for effective density and settling velocity of flocs," *J. Hydraul. Res.* **44**, 390–401 (2006).
21. F. Maggi, "Variable fractal dimension: A major control for floc structure and flocculation kinematics of suspended cohesive sediment," *J. Geophys. Res.* **112**(C7), C07012 (2007).
22. D. Risovic, and M. Martinis, "Fractal dimensions of suspended particles in seawater," *J. Colloid Interface Sci.* **182**(1), 199–203 (1996).
23. G. A. Jackson, R. Maffione, D. K. Costello, A. L. Alldredge, B. E. Logan, and H. G. Dam, "Particle size spectra between 1 μ m and 1 cm at Monterey Bay determined using multiple instruments," *Deep Sea Res. Part I Oceanogr. Res. Pap.* **44**(11), 1739–1767 (1997).
24. J. M. Fox, P. S. Hill, T. G. Milligan, A. S. Ogston, and A. Bldrin, "Floc fraction in the waters of the Po River prodelta," *Cont. Shelf Res.* **24**(15), 1699–1715 (2004).
25. X. Li, U. Passow, and B. E. Logan, "Fractal dimensions of small (15–200 μ m) particles in Eastern Pacific coastal waters," *Deep Sea Res. Part I Oceanogr. Res. Pap.* **45**(1), 115–131 (1998).
26. X. Zhang, M. Lewis, and B. Johnson, "Influence of bubbles on scattering of light in the ocean," *Appl. Opt.* **37**(27), 6525–6536 (1998).
27. C. F. Bohren, and D. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, 1987).
28. L. E. Paramonov, "On optical equivalence of randomly oriented ellipsoidal and polydisperse spherical particles. The extinction, scattering and absorption cross sections," *Opt. Spectrosc.* **77**, 589–592 (1994).
29. N. V. Shepelevich, I. V. Prostavkova, and V. N. Lopatin, "Light-scattering by optically soft randomly oriented spheroids," *J. Quant. Spectrosc. Radiat. Transf.* **70**(4–6), 375–381 (2001).
30. E. Aas, "Refractive index of phytoplankton derived from its metabolite composition," *J. Plankton Res.* **18**(12), 2223–2249 (1996).
31. M. S. Twardowski, J. M. Sullivan, P. L. Donaghay, and J. R. V. Zaneveld, "Microscale quantification of the absorption by dissolved and particulate material in coastal waters with an ac-9," *J. Atmos. Ocean. Technol.* **16**(6), 691–707 (1999).
32. F. P. Chavez, D. M. Karl, D. Hebel, M. Latasa, and L. Campbell, "On the chlorophyll-a retention properties of glass-fiber GF/F filters," *Limnol. Oceanogr.* **40**, 428–433 (1995).
33. D. Stramski, and D. A. Kiefer, "Light scattering by microorganisms in the open ocean," *Prog. Oceanogr.* **28**(4), 343–383 (1991).
34. M. S. Twardowski, E. Boss, J. B. MacDonald, W. S. Pegau, A. H. Barnard, and J. R. V. Zaneveld, "A model for estimating bulk refractive index from optical backscattering ratio and the implications for understanding particle composition in case I and case II waters," *J. Geophys. Res.* **106**(C7), 14129–14142 (2001).
35. E. Boss, W. H. Slade, M. Behrenfeld, and G. Dall'Olmo, "Acceptance angle effects on the beam attenuation in the ocean," *Opt. Express* **17**(3), 1535–1550 (2009).

1. Introduction

Many particles found in the world's oceans are not single solid particles. Rather, they are amorphous agglomerations of many different particles. These agglomerations are termed aggregates or flocs. The components of such aggregates may be large polymers, clay minerals and other inorganic particles, viruses, single celled organisms such as bacteria and phytoplankton, pieces of organisms, shells, discarded feeding structures, and excreta.

There are few studies of the optical properties of ocean aggregates in the laboratory or field. Early work by Carder and Costello qualitatively considered the effects that aggregation could have on observational closure of optical properties by packaging mass into particles that are large and rare relative to the measurement sample volume [1]. Costello et al. [2] examined variability of optical properties during a controlled diatom bloom mesocosm study and found beam attenuation to be an excellent indicator of particulate organic carbon despite changes in particle size distribution (PSD) as the diatom population aggregated [2]. In a follow-up study, Hou et al. used a specialized instrument to measure the scattering properties and particle size distribution of marine snow particles greater than 280 μm throughout the water column and concluded that these large particles could contribute up to 20% of total scattering as well as enhance backscattering efficiency [3]. More recently, Hatcher et al. examined the optical backscattering of phytoplankton-drill mud aggregates created in the laboratory using an upwelling tank [4]. Over the course of the 37 day experiment, during which the aggregates formed and aged, the relationship between backscattering and projected cross-sectional area for particles greater than 10 μm in diameter remained constant. A subsequent experiment during a spring phytoplankton bloom observed the particulate backscattering and PSD (for particles greater than approximately 100 μm in diameter), also finding evidence that the effect of large particles on the backscattering coefficient is substantial [5].

It is expected that aggregates differ in optical properties from the particles that comprise them and from a solid particle of the same size for two primary reasons: First, the packing of particles within aggregates is dense enough that coherent interactions between scattered waves emanating from individual particles within the aggregate will cause a different scattering pattern than the simple superposition of scattering by the individual particles in suspension. This coherent scattering is due to the fact that neighboring particles are affected by each other's electro-magnetic fields and hence their scattered waves cannot be assumed to have random phase relative to each other [6]. Second, aggregate porosity is observed to grow with increasing aggregate size, so the cross-sectional areas of aggregates can be significantly larger than that derived by assuming that the solid mass is packed into a sphere of the same density as the component particles.

Expanding the second reason above, it is useful to consider a cotton ball as a conceptual model for an oceanic aggregate. When compressed to a solid particle with no empty space between cotton strands, the cross section of the ball is minimal. As the cotton ball is 'fluffed' into a larger size, it occupies a bigger and bigger volume, although its solid mass remains constant. Even when fluffy, however, the cotton ball remains opaque because on average, there is a strand of cotton occupying every part of the cross sectional area. Eventually, the cotton ball is expanded to the point that some light can go through without interacting with any strand, and the aggregate becomes largely transparent [7].

The theory of light scattering by aggregates in the earth sciences has focused on scattering by aerosols, which are usually constructed from single elementary particles (monomers) that are smaller than the wavelength of light (e.g [8]). Unfortunately, the last assumption does not hold true for marine aggregates, which often comprise solid particles larger than the wavelength of visible light such as phytoplankton, bacteria, clays, and other large hydrosols.

Latimer pioneered and validated a model of light attenuation by aggregates composed of latex spheres of equivalent size or larger than the wavelength of light [9]. His approach approximated aggregates using two models: (1) a coated spherical particle with an inner core representing the interstitial fluid and an outer core having the same volume fraction and index of refraction as the component particles; and (2) a randomly oriented prolate spheroid with axis ratio of 3 to 1 and an index of refraction that takes into account the interstitial fluid. The average of these two models is the optical model for the aggregate. Latimer tested this model for aggregates composed of a single primary latex particle (with two sizes of primary particles of 0.26 or 1.1 μm) and found it to provide an adequate prediction for the attenuation and the

side and forward scattering properties of populations of aggregates of five different sizes. Based on these results Latimer argued that the details of the inner structure of aggregates have little influence on their near forward scattering and the beam attenuation.

Historically, good quantitative agreement has been found between Mie theory, which describes the interaction of light with solid, homogeneous spherical particles, and measurements of optical properties in the ocean (e.g [10–13].), and models of solid particles are still the cornerstone of theoretical approaches in ocean optics [10,14,15]. Our goal here is to provide a qualitative assessment of how aggregates differ from solid particles in both measurements and theory. In particular, we focus on the mass normalized beam attenuation as the beam attenuation is often used as a surrogate for particulate mass.

A primary motivation for this paper is the observation of relatively tight correlations between total scattering or beam attenuation and suspended mass in coastal environments (e.g [13,16].). In this paper we demonstrate that aggregation can provide an explanation for this consistency whereas attenuation by solid particles, modeled by Mie theory, does not.

2. Methods

2.1 Observations

The qualitative effect of aggregation on beam attenuation was observed by deploying two Sequoia LISST-100 type B instruments side by side in an estuary over a tidal cycle. The instrument package was deployed in the Damariscotta river estuary at 1m above bottom near the dock of the University of Maine’s Darling Marine Center (approximate mean water depth 10m) on 2-3 August 2007. The LISST-100 measures near forward scattering at 32 angles as well as light transmission. One of the instruments was open to the environment (typical deployment method) while the other sampled from the same depth with the sample circulated through a pump (SeaBird SBE 5T, set at 3000rpm) prior to entering a sampling chamber. The purpose of the pump was to break aggregates through turbulence-induced shear. A comparison of measurements with and without the pump provides a qualitative indication of the aggregation effect on the optical properties measured by the LISST. Before conclusion of the experiment, deploying the two instruments together with no chamber served as an experimental control and provided for the determination of a cross-calibration offset. This offset was then applied to the entire experiment. The LISST near-forward scattering measurements were inverted to obtain a particulate area size distribution [17] and volume-weighted particle size (a proxy for mass weighted particle size). The first and last three bins of the size distribution were ignored due to possible contamination by aliased particles (e.g [18].). The phase function was computed by dividing the calibrated volume scattering measurements (obtained using the method of [19]) by the integrated volume scattering function, an estimate of the scattering coefficient.

2.2 Theory

Natural aggregates are complex and do not lend themselves to simple description. Nonetheless, to understand how the voids within aggregates affect their physical properties (e.g. settling velocity, optical properties), simplified models of aggregates have been constructed. We use such a simplified model here (see below).

Assume that an aggregate of a characteristic size L (e.g. the diameter of a sphere with the volume enclosing the aggregate) is made of n identical particles (the primary particles) of size L_p . A ‘fractal’ dimension, d_3 , sometimes called the ‘capacity dimension’ relates them via:

$$n = \left(\frac{L}{L_p} \right)^{d_3} . \quad (1)$$

The fractal dimension ranges from 1 to 3, where the value 3 corresponds to the case of no voids between the primary particles comprising the aggregate (i.e. a solid particle), and a value of 1 represents the case where the particles are not connected.

The solid fraction of such an aggregate, F , is the ratio of the volume of the component particles to the volume of the aggregate, $n(L_p/L)^3$, and can be related to d_3 via Eq. (1), namely:

$$F = n \left(\frac{L_p}{L} \right)^{3-d_3} = \left(\frac{L_p}{L} \right)^{3(d_3-1)}. \quad (2)$$

The porosity of the aggregate (the fraction of the aggregate volume made up of water) is simply $e = 1-F$.

Natural marine aggregates have d_3 that co-varies with size. The larger the aggregate the smaller is d_3 (e.g [20,21], but see [22]). In the model used here we will assume that $d_3 \geq 2$ (e.g [23,24].), though some studies suggest marine aggregated may have smaller fractal dimensions (e.g [22,25]); this fact is important as aggregates with $d_3 < 2$ are optically very different from those with $d_3 \geq 2$ and the transition is abrupt (see [7]).

Following Latimer [9] we constructed two optical models for aggregates: (1) shelled spheres with water cores and outer shells made of the particulate material; and (2) homogeneous oblate spheroids with an index of refraction decrease to account for the fraction of water within the aggregates. Latimer averaged these two models to find the best fit with observations of aggregates of polystyrene beads [9]. For the shelled-sphere model we use a code provided by Zhang (details in [26]). We compared it to the layered-sphere code found by Bohren and Huffman [27] and found both to agree where they overlapped. However, due to differences in implementation of the layered-sphere model, Zhang's code could be applied to larger particles. For the spheroid model we use a method based on the work of Paramonov [28] that computes the optical properties of a randomly oriented spheroid from that of an appropriate population of spheres [15,29]. Our numerical solution method is different from that used by Latimer [9], particularly our approach to modeling a spheroid (not available to Latimer) is expected to be more exact.

We use different values of the index of refraction to represent three types of oceanic particles comprising a given aggregate. The values are representative of a phytoplankton at a wavelength of an absorption peak ($m = 1.05 + 0.005i$), a bacteria (or phytoplankton at a wavelength of minimal absorption, $m = 1.05 + 0.0001i$) and a clay mineral ($m = 1.15 + 0.0001i$) (e.g., [13,30]). The wavelength we choose is 660 nm, the most common wavelength for beam-transmissometers used to estimate particulate mass. Density of the inorganic particles is assumed to be 2650 kg/m³ while and the dry density of the organic particles is assumed to be 1380 kg/m³ [13].

For the homogeneous spheroid model we need the average index of refraction of the aggregate ($m_{aggregate}$). Given that oceanic particles are soft (their index of refraction is close to that of the medium) we use the simple Gladstone-Dale relationship (used by [8], to model aggregates, and by [30] to model phytoplankton):

$$(m-1)_{aggregate} = F(m_p - 1), \quad (3)$$

where m_p denotes the index of refraction of the particles comprising the aggregate and F is the solid fraction of the aggregate (2). Using more complicated formulas (e.g. Bruggeman's or Maxwell-Granet rule, see [14]) did not change the results significantly.

We constrain the fractal dimension of the aggregates using observed relations between the aggregates' fractal dimension and their size as observed and suggested by [20] and [21]. The simplest such relation is of the form [20]:

$$d_3 = 3 \left(\frac{L}{L_p} \right)^\beta, \quad \beta = \frac{\log(F_c / 3)}{\log(L_{fc} / L_p)}, \quad (4)$$

where F_c is the lowest value of the fractal dimension and L_{fc} the size where it is reached [20]. recommended the following values (based on a variety of historical data) to be used when no direct measurements are available:

$$F_c = 2, \quad L_{fc} = 2000 \mu\text{m}, \quad L_p = 1 \mu\text{m}. \quad (5)$$

Substituting these values into Eq. (4) when $L > L_p$, we obtain:

$$d_3 = 3L^{-0.0533}, \quad (6)$$

where L is the diameter of the aggregate in μm [21]. found that such a power-law model fits laboratory generated clay aggregate data with an exponent varying between -0.08 and -0.11 (note that in [21] the aggregates were smaller than $200 \mu\text{m}$).

Given the diameter of a solid particle with the same mass (L_s) we can find the diameter for the aggregate (L) by numerically solving (derived using Eq. (4) and Eq. (1):

$$3 \left(\frac{L}{L_p} \right)^\beta \log \left(\frac{L}{L_p} \right) = \log n. \quad (7)$$

In total suspended mass analysis the filter of choice is often a $0.7 \mu\text{m}$ GF/F filter. Measurements of the beam-attenuation often use a pre-filter of $0.2 \mu\text{m}$ (e.g., [31]). We will therefore limit our analysis to particles bigger than $0.2 \mu\text{m}$ or $0.7 \mu\text{m}$ though it is well known that these filters do not have a perfect cutoff (e.g., [32]).

We compare the results of the aggregate model to the optical properties of solid particles of the same size. Randomly oriented prolate spheroids with an axis ratio of 3 are used as the model for the solid particles in order to average out oscillations associated with resonant interactions in spheres. Comparisons are made between dry-mass normalized beam attenuations in order to reveal the effects of aggregation on mass normalized attenuation.

3. Results

3.1 Observations

Beam attenuation at 670nm increased by an average of 30% (16th percentile = 20% , 84th percentile = 40%) in the LISST with the pump relative to that the LISST that was open to the environment (Fig. 1). Beam attenuations for both instruments agree during the control period at the end of the experiment, when the pump was removed from the intake of the first instrument. The phase function also differs between the two instruments. Near forward scattering is reduced when the sample is pumped, while at larger angles scattering is increased, consistent with destruction of particles with large cross-sectional area and formation of particles with small cross-sectional area. Volume-weighted mean size (a proxy for mass-weighted-size) averages $62 \mu\text{m}$ for the open environment while only $31 \mu\text{m}$ for the pumped samples. This field manipulation experiment indicates that a large fraction of the particles in the water sampled were aggregates and that breaking them has an effect on the measured beam attenuation and near forward scattering. The presence of large numbers of aggregates in this estuary, during a similar time of year, was confirmed independently by a submersible camera during a previous deployment (4-5 August 2003, data not shown).

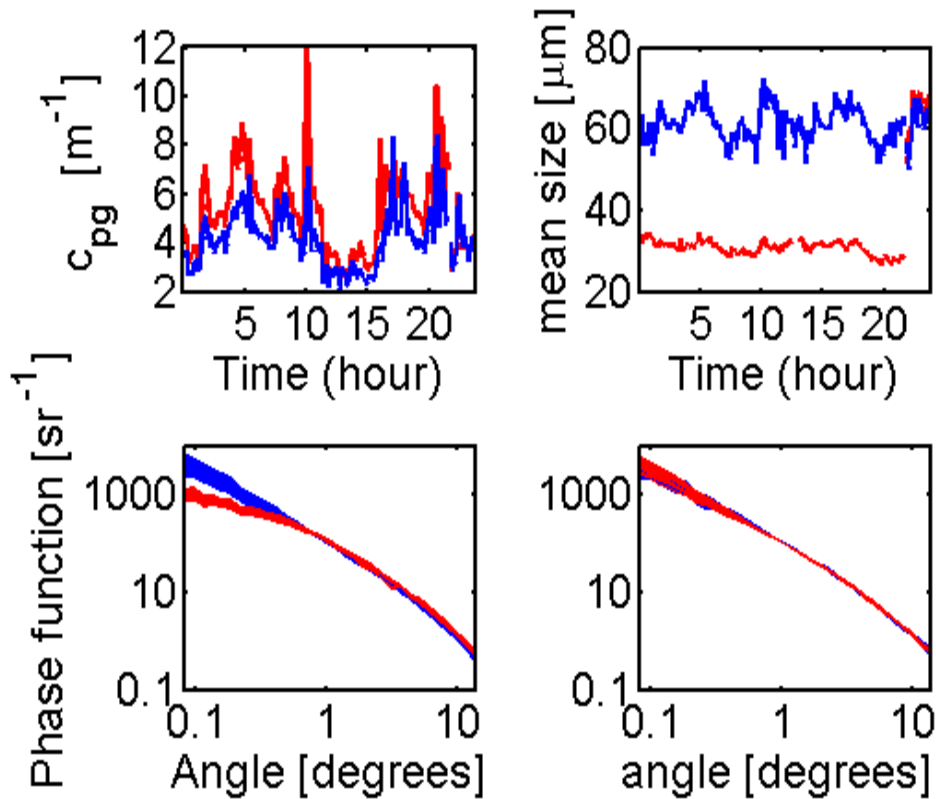


Fig. 1. Time series of beam attenuation at 670 nm (left top) and inverted volume-weighted particle size (right top) based on measurements co-deployed LISST-100 instruments. During the manipulation experiment (first segment) one instrument measured local waters that flowed through an underwater pump (measurements denoted by red lines) while the other (measurements denoted by blue lines) was open to the environment. During the last two hours both were deployed side by side open to the environment, providing a control. Phase function during the experiment (bottom left) and control (bottom right).

3.2 Theoretical results

The two different aggregate models (the coated sphere and the dilute spheroid model), which when averaged comprise Latimer's model [9], provide similar dry-mass normalized beam attenuation (Fig. 2, note: this is the dry-mass normalized beam-attenuation of a population of particles all with the same size). Over the whole range of sizes, fractal dimension and particle compositions we investigated, the relative difference between the two aggregate models is at worst 70% with a mean difference of less than 20%. These differences should be contrasted with dry-mass normalized attenuation changes of two orders of magnitude over the range of sizes investigated (Fig. 2).

The theoretical beam attenuation per mass of solid fraction of aggregates with high water fraction ($F \ll 1$) differs markedly from those with low water fraction ($F = 0.99$, Figs. 2 and 3). Generally speaking, all the curves exhibit a resonant response in which there is a size for which a maximum in attenuation per mass exists. The position of this maximum increases with fluid fraction ($1-F$), while the peak amplitude varies relatively little (decreases by less than a factor of 2 as fluid fraction increases from 1% to 99%). For small size aggregates made of the same primary particle but differing in fluid fraction, low fluid fraction aggregates attenuate more per mass than those with high fluid fraction while high fluid fraction

aggregates attenuate more per unit mass than low-fluid fraction aggregates for larger sizes (Figs. 2,3). Changes in particle composition (changes in the real part of the index of refraction) have two general consequences: (1) organic particles appear to have maximal mass-specific attenuation at larger sizes compared to inorganic particles; and (2) organic particles have reduced peak mass-specific attenuation (Fig. 2). From Fig. 3 onwards, results for the average of the coated-sphere and the dilute spheroid models (that is the model in [11]) are presented.

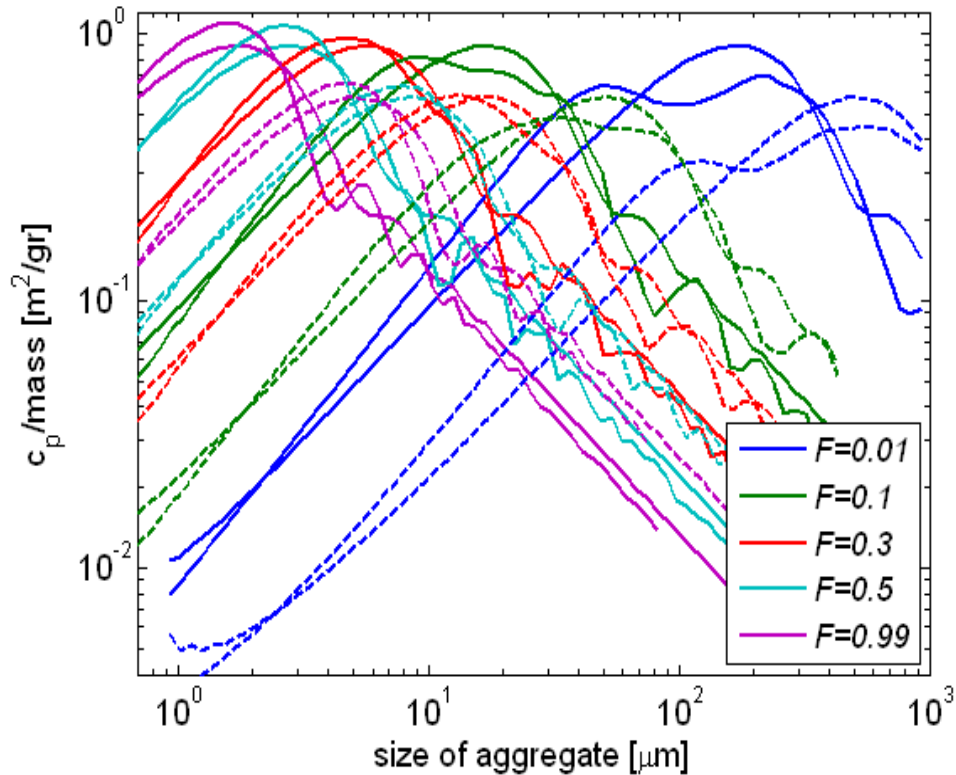


Fig. 2. Particulate mass normalized beam-attenuation as a function of particle size for particles differing in their index of refraction ($m = 1.15 + 0.0001i$, solid, $m = 1.05 + 0.0001i$, dashed), water fraction (color), and aggregate model (spheroid and coated sphere). Each couple of curves with the same color represents the results of the two different aggregate models (coated sphere and dilute spheroid). The model we use herein is computed from the two different aggregate models.

For many particle sizes the difference between the results with differing fluid fraction is larger than that due to composition at a fixed fluid fraction, suggesting aggregation (through its change of the index of refraction of the aggregate particle) could have as important or larger an effect on the mass normalized attenuation of aquatic particles as the index of refraction of the primary particle. Absorption effects can be significant, and are most pronounced for particles with size smaller than the peak response (Fig. 3).

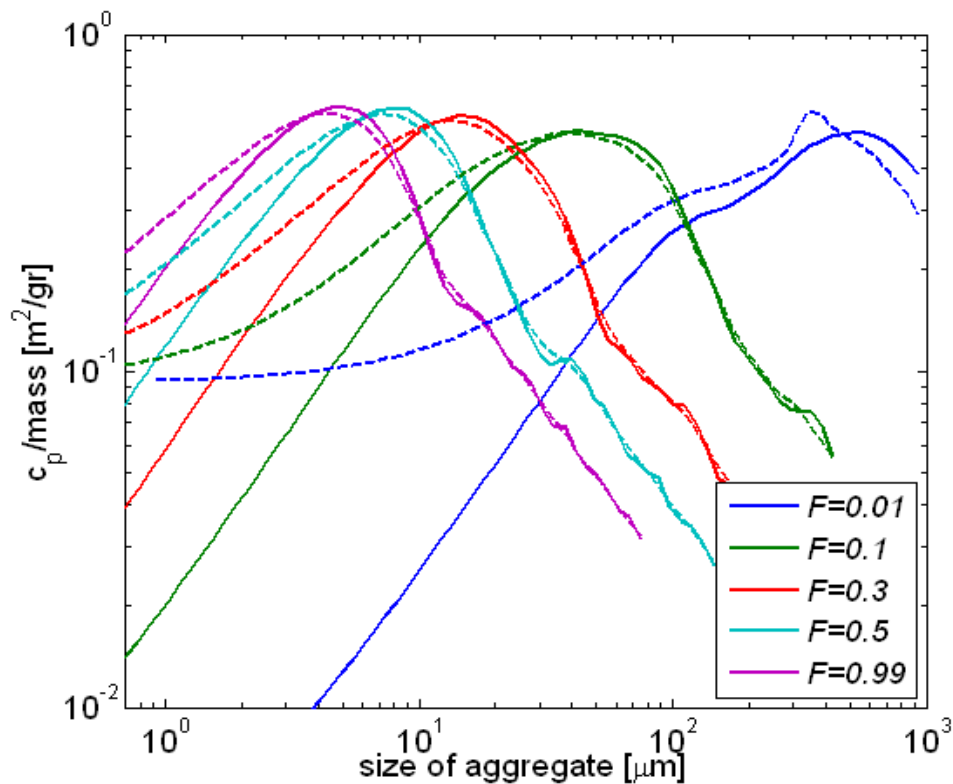


Fig. 3. Mass normalized attenuation for particles as a function of size, with two different imaginary indices of refraction ($m = 1.05 + 0.0001i$, solid, $m = 1.05 + 0.005i$, dashed) and variable water fraction (color), and using Latimer's [9] aggregate model (the average of the spheroid and coated sphere models of a given fluid fraction).

For particles with a fluid fraction that varies with size according to [20] (Eqs. (2), (6), and (7)) aggregate mass normalized attenuation is much less varied as a function of size than relative solid particles of the same size (Fig. 4). Sensitivity to composition for particles bigger than $8 \mu\text{m}$ is weak in comparison to the sensitivity to aggregation (compare dispersion among blue curves from that between blue and red). For particles close to the size of the primary particle the fractal dimension is close to 3 and thus the aggregate model converges to that of solid particles, where there is strong sensitivity to size and composition.

These single-size aggregate results are consistent with observed mass specific beam attenuation at 660 nm for bulk particles in the ocean ($0.2\text{-}0.6 \text{ m}^2/\text{gr}$, e.g., [15]), which is not the case for the solid particles (red curves in Fig. 5).

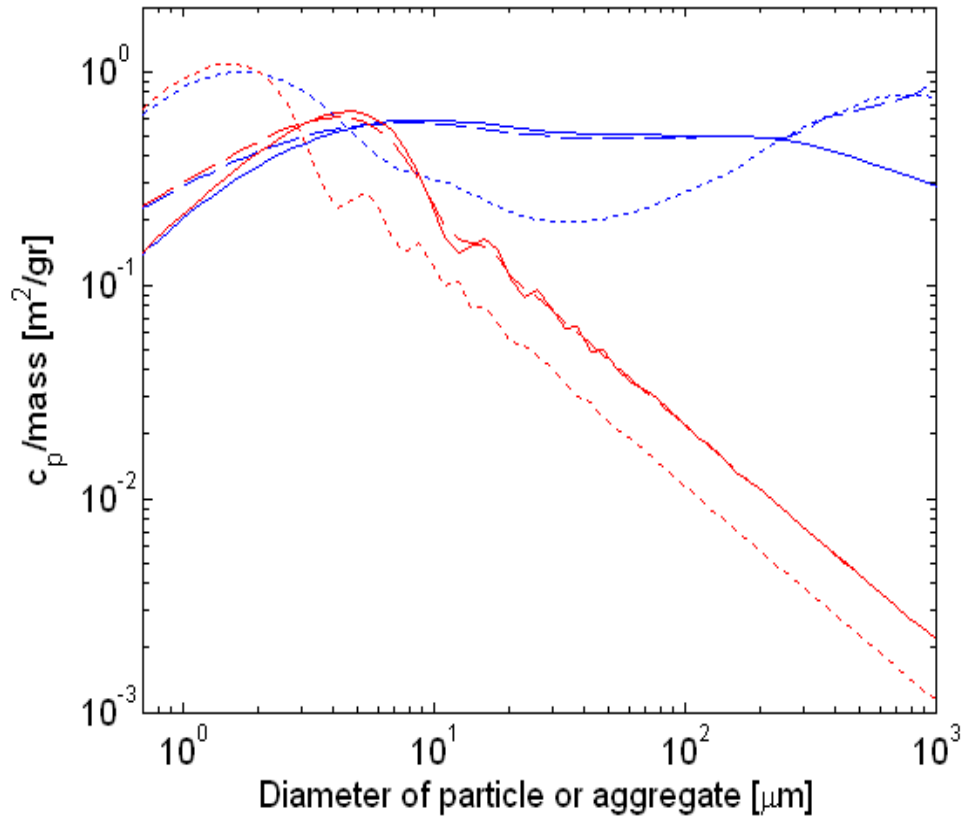


Fig. 4. Mass normalized beam attenuation at 660nm for aggregates assuming a relationship between fractal dimension and size as in Khelifa and Hill [20] (blue lines) and solid particles (red lines). Solid lines denote particles with $m = 1.05 + 0.0001i$, dashed lines $m = 1.05 + 0.0005i$ and dotted lines $m = 1.15 + 0.0001i$.

3.3 Populations of particles

The above results for single particles indicate that details of the specific size distribution are unlikely to greatly change the mass specific beam attenuation of aggregates (as they are only weakly size dependent). To model a particle population (denoted by $N(D)$, the number of particles of size between D and $D + dD$) we use a simplistic power-law size distribution with a differential exponent for the population (denoted by ζ) varying between 2.5 to 5 and a diameter range varying from $D_{min} = 0.2 \mu\text{m}$ to $D_{max} = 200 \mu\text{m}$:

$$N(D)dD = \begin{cases} N_0(D_0) \left(\frac{D}{D_0} \right)^{-\zeta} & D_{min} \leq D \leq D_{max} \\ 0 & D > D_{max} \text{ or } D < D_{min} \end{cases} \quad (8)$$

Here $N_0(D_0)$ denotes a reference particulate concentration at a reference size D_0 . This PSD has been used by [14] with, however, $D_{min} = 0.02 \mu\text{m}$. Observed PSD power-law exponents vary between 2.5 and 5 with 4 being the ‘classic’ oceanic value (e.g [33]. and see discussion in [34]). We find relatively little change in mass normalized beam attenuation across populations with different PSD exponents for the aggregate model, particularly for organic particles (Fig. 5). The value of the mass normalized beam attenuation is also consistent with the range observed in nature (e.g., 0.2-0.6 m^2/gr at 660nm). On the other hand we find results

for solid particles to be highly variable and consistent with observations only at a smaller range of particle sizes, those enriched with small particles (slope of PSD bigger than 3.75).

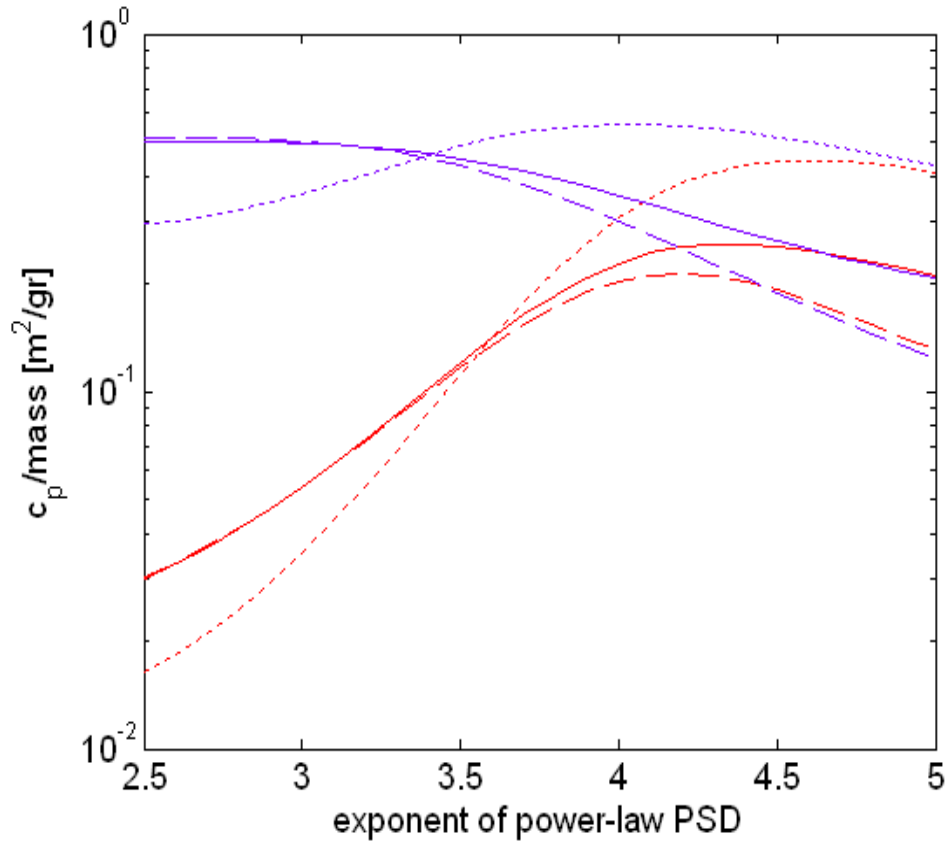


Fig. 5. Mass normalized beam attenuation for populations of aggregates with a relationship between solid fraction and size as in Khelifa and Hill [20] (blue lines) and populations of solid particles (red lines). Both have particulate size distributions that are power-law functions with the x-axis denoting its exponent. Solid lines denote particles with $m = 1.05 + 0.0001i$, dashed lines $m = 1.05 + 0.005i$ and dotted lines $m = 1.15 + 0.0001i$. Parameters are: Wavelength = 660 nm, minimum diameter = 0.2 μm , maximum diameter = 200 μm .

4. Discussion

Field observations suggest an average increase of 30% in beam attenuation when aggregates are broken. If all particles were solid, we would expect a larger increase, since for large solid particles much of the material is shaded (Fig. 4, red curves).

Optical properties of aggregates based on Latimer's model are significantly different than those of a particle of the same size, with the resonance-peak at larger sizes (Fig. 2). The real and imaginary parts of the index of refraction have significant influence on the attenuation but have less impact than the particle's fluid fraction.

Latimer's model is a simplistic representation of oceanic aggregates; it assumes in its core a single primary particle for all aggregates and that the aggregate can be well represented as a combination of two large particles (a hollow sphere and a dilute spheroid). Its combination with an empirical relationship providing the relationship between size and solid fraction provides its quantitative appeal. Indeed, we find that this simple semi-empirical aggregation model is quantitatively more consistent with observations of mass specific beam-attenuation

than that based on modeling oceanic particles as solid homogeneous particles (the practice to date). The agreement between the model and observations suggests, as in Latimer's own work, that the aggregate's fluid fraction is a first order determinant of its beam attenuation (more important than the index of refraction of the primary particle for aquatic particles).

In addition, our results suggest that the mass specific beam attenuation may be less sensitive to changes in size than previously thought (e.g., [16]). The relative insensitivity to composition has been previously demonstrated by [13]. However, this latter study had to invoke small particles ($D_{min} = 0.02 \mu\text{m}$) to obtain mass normalized scattering coefficients consistent with field observations.

The model assumption of a spherical primary particle only affects the results of the model at the small diameter end of the particulate size distribution. The aggregates have the same fluid fraction (and hence model) whether we use a spherical or non-spherical primary particle. In any case, differences between the attenuation of spherical or non-spherical primary particle are expected to be small and constrained to micron sized particles [15].

A sensitivity analysis to the parameters of the aggregation model provides an evaluation for its robustness (Fig. 6). Varying the primary particle size (L_p) and the exponent of the fractal dimension-size relationship (β , Eq. (6)) it is found that the model is most sensitive to changes in L_p (an order of magnitude for the largest particles, Fig. 6), yet it is smaller than the differences between solid particles and aggregates (Fig. 4). In general, smaller values of L_p and β tend to reduce the change of mass normalized attenuation as function of size.

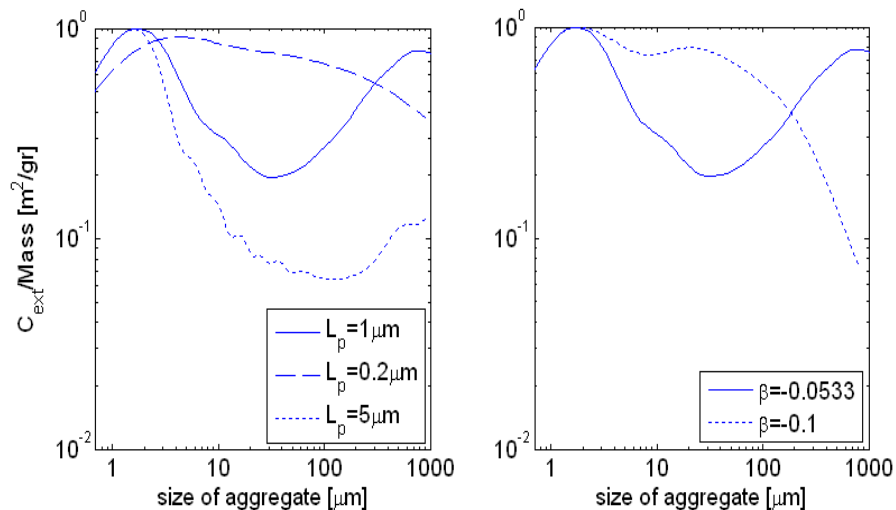


Fig. 6. Mass normalized beam attenuation for aggregates as function of aggregate size assuming a relationship between fractal dimension and size as in Khelifa and Hill [20] but with a different primary particle size, L_p , in Eq. (6) (left panel) or a different β in Eq. (6) (right panel). All runs of inorganic-like particles with $m = 1.15 + 0.0001i$.

There are many additional practical issues associated with measuring and modeling the beam attenuation. The minimal and maximal sizes chosen, D_{min} and D_{max} , can affect the results associated with modeled particle populations. Here, we choose $D_{min} = 0.2 \mu\text{m}$ based on the protocol for measuring particulate beam attenuation with spectral transmissometers and the fact that, most often, attenuation by the fraction smaller than $0.2 \mu\text{m}$ is negligible in the red (where most single wavelength transmission measurements are done). D_{max} (here chosen as $200 \mu\text{m}$) is harder to specify and can have a significant effect on mass normalized beam attenuation (see the sensitivity of c_p/volume to D_{max} in [12]). De-facto, the acceptance angle of beam transmissometers is a filter on the size distribution, as the portion of forward scattered light into the receiver increases with size for particles significantly larger than the wavelength

[35]. The sample volume when making measurements is itself a filter on the size distribution as large rare particles are less likely to be sampled (see additional discussion in [13]). Due to the relative constancy of mass normalized beam attenuation with size (in particular when compared to solid particles), the results of the aggregate model are much less sensitive to the specifics of the function chosen as a model of the particulate size distribution than results based on Mie theory (e.g. one could use a gamma distribution, power-law, or multi-modal for PSD with relatively little change in the results).

5. Summary

We have presented data documenting the role aggregates play in the observed beam attenuation and a model of aggregate beam attenuation that is consistent with the observation that mass normalized beam attenuations are relatively constant in the environment despite large environmental changes in particle index of refraction and size. This consistency suggests that the beam-attenuation of aggregates significantly larger than the wavelength of light is most sensitive to the aggregates' solid fraction and less sensitive to the physical and optical properties of the particles comprising the aggregate. These results are important as they support the practice of measuring a single optical property (here beam attenuation) as a proxy of particulate matter, an important water quality indicator. In addition, we have provided a framework with which to model aquatic aggregates.

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