

Responses to comments on the manuscript “Inversion of the volume scattering function and spectral absorption in coastal waters with biogeochemical implications” by the Anonymous Referee #1

Dear Referee,

Thank you for your thoughtful comments. We have tried to address your comments in the revised manuscript. In the following, we will report these changes in details.

Sincerely,

Xiaodong, Yannick, Deric, Alan and Joe

----- Comments by the Referee #1 -----

I. General comments.

The manuscript presents various bio-optical properties of suspended matter (e.g., volume scattering function-VSF, absorption and scattering coefficients) acquired in a coastal environment, namely the Chesapeake Bay (USA). The inversion of the in-situ measurements is performed using a previously developed methodology (Zhang et al., 2012) to retrieve biogeochemical parameters (chlorophyll concentration) and some pieces of information on the particle size distribution. The main results of the study are as follows : (i) the chlorophyll concentration could be derived satisfactorily from the VSF in coastal waters despite the fact that this parameter does not primarily drives the variation of the VSF in the study area, (ii) it is suggested that one fraction of the Colored Dissolved Organic Matter (CDOM) could induced some significant backscattering in such environment while CDOM is often considered as a non-scattering material when dealing with open ocean water type.

The manuscript is very well written, documented and pleasant to read. In particular, the authors clearly justify the assumptions or approximations they do; they discuss as well nicely their results over the course of the manuscript. They provide good perspectives to their work. Despite the fact that the methodologies used in this manuscript are not new (they were already published previously), the interpretation of the inversion of the bio-optical properties of marine particles in term of biogeochemical applications is of great interest for the community. From this point of view, the manuscript is original and is a significant contribution to the ocean optics field of research. I do not see any major errors in their analysis. Based on the high quality and on the originality of the discussion of the results outlined in the manuscript, I recommend the manuscript for publication in Biogeosciences journal. I have a few general comments and many specific comments (section II) which could help to improve the manuscript and which should not be so difficult to address by the authors.

Thank you for the kind words and assessment of potential contribution of our work to the ocean optics field of research.

1. Influence of the multispectral data on the VSF inversion results.

*The instrument that is used to measure the full VSF, the MVSM instrument, is able to measure the VSF at several wavelengths which are of great interest for the objectives of the authors. However, the multispectral information is not really exploited in the inversion technique (just one wavelength, namely 532 nm, is used). This is too bad since such spectral information could help to better constrain any inversion technique to increase its performance. As an example, the wavelength dependence of the VSF might be useful to better identify the type of marine particles, the size of particles and the absorption effects of particles (as shown for example by Chami et al., “Spectral variation of the volume scattering function measured over the full range of scattering angles in a coastal environment,” *Applied Optics*, 45, 3605-3619, 2006). So, it would be interesting to mention in the manuscript whether (and how) the inversion technique could be improved by taking into account all the multispectral VSF information. Would it be feasible to include all the wavelengths in the inversion procedure? If yes, do the author could mention if the performance of their inversion procedure would be weakly or significantly improved?*

To the first order of approximation, the dominant variability in scattering by a particular particle population is in the angular domain while the dominant variability in absorption is in the spectral domain. Compared to these first order variability, the spectral variation of the VSFs, if present, is secondary. Therefore, the angular scattering and spectral absorption are the main optical signals that were used in our paper. We are well aware of reports by Chami et al. (2006), which is cited in our manuscript. Conceptually and potentially, multi-spectral VSF data measured by MVSM should improve the inversion because it provides additional constraints. However, there are a few practical difficulties currently limiting us from fully utilizing the potential offered by the MVSM instrument. First, our MVSM instrument has issues with measurements at forward angles up to 9.5 deg. Therefore, the full VSFs were obtained by merging LISST and MVSM. Since our LISST data are only available at 532 nm, technically, we have full VSF data only at this wavelength. Second, a convenience in operating at 532 nm (or better yet a longer wavelength) is that absorption by different particles at this wavelength is low in general. Therefore, in applying VSF-inversion, it can be justified by assuming a small imaginary refractive index (0.001i) for all the candidate particle populations. This will not be the case for shorter wavelengths, where absorption by algal and organic particles could be very high. In Zhang et al. (2012), we briefly discussed this issue and offered another way for using the multispectral VSF data qualitatively during the validation of the inversion (see Section 3.B and Figure 8-f in that paper). Zhang et al. (2012) used the PSDs inverted from VSFs at 532 nm to estimate the particle scattering at other wavelengths. Comparison of estimated VSFs at other wavelengths with the measurement serves as a validation of the VSF-inversion results.

We are thus limiting ourselves to one wavelength for this paper. Future contributions may tackle the multispectral effects, if we can avoid biases in the near forward angles associated with our instrument.

2. Consideration of VSF shapes for mineral-like particles.

It seems that the inversion procedure does not take into account the VSF of inorganic mineral-like particles for which the angular distribution of the scattering properties could

be significantly different from that of phytoplankton-like particles. In the manuscript, it is mentioned (end of section 2.4) that one limitation of the inversion technique is that the NAP (Non-Algal Particles) that are modelled have a similar angular distribution of VSF as phytoplankton (or maybe, I misunderstood). However, in their study area, it is likely that mineral-like particle could represent a significant fraction of the suspended matter (as the authors say, the contribution of phytoplankton-type particles is not dominating in these coastal waters). It would be interesting if the authors could simply clarify or discuss how the mineral-like particles are accounted for in their inversion procedure since these particles should play a major role in the scattering properties of the study area (i.e., the scattering coefficients values are high while they are not correlated with chlorophyll).

Yes, we are using different VSF for angular distribution by NAP (which include mineral particles) from that by phytoplankton-like particles. And the differences mainly arise from 1) the difference in the refractive index, which is typically higher for mineral-type particles than phytoplankton-like particles and 2) the difference in the size distribution. However, from an optical point of view, under the assumptions of the manuscript, a mineral particle and a phytoplankton particle would behave exactly the same if they have the same index and size. Or in other words, the inversion will not be able to differentiate these two particles.

We read over the relevant sections (introduction and section 2.4) and we feel that this is clearly stated.

II. Specific comments

- Title (p.9003) : When reading the title, one could think that an inversion method is developed and applied to the retrieval of inherent optical properties and biogeochemical properties of particles. However, the manuscript is not really dealing with the development of an inversion methodology since it was previously published. I suggest to slightly modify the title which should focus more on the new results obtained in the manuscript.

The title has changed to “Biogeochemical origins of particles obtained from the inversion of the volume scattering function and spectral absorption in coastal waters”

- p. 9006, line 1: I think that the word “absorption” is missing after “NAM”

Agree. It now reads: “Absorption by NAM”

- p. 9007, line 16: the reference Twardowski et al., 2012 is missing in the reference section at the end of the manuscript.

Thank you. Don’t know why Endnote software did not populate this reference in the reference list. It is included now.

- p.9009 : line 10 to 17 : since the samples were collected in turbid waters (i.e., the scattering coefficient values are up to 4 m⁻¹, see figure 3), it is likely that multiple scattering effects could significantly alter the measurement of the VSF using the MVSM instrument (figure 4 shows a “smooth” VSF with angles). In other words, the VSF is supposed to be measured for a primary scattering regime of ambient light and turbid samples may change this primary scattering regime into a strong multiple scattering regime within the chamber of the instrument (despite the pathlength of the instrument is

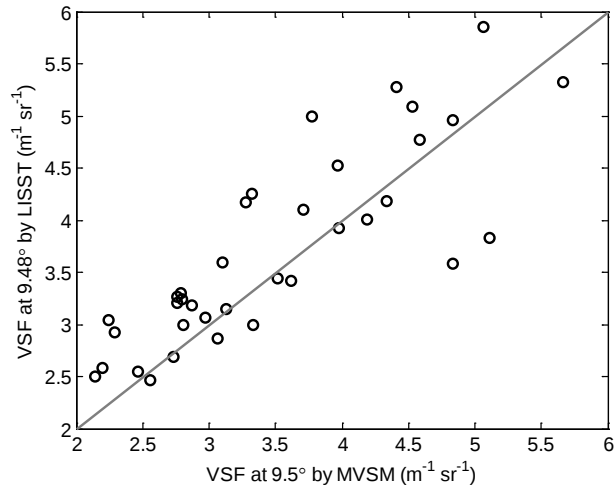
relatively low). So, the measured VSF may not be fully representative of particulate VSF. Did the authors use a specific protocol for measuring the VSF of turbid samples ? Since the MVSM measured continuously near the surface, it was probably not possible to dilute the samples to reduce the multiple scattering regime. At least, did the authors perform some experiments in the lab using beads to determine a threshold concentration of suspended matter from which the multiple scattering processes strongly affect the VSF measurements by MVSM ? It would be interesting if the authors could discuss this point relative to the possible influence of the multiple scattering effects on the VSF measurements in the manuscript; at least, they could mention that multiple scattering effects could be a limitation of the VSF measurements in their study area.

We have performed concentration tests in the laboratory and comparison tests between the MVSM and other instruments (ECO-VSF, Hydrosat-6) in the field, and found the upper operating range to be a scattering coefficient of about 4 m^{-1} . Waters with larger values were sampled during the deployment, but were excluded from the analysis due to the very reason the reviewer highlighted. The MVSM has an optical pathlength of 13 cm in the water, which translates to a scattering optical depth of 0.52, outside the single scatter limit, but not impractically so. On the low end, the LISST has an optical pathlength in the water of 5 cm, and hence there is also a minimum scattering coefficient, which was found to be around 0.1 m^{-1} , though a range of $0.2 - 0.3$ is a better cutoff. The “sweet spot” in a combined VSF measurement is a scattering coefficient around $1 - 2 \text{ m}^{-1}$. In practical terms, at the low end the results suffer from low signal to noise (or signal to background). At the high end, the main problem is that multiple scattering leads to beam spreading of the incident beam, which causes a change in the scattering volume seen by the detector. This effect appears first at scattering angles near 180° , where the common volume between the beam and detector is quite large. The effect of the beam spread is to cause an increase in the measured VSF at these large angles. As the scattering coefficient increases, the affected angular range increases as well – the increase in VSF tends to move from 180° towards lower angles, down to around 165° . As always, there is no definitive or hard cut-off; instead it is a gradual change. The reviewer is correct that the VSF measured at the higher attenuation values can have multiple scattering contamination, but most of the it would occur at larger scattering angles ($> 165^\circ$).

- p 9009, line 24 : “no scaling was applied to the data from either instrument” :does it mean that the LISST and the MVSM instruments were systematically consistent and matched exactly in term of absolute geophysical values of VSF (in $\text{m}^{-1} \text{ sr}^{-1}$) ? One could expect some discrepancies between both instruments (even within few percents) which should not help the merging of data of both instrument unless the data are normalized to a given scattering angle. How was the MVSM calibrated in geophysical units (did you use beads calibration for that ?) ? Did you normalize the VSF data to a given scattering angle (e.g., 90°) to perform the merging between LISST and MVSM ? You need to clarify with one or two sentences these points in the manuscript.

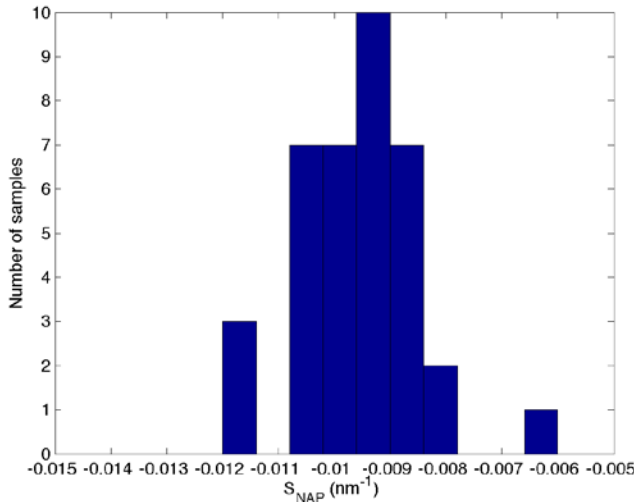
Yes, each instrument was indeed calibrated in terms of the absolute geophysical unit of VSF ($\text{m}^{-1} \text{sr}^{-1}$). Due to stray light contamination to the two largest angles of the LISST and the measurement issues at near forward angles of the MVSM, there is no overlap of angles between the two instruments that can be used for scaling. The closest two angles are LISST measurements at 9.48° and MVSM measurements at 9.5° .

As shown in the figure at right, the measurements at these two angles by the two instruments are very similar. This gives us confidence in merging two datasets without any scaling.



We added text stressing that the each instrument was absolutely calibrated.

- p. 9011, line 17 : “ $\text{Snap} < 0.012 \text{ m}^{-1}$ ” : Is this upper limit for Snap not too weak compared to what was found in other coastal waters (Snap up to 0.019) (e.g., Babin et al., 2003)?



The figure above shows the variation of S_{NAP} from the inversion of absorption spectra. As can be seen, they are well distributed. If the upper limit was constraining the fit of most spectra, the inversion results would be mostly near -0.012. Therefore, we believe the upper limit, $S_{\text{NAP}} < 0.012 \text{ nm}^{-1}$ used in our study, is realistic and does not affect the result, even though it is less than Babin et al. (2003) value of 0.019 nm^{-1} . This upper value was taken from the large dataset published by Magnuson et al. (2004) in Cheasapeake Bay.

- p. 9012, line 18-19 : *Here, the authors seem to compare optical properties of mineral aerosols (including in polarization states) with oceanic hydrosols (phytoplankton and NAP). It is confusing since the hydrosols optical properties may significantly differ from those of aerosols (especially in their polarization states). I understand that it is difficult to know what shape of particles should be used for marine particles but it may be confusing here to suggest that oceanic particles could have similar properties as aerosols. I do not question what the authors did but I just think that this sentence should be moderated and re-written to highlight that aerosols and hydrosols optical properties are different.*

That part has been revised and now reads: “In computing the kernel function, the particles (except for bubbles) were assumed to have an asymmetric hexahedral shape. Real oceanic particles are in general nonspherical and cannot be represented simply by a single shape. The reason we chose asymmetric hexahedral shape is because it has been shown to simulate well the optical properties and polarization states of mineral aerosol particles, which do not possess a particular shape either (Bi et al., 2010)”

- p. 9013, line 7-10 : *based on their results, it seems that NAP particles could be mostly inorganic and mineral in the study area. However, it is not clear to me if the authors used optical properties which are representative of mineral-like particles. How did the authors account for mineral-like particles in their inversion procedure (see also my general comment #2) ?*

As explained in the text and in addressing your general comment #2, different particle populations are differentiated by the refractive index and the size distribution. For example, the scattering phase function by an NAP population with a representative index of 1.14 will be very different from that by a phytoplankton population, say, with an index of 1.05, even these two populations have very similar size distributions.

- p. 9014, line 19 : *I agree with the authors that the errors associated with the omission of angles close to 0 and 180 are small when calculating the scattering coefficient from the integration of the VSF. One reason could be because due to the fact that the VSF is weighted by a sinus function in the integral which thus reduces the importance of the VSF values when summing the integral to get the scattering coefficient.*

Thank you for reminding us this mathematical fact, which we now mention in the text.

- p. 9015, line 28 : *“multiplied by ~1.20” : this number is interesting since it could be informative on the error bar of AC-S measurements of the scattering coefficient. Is it right ?*

The sentence was confusing. It now reads: “Since the 1st correction is routinely applied to the ac measurements, we estimated that the typical ac-s estimates of the scattering coefficient (grey circles in Fig. 3-(a)) would have to be multiplied by ~1.20 to match the estimates based on the full angular measurement of the VSF.” Basically it means that typical estimates of scattering coefficient by an ac meter would underestimate the true b because the acceptance angle (0.93°) of the c meter. We found from our dataset that estimates of b from the AC-S multiplied by ~1.20 would approximately agree with estimates of b based on the full angular VSFs.

p. 9016, line 5-18 : As discussed by the authors here, it is not easy to perform an optical closure and to find consistent results between various instruments. The agreement they have is satisfactory to my point of view. It is likely as well that the noise in their data is probably reduced because the samples are collected in turbid waters which induce strong scattering signals. Perhaps, the bias between the instruments would have been larger in clear waters.

We are glad too that we were able to achieve an instrumental closure for IOPs. Overly high (not enough light at the detector) and overly low (no discernable loss of light in the instrument path) scattering certainly would increase the potential for biases.

- p. 9017, line 1 “the modelled VSF...” and p. 9037, figure 4: it is very difficult to distinguish the modelled VSF (dashed line) from the measured VSF in figure 4. To better see both VSF, the authors could plot the measured VSF using dots and degrading the angular resolution of their data (i.e., plot the VSF for an angle step of 1 for example) and superimposed the modelled VSF using a solid line so one could better see the comparisons between modelled and measured VSF.

Thank you for the suggestions on improving Fig. 4. Figure 4 has been redone to make it easy to distinguish the modeled VSFs from the measured VSFs.

- p. 9017, line 13 : “ the angular scattering in the backward directions...increased” : this statement is not so obvious to see in figure 4. Could you clarify ?

If you compare the green curves in Fig. 4-(a) and (c), you would notice that the scattering in the backward angle increases more in (c) than in (a).

- p. 9017, line 24-25 : here, you show that phytoplankton is not the dominant particle type. So, it corroborates that the limitation of the VSF inversion procedure (p. 9013, line 9-10) to take into account a different angular scattering shape for VSF of NAP relatively to that of phytoplankton may be a critical point. It would be interesting if the authors could discuss in few sentences the possible impact of this limitation on their results with regard to the fact that NAP contribution is dominating in the coastal waters of their study area.

We added after the sentence: “Yet, this non-dominant population was able to be identified and quantified through the VSF-inversion because phytoplankton particles exhibit an angular scattering signature that is generally distinctive from other particles (e.g., Fig. 4-(a) and (c)).”

- p. 9018, line 8-28 : the results discussed here are consistent to what we could expect. The explanations provided by the authors are convincing.

Thank you.

- p. 9019, line 4-5 : the values of the backscattering ratio used for NAP (0.002 to 0.005) seem weak if inorganic material such as mineral like particles are a major contributor to NAP. If mineral like particles are present in the study area, they may have a much higher backscattering ratio (it could reach sometimes several percents) while the values used here are less than 0.5% which are typical of organic material. Perhaps, the mineral like particles are included in the Very Small Particles (VSP) component? The values used for phytoplankton backscattering ratio (0.0007 to 0.0034) seem weak as well for this type of

particle where we could expect values about 5 times larger (up to 0.015). It would be good if the author could justify briefly the choice of their values that do not seem to be in the representative range of variation for this type of water.

The values of backscattering ratio for phytoplankton and NAP particles are lower than the published values. For example, Whitmire et al. (2010) measured the backscattering ratio of marine phytoplankton cultures in the range of 0.002 to 0.02. However, they also admit that *“achieving a ‘pure culture’ and distinguishing the phytoplankton signal from nonalgal particles in culture is probably our greatest challenge in determining the optical properties of marine phytoplankton on a per-cell or per-species basis”*. It is conceivable that the backscattering ratio could have been greatly overestimated if the phytoplankton culture is contaminated with VSP particles, which tend to have a high backscattering ratio. On the other hand, it is possible that our model underestimates the backscattering ratio because it assumes the particles are homogeneous. We have added this discussion in the text.

-p. 9019, line 17: “...hexahedral shape...” :See my previous comment about the possible confusion between the oceanic hydrosols and aerosol optical properties.

Please see our response above.

- p. 9020, line 20-26 : the results obtained here seem counter-intuitive. I would not expect that VSF could be inverted to retrieve satisfactorily the chlorophyll concentration in waters dominated by NAP contribution; the variation of VSF is not primarily driven by chlorophyll (at a 1st order). Do the authors use a specific additional constrain on the inputs parameters of their VSF inversion procedure that could explain the fact that their method is highly sensitive to variables which drives at second (or third) order the variations of the VSF ?

Though, we were originally also surprised by this finding we found that the “strength” of the VSF-inversion method is that it identifies and quantifies different particles based on the angular scattering signature by different particle populations. Even though phytoplankton particles are not the dominant species (numerically and optically) in the Chesapeake Bay, sufficient scattering signature is contained in the measured VSFs caused mostly by the different index of refraction. Not also that the concentration of phytoplankton are quite high despite there low contribution to the total such that their absolute contribution to scattering is significant.

- p. 9022, line 10 : “fig. 6” : I think that the sentence refers to figure 5 rather than figure 6 ?

Yes, you’re right. It has been changed.

- p. 9023, line 23-25 : “:::VSF method was demonstrated...” : I suggest here to moderate the sentence and to use the verb “highlighted” rather than “demonstrated” since the explanation given for the idea mentioned in this sentence is not so convincing (see my previous comment on p. 9022).

We adopted your suggestion.

- p. 9037, figure 4 : *see my previous comment of p. 9017 with regard to the quality of the plots to better distinguish between the modelled and measured VSF.*

Figure 4 has been improved following your suggestion.