

Optical Properties of size and chemical fractions of suspended particulate matter in littoral waters of Quebec

by

Mohammadpour, Gagné, Larouche, and Montes-Hugo

General Comments:

Interesting relations are reported in this paper which, however, should be used to reach better conclusions. The significance of this paper is the investigation of the partition of Suspended Particulate Matter (SPM) into its major chemical class composition of Particulate Inorganic Matter (PIM) and Particulate Organic Matter (POM) to determine true optical properties (cross sections) of the suspended matter. These true optical relations are then correlated with empirical absorption and scattering coefficients of total SPM. The true optical coefficients taken with the empirical ones allow a reasonable interpretation of the empirical coefficients of the St. Lawrence Estuary. However, the particular form taken here is to advocate a model of empirical properties of SPM that has no generality, i.e. it cannot be applied beyond the St. Lawrence Estuary. I will expand on this as I comment on specific lines and portions of the manuscript. The results of this paper document the fact that the empirical optical coefficients do not allow a general model. In sum, this paper requires a massive reanalysis of the data and a massive effort at rewriting.

Specific Comments:

Page 1, lines 7-9. The language in this manuscript can be pretty cryptic. Some expansion is required here and below for clarity even though I realize abstracts are supposed to be kept as short as possible.

Suggested wording: **Abstract.** Empirical mass-specific absorption (a_{SPM}^*) and scattering (b_{SPM}^*) coefficients of suspended particulate matter (SPM) were measured for different size fractions (proposed to be 0.2-0.4 μm , 0.4-0.7 μm , 0.7-10 μm , and >10 μm) in the surface waters (0-5 m depth) of the Saint Lawrence Estuary and Saguenay Fjords (SLE-SF) during the spring of 2013. True optical absorption and scattering cross sections were determined for the total PIM and POM, in addition to mass-specific absorption and scattering coefficients.

Page 1, line 10. A synopsis of the results of the determination of the true optical absorption cross sections also needs to be reported here. It requires pulling together the results on the spectral range of absorption cross sections of at least PIM to document the effects of adsorbed iron on clay minerals or suspended iron oxides in the PIM. That is, an analysis of the true absorption cross section, σ_a^j , for chemical fraction j, organic or inorganic. The true optical cross sections determined here provide the information to interpret the empirical coefficient ratios reported for size fractionation, etc. This information documents the statements in the final sentence of the abstract such as for the effects of chemical composition and absorption variability on what is reported here.

Page 1, lines 13-14. It is not at all clear here what the authors mean when identifying variability of the empirical mass-specific absorption and scattering coefficients. In addition, the results of this study call into question the utility and feasibility of utilizing these empirical coefficient ratios.

Suggested wording: (Gironde River). a_{SPM}^* ... particulates. Correlation analysis of the optical

properties and the empirical ratios of this study suggests that particle composition has the most significant impact on variability of a_{SPM} * and particle size distribution has the most significant impact on b_{SPM} * variability. The fact that knowledge of the optical cross sections is necessary to interpret these empirical ratios calls into question the utility of a_{SPM} * and b_{SPM} * in general models of microphysical and biogeochemical processes proposed for all coastal/estuarine systems.

A fundamental problem with all correlational analyses, as opposed to a well-defined regression analysis, is the fact that correlational analysis merely records the co-occurrence of phenomena without postulating a fundamental relationship between variables of the phenomena. High correlations simply mean that other, more fundamental relationships may be causing the co-occurrence of unrelated phenomena. An analysis based on a_{SPM} * and b_{SPM} * will always be correlational and limited to the specific region where the relationships were defined.

Page 2, lines 1-2. Algorithms based only on C_{SPM} will never have the accuracy required for optical inversions because SPM is undefined optically, an unknown mixture of inorganic and organic matter. Therefore partition of SPM into at least major chemical composition classes (PIM and POM) and estimation of size distribution are required independently for optically-based remote sensing algorithms of primary productivity and suspended mineral dynamics of “disappearing shorelines” etc.

Page 2, lines 13-17. A fundamental issue here, not often discussed in the literature but should be, is consideration of what constitutes Inherent Optical Properties and how this concept should be applied to the measurements taken in the field. One can take a bulk absorption or scattering coefficient of an undefined mixture of material suspended in water and easily determine their mass-specific coefficients but what do they really mean? The absorption coefficient of dissolved matter such as CDOM can be related to a general chemical class of dissolved compounds and we can come up with a measurement of absorption that can be related by refractive index or whatever to a similar group of compounds and the absorption coefficient of CDOM can be analyzed in a quantitative manner. That is, an absorption coefficient of CDOM from one region can be related quantitatively (absorption cross section, etc.) to an absorption coefficient of CDOM from an entirely different region. So an absorption coefficient of CDOM can be called an optical property as per the definition of Bohren and Huffman (1983, p. 227), “There are two sets of quantities that are often used to describe optical properties: the real and imaginary parts of the complex refractive index $N = n + ik$ and the real and imaginary parts of the complex dielectric function (or relative permittivity) $\epsilon = \epsilon' + i\epsilon''$.” In other words, genuine optical properties must have defined complex refractive indices and permittivities which the absorption and scattering coefficients of SPM do not have. Again, SPM is an unknown mixture of both mineral and organic matter and the SPM composition varies from point to point in the same region and furthermore varies between different regions. If we separate out mineral and organic matter we can approach true optical properties of this material by having more narrowly defined complex refractive indices and relative permittivities. By this definition the absorption and scattering coefficients of SPM cannot be called optical properties and their mass-specific versions, a_{SPM} * and b_{SPM} *, should only be called empirical mass-specific ratios. At best the absorption and scattering coefficients of unpartitioned SPM can be referred to as “optical proxies.” Thus the term “optical properties” should be limited to the optical cross sections and absorption and scattering coefficients for PIM and POM only. This rationale will be followed in my subsequent comments.

Page 3, lines 15-20. The description of the procedures utilized here is confusing. The process of size-fractionation of suspended matter in water is tricky (Sheldon and Sutcliffe, 1969; Sheldon, 1972). It is important to recognize the difference between screens and filters as was pointed out by Sheldon and Sutcliffe (1969). A screen is designed for separation of materials in suspension of a particular diameter

and a filter is designed for retention of all materials in suspension greater than a given diameter. That is, the manufacturer guarantees that a filter of a given nominal pore size will retain all material larger than the nominal pore size. However, as a filter slowly gets clogged it will retain material smaller than the nominal pore size. All the filters mentioned in this section were not designed to be screens and the nominal manufacturer's pore size is not the median pore size for retention as demonstrated by Johnson and Wangersky (1985), Sheldon (1972), and Sheldon and Sutcliffe (1969). The median size of particles retained is a function of the volume of sample filtered and the concentration of particles in the sample. The use of manufacturer's nominal pore size to delineate the size fractionation, as is done in this paper, does not correctly give the limits of the size fractions unless the authors did extensive tests on the particle size-range and retention capacity of the filters they utilized under their particular conditions of filtration. It is not clear which filter was used for the loss-on-ignition determination of the total suspended mass and partitioning of it into PIM and POM. If the Whatman GF/F filter were used for SPM, PIM, and POM determination then why was the same filter used for fractionation into the supposed 0.4-0.7 and 0.7-10 μm size ranges? The Whatman GF/F filter can work well for removing nearly all particles down to about 0.2 μm out of suspension. Chavez et al. (1995) reported about 95% particle retention down to 0.2 μm by Whatman GF/F filters. Johnson and Wangersky (1985) derived a theory, involving diffusion and adsorption of suspended materials and filter pore walls, demonstrating that filters will retain particles much smaller than the nominal pore size reported by the manufacturer. One of their conclusions was that a Whatman GF/C filter of nominal pore size 1.2 μm , depending on concentration of materials in suspension and flow rate of filtration, could be an efficient method of separating out materials in suspension larger than 0.7 μm

The authors need to give a table of the suspended masses retrieved by the various filter sizes and compare it with the total mass retrieved on a single filter. Given the fact that the nominal pore sizes of the filters do not correspond to the actual sizes of material retained on the filters, I would be surprised if the masses of the sub samples from various filters added up to the total mass retrieved from one filter. Since the masses retained by the filters are the key to the results reported in this paper, I suggest some sort of optimization scheme to adjust the total mass and the sum of the subsample masses so that a probable mass partition can be utilized based on the masses retained on the filters, i.e. adjusting the various masses to sum up to the total mass filtered. This would presumably require various weighting factors to be applied to the measured masses. It appears the Whatman GF/F filters were used for both total mass filtration and for determining two sub-sample ranges. The authors must explain carefully just how this was accomplished.

Page 3, lines 22-23. The authors point out that they did not use the correction factors discussed by Barille-Boyer et al. (2003) to account for the loss of structural water by the suspended clay minerals. The authors state that an error of about 10% will accrue to the PIM and POM estimates if ignored. The 10% error is only for the inorganics while the 10 % error in inorganic mass will generate a greater error in the organic mass, easily as much as 30% overestimation error in the POM estimate. I suggest the authors utilize the extensive geochemical publications on the St. Lawrence Estuary to estimate the probable concentration of the various clay mineral species in their samples in order to calculate this error. One possible source is Danglejan and Smith (1973).

Page 3, line 30. The weightings used to correct the mass fractionation of the filters should be applied here to the estimates of spectral absorption by the various estimated size fractions.

Page 4, lines 4-5. The spectral measurements of c should also be adjusted by the weightings for the SPM size fractions as mentioned above for the absorption coefficient. Of course this then results in

weighted values of b for the size fractions. Then one should check this with the known optical relation that the various b values measured for the sub fractions should add up to the b value recorded for the total SPM. All of this information about a and b values should be recorded in a table.

Page 4, lines 5-7. The authors mention the use of a LISST-100X for determining particle size spectra in the range 3-170 μm and then never mention these data again. If the data were important they should be brought into the discussion, especially considering the lack of precision and accuracy in the attempt to do size fractionation of suspended matter in this study. Were the LISST data used to estimate the Junge slope γ ? If so the extensive analysis of submicron materials in this study will not have relevance to γ and these correlations must be removed from the analysis. If the LISST-100X data were not used then the use of the LISST-100X is irrelevant to this study and should not be mentioned.

Page 4, lines 15-30. This section is totally obscure as many relationships are brought in that do not directly reflect on the studies proposed here and may have some relevance to the material at hand but I am hard put to find relationships or relevancies. The introductory material introduces the Morel and Prieur (1977) formulas for estimating R_{rs} that depend on measurements of backscattering b_b which, however, are not used in this study. Further on, the equations (1) and (2) are supposedly used to derive Eqs. (3) – (5), the biogeo-optical (BOI) indices which do not utilize b_b . Clearly, the reader requires a derivation of how one gets from a backscattering formulation to a scattering formulation. The BOI indices are proposed to estimate changes in bulk chemical composition and size distribution of SPM. From these formulas of BOI indices to the end of the page the argument becomes increasingly obscure and hard to follow. It would help to write the variables used in the manuscript into fractions created by a math editor rather than the plethora of inline fractions. The inline fractions contribute to the obscurity of the argument. The relation between formulations with backscattering to derive formulations with total scattering have to be laid out clearly. The BOI for “size 1” and “size 2” have to be explained clearly. Does this refer to all the size fractionations attempted here or to just one or two? If so, which size fractions? Where does the polynomial function F come in and how do we get this from the derivation of Eqs. (4) and (5)? What is the relevance of Gordon's (1988) formulation for R_{rs} , in terms of b_b and Eqs. (4) and (5) in terms of b ? Again, the reader has to be led carefully from a backscattering formulation to a total scattering formulation. This section requires expansion and a total rewrite.

Page 5, line 3. Utilizing empirical relations involving POC (essentially the CO_2 from ashed organic matter) generalized to POM is difficult in marine systems because the crude relations between POC and POM are based on chemical analysis of detritus from higher plants. The relation between the two variables is not straightforward in marine systems because the organic content of phytoplankton differs in quantity and quality from higher plants and the various groups of phytoplankton, diatoms and prochlorophytes for example, differ from each other. I always recommend coupling POC data with POM data because of this difficulty. So relations coupling $a_{\text{SPM}}(\lambda)$, C_{SPM} , and POC become increasingly problematic and definitely region-specific. The derivation of the BOI^{size} indices for particle size being based on the unknown spectral slope of backscattering also becomes problematic. For that matter, there is still controversy about whether there actually is a spectral slope associated with the backscattering coefficient. These indices along with BOI^{comp} may be of some empirical use but they will always be regionally limited without independent information on chemical composition and size distribution to interpret them. The problem with the indices proposed here and similar indices proposed elsewhere is that they are qualitative in nature. At best, ignoring all the problems, one can only come up with qualitative “greater than or lesser than” estimates of size or chemical composition without any quantitative information which is what is needed for valid and accurate predictions of particle and biogeochemical dynamics.

Page 5, line 9. Since the empirical mass normalizations reported here do not fit the Bohren and Huffman definition of optical properties, I suggest the following, **2.6 Optical cross sections and mass-normalized coefficients**, and the substitution of “optical coefficients or mass-specific ratios” throughout the manuscript when the term “IOP” is used to refer to the empirical mass-normalized coefficients or absorption and scattering coefficients determined for SPM.

Page 5, lines 10-11. The mass-specific absorption and scattering cross sections were estimated with Model I multiple regression. Just as Model II regression was used elsewhere in this paper, Model II multiple regression must be used for the best estimates of the mass-specific cross sections (σ). The only time that Model I regressions can be used in place of Model II regressions is with a high R^2 value between the proposed dependent and independent variables, say $R^2 > 0.95$. That is not the case here. It is my experience that the best estimate of slopes (as used to estimate σ values) with R^2 values as low as reported here is definitely with Model II multiple regression (Stavn and Richter, 2008; Richter and Stavn, 2014).

Page 5, line 12. In light of above I suggest in this line the replacement of “optical property” with “optical coefficient.”

Page 5, line 16. As suggested earlier, the masses used for calculating the mass-specific absorption and scattering coefficients of size-fractionated SPM should be optimized and weighted for these calculations.

Page 5, lines 23-25. Although the slope of the power-law formulation is often used to describe the particle size distribution (PSD), the actual PSD's for estuarine systems as reported previously (Risović, 2002; Zhang et al. 2014; Zhang et al. 2017) should be mentioned. The power-law distribution is a first-order approximation of the PSD for particles greater than about 2 μm diameter. Therefore it will often work for total scattering with calculations involving only particles in the 2 μm + range. It fails for sub-micron particles and since assertions are made for size fractions less than 2 μm diameter, the use of this assumption becomes questionable. Again, the use of the γ slope gives a qualitative feeling for a relative distribution of large and small particles in suspension but fails when quantitative relations are desired. This is especially true of backscattering estimates as demonstrated by Risović (2002) and there seem to be analogies being made for parameters proposed and used in this paper that are based on backscattering. The bottom line again is a development here that is qualitative at best and regionally limited.

Page 5, lines 25-27. It is important to keep in mind here that the SPM parameters proposed and the SPM relations utilized in this paper are only useful when correlated with actual determinations of chemical species and some independent estimation of the size-classes of PSD. The authors claim that functionalities between “IOP's” and BOI indices were investigated with linear regression analyses. However, I see no report of regression coefficients in the data tables, only correlation coefficients.

Page 6, lines 7-11. How were the γ slope's calculated? Were they from the masses of the various size sub-ranges or from the LISST data? This is important because of the rampant inconsistencies between the size fraction masses and the γ slope estimates. The mode of calculation must be delineated and the data shown in a table to be able to evaluate what is reported here. Even though the largest mass of 0,2-0.4 mm particles is reported for the LE the smallest γ slope is reported for this region. The 90% error for the γ coefficient, for which the area is not delineated here, is strong evidence for the inability of the

Junge-type slope to describe, even qualitatively, the PSD patterns for this study. A table is required for the γ slopes and their errors.

Page 8, lines 7-9. Even if the n value is low for correlations between the BOI indices and the optical cross sections, this is the only way to validate the BOI indices and the correlations should be given with proper caveats.

Page 8, line 10. The Discussion section, in general, reads too much like a Results section. We should assume that the relevant statistical relations are in the results section and here we are interested only in the overall pattern of the results and the explanation of the patterns laid out in the results section.

Page 9, lines 22-23. The assertion here is that a larger portion of large particles and lower γ slope's (how were they calculated?) were found in the LE region. Yet Table 2 indicates that parts of the LE region had the greatest contribution of 0.2-0.4 μm particles and a contribution of particles greater than 10 μm equivalent to or less than that of SF and UE. Here is an obvious problem with the γ slope. The interpretation that these large particles may have been organic in nature contributes to the uncertainty of the interpretation of the SPM-based coefficients and measurements advocated in this paper.

Page 10, lines 16-17. Table 4 is nearly incomprehensible. The extensions of the table without the columns being identified is what makes the table incomprehensible. And again, in this section the statistical tests should be in the results section and we are interested only in the interpretations of the patterns in the results. The correlation coefficients reported in the table are low even though presumably significant. Again, if γ were determined from the LISST data then any analysis of submicron particles and γ is simply invalid.

Page 10, lines 24-25. The theoretical calculations of Babin et al. (2003) assumed the Junge slope γ when estimating particle concentrations and calculating the Mie scattering based on the particle concentrations predicted by the Junge slope. Since the PSD has been demonstrated to not be Jungian (Risović, 2002; Zhang et al. 2014; Zhang et al. 2017), especially in coastal waters, the Babin et al. (2003) results are not relevant here. Table 4 does not show any relationship between b_{SPM}^* and γ , i.e. γ is not in the table at all. This closest approach is apparently in Table A1. Here we see that the correlations of the optical coefficients of nominal size fractions of SPM and γ vary all over the map, from positive to negative, significant and non-significant, not at all supporting the hypothesis of γ being a significant and explanatory variable in this analysis. This also falsifies the hypothesis that absorption coefficients and ratios are parameters of use in general models of the occurrence and dynamics of suspended matter.

Page 11, lines 2-4. Again, the empirical indices proposed in this paper are poorly described and defined. What do the superscripts “size 1” and “size 2” mean? The BOI indices may be of some utility but again, like all similar indices based on empirical coefficients of total SPM, they are strictly qualitative in nature. The unknowns in the bulk coefficients in their definition will always cast doubt on their interpretation if ancillary evidence on PSD and composition are not available.

Page 11, lines 20-21. Suggested wording: These relationships will be useful in investigating local and regionally-limited relationships and properties of SPM. Without separate independent studies of true optical properties of PIM and POM, and of PSD, these relationships will remain problematical.

Technical Corrections:

Page 2, line 5. Bowers et al. (2009) reported estimates of mass-specific scattering coefficients of and biogeo-physical characteristics of PIM, not SPM.

Page 6, line 26. Replace “properties” with “coefficients.”

Page 9, lines 9-10. The English usage here is nearly incomprehensible. Correct this and similar constructions with a native speaker of English.

Pages 19-30. The tables presented here are nearly impossible to interpret. The table extensions to multiple pages have incomplete columns and no captions to the columns. The the table captions are limited and cryptic.

References:

Bohren, C.H. and D.R. Huffman. 1983. Absorption and Scattering of Light by Small Particles. John Wiley and sons, New York. *Xiv* + 530 pp.

Chavez, F.P., Buck, K.R., Bidigare, R.R., Karl, D.M., Hebel, D., Latasa, M., and Campbell, L. 1995. On the chlorophyll a retention properties of glass-fiber GF/F filters. *Limnol. Oceanogr.*, 40: 428–433.

Johnson, B. D. and P. J. Wangersky. 1985. Seawater filtration: Particle flow and impaction considerations. *Limnol. Oceanogr.* 30: 966-971, doi:10.4319/lo.1985.30.5.0966.

Richter, S.J. and R.H. Stavn. 2014. Determining functional relations in multivariate oceanographic systems: Model II multiple linear regression. *Journal of Atmospheric and Oceanic Technology*, 31: 1663-1672.

Risović, D. 2002. Effect of suspended particulate-size distribution on the backscattering ratio in the remote sensing of seawater. *Appl. Opt.*, 41(33): 7092-7101.

Sheldon, R.W. 1972. Size separation of marine seston by membrane and and glass-fiber filters. *Limnol. Oceanogr.*,17(6): 494-498.

Sheldon, R.W. and W.H. Sutcliffe, Jr. 1969. Retention of marine particles by screens and filters. *Limnol. Oceanogr.*, 14(3): 441-444.

Zhang, X., Stavn, R.H., Falster, A.U., Rick, J.J., Gray, D. and R.W. Gould, Jr. 2017. Size distributions of coastal ocean suspended particulate inorganic matter: Amorphous silica and clay minerals and their dynamics. *Estuarine, Coastal and Shelf Science*. DOI: 10.1016/j.ecss.2017.03.025