October, 9, 2017

Dear Dr. Emmanuel Boss

Editor Associate

Biogeosciences

The whole manuscript was revisited and corrected according to your last suggestions.

The text was shortened and clarified and the speculations about iron or other topics were eliminated. Figure 6 was eliminated because it was redundant. Lastly, the english style was carefully reviewed and corrected as needed.

We are very grateful for your help throughout the reviewing process

We hope this version meets the quality of your journal and we look forward to receive a favorable response

My best regards,

Dr. Martin Montes

Professor

ISMER

University of Quebec at Rimouski

Optical properties of size fractions of suspended particulate matter in littoral waters of Quebec

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Abstract. Empirical mass-specific absorption ($a_i^*(\lambda)^*$) and scattering ($b_i^*(\lambda)^*$) coefficients ~~of suspended particulate matter (SPM)~~ were ~~measured~~ derived for four size fractions (i = 0.2-0.4 µm, 0.4-0.7 µm, 0.7-10 µm, and >10 µm, λ = wavelength in nm) of suspended particulate matter (SPM) ~~in~~ and with samples obtained from surface waters (i.e., 0-2~~5~~ m depth) of the Saint Lawrence Estuary and Saguenay Fjords (SLE-SF) ~~and~~ during June of 2013. ~~The response of two optical proxies (the spectral slope of particulate beam attenuation coefficient and mass-specific particulate absorption coefficient, hereafter γ and *Svis*, respectively) to changes on particle size and chemical composition was also examined.~~ For the ~~spectral range~~ visible-near-Infrared spectral range (i.e., λ = 400-710 nm), mass-specific absorption coefficients of total SPM (i.e., particulates > 0.2 µm) (hereafter a_{SPM}^*) had low values (i.e., 0.01-0.02 m^2 g^{-1}) in areas of the lower estuary dominated by ~~large-sized~~ particle assemblages with relatively large mean grain size~~with~~ ~~relatively~~ and high particulate organic carbon and chlorophyll a per unit of mass of SPM. Conversely, largest a_{SPM}^* values (i.e., > 0.5 m^2 g^{-1}) corresponded with locations of the upper estuary and SF where particulates were mineral-rich and/or their mean diameter ~~particulates~~ was~~are~~ relatively small. ~~-sized and/or mineral-rich .~~ The variability of two optical proxies (the spectral slope of particulate beam attenuation coefficient and mass-specific particulate absorption coefficient, hereafter γ and *Svis*, respectively) with respect to changes on particle size distribution (PSD) and chemical composition was also examined. The power-law exponent of the exponential fit to the differential particle ~~differential Junge slope of particle~~ size distribution had a larger correlation with b_i^* estimates computed at a wavelength of 550 nm (Spearman rank correlation coefficient ρ_s up to 0.37) ~~with respect~~as opposed to a_i^* estimates derived at a wavelength of 440 nm (ρ_s up to 0.32). Conversely, the contribution of particulate inorganic matter to total mass of SPM (F_{SPM}^{PIM}) ~~the ratio between particulate inorganic matter and SPM concentration~~ had a stronger ~~influence on~~correlation with a_i^* coefficients as derived at a wavelength of 440 nm (ρ_s up to 0.50). The magnitude of γ was ~~sensitive~~ positively related to changes of~~n~~ weight contributions of different size fractions of SPM (ρ_s up to 0.53 for i = 0.2-0.4 µm). Also, ~~mass, and~~ the re~~sponse~~lation between~~of~~ γ and~~to~~ F_{SPM}^{PIM} ~~particle composition~~ variability was secondary (ρ_s = -0.34, *P* > 0.05). Lastly, the magnitude of *Svis* was inversely correlated with $a_{SPM}^*(440)$ (ρ_s = -0.55, *P* = 0.04) and F_{SPM}^{PIM} ~~Lastly, in~~

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(ρ_S = -0.62, P = 0.018) in sampling locations ~~areas of the estuary~~ having~~with~~ a larger marine influence (i.e., lower estuary).~~, the magnitude of *Svis* was inversely correlated with a_{SPM}^*(440) values and the mineral content of SPM. Functionalities between *Svis* and a_{SPM}^*(440) distributions and unusual high values of a_i^* measured in SF waters suggest that iron bound to particles is likely a major factor explaining relatively high values of a_{SPM}^*(440) in our study area.~~

1 Introduction

The distribution of suspended particulate matter (SPM) (Table 1) in coastal and estuarine environments has a major influence on several biogeochemical processes (e.g., phytoplankton blooms) (Guinder et al., 2009), ecosystem structure (e.g., food webs) (Dalu et al., 2016) and dispersion of pollutants (e.g., copper, mercury, polycyclic aromatic hydrocarbons) (Ma et al., 2002; Ramalhosa et al., 2005). Light absorption by suspended particulates is essential for several photochemical processes related to the carbon cycle (e.g, photosynthesis, production of dissolved inorganic and organic carbon) (Estapa et al., 2012). Lastly, the concentration of SPM ~~(CSPM) (Table 1)~~ is an important variable for modeling thermodynamic processes and computing heat budgets (Löptien and Meier, 2011) due to its influence on underwater light attenuation (Morel and Antoine, 1994; Devlin et al., 2008).

~~Remote sensing allows synoptic mapping of SPM in littoral environments where~~ T~~t~~he spatial and temporal variability of suspended particulates is relatively high (i.e., >100-fold) in littoral environments (Doxaran et al., 2002; Montes-Hugo and Mohammadpour, 2012). This represents a challenge for traditional methods of measuring SPM based on gravimetry (Strickland and Parson, 1972) as the analysis of a large number of samples is time- consuming and costly. Thus, these studies are commonly based on a relatively small dataset that may partially represent the in situ distributions of SPM. Due to these difficulties, several techniques have been developed for synoptic and large-scale mapping of SPM based on satellite-derived optical measurements (Doxaran et al., 2002; Miller and McKnee, 2004; Montes-Hugo and Mohammadpour, 2012). SPM is an unknown mixture of inorganic and organic matter that varies between locations and as a function of time due to diverse physical (e.g., tides) and biogeochemical (e.g., phytoplankton growth) factors (D'Sa et al., 2008;Eleveld et al, 2014). Thus, ~~However,~~ optical remote sensing~~ocean color~~ algorithms for estimating ~~C~~SPM ~~will never have the accuracy required for optical inversions because SPM is undefined optically (i.e., an unknown mixture of inorganic and organic matter).~~are more region-specific and generally less accurate than those conceived for estimating specific fractions of SPM (e.g., particulate inorganic matter or PIM). - This highlights the need for a better understanding ~~Therefore, partition of SPM into at least major chemical composition classes (particulate inorganic and organic matter or PIM and POM, respectively) and estimation of size distribution are required independently for optically-based remote sensing models of primary productivity and suspended mineral dynamics.~~

~~Likewise and unlike optical inversions of SPM, remote sensing estimates of specific fractions of SPM (e.g., PIM and POM) have a definable and reproducible measurement error and are less influenced by regional variability of optical properties.~~

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~~Despite this, there is still a lack of understanding regarding how~~of optical properties of SPM components that can be later used for estimating second-order attributes of SPM (i.e., chemical composition, size distribution) and designing more general remote sensing algorithms for retrieving total concentrations of particulates per unit of volume and across different water types.

In general, four techniques have been proposed for characterizing ~~SPM microphysical characteristics (e.g., particle chemical composition and size distribution) relate to mass-specific optical properties. This knowledge is essential for deriving new optical inversions for retrieving second-order attributes of SPM (i.e., chemical composition, size distribution).~~

~~Lastly, the biogeo-optical modeling of size and chemical fractions of SPM has a major scientific interest for understanding the dynamics of different mineral iron forms in coastal waters (Estapa et al., 2012) as particle-associated iron has two specific light absorption bands (wavelength, λ = 360-390 nm and λ = 400-450 nm). Also, Estapa et al. (2012) demonstrated that optical proxies such as the spectral slope of particulate absorption (*Svis*) within the visible spectral range (λ = 400-700 nm) could be used for estimating dithionite-extractable iron and organic carbon content in marine samples. Iron can be part of organic (e.g., complexed forms) or inorganic (e.g., silicate sheets) particulates having a broad size range (e.g., from clays to amorphous aggregates) (Bettiol et al., 2008). Thus, the analysis of different fractions of SPM is essential for understanding the complex fate of iron in aquatic systems. Linking iron distributions with optical properties of size and chemical fractions of SPM may allow the development of proxies for mapping iron based on optical (*in water* and remote sensing) measurements. This is particularly advantageous for long-term monitoring projects as direct iron measurements are very expensive, difficult, and demand highly trained technicians.~~

~~The optical characterization of~~ particle size distribution (PSD) and/or~~/or~~ chemical composition of SPM ~~in coastal and oceanic waters has been attempted based on four main methodologies~~based on optical measurements: (1) ~~: (1)~~ optical proxies (e.g., the ~~analysis of~~ spectral ~~changes~~ slope of ~~inherent optical properties~~particulate beam attenuation, γ, mass-specific absorption, *Svis*, and backscattering coefficients) (Boss et al., 2001; Loisel et al., 2006; Estapa et al., 2012), (2) ~~empirical relationships between~~ mass-specific optical ~~cross sections~~coefficients (e.g., mass-specific particulate scattering, backscattering and beam attenuation coefficients) ~~and biogeo-physical characteristics of PIM (e.g., mean diameter)~~ (Bowers et al., 2009;~~) and SPM (e.g. apparent density of particulates) (~~Neukermans et al., 2012), (3) particulate ~~optical inversions of different~~ volume scattering functions (Zhang et al., 2014), and (4) ~~changes on~~ water leaving polarized reflectance (Loisel et al., 2008). ~~A widely used methodology for estimating particle size spectra changes is the use of the spectral slope of particulate beam attenuation coefficient (γ) due to its relationship with the differential Junge slope of particle size distribution (ξ) (Boss et al., 2001).~~

The Saint Lawrence Estuary (SLE) and the Saguenay Fjords (SF) constitute a large sub-Arctic system characterized by relatively high concentrations of chromophoric dissolved organic matter (CDOM) (Nieke et al., 1997). The remote sensing of physical attributes of SPM ~~microphysical characteristics~~(e.g., PSD) in these waters is crucial for ~~understanding~~ studying regional climate effects on coastal erosion ~~(Bernatchez and Dubois, 2004)~~ and occurrence of harmful algae blooms ~~(Fauchot et al. 2008)~~. However, in order to accomplish this task it is essential to know how ~~mass-specific optical coefficients~~optical characteristics ~~-~~of suspended particulates (e.g., mass-specific optical coefficients) are influenced by particle composition and size distribution changes. To our knowledge, mass-specific absorption and scattering coefficients of SPM size fractions have never been reported in the literature even though it has a potential application in biogeo-optical ~~inversions~~ modeling and biogeochemical studies regarding the dynamics of trace metals, sediment transport and primary productivity models.

This study has t~~wo~~hree main objectives: (1) to characterize the mass-specific absorption (a_i~~*~~$(\lambda)^*$) and scattering (b_i~~*~~$(\lambda)^*$) coefficients of four size fractions of SPM (i = 0.2-0.4 µm, 0.4-0.7 µm, 0.7-10 µm, and >10 µm, λ = wavelength in nm) at~~in~~ different locations of the SLE-SF and during spring conditions, (2) to establish relationships between mass-~~independent~~specific optical coefficients calculated in (1) and ~~microphysical properties~~characteristics of ~~of particulates~~particle assemblages related to PSD and mineral content of SPM, and (3) to examine the ~~response~~ correlation ~~of~~ between optical proxies γ and *Svis*, and ~~two optical proxies (γ and *Svis*)~~ variables linked to~~to~~ ~~changes on~~ P~~P~~SD and chemical composition of SPM. ~~as inferred from PIM~~. ~~and POM contributions.~~

This study is organized in three sections. In the first section, mass-specific absorption (a_{SPM}*) and scattering (b_{SPM}*) coefficients of total SPM (i.e., particulates >0.2 µm) are calculated for different optical environments of the SLE-SF that are characterized by distinct particle assemblages and variable contributions of CDOM, non-algal particulates (NAP) and phytoplankton to light attenuation. In the second section, ~~the response~~ relationships between~~of~~ mass-specific optical coefficients of different SPM size fractions and parameters related to ~~to variations in~~ PSD and mineral-content of suspended particulates are~~is~~ investigated. Lastly in the third section, ~~the influence~~ relationships between~~of~~ optical proxies γ and *Svis* ~~PSD and mineral enrichment of particulates on γ and *Svis* is examined.~~and second-attributes of SPM linked to particle chemical composition and PSD are analyzed.

2 Data and methods

2.1 Study area

The SLE can be divided in two main regions having contrasting biological productivity and bathymetry: the upper (UE) and the lower (LE) estuary (Levasseur et al., 1984). NAP and CDOM dominate the ~~underwater~~ diffuse light attenuation of SLE ~~UE~~ waters (Nieke et al., 1997). This is ~~in~~ partially related to the inflow of CDOM-rich and NAP-rich waters coming from the St. Lawrence River and Saguenay Fjord (Tremblay and Gagné, 2007; Xie et al., 2012). Unlike NAP and CDOM, contribution of phytoplankton to inherent optical properties increases towards the mouth of the SLE (Montes-Hugo and Mohammadpour, 2012; Xie et al., 2012).

The study of optical properties of suspended particulates in SLE waters began during the late 80's. Babin et al. (1993) investigated the horizontal variability of the specific absorption coefficient of phytoplankton (i.e., absorption coefficient normalized by concentration of chlorophyll + phaeopigments) in surface waters during summer of 1989 and 1990. During the summer of 1990, Nieke et al. (1997) ~~studied the spatial variability of CDOM in terms of fluorescence and absorption spectra. Also, this study~~ reported for the first time relatively high values (up to 3 m^{-1}) of particulate beam attenuation coefficients (c_{SPM}) and inverse relationships between salinity, c_{SPM}, and CDOM absorption coefficients (a_{CDOM}). Larouche and Boyer-Villemaire (2010) proposed remote sensing models for estimating PIM in the SLE and the Gulf of Saint Lawrence. Xie et al. (2012) showed inverse relationships between salinity and absorption coefficients of NAP and highlighted the extremely high values of ~~-~~a_{CDOM} (i.e., up to 5.8 m^{-1} at λ = 412 nm) along the Saguenay Fjord.

Historical studies performed during summer of 1975 suggest that size distribution of SPM differs between UE, LE and SF subregions (Poulet et al., 1986). Based on surface samples, Poulet et al. (1986) found a dominance of relatively 'small-sized' (i.e., mode diameter < 10 µm) and 'large-sized' (i.e., > 30 µm) particulates over the UE and the mouth of the SLE, respectively. Conversely, the remaining locations of the LE were characterized by particulates having an intermediate size. In surface waters of SF and during spring~~ months~~, Chanut and Poulet (1982) found that SPM is commonly composed by very small particles (i.e., 2-3 µm)~~ (Chanut and Poulet, 1979)~~. Several investigations point out that suspended particulates in SLE-SF regions are principally composed by inorganic matter (D'Anglejan and Smith, 1973; Larouche and Boyer-Villemaire, 2010; Mohammadpour et al., 2015). This mineral contribution ~~varies~~ may vary between 60 and 95% of dry weight depending on the geographic location and period of the year (Yeats, 1988; Larouche and Boyer-Villemaire, 2010). Despite their important contribution to the study of physical and chemical properties of SPM, none of these studies investigated relationships between chemical composition, size distribution, mass-normalized optical coefficients and optical proxies of second-order attributes of SPM.

~~**Despite their important contribution, none of these studies reported mass-normalized optical coefficients for different size fractions of SPM nor an assessment of particle composition and size distribution effects on these coefficients.**~~

2.2 Field surveys

~~2.2 Field surveys~~

Discrete water samples for biogeochemical and optical measurements were obtained in 22 locations distributed throughout the SLE (N =17) and SF (N = 5) regions (Fig. 1). One discrete sample was obtained in each sampling locations but in site 6 where 2 measurements were made during June 3 and 6 of 2013. Surface s~~S~~amples ~~corresponding to a sampling depth of~~(i.e., 0-2 m depth) were collected during June 3-9 of 2013 by using an oceanographic rosette equipped with Niskin bottles (volume = 12 L). For each ~~sampling~~ study location~~location~~, PSD of unfractionated water samples, and ~~mass~~ optical properties of different size fractions of SPM~~,~~ ~~optical coefficients for different SPM size fractions, and particle size distribution spectra~~ were ~~measured~~determined ~~inside the wet lab of the vessel~~onboard of the ship.

2.3 Biogeochemical analysis

Size fractionation of SPM was done after sequentially filtering the original samples through pre-weighted membranes having a diameter of 47 mm and a pore size of 10 µm (Whatman, polycarbonate), 0.7 µm (GF/F, Whatman, glass fiber), 0.4 µm (Whatman, polycarbonate), and 0.2 µm (Nucleopore, polycarbonate). The contribution of size fraction i to the total mass of SPM (F_{SPM}^{i}, i = 0.2-0.4 µm, 0.4-0.7 µm, 0.7-10 µm, and >10 µm) was computed by normalizing the weight of the fraction i by the sum of weights derived from each size fraction. The ~~mineral and organic~~contribution of PIM to total mass of SPM ~~composition of suspended particulates~~ (F_{SPM}^{PIM}~~^{j}, where j superscript symbolizes PIM or POM, respectively~~) was only computed for particulates with a grain size greater than 0.7 µm (i.e., after filtering the original unfractionated sample trough a GF/F filter membrane). In this case, the mass of PIM and particulate organic matter (POM)~~POM~~ was assumed to be negligible for particulates with a diameter smaller than 0.7 µm. ~~Thus, resulting PIM and POM determinations correspond to total suspended particulates.~~ This approximation should be verified in the future since the authors are not aware of publications addressing the contribution of relatively small particulates (i.e., < 0.7 µm) to PIM and POM. The mass of PIM was obtained after removing the organic mass ~~(i.e., POM)~~ by combustion of original samples at 450°C and during 6 h (Mohammadpour et al., 2015). The mass of POM was calculated as the difference between the dry mass of ~~particulates~~ SPM concentrated in GF/F filters minus the dry mass of PIM.

The precision of SPM mass determinations based on GF/F filters was 15% (Mohammadpour et al., 2015). This precision was computed as the percentage of ± 1 standard deviation with respect to the arithmetic average of weight corresponding to 10 replicas. Based on loss on ignition factors (Barillé-Boyer et al., 2003) and clay composition data obtained in the Saint Lawrence Estuary (D'Anglejan and Smith, 1973), the estimated error of PIM determinations due to dehydration of clays was 3.1%. Thus, PIM mass determinations have a maximum uncertainty of 18.1% due to the additional error of SPM mass measurements~~ by gravimetry~~. Notice that error in POM mass estimates was slightly greater than that associated to PIM mass estimates (18.2%).

2.4 Optical measurements

Total absorption (*a*) and beam attenuation (*c*) coefficient measurements were done on unfractioned~~iltered~~ and size-fractioned ~~filtered~~ water samples previously described in section 2.3. Discrete samples for optical coefficients were measured ~~onboard~~ by using an absorption-beam attenuation meter (ac-s, WetLabs, λ = 400.3-747.5 nm, average spectral resolution = 4 nm, path-length = 10 cm, accuracy ± 0.001 m^{-1}). In order to minimize the presence of bubbles, a pump (ISMATEC MCP-Z) was used to gently circulate the samples ~~through the ac-s tubes~~during the measurements. Spikes on raw signal associated to bubbles were removed by visual inspection. The r~~R~~esidual scattering on absorption measurements was removed by applying a flat baseline at a reference wavelength of 715 nm (Bricaud and Stramski, 1990). This is a first order correction for scattering effects on non-water absorption coefficient estimates. Thus, the calculation of particulate absorption coefficients in this study is expected to have a bias with respect to true values measured using absorption-meter instruments that are less influenced by particulate scattering (e.g., point-source integrating-cavity absorption meters) (Röttgers et al., 2013). Lastly, values of a and c were corrected by water temperature and salinity variations (Pegau et al. 1997). Spectral values of a_{SPM} in m^{-1} were derived ~~in~~ from ~~unfiltered~~ unfractionated samples by subtracting the contribution of CDOM ~~a_{CDOM} and~~and pure seawater to ~~the absorption coefficient for pure seawater (a_{w}) to~~ a ~~at each wavelength~~. ~~The contributions a_{CDOM} + a_{w} were~~The magnitude of a_{CDOM} ~~measured~~ was determined ~~by using the a-tube (i.e., reflective tube) of the ac-s and~~ after pre-filtration of ~~total~~ size-fractionated samples through a membrane having a pore size of 0.2 µm (nucleopore, Whatman). Similar to a_{SPM} calculations, ~~the magnitude~~values of c_{SPM} ~~was~~ were derived ~~computed in~~from unfractioned~~iltered~~ samples after subtracting CDOM and pure seawater contributions to c ~~as derived by using the c-tube (i.e., opaque tube) of the ac-s instrument~~. Lastly, particulate scattering coefficients (b_{SPM}) in m^{-1} were derived by subtracting a_{SPM} to c_{SPM} values. Notice that pure seawater contributions to a and c values are initially removed when the ac-s instrument is calibrated by the manufacturer. Seawater absorption and scattering coefficients are derived from tables (Morel, 1974; Pope and Fry, 1997).. ~~Lastly, particulate scattering coefficients (b_{SPM}) in m^{-1} were derived by subtracting a_{SPM} to c_{SPM} values.~~

~~The~~Bench determinations of ~~particle size spectra~~PSD ~~within the size range 3-170 µm were measured~~were made ~~on unfiltered samples and~~ by using a red laser (wavelength = 670 nm) diffractometer (LISST-100X, type B, Sequoia Scientifics) (Agrawal et al. 1991). ~~LISST bench determinations were discrete and performed on board of the ship.~~ Lab measurements were performed by using a chamber and a magnetic stir bar in order to homogenize the samples and avoid sinking of particulates. The optical path was covered with a black cloth to minimize ambient light contamination during the scattering measurements. The LISST-100X instrument can measure 32 scattering angles within an angular range of 0.08-13.5°, thus, particulates with a diameter between 1.25 and 250 µm can be quantified. However only the interval 3-170 µm was analyzed due to stray light effects and variability of particle shape and refractive index in the first bins (i.e., < 3.2 µm) (Agrawal et al., 2008; Andrews et al., 2010~~), stray light effects in the first bins (~~; Reynolds et al. 2010), and bias related to particle sinking in the last bins (i.e., 170-250 µm) (Reynolds et al. 2010). The Hampel filter algorithm was applied to the original measurements in order to ~~Measurements~~ eliminate potential outliers (Pearson, 2005). Lastly, each final PSD estimate was computed as the average of measurements made during 3 minutes at 1 Hz sampling rate.

~~were made during a period of 3 minutes at 1 Hz, and resulting raw data were quality controlled by using the Hampel filter algorithm for eliminating outliers (Pearson, 2005).~~ The number of particles per unit of volume within each size class (N(D)) was computed by dividing the particle volume concentration (V(D)) by the diameter (D) of a volume-equivalent sphere ~~for~~ corresponding to the midpoint of each individual class:

$$N(D) = 6\,V(D)\,(\pi\,D^3)^{-1} \qquad (1)$$

A total of 25 particle size bins were calculated ~~based on~~from ~~inversions of the scattering pattern and by applying an inversion kernel matrix derived from~~ scattering patterns of spherical homogenous particles as predicted from Mie theory and a realistic range of index of refraction. The particle size distribution (N'(D)) was defined as the average number of particles within a given size class of width ΔD and per unit of volume (Reynolds et al., 2010):

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$$N'(D) = N(D)\ \Delta D^{-1} \quad (2)$$

The ~~parameter~~ power-law exponent of the exponential fit to the differential PSD (ξ) was computed ~~as the exponent of the following power-type function~~as follows:

$$N'(D) = N'(Do)\ (D/Do)^{-\xi} \quad (3)$$

where Do is the reference particle diameter and was set to ~~35.17 µm because is~~ the midpoint of the size logarithmic size range (i.e., 35.17 µm). Calculations of ξ were done by least square minimization of log-transformed data (Reynolds et al., 2010). The uncertainty of ξ calculations, as estimated from 2 standard errors, varied between 1.6 and 10.2% with smaller errors in samples obtained in LE locations. Although ~~particle size distribution~~PSD in natural waters may not follow the model proposed in equation (3)~~a Junge-type slope~~, its use here was justified ~~since~~ as our main interest was to have a first-order assessment of size effects of particulates on optical coefficient's variability. ~~Indeed~~Also, the definition of ξ based on LISST measurements applies for particulates greater than 2 µm. A more realistic representation of PSD is the model proposed by Risovic (1993). This parameterization mainly includes two particle populations ('large' and 'small') having different refractive index and has been recently applied in littoral environments by different studies (Zhang et al., 2013; Zhang et al., 2014; Zhang et al., 2017). Thus, relationships between ξ and optical coefficients in this study are local and should not be generalized to other littoral environments.

2.5 Optical proxies and ~~particle microphysical~~ characteristics of particle assemblages

A widely used methodology for estimating size spectra of suspended particulates is the calculation of γ (Boss et al., 2001). The parameter γ is positively correlated with ~~the~~ the power-law exponent fit to the particle number size distribution (ξ) ~~exponent of the particle number size distribution~~ ($\xi = \gamma + 3 - 0.5\ e^{-6\gamma}$, Boss et al., 2001) and negatively related with the mean particle size for particles smaller than 20 µm (Boss et al., 2013). The parameter γ was derived as ~~the exponent of a power-type regression model of c_{SPM} as a function of wavelength~~follows:

$$c_{SPM}(\lambda) = c_{SPM}(488)\ (\lambda/\lambda r)^{-\gamma} \quad (4)$$

where λr is the reference wavelength at ~~=~~ 488 nm ~~and it is the reference wavelength~~ (Boss et al., 2013).

The uncertainty of γ determinations ~~varied~~ varied between 2.2% and 6.4% with largest errors computed ~~for~~ in samples obtained in LE waters. The spectral slope of ~~empirical~~ mass-specific particulate absorption coefficients (*Svis*) was calculated by nonlinear fitting of a single-exponential decay function over the visible range 400-700 nm:

$$a_x^*(\lambda) = A\ e^{-Svis\,(\lambda-400)} + B \quad (5)$$

where x corresponds to total SPM or the size class i, the term *B* corresponds to an offset at near-IR wavelengths to account for nonzero absorption by mineral particles (Babin et al. 2003; Röttgers et al., 2014). The uncertainty of *Svis* estimates varied between 0.5 and 21.5% with largest errors ~~corresponding~~ associated ~~with~~ to samples obtained in LE locations. The equation (5) is only valid in waters where non-algal particulates are the main optical component contributing to light absorption coefficient of SPM. ~~The magnitude of *Svis* is inversely correlated with extractable iron from crystalline and amorphous iron~~

~~oxides and organic-iron complexes in measurements corresponding to marine samples (Estapa et al., 2012). Also for the same environments, *Svis* is expected to have a negative covariation with the organic carbon content of particulates (Estapa et al., 2012).~~

2.6 Mass-specific optical coefficients

The s~~S~~pectral ~~values of~~ mass-specific absorption ($a_i^*(\lambda)$) and scattering ($b_i^*(\lambda)$) coefficients~~s~~ in m^2 g^{-1} and for different size fractions of SPM ~~were calculated as~~are defined as follows:

$$a_i^*(\lambda) = a_i(\lambda)\ (wp_i)^{-1} \qquad (6)$$

$$b_i^*(\lambda) = b_i(\lambda)(wp_i)^{-1} \qquad (7)$$

For each size class i, a_i and b_i are the coefficients of particulate absorption and scattering, respectively, and wp_i is the mass of particulates per unit of volume in g m^{-3}.

2.7 Statistical analysis

~~The influence of~~Relationships between PSD,~~ particle size~~ , particle~~and~~ chemical composition, ~~variations on~~ optical proxies (γ and *Svis*) and empirical mass-specific optical coefficients ~~of particulates~~ for different size fractions (i.e., a_i^* and b_i^*) of SPM ~~and optical proxies (γ and *Svis*)~~ w~~as~~ere investigated based on correlations with respect to ξ and F_{SPM}^{PIM} variables~~, respectively~~. In all cases, the intensity and sign of correlations were quantified based on non-parametric Spearman rank coefficient (ρ_s) (Spearman, 1904).

3 Results

3.1 Spatial variability of ~~microphysical~~ physical and chemical ~~properties~~ characteristics of SPM

The~~In terms of particle~~ size distribution of particulates presented~~,~~ contrasting ~~areas~~ changes among different subregions of the study area~~in the SLE-SF were identified~~. In general, particulates with a diameter larger than 10 µm had a relatively large contribution to the total SPM mass in UE locations ($F_{SPM}^{>10\ \mu m}$ as percentage up to 17%). This proportion was lower in the LE (up to 11%) and SF (up to 15%) subregions. The largest mass contribution of smallest-sized particulates (i.e., diameter < 0.4 µm) was calculated in the lower estuary (up to 27%). Lastly, the intermediate size classes 0.4-0.7 µm and 0.7-10 µm were in average the fractions having the largest mass contributions to SPM in SF locations (up to 14 and 87%, respectively). In general, ~~the Junge slope calculations~~the magnitude of ξ suggested the presence of ~~relatively~~ larger~~r~~ particulates in the LE (arithmetic average ± standard deviation = 3.28 ± 0.38, N = 15) with respect to UE (3.46 ± 0.36, N = 3) and SF (3.42 ± 0.39, N = 5) subregions. Unlike PSD, ~~chemical composition of SPM~~the mineral content of SPM was less variable throughout the study area (F_{SPM}^{PIM} range = 37 to 87 %). In average, particle chemical composition in UE, SF and LE subregions was dominated by minerals (F_{SPM}^{PIM} = 0.65 ± 0.13, 0.67 ± 0.14 and 0.67 ± 0.14 for SF, UE and LE, respectively).

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3.2 Mass-specific optical ~~properties~~ coefficients of particulates~~of SPM~~

In general for the visible spectrum, ~~For the spectral interval 400-710 nm,~~ the sub~~magnitude of~~ regionall~~y~~ ~~-~~average of~~d~~ mass-specific absorption particulate coefficients ~~a_{SPM}^{*}~~ was higher in SF (e.g., $a_{SPM}^{*}(440)$ = ~~for at λ = 440 nm, arithmetic average ± standard error =~~ 0.523 ± 0.102 m^{2} g^{-1}, arithmetic average ± standard error)~~)~~ with respect to UE (0.12~~2~~2 ± 0.069~~8~~ m^{2} g^{-1}) and LE (0.062~~50~~ ± 0.010 m^{2} g^{-1}) ~~-~~locations (Fig. 2a). Conversely, the subregional average ~~regionally-averaged~~of mass-specific particulate scattering coefficients ~~b_{SPM}^{*} values~~ was comparable ~~ere~~ ~~highly variable within~~between different spatial domains of the SLE~~ spatial domains~~ ~~even though~~ (Fig. 2b). However, the highest and lowest values subregional averages of b_{SPM}^{*} tended to be associated with UE (e.g., $b_{SPM}^{*}(440)$ = 0.499 ± 0.278 m^{2} g^{-1}) and LE (0.181~~29~~ ± 0.046 m^{2} g^{-1}) locations, respectively~~ (Fig. 2b)~~. In general for all size fractions of SPM, mass-specific absorption coefficients ~~tended to~~were usually ~~be~~ higher in SF (e.g., $a_{i}^{*}(440)$ ~~at λ = 440 nm,~~ up to 2.81 m^{2} g^{-1})~~)~~ with respect to UE and LE ~~other~~ subregions ~~of the SLE~~ (up to 2.11 m^{2} g^{-1}) (Fig. 3~~a~~). However, this pattern was reversed when the grain size of particulates was smaller than 0.4 µm (Fig. 3a). Indeed, the ~~for the smallest size range 0.2-0.4 µm,~~ highest $a_{0.2\text{-}0.4\,\mu m}$* ~~values~~estimates in this study ~~where measured in~~corresponded to UE waters (e.g., st 14) (2.19 m^{2} g^{-1}) (Fig. 3a).

In general, very high ~~Spectral curves with the highest~~ a_{i}* values (e.g., up to 4 m^{2} g^{-1} at λ = 400 nm) ~~corresponded~~ were associated with the~~with the smallest-sized and~~ ~~largest~~s~~-~~size~~d~~ fraction~~s~~ of SPM having particulates with a diameter greater than 10 µm (Fig. 3~~a,~~d). These values were up to 8 and 5 times higher than those characteristic of size fractions 0.4-0.7 µm and 0.7-10 µm, respectively (Fig. 3b-c). In general, ξ and F_{SPM}^{PIM} correlations with mass-specific absorption coefficients of different size fractions of SPM suggest that particle chemical composition has a larger influence on $a_{i}^{*}(440)$ (ρ_{s} up to 0.50, $P = 0.0009$) with respect to PSD (ρ_{s} up to 0.32, $P = 0.0033$) (Table 2).

Similar to a_{i}*, highest b_{i}* values (up to 5.70 m^{2} g^{-1} at λ = 400 nm) were ~~computed in~~associated with particulates within two size ranges, 0.2-0.4 µm and >10 µm ~~size-fractionated samples corresponding to particle size ranges of 0.2-0.7 µm and >10 µm~~ (Fig. 4). Notice that mass-specific optical coefficients in the near-Infrared (NIR) spectral range are not shown due to the presence of negative values at some wavelengths. For the same size range of particulates, the h~~H~~ighest b_{i}* values ~~scattering efficiencies in terms of b_{i}*~~ were not always measured in the same region. Indeed, maximum b_{i}* values for the size fractions 0.7-10 µm (up to 1.25 m^{2} g^{-1} at λ = 556 nm) and >10 µm (up to 4.58 m^{2} g^{-1}) were obtained in UE and LE domains, respectively. Unlike $a_{i}^{*}(440)$, $b_{i}^{*}(550)$ variability was less influenced by changes on particle composition (ρ_{s} up to 0.42, $P = 0.0015$) (Table 2). Conversely, the impact of changing particle dimensions, as inferred from ρ_{s} correlations, had a larger effect on $b_{i}^{*}(550)$ (ρ_{s} up to 0.37, $P = 0.006$) with respect to $a_{i}^{*}(440)$ (ρ_{s} up to 0.32, $P = 0.009$) values.

~~Notice that mass-specific optical coefficients in the near-Infrared (NIR) spectral range are not shown due to the presence of negative values at some wavelengths.~~

The s~~S~~pectral variability of mass-specific optical coefficients for two size fractions of SPM and averaged over the whole study area is illustrated in Fig. 5. For the spectral range of 440-556 nm, a_{i}* values for the size range 0.2-0.4 µm tended to be higher with respect to those associated with ~~the~~ particulates larger than 10 μm (Fig. 5a). Conversely, this trend appeared to be reversed at wavelengths within the red-NIR spectral range. In general for the visible-NIR wavelengths, the arithmetic average of b_i* for the size fraction 0.2-0.4 μm were consistently larger with respect to that associated to the size fraction >10 μm (Fig. 5b).

~~**The subregional variation of mass-specific optical coefficients for different size fractions of SPM are depicted in Fig. 6. For all size fractions of SPM, the regionally-averaged magnitude of $a_i^*(440)$ was higher in UE-SF with respect to LE locations (Fig. 6a). These differences are consistent with spatial changes of a_{SPM}^* in Fig. 2a and 3. In Saguenay Fjord waters, the maximum regionally-averaged $a_i^*(440)$ values (up to 4.6 m^2 g^{-1}) were associated with the size fraction of SPM having particulates with a size grain larger than 10 μm (Fig. 6a). In general, ξ and F_{SPM}^{PIM} correlations with mass-specific optical coefficients of different size fractions of SPM suggest that particle chemical composition has a larger influence on $a_i^*(440)$ (ρ_s up to 0.50, $P = 0.0009$) with respect to particle size (ρ_s up to 0.32, $P = 0.0033$) (Table 2).**~~

~~**Geographically-averaged $b_i^*(550)$ values were generally comparable among subregions (Fig. 6b). However for the size fraction 0.7-10 μm , averaged $b_i^*(550)$ values of UE-SF (0.432-0.501 m^2 g^{-1}) domains were larger with respect to the arithmetic average computed for LE waters (0.136 ± 0.027 m^2 g^{-1}). Unlike $a_i^*(440)$, $b_i^*(550)$ variability was less influenced by changes on particle composition (ρ_s up to 0.42, $P = 0.0015$) (Table 2). Conversely, the impact of changing particle dimensions, as inferred from ρ_s correlations, was greater for $b_i^*(550)$ (ρ_s up to 0.37, $P = 0.006$) with respect to $a_i^*(440)$ (ρ_s up to 0.32, $P = 0.009$) values.**~~

3.3 Optical proxies

Correlations between size and chemical fractions of SPM ~~,~~ as derived from mass ~~ratios,~~ratios, and optical proxies are presented in Table 3. Over the whole study area, there was not a clear relationship between γ and F_{SPM}^{PIM} values ~~chemical fractions of SPM fractions~~ (ρ_s = -0.34, P = 0.11). However, γ changes ~~responded~~ were associated to variations of size-fractionated mass contributions of ~~on size fractions for~~ particulates within the ~~the~~ range 0.2-10 μm (ρ_s up to 0.53, P = 0.01). The sign of this ~~response~~ correlation ~~changed~~ varied depending on the size class under investigation (e.g., positive and negative ρ_s values for small-sized and~~,~~ ~~negative for~~ intermediate-sized particulates, respectively). ~~Although positively correlated, t~~There was not a clear relationship between γ and ξ ~~determinations~~ values calculated with samples obtained over the whole study area (ρ_s = 0.15, P = 0.49, N = 23). The range of γ values was 0.759-3.282, 1.389-1.534, 2.873-3.282 and 0.759-1.802 nm^{-1} for the SLE, UE, SF and UE domains, respectively. The spectra slope of a_{SPM}^* was not ~~substantially~~statistically ~~affected~~ related to~~by~~ F_{SPM}^{PIM} changes (ρ_s = -0.06, P = 0.78, N = 23). H~~, h~~owever *Svis* variability was strongly ~~influenced~~ connected with changes on mass contribution of different size classes of SPM~~by particle size changes (Table 3).~~,and in particular those associated to ~~Also, size effects on *Svis* were more remarkable for relatively~~ small-sized particulates (i.e., 0.2-0.7 μm) (Table 3). This pattern was consistent with a positive correlation between γ and *Svis* (ρ_s = -0.489, P = 0.018, N = 23). However, there was not a clear relationship~~s~~ between *Svis* and ξ values (ρ_s = 0.123, P = 0.57, N = 23).

The r~~R~~ange of *Svis* values ~~of total SPM~~for unfractionated samples of SLE-SF, UE, SF and UE domains was 0.005-0.051, 0.009-0.017, 0.014-0.051 and 0.005-0.016 nm^{-1}~~ for the SLE, UE, SF and UE domains~~, respectively. Over the whole study area, the range of *Svis* values for SPM size fractions 0.2-0.4 µm, 0.4-0.7 µm, 0.7-10 µm and > 10 µm was 0.004-0.026, 0.007-0.052, 0.004-0.109 and 0.001-0.028 nm^{-1}~~ for size fractions 0.2-0.4 µm, 0.4-0.7 µm, 0.7-10 µm and > 10 µm~~, respectively. In general, *Svis* slopes were not correlated between size fractions even though the ~~magnitude ~~variation of *Svis* for ~~total ~~unfractionated samples~~SPM~~ was strongly~~ influenced~~ linked to changes on~~by~~ *Svis* estimates associated ~~calculated ~~to particulates within the size range ~~for the ~~0.7-10 µm ~~ fraction~~ ($\rho_s = 0.66$, $P = 0.004$).

4 Discussion

4.1 Uncertainty of optical measurements

Inherent optical properties in this study were derived from an ac-s instrument. Thus, large errors on absorption coefficients may be anticipated in relatively turbid waters if original measurements are not corrected by scattering effects (Boss et al., 2009; McKee et al., 2013). These effects are mainly attributed the acceptance angle of the transmissometer and the multiple scattering of photons. The acceptance angle of the ac-s instrument is ~0.9° and much larger than that corresponding to the LISST-100X diffractometer (~0.027°). Thus, a larger underestimation on *c* magnitude is expected in ac-s with respect to LISST-100X measurements due to a larger contribution of forward-scattered photons arriving to the detector of the former optical instrument. Further comparisons of *c*(532) measurements derived here by ac-s and LISST-100X showed that *c* values as derived from ac-s were 23-84% lower with respect to those determinations based on LISST-100X. This is consistent with Boss et al. (2009) who reported that uncorrected Wet Labs ac-9 attenuation values are approximately 50%-80% of equivalent LISST attenuation data. Unfortunately, *c* deviations due to acceptance angle variations were not corrected in this study due to the lack of true *c* values as obtained by using an integrating cavity absorption meter (e.g., PSICAM) (Röttgers et al., 2005). Notice that these errors are much greater with respect to the standard deviation of~~the optical variability associated to~~ each ~~sample ~~sample determination ~~in SLE~~in this study and ~~ SF waters and ~~computed based on ac-s measurements (e.g., < 1% at $\lambda = 532$ nm).

In this investigation, the 'flat' baseline correction was selected for correcting the residual scattering in absorption coefficient estimates as derived from ac-s measurements. This technique was chosen due to the lack of PSICAM measurements or ~~critical ~~ancillary optical information (e.g., particle backscattering efficiency) to tune up a Monte Carlo scattering correction approach (McKee et al., 2008). The 'flat' scattering correction approach is expected to provide a fair correction of *a* values in oceanic waters (e.g., up to 15% underestimation at wavelengths shorter than 600 nm, see Fig. 8b, McKnee et al., 2013) but may result in large deviations (e.g., up to 100% decrease in the NIR spectral range) of *a* values in relatively turbid waters (e.g., $a > 0.2$ m^{-1}) such as the Baltic/North Sea. Also, this issue is present when the proportional correction method of Zaneveld et al. (1994) is applied. Unlike the 'flat' baseline, the scattering residual of the proportional method is spectrally dependent but still relying in one reference wavelength in the NIR spectral range. Approximations justifying the use of the ‘flat’ (i.e., zero absorption signal in the NIR) and ‘proportional’ (i.e., wavelength-dependent scattering phase function) method are still in debate (McKnee et al., 2013). Lastly, the Monte Carlo correction method (McKee et al., 2008) has in general a better agreement (error <10%) with true *a* values as derived from an integrating cavity absorption meter. However, this approach may also have major uncertainties due to assumptions regarding optical coefficients (e.g., particulate backscattering ratio and volume scattering function) and changes on scattering efficiency due to factors related to the optical instrument (e.g., aging of the reflective tube of the absorption-attenuation meter) ~~by the inner wall of the reflective tube due to aging~~ (McKnee et al., 2013). Thus in conclusion, the resulting optical coefficients and mass-specific optical coefficients of particulates measured in SLE-SF waters may present large errors (i.e., > 50%) with respect to true values and at wavelengths longer than 550 nm. This bias is anticipated to be maximum (minimum) in UE (LE) locations.

4.2 Variability of ~~microphysical~~ physical and chemical ~~properties~~ characteristics of SPM

A striking finding in this study was the important weight contribution of relatively large particulates (i.e., >10 µm) to the total mass of SPM in UE waters. This phenomenon was likely attributed to the active resuspension of sediments associated with vertical mixing produced by tidal currents and winds (Yeats, 1988). Conversely, this effect was secondary in relatively deep waters of SF and LE where large and heavy particulates are rapidly removed from the water column and deposited along submarine canyons (Gagné et al., 2009). ~~Although~~ The chemical composition of size-fractioned SPM was not analyzed in this study. However~~,~~, ~~additional~~ additional correlations between ~~with~~ F_{SPM}^{PIM} and $F_{SPM}^{0.2\text{-}0.7\ \mu m}$ values suggest that mineral content of SPM increases as the contribution of particulates with a diameter smaller than 0.7~~10~~ µm ~~were richer in inorganic matter~~becomes larger (ρ_s = 0.30~~62~~, *P* = ~~<~~ 0.035~~01~~, N = 23). ~~with respect to particulates with a diameter greater than 10 µm~~. This finding ~~confirms~~ is consistent with previous studies in the SLE showing that relatively small (i.e., diameter ~2 µm) particulates ~~in the SLE~~ are mainly composed by ~~minerals~~ inorganic matter (Yeats, 1988; Gagné et al., 2009). In this contribution, a large proportion of particulates with a diameter above 50 µm and lower ξ values were typically found in LE locations. These results ~~also support~~go along with historical ~~observations~~ datasets ~~made during July and August~~ and showing a greater proportion of relatively large particulates (i.e., > 5 and < 50 µm) over the LE locations and during the same period of the year (Chanut and Poulet, 1982~~79~~).

4.3 Spatial variability of mass-normalized optical coefficients

In this study, a_{SPM}^* measurements in the visible and near-IR range had a large variability that was comparable to the range of values reported in the literature for temperate coastal waters (e.g., Mobile Bay, ~~River of La Plata,~~ Elbe Estuary, Gironde Estuary) (Stavn and Richter, 2008; Doxaran et al., 2009) (Table 4). This is remarkable given the large diversity of methodologies used by different research teams ~~to~~ for estimating~~e~~ a_{SPM}^* ~~and b_{SPM}^*~~ values. In general, the lowest a_{SPM}^* values (i.e., 0.01-0.02 m^2 g^{-1} at λ = 440 nm) commonly corresponded with samples obtained in very turbid environments (i.e., > 100

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g m^{-3}, Mississippi River and Delta, Gironde River~~, La Plata River~~) (Bowers and Binding, 2006; D'Sa et al. 2006; Doxaran et al., 2009). Notice that part of this decrease can be attributed to an incomplete removal of multiple scattering effects. Relative low a_{SPM}^* values have been linked to high POC/SPM (Wozniak et al., 2010) and chl/SPM concentration ratios, where chl means chlorophyll a concentration (Estapa et al., 2012). In this study, chl/SPM values are relatively high (up to as 2 10^{-3}) with respect to those reported in the literature (~10^{-3}) (D'Sa et al., 2006) and are consistent with low a_{SPM}^* estimates. ~~presented values as high as 2 10^{-3} that are comparable to relatively high ratios reported by D'Sa et al. (2006)~~.~~.~~ ~~Thus, it is suggested that some locations in our study area are characterized by relatively high POC/SPM as other turbid coastal environments such as adjacent waters to the Mississippi Delta (D'Sa et al. 2006).~~

A well-known mechanism explaining the general decrease of a_{SPM}^* in very turbid waters is related to packaging effects (Morel, 1974; Zhang et al., 2014). At higher turbidities, larger particulates contribute to PSD variations, thus as mean diameter of particles increases, the light absorption efficiency per averaged particle decreases (i.e., the interior of larger particles has a greater 'shading'). This could also explain the spatial differences of $a_{SPM}^*(440)$ in our study area where larger values corresponded with surface waters dominated by particles assemblages having a smaller mean diameter (e.g.,~~i.e.~~, UE and SF). In nearshore waters of California, Wozniak et al. (2010) demonstrated inverse relationships between $a_{SPM}^*(440)$ and the median particle diameter of~~for~~ inorganic- ~~-~~and organic-dominated assemblages. ~~Also and consistent with our previous discussion regarding particle composition, Wozniak et al. (2010) observed that POC/SPM was positively correlated with the median particle diameter.~~

Indirect size effects on $a_{SPM}^*(440)$ due to changes on iron content per particle have been discussed by Estapa et al. (2012) in environments where optical properties are dominated by NAP. In general, smaller particulates have a greater surface for adsorbing organic compounds where iron can accumulate (Mayer, 1994; Poulton and Raiswell, 2005). Thus, SPM fractions with small-sized~~er~~ particulates are expected to have an enhancement of $a_{SPM}^*(440)$ due to relatively high iron concentrations. This phenomenon could probably explain part of the ~~likely explained our higher~~ $a_{SPM}^*(440)$ variability in some locations of our study area where relatively high concentrations of iron bound to particulates have been measured (e.g., SF~~) regions with respect to LE waters where the water salinity range is 0-29 and 29-33.5, respectively (El Sabh, 1988). Indeed, relatively high concentrations of iron bound to particulates have been measured in surface waters of the Saguenay Fjord~~ (Yeats and Bewers, 1976; Tremblay and Gagné, 2009). ~~In coastal Louisiana and the lower Mississippi and Atchafalaya rivers, Estapa et al. (2012) found that magnitude of a_{SPM}^* within the UV (λ ~ 360-390 nm) and blue (λ ~ 400-450 nm) spectral range is commonly higher in freshwater with respect to marine samples. This difference was related to the greater concentration of particulate iron oxides and hydroxides derived from terrestrial sources in freshwater samples and later transport and reduction in marine environments. Notice that unlike our study, Estapa et al. (2012) used a different method for measuring a_{SPM}^* and based on absorbance changes inside an integrating spehere. Iron oxide and hydroxide minerals have a major light absorption within the spectral range of 400-450 nm due to the absorption bands of iron (Estapa et al., 2012). Pigmentation of mineral particulates due to iron hydroxides has been suggested to be a major factor increasing a_{SPM}^* (Babin and Stramski, 2004; Estapa et al., 2012). Unfortunately, no chemical determinations of iron hydroxides were performed during our study in~~

~~order to test these relationships. Likewise and and unlike optical measurements made by Estapa et al. (2012), the resolution of our ac-s measurements (~4 nm) did not allow a quantification of iron bound to particulates.~~

Similar to a_{SPM}^*, b_{SPM}^* values were highly variable between locations and within the range of measurements obtained in other environments (Table 4). In this study, the spectral variation b_{SPM}^* between regions showed a spectral flattening as particle assemblages become dominated by organic matter (i.e., LE). This finding is consistent with Wozniak et al. (2010) ~~measurements~~ determinations made in Imperial Beach, California.

4.4 Relationships between ~~Particle size~~PSD, particle ~~and~~ chemical composition ~~effects on~~and mass-specific optical coefficients

~~Correlations of ξ and F_{SPM}^{PIM} with mass-specific optical coefficients for different SPM size fractions were shown in Table 2.~~ For all size fractions of SPM, ξ was positively correlated with $a_i^*(440)$ (ρ_s up to 0.32, $P = 0.006$). This pattern suggests a higher absorption efficiency of relatively small-sized particulates. As previously discussed, these particulates have a greater light absorption per unit of particle mass due to a lesser role of shading effects~~ and presumably a greater iron enrichment~~. Since particle aggregates were altered during our experiments, the influence of particle density on mass-specific optical coefficients cannot be quantified as this effect is mainly observed in undisrupted marine aggregates (Slade et al. 2011; Neukermans et al., 2012, Neukermans et al 2016). However and based on Estapa et al. (2012) simulations, the impact of aggregation on a_{SPM}^* is anticipated to be small (i.e., ~10%) with respect to the spatial variability of a_{SPM}^* in SLE-SF waters (>500%).

In general, ξ was positively correlated with $b_i^*(550)$ (ρ_s up to 0.37, $P = 0.008$) and ~~pointed out as expected~~suggests an increase of scattering efficiency as particulates become smaller and the influence of packaging effects is less important. Notice that ξ correlations with $b_i^*(550)$ were greater with respect to $a_i^*(440)$ and more remarkable for relatively large-sized particulates. In Arctic waters, Reynolds et al. (2016) observed an increase on mass-specific particulate backscattering for mineral-rich particle assemblages that tend to exhibit steeper ~~size distributions~~PSDs. Although no particulate backscattering measurements were available in this study, Reynolds et al. (2016) highlight the importance of ~~relatively small-sized particulates~~PSD for driving variations on mass-specific optical coefficients linked to scattering processes.

~~In all cases~~A common pattern in all size fractions of SPM was the ~~,~~ ~~F_{SPM}^{PIM} had a~~ stronger correlation of F_{SPM}^{PIM} with $a_i^*(440)$ compared with $b_i^*(550)$ values~~, and these relationships were stronger when SPM was dominated by particulates with an intermediate size (i.e., 0.4-10 µm).~~. The enrichment of suspended particulates on inorganic matter and concomitant variations $a_i^*(440)$ may be ~~explained~~ attributed ~~by by a greater contribution of~~ to mineral-associated iron (Babin and Strasmki, 2004; Estapa et al., 2012) or/and organic-associated iron (Estapa et al., 2012).~~. to light absorption~~. Also, the combustion method used to measure PIM in our study could be another factor explaining the increased particle absorption in the blue range (Babin et al. 2003). ~~Iron can take many forms in mineral particulates (oxides, hydroxides, monosulfides) and can be deposited over the particle surface or be part of its internal structure (e.g., clays). Since the mean diameter of clay particles is less than 2 µm, the aforementioned F_{SPM}^{PIM}—$a_i^*(440)$ correlations were also likely affected by iron associated~~

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~~(adsorbed or structural) to other types of inorganic particulates that are characterized by larger dimensions.~~ In SF locations, reduced iron is mainly associated to dissolved organic compounds that can be strongly adsorbed to hydrous metal oxides (Deflandre et al., 2002). ~~Babin and Stramski (2004) obtained positive correlations between a_{SPM}^* and iron content of dust and soil particles suspended in seawater. Estapa et al. (2012) found a strong covariation between a_{SPM}^* values and dithionite-extractable iron content of oxides and hydroxides.~~

An important objection to correlations of ξ and F_{SPM}^{PIM} with mass-specific optical coefficients of SPM for different ~~SPM~~ size fractions was related to differences in terms of particle size range used to compute ξ and F_{SPM}^{PIM} and particle size classes derived by sequential filtration of water samples. More specifically, ξ is not representative of submicron particles less than 2 µm. Also, F_{SPM}^{PIM} is only a valid ~~particle composition~~ parameter for particles mostly larger than 0.7 µm. Thus, correlations ξ and F_{SPM}^{PIM} with mass-specific optical coefficients of 0.2-0.4 µm and 0.4-0.7 µm may only reflect indirect dependencies between mass-normalized optical coefficients of different size classes. This possibility (i.e., correlations between a_i^* or b_i^* values of different size classes) was confirmed *a posteriori* based on samples obtained in UE, LE and SF waters.

Lastly, it is important to discuss the potential bias on a_i^* and b_i^* determinations due to size fractionation and ~~a posteriori~~subsequent impact on correlations with respect to F_{SPM}^{PIM} and ξ values. No measurements of F_{SPM}^{PIM} and ξ were done in size fractions of SPM, thus it is difficult to compare ~~particulate size distribution~~ PSD and particle chemical composition changes before and after the size fractionation of the samples. Size fractionation is anticipated to cause retention of smaller particulates in membranes having a larger pore size. These primary particles will overestimate the weight of the filtered sample and underestimate the weight of the next filtration step consisting in a membrane having a smaller pore size. Since particle sieving begins with large-sized particles and finishes with small-sized particles, the magnitude of a_i^* and b_i^* for relatively large (small) particulates is likely to be under-(over-) estimated. Bias on mass of particulates for each~~of~~ size fraction~~s~~ was verified by comparing the sum of ~~masses~~ weights ~~for~~ of 0.7-10 µm and >10 µm fractions with the weight of~~total~~ an independent sample after ~~filtered~~ filtering it trough a GF/F ~~filter~~ membrane (i.e., 0.7 µm nominal pore size). In this case, t~~T~~he arithmetic average (median) of the relative bias for the whole ~~study area~~dataset was 29.7% (24.9%) or a 29.7% (24.9%) overestimation with respect to samples without a previous size fractionation. ~~of mass for particulates > 0.7 µm when total weight is computed based on sum of partial weights corresponding to different size fractions~~. An optimization scheme to adjust the mass for each size fractions (i.e. adjusting the various ~~masses~~ weights to sum up to the total mass filtered) was not attempted since we didn't filter ~~total~~ unfractionated samples through 0.2 or 0.4 µm membranes due to the sequential mode of our filtration. Thus, 'filtration weighting factors' for size fractions > 0.2 µm or > 0.4 µm could not be calculated.

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4.5 Optical proxies of ~~particle~~ SPM characteristics

In terms of fractioned mass, the size of particulates was the dominant variable driving changes on γ (ρ_s up to 0.53, P = 0.004). Conversely, the mineral content of SPM did not have a statistically detectable impact on γ at 95% confidence ~~interval~~level. In particular, the strongest ~~response~~ relationship betwen~~of~~ γ ~~to~~ and F_{SPM}^{i} ~~size effects~~ was ~~manifested~~ associated ~~for the mass fraction having~~to the fraction ~~the~~ having the smallest ~~particulates~~ particles (i.e., 0.2-0.4 µm). Despite the major effects of particle size classes on γ, values of γ were not clearly correlated with ξ ~~slopes~~values. In oceanic waters, ξ and γ values are expected to covary in a linear way for a specific range of refractive index and ξ (Boss et al., 2001; Twardowski et al., 2001). Our range of ξ values was within the natural variability reported in coastal and oceanic environments (ξ = 2-4.5) (Reynolds et al., 2010; Neukermans et al., 2012; Xi et al., 2014). Also, the magnitude of γ in our samples (0.29-2.22 nm^{-1}) was within the range of values that characterize oceanic environments (0.2-2) (Twardowski et al., 2001, Boss et al., 2013). Unlike oceanic waters, the poor correspondence between ξ and γ values in this study was linked to different ~~responses~~ relationships between~~of~~ γ, ξ ~~spectral c_{SPM} and particle size distribution slopes~~ and~~to~~ changes of two non-covarying optical contributions: minerals and phytoplankton. Also, the reduced number of sampling locations and the geographic variability of ξ-γ relationships were additional factors likely explaining the lack of ~~a general functionality~~ correlation for the study area. Lastly, ξ and γ were not substantially correlated in our samples due to deviations on Mie-based models (e.g, absorbing spheres) of γ as a function of ξ (Twardowski et al., 2001). Indeed during our surveys, high absorbing particulates were present in SLE-SF waters.

The variability of *Svis* values in this study was relatively high (~10-fold) with respect to other littoral environments (1.3-fold, *Svis* = 0.009-0.0113 nm^{-1}) (Estapa et al., 2012). *Svis* was inversely related to $a_{SPM}^{*}(440)$ in surface waters of the SLE having a major marine influence (i.e., salinity range = 29-33.5, LE locations) (ρ_s = -0.55, P = 0.04, N = 14). In coastal waters of the Gulf of Mexico, Estapa et al. (2012) found that $a_{SPM}^{*}(440)$ (*Svis*) tends to increase (decrease) in iron-enriched particle assemblages of marine samples. Whether this phenomenon is also occurring in the SLE is unknown and should be investigated in future studies.

~~**No statistically significant correlations at 95% confidence level were computed between F_{SPM}^{PIM} and *Svis* (ρ_s = -0.06, P = 0.781).. This is counterintuitive as F_{SPM}^{PIM} is strongly correlated to $a_i^{*}(440)$ (see Table 2) and presumably iron content of particulates. This discrepancy might be related to the inclusion of freshwater or brackish samples into the correlation analysis as *Svis* is only expected to change with extractable-iron of measurements made in marine samples (Estapa et al., 2012). Additional correlations between F_{SPM}^{PIM} and *Svis* values measured in LE locations confirmed this hypothesis (ρ_s = -0.62, P = 0.018, N = 14) and suggest a direct link between PIM content of SPM and $a_i^{*}(440)$ variations. Likewise as expected, *Svis* was inversely related $a_{SPM}^{*}(440)$ in marine waters of the SLE (ρ_s = -0.55, P = 0.04). Since $a_{SPM}^{*}(440)$ tends to increase in iron-enriched particulates (Estapa et al., 2012), lower *Svis* values in LE locations are likely associated with mineral particle assemblages having a greater proportion of iron.**~~

5 Conclusions

~~5 Conclusions~~

The measure of mass-specific optical coefficients of SPM is essential for developing optical inversions for mapping biogeo-chemical components in surface waters and improvinges our understanding regarding the origin of optical signatures in remote sensing studies~~ and map biogeo-chemical components in surface waters~~. In this contribution, we presented for the first time, mass-specific scattering and absorption coefficients of size-~~–~~fractioned SPM in estuarine waters of the Saint Lawrence River and a major SLE tributary, the Saguenay Fjord.

Despite the intrinsic variability of weight-normalized optical coefficients due to variations of physical and chemical properties of particle assemblages~~le micro-physical attributes~~, ~~the following~~the following patterns were identified: 1)~~: 1.~~ the mass-specific absorption coefficient of different size fractions of SPM was preferentially ~~influenced~~ related ~~by~~ to changes on~~in~~ particle chemical composition as inferred from changes on F_{SPM}^{PIM} and at a wavelength of 440 nm~~;~~, 2) the magnitude of ~~ξ2. changes on PSD~~ had a ~~larger impact~~stronger correlation with~~on~~ b_{iSPM}^{*}(550) ~~with respect~~compared to a_{iSPM}^{*}(440) ~~variation~~, and 3) the magnitude of *Svis* was inversely correlated with a_{SPM}^{*}(440) in areas having a larger marine influence (i.e., lower estuary). ~~s, and 3. regional variations on *Svis* are likely suggesting iron-enrichment of suspended particulates in LE waters..~~ In summary, these relationships will be useful for investigating local and regionally-limited ~~functionalities~~ biogeo-optical~~and~~ properties of SPM. Thus, additional research based on~~ Without separate independent studies of~~ true optical properties of PSD will be needed in order to propose more general relationships that can be applied to other littoral environments.~~, the application of the relationships to other littoral environments will remain problematical.~~

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Table 1. Summary of acronyms

Abbreviation	Definition	Unit
SLE	St. Lawrence Estuary	
UE	Upper e~~E~~stuary	
SF	Saguenay Fjord	
LE	Lower e~~E~~stuary	
~~CSPM~~	~~Concentration of suspended particulate matter~~	~~$g\ m^{-3}$~~
POM	Particulate organic matter	
PIM	Particulate inorganic matter	
PSD	Particle size distribution	
F_{SPM}^{i}	Contribution of size fraction i to total mass of SPM	dimensionless
F_{SPM}^{j}	Contribution of chemical fraction j to total mass of SPM	dimensionless
NAP	Non-algal particulates	
CDOM	Chromophoric dissolved organic matter	
λ	Light wavelength	nm
a_{SPM}	Absorption coefficient of total SPM	m^{-1}
b_{SPM}	Scattering coefficient of total SPM	m^{-1}
c_{SPM}	Particulate beam attenuation coefficient of total SPM	m^{-1}
a_{SPM}^{*}	Mass-specific absorption coefficient of total SPM	$m^{2}\ g^{-1}$
b_{SPM}^{*}	Mass-specific scattering coefficient of total SPM	$m^{2}\ g^{-1}$

ξ	Power-law exponent of the exponential fit to the differential particle size distribution~~Differential Junge slope of particle size distribution~~	Number of particulates per µm
D	Diameter of a volume-equivalent sphere at mid point of size class	µm
V(D)	Volume concentration at size class D	µL L^{-1}
N(D)	Particle number concentration at size class D	m^{-3}
N'(D)	Particle number density at size class D	m^{-3} µm^{-1}
γ	Spectral slope of particulate beam attenuation coefficient	nm^{-1}
Svis	Spectral slope of mass-specific particulate absorption coefficient within the visible spectral range	nm^{-1}

Table 2. Particle size and chemical composition effects on mass-specific optical coefficients. Spearman rank correlations for a_i^* and b_i^* are computed at a wavelength of 440 and 550 nm, respectively.

Mass-specific Optical fraction	ξ	F_{SPM}^{PIM}
$a_{0.2-0.4\ \mu m}^*$	0.32 *	0.31 *
$a_{0.4-0.7\ \mu m}^*$	0.28 *	0.50 **
$a_{0.7-10\ \mu m}^*$	0.26 *	0.49 *
$a_{>10\ \mu m}^*$	0.31 *	0.44 *
$b_{0.2-0.4\ \mu m}^*$	0.15	-0.17 *
$b_{0.4-0.7\ \mu m}^*$	0.05	-0.06
$b_{0.7-10\ \mu m}^*$	0.23 *	0.42 *
$b_{>10\ \mu m}^*$	0.37 *	0.26 *

Table 3. Correlation of optical proxies with mass-derived size and chemical fractions of SPM. Spearman rank correlations based on 23 samples.

Mass fraction ~~of particulates~~	γ	*Svis*
F_{SPM}^{PIM}	-0.34	-0.06
$F_{SPM}^{0.2\text{-}0.4\ \mu m}$	0.53*	0.49**
$F_{SPM}^{0.4\text{-}0.7\ \mu m}$	-0.43*	-0.49**
$F_{SPM}^{0.7\text{-}10\ \mu m}$	-0.38*	-0.30*
$F_{SPM}^{>10\ \mu m}$	0.13	0.19

Table 4. Mass-specific optical coefficients of suspended particulates for different littoral environments. Acronyms and units are defined in Table 1.

Location	λ	a_{SPM}^{*}	b_{SPM}^{*}	[~~C~~SPM]^{k}~~^{i}~~	References
UE	440	0.01 – 0.25[a]	0.01 – 1.06 [a]	2.28 – 30.6	This study
	488	0.01 – 0.14	0.01 – 0.97		
	556	0.01 – 0.06	0.01 – 0.86		
	665	0.01 – 0.02	0.01 – 0.73		
	708	0.01 – 0.012	0.01 – 0.68		
SF	440	0.32 - 0.73	0.20-0.56		
	488	0.17 - 0.39	0.18-0.49		
	556	0.08 – 0.17	0.15-0.42		
	665	0.02 – 0.04	0.13 – 0.34		
	708	0.01 – 0.02	0.12 – 0.31		
LE	440	0.03 – 0.07	0.04 – 0.22		
	488	0.02 – 0.04	0.04 – 0.21		
	556	0.01 – 0.02	0.04 – 0.19		
	665	0.003 – 0.006	0.04 – 0.18		

	708	0.015 – 0.002	0.04 – 0.17		
Elber River,	650	0.001 – 0.020^{b}		0.5-10	Röttgers et al. (2014)
German Bight,	750	0.001 – 0.019			
Baltic Sea, New Caledonia lagoon	850	0.001 – 0.014			
Monterey Bay, US	532		0.46 – 2.54^{c}	0.11 – 2.37	Zhang et al. (2014)
Mobile Bay, US	532		0.40 – 1.78	0.26 – 7.36	
Mobile Bay,	440	0.44 – 1.95^{d}		0.23-25.32	Stavn and Richter (2008)
Southwest Pass, US	488	0.41 – 1.89			
	550	0.40 – 1.80			
	676	0.36 – 1.63			
	715	0.34 – 1.61			
Coast of New Jersey,	440			0.44 – 6.6	Snyder et al. (2008)
Monterey Bay,	488				
Great Bay	556				
Mobile Bay	665	0.05 ± 0.01^{d} (arithmetic			

		mean ± standard deviation)			
Irish sea, UK	665		0.08 – 0.45[e]	1.9 – 26.5	Binding et al. (2005)
Irish sea, UK	443	0.062 ± 0.013[f]	0.17 – 0.19	1.6 – 50	Bowers and Binding (2006)
	490		0.20 – 0.22		
	555		0.20 – 0.24		
	665		0.14 – 0.15		
Coast off Europe and French Guyana	676		0.63 – 2.07[g]	1.2 – 82.4	Neukermans et al. (2012)
Elbe Estuary, Germany	555	0.05 – 0.07[d]	0.35 – 0.47	73.5 – 294.2	Doxaran et al. (2009)
	715	0.01 – 0.03	0.32 – 0.44		
Gironde Estuary, France	555	0.02 – 0.06	0.28 – 0.50	21.9 – 344.1	
	715	0.01 – 0.02	0.27 – 0.45		
Coastal Louisiana and lower Atchafalaya and	440	0.056 ± 0.012[g] (0.05 - 0.065)			Estapa et al. (2012)

Mississsippi Rivers					
	488	0.035 - 0.05			
	556	0.25 - 0.35			
	665	0.125 - 0.02			
West of Mississippi Delta	443	0.01 2 -0.079 [d]			D’Sa et al. (2006)
Imperial Beach, California	440	0.03 – 0.1[h]	0.1 - 1.2	3-90	Wozniak et al. (2010)
	488	0.02 – 0.08	0.18 - 0.9		
	556	0.01 – 0.03	0.2 - 0.9		
	665	0.004 - 0.02	0.2 - 0.8		
	708	0.001 - 0.02	0.2 - 0.8		

[a]ac-s measurements and sum of weights of SPM size fractions 0.2-0.4 µm, 0.4-0.7 µm, 0.7-10 µm and >10 µm, [b]integrating sphere coupled to spectrophotometer for suspensions and pad-technique, SPM weight based on GF/F (pore size = 0.7 µm) and nucleopore Whatman (pore size = 0.4 µm) filters, [c]Multispectral volume scattering meter and optical models for different particle subpopulations with assymetrical shape, [d]ac-9 measurements and SPM weight based on GF/F filters, [e]Irradiance meter PRR600 and optical models for estimating inherent optical properties and SPM weight based on GF/F filters, [f]comparable to [e]but pad-technique for estimating absorption coefficients of SPM, [g]comparable to [d] but using ac-s measurements, [g] comparable to [b] but using only suspensions and weight based on GF/F filters, [h]comparable to [b] but using only GF/F filters for SPM weight, [k]~~[i]~~concentration of SPM in g m^{-3} and for particulates retained in glass-fiber filters with a pore size of 0.7 µm.~~concentration of SPM for particulates >0.7 µm.~~

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Figure captions

Figure 1. Study area. UE (red~~green~~ triangles), SF (green circles) and LE (blue rectangles)~~ and SF (red circles)~~. GSL is the Gulf of St. Lawrence.

Figure 2. Spectral variation of mass-specific optical coefficients for total SPM. (a) a_{SPM}^* ~~particulate absorption at λ = 440 nm~~ and~~,~~ (b) b_{SPM}^* ~~particulate scattering at λ = 550 nm~~. Each bar is the arithmetic average ± 2 standard errors as computed for SLE-SF (black circles), UE (red circles), SF (green circles) and LE (blue circles).~~different regions of the study area.~~ The number~~Number~~ of observations for UE, SF and LE are 3, 5 and 15 respectively.

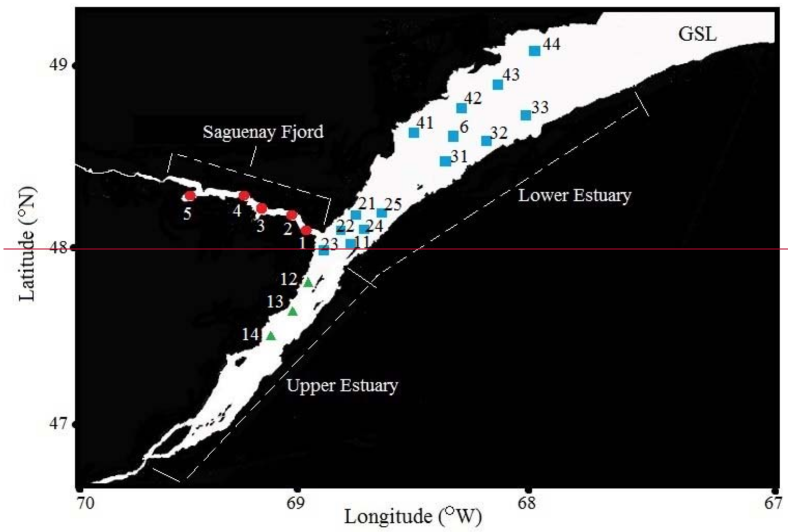
Figure 3. Spectral variation of mass-specific absorption coefficients for different size classes of suspended particulates. (a) 0.2-0.4 µm, (b) 0.4-0.7 µm, (c) 0.7-10 µm and (d) >10 µm. ~~Curves presenting negative values at some wavelengths are not depicted. SF (black line), UE (red line) and LE (blue line).~~Color coding of symbols idem as Fig. 2. Curves presenting negative values at some wavelengths are not depicted.

Figure 4. Spectral variation of mass-specific scattering coefficients for different size classes of suspended particulates. Size classes and color coding of symbols idem as Fig. 3. Curves presenting negative values at some wavelengths are not depicted.

~~Symbols of size classes idem as Fig. 3. Curves presenting negative values at some wavelengths are not depicted~~

Figure 5. Spectral variation of m~~M~~ass-specific optical coefficients ~~for size fractions~~ of SPM averaged over the entire study area ~~and as a function of wavelength~~. (a) a_i^* and (b) b_i^*. ~~particulate absorption, (b) particulate scattering~~. Each bar is the arithmetic average ± 2 standard errors as computed for the size fractions 0.2-0.4 µm (solid symbol) and >10 µm (empty symbol)~~s. as computed over the whole study area~~.

~~Figure 6. Subregional variation of mass-specific optical coefficients for size fractions of SPM . (a) particulate absorption at λ = 440 nm, (b) particulate scattering at λ = 550 nm. Each bar is the arithmetic average ± 2 standard errors as computed for each spatial domain.~~


GSL
44
43
42
33
41
6
32
31
Saguenay Fjord
Lower Estuary
5
4
3
2
1
23
22
21
25
24
11
12
13
14
Upper Estuary
49
48
47
70
69
68
67
Latitude (°N)
Longitude (°W)

Field Code Changed

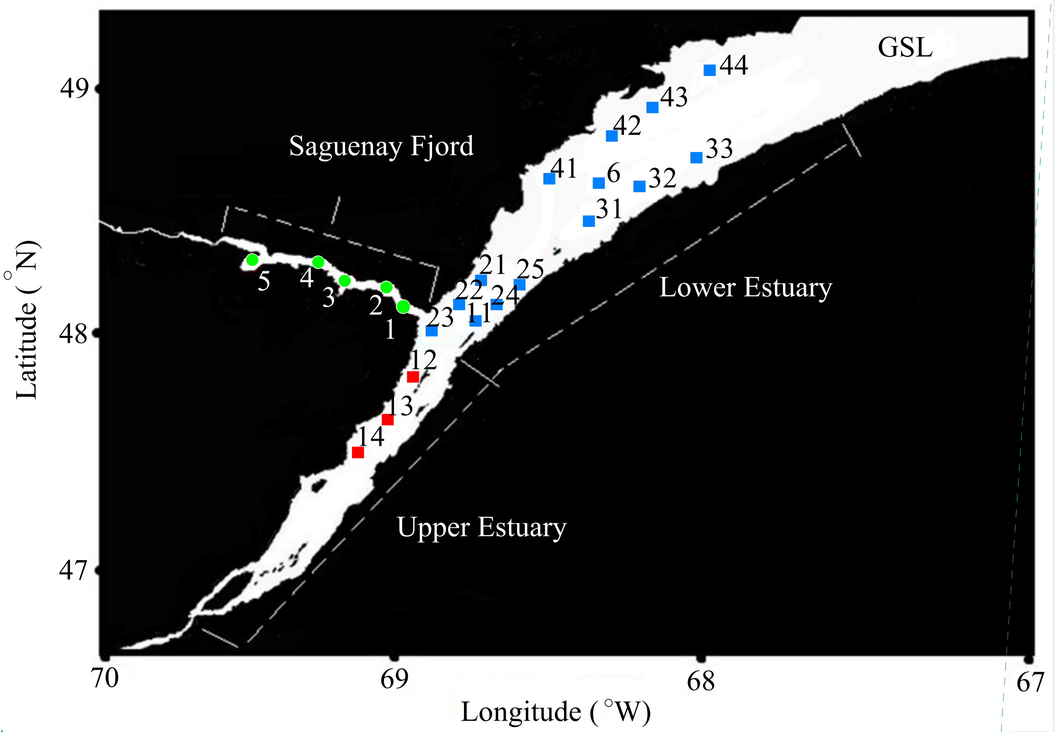
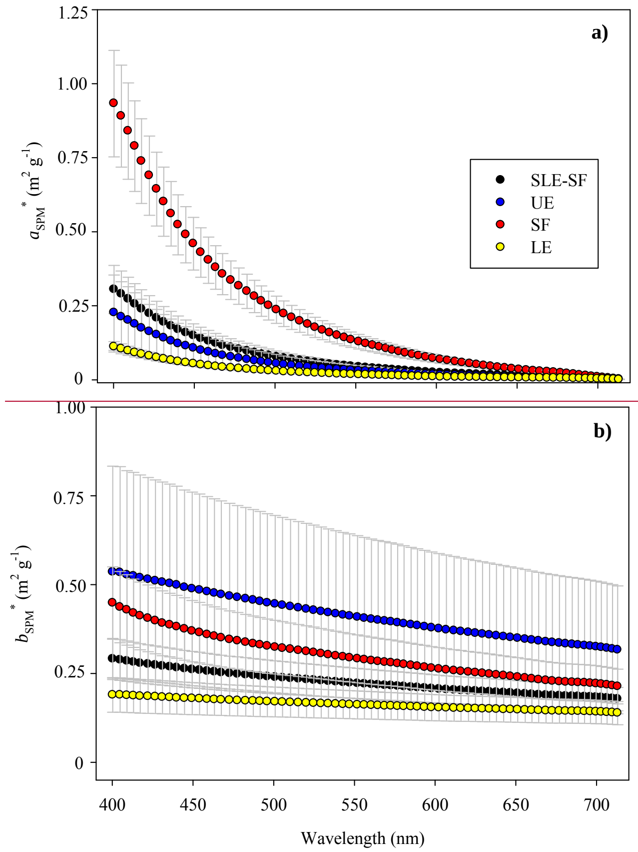


fig. 1


a)
b)
a_{SPM}^{*} (m^2 g^{-1})
b_{SPM}^{*} (m^2 g^{-1})
SLE-SF
UE
SF
LE
1.25
1.00
0.75
0.50
0.25
0
Wavelength (nm)
400
450
500
550
600
650
700

Field Code Changed

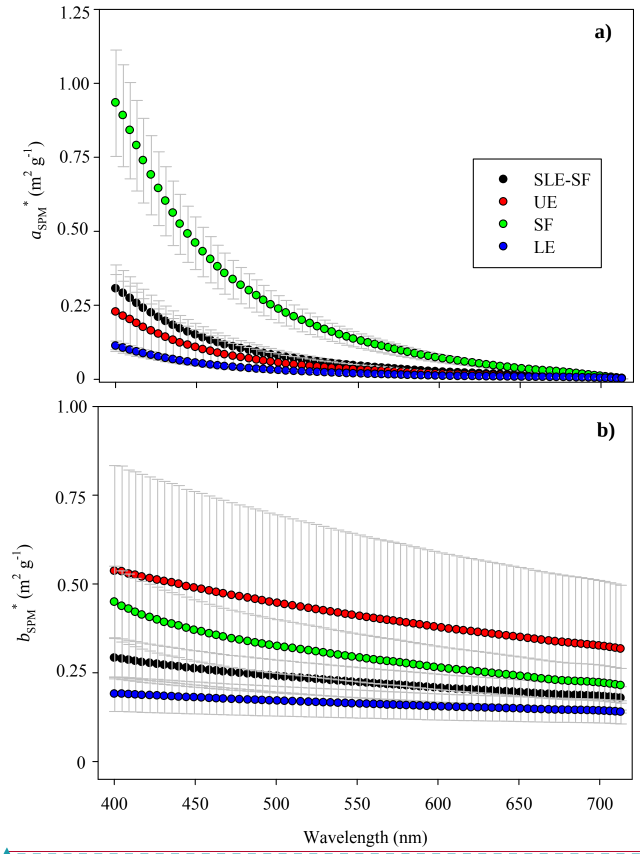
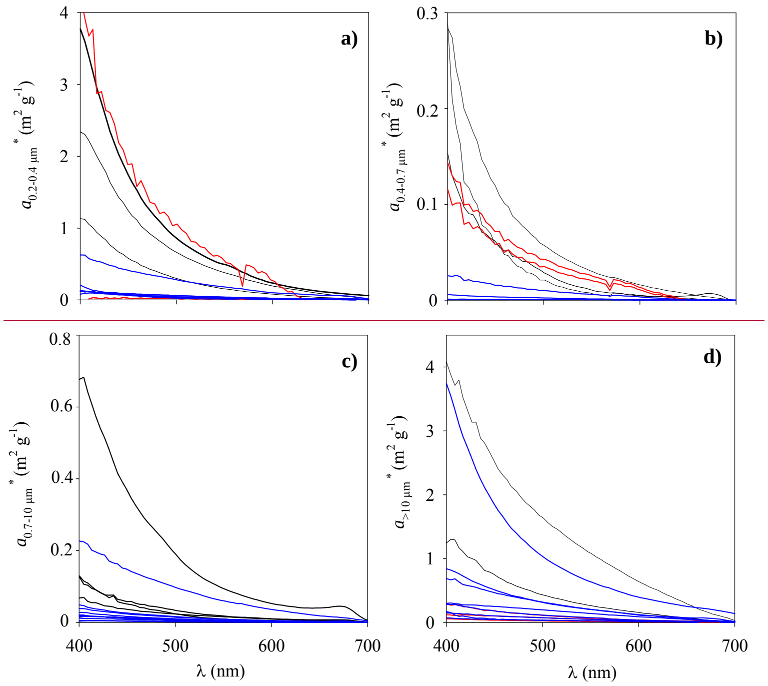


Fig. 2

5


a)
b)
c)
d)
$a_{0.2\text{-}0.4\ \mu m}^{*}$ (m^2 g^{-1})
$a_{0.4\text{-}0.7\ \mu m}^{*}$ (m^2 g^{-1})
$a_{0.7\text{-}10\ \mu m}^{*}$ (m^2 g^{-1})
$a_{>10\ \mu m}^{*}$ (m^2 g^{-1})
0
1
2
3
4
0
0.1
0.2
0.3
0
0.2
0.4
0.6
0.8
0
1
2
3
4
400
500
600
700
400
500
600
700
λ (nm)
λ (nm)

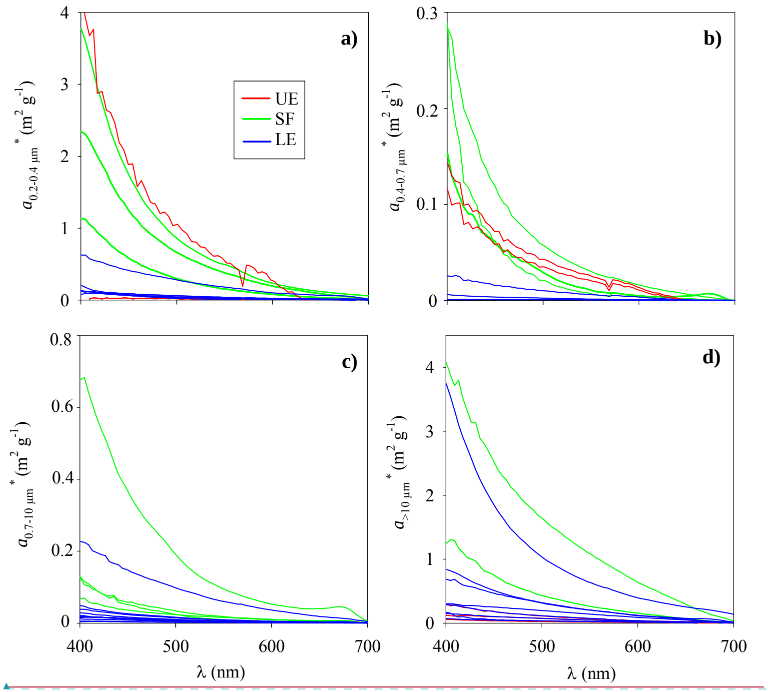
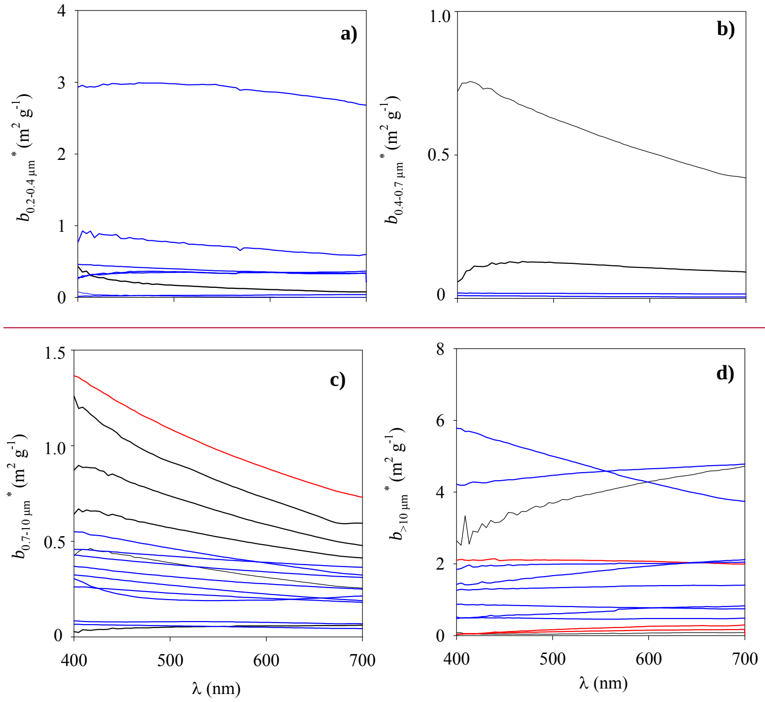


Fig. 3

Field Code Changed


a)
b)
c)
d)
4
3
2
1
0
1.0
0.5
0
1.5
1.0
0.5
0
8
6
4
2
0
400
500
600
700
$b_{0.2\text{-}0.4\,\mu m}{}^{*}$ (m^2 g^{-1})
$b_{0.4\text{-}0.7\,\mu m}{}^{*}$ (m^2 g^{-1})
$b_{0.7\text{-}10\,\mu m}{}^{*}$ (m^2 g^{-1})
$b_{>10\,\mu m}{}^{*}$ (m^2 g^{-1})
λ (nm)
λ (nm)

Field Code Changed

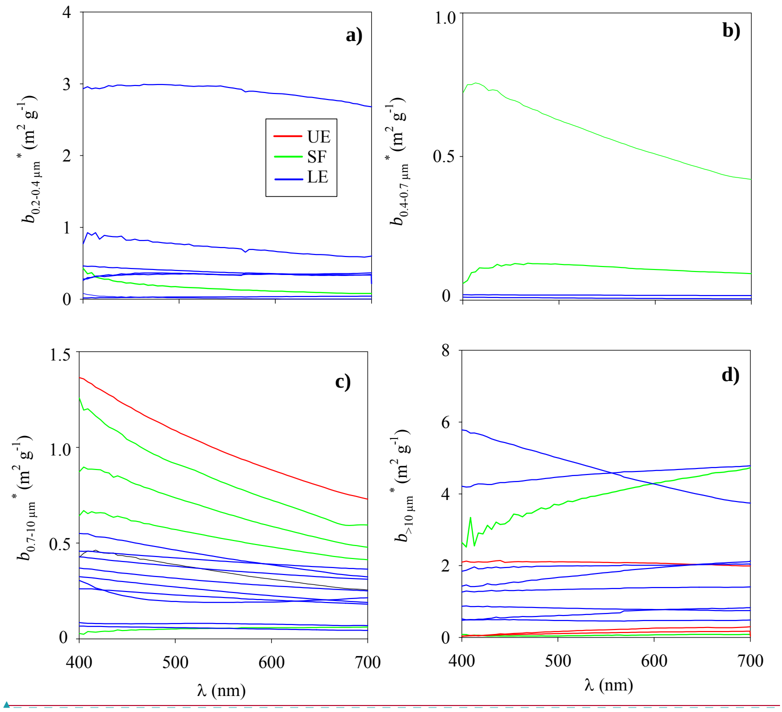


Fig. 4

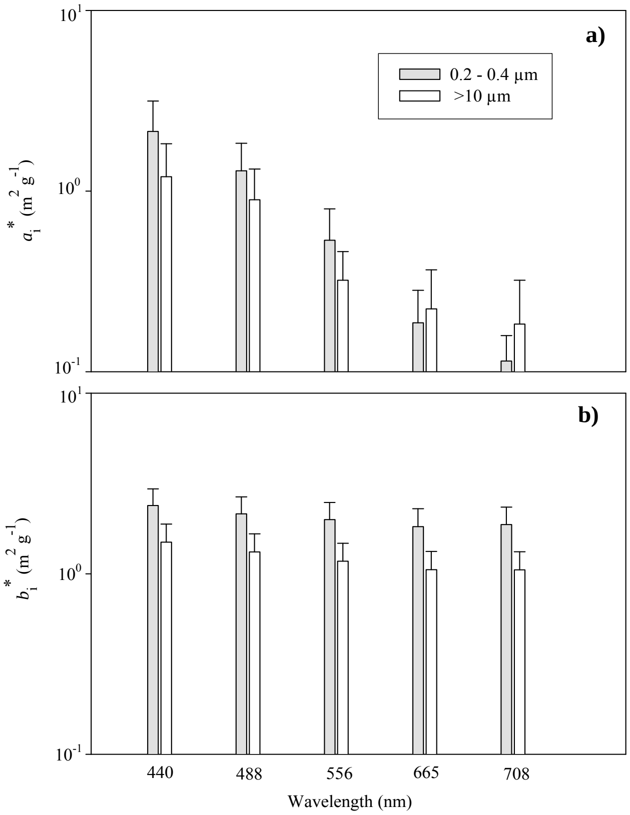
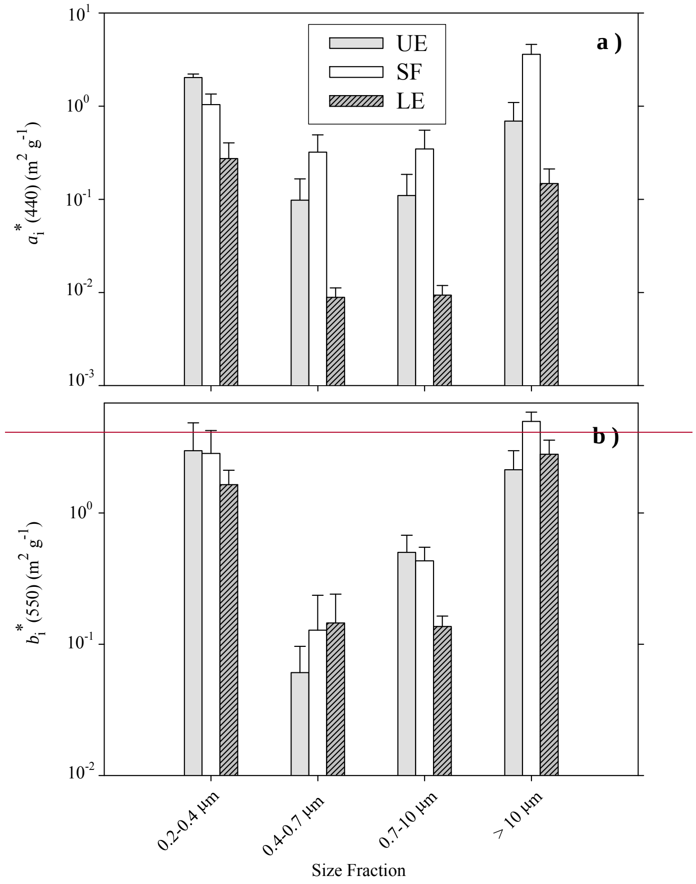
10¹
10⁰
10⁻¹
a)
0.2 - 0.4 µm
>10 µm
a_i^* (m² g⁻¹)
b)
b_i^* (m² g⁻¹)
440
488
556
665
708
Wavelength (nm)

fig. 5

5


a)
b)
UE
SF
LE
a_i^* (440) ($m^2\ g^{-1}$)
b_i^* (550) ($m^2\ g^{-1}$)
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^0
10^{-1}
10^{-2}
0.2-0.4 µm
0.4-0.7 µm
0.7-10 µm
> 10 µm
Size Fraction

~~Fig. 6~~