

October, 19, 2017

**Dear Dr. Emmanuel Boss**

**Editor Associate**

**Biogeosciences**

The english style of the manuscript was reviewed by a native english speaker. Figure 6 was removed and the text was shortened. Speculations were removed.

Thank you again for your support and advice during the entire review.

My best regards,

A handwritten signature in black ink, appearing to read 'M. Montes', is written over a thin horizontal line.

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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10 | **Abstract.** Mass-specific absorption ( $a_i^*(\lambda)$ ) and scattering ( $b_i^*(\lambda)$ ) coefficients were derived for four size fractions ( $i = 0.2$ -  
0.4  $\mu\text{m}$ , 0.4-0.7  $\mu\text{m}$ , 0.7-10  $\mu\text{m}$ , and  $>10 \mu\text{m}$ ,  $\lambda =$  wavelength in nm) of suspended particulate matter (SPM) and with  
samples obtained from surface waters (i.e., 0-2 m depth) of the Saint Lawrence Estuary and Saguenay Fjords (SLE-SF)  
15 | during June of 2013. For the visible-near-Infrared spectral range (i.e.,  $\lambda = 400$ -710 nm), mass-specific absorption  
coefficients of total SPM (i.e., particulates  $> 0.2 \mu\text{m}$ ) (hereafter  $a_{\text{SPM}}^*$ ) had low values (e.g.,  $\leq 0.01 \text{ m}^2 \text{ g}^{-1}$  at  $\lambda = 440$  nm) in  
areas of the lower estuary dominated by particle assemblages with relatively large mean grain size and high particulate  
organic carbon and chlorophyll a per unit of mass of SPM. Conversely, largest  $a_{\text{SPM}}^*$  values (i.e.,  $> 0.05 \text{ m}^2 \text{ g}^{-1}$  at  $\lambda = 440$   
nm) corresponded with locations of the upper estuary and SF where particulates were mineral-rich and/or their mean  
20 | diameter was relatively small. The variability of two optical proxies (the spectral slope of particulate beam attenuation  
coefficient and the mass-specific particulate absorption coefficient, hereafter  $\gamma$  and  $S_{\text{vis}}$ , respectively) with respect to changes  
in particle size distribution (PSD) and chemical composition was also examined. The slope of the PSD had a larger  
correlation with  $b_i^*$  estimates computed at a wavelength of 550 nm (Spearman rank correlation coefficient  $\rho_s$  up to 0.37) as  
opposed to  $a_i^*$  estimates derived at a wavelength of 440 nm ( $\rho_s$  up to 0.32). Conversely, the contribution of particulate  
inorganic matter to total mass of SPM ( $F_{\text{SPM}}^{\text{PIM}}$ ) had a stronger correlation with  $a_i^*$  coefficients at a wavelength of 440 nm ( $\rho_s$   
up to 0.50). The magnitude of  $\gamma$  was positively related to  $F_{\text{SPM}}^i$  or the contribution of size fraction  $i$  to the total mass of SPM  
( $\rho_s$  up to 0.53 for  $i = 0.2$ -0.4  $\mu\text{m}$ ). Also, the relation between  $\gamma$  and  $F_{\text{SPM}}^{\text{PIM}}$  variability was secondary ( $\rho_s = -0.34$ ,  $P > 0.05$ ).  
Lastly, the magnitude of  $S_{\text{vis}}$  was inversely correlated with  $a_{\text{SPM}}^*(440)$  ( $\rho_s = -0.55$ ,  $P = 0.04$ ) and  $F_{\text{SPM}}^{\text{PIM}}$  ( $\rho_s = -0.62$ ,  $P =$   
0.018) in sampling locations having a larger marine influence (i.e., lower estuary).

## 1 Introduction

The distribution of suspended particulate matter (SPM) (Table 1) in coastal and estuarine environments has a major influence on biogeochemical processes (e.g., phytoplankton blooms) (Guinder et al., 2009), ecosystem structure (e.g., food web) (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 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).

10 The 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  
15 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).

20 Thus, optical remote sensing algorithms for estimating SPM are region-specific and generally less accurate when applied to unknown littoral environments. This highlights the need for a better understanding 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 particle size distribution (PSD) and/or chemical  
25 composition of SPM based on optical parameters: (1) optical proxies (e.g., the spectral slope of particulate beam attenuation coefficient,  $\gamma$ , the spectral slope of mass-specific absorption coefficient,  $S_{vis}$ , and particulate backscattering/scattering ratio) (Boss et al., 2001; Twardowski et al., 2001; Loisel et al., 2006; Estapa et al., 2012), (2) mass-specific optical coefficients (e.g., mass-specific particulate scattering, backscattering and beam attenuation coefficients) (Bowers et al., 2009; Neukermans et al., 2012), (3) particulate volume scattering functions (Zhang et al., 2014), and (4) water leaving polarized  
30 reflectance (Loisel et al., 2008).

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 (e.g., PSD) in these waters is crucial for studying regional climate effects on coastal erosion

and occurrence of harmful algae blooms. However, in order to accomplish this task it is essential to know how mass-specific optical coefficients of suspended particulates are influenced by particle composition and size distribution changes. To our knowledge, mass-specific absorption and scattering coefficients of different SPM size fractions have never been reported in the literature even though it has a potential application in biogeo-optical modeling and biogeochemical studies regarding the dynamics of trace metals, sediment transport and primary productivity models.

This study has three main objectives: (1) to characterize the mass-specific absorption ( $a_i^*(\lambda)$ ) and scattering ( $b_i^*(\lambda)$ ) coefficients of four size fractions of SPM ( $i = 0.2-0.4 \mu\text{m}$ ,  $0.4-0.7 \mu\text{m}$ ,  $0.7-10 \mu\text{m}$ , and  $>10 \mu\text{m}$ ,  $\lambda =$  wavelength in nm) at different locations of the SLE-SF during spring conditions, (2) to establish relationships between mass-specific optical coefficients and characteristics of particle assemblages related to PSD and mineral content of SPM, and (3) to examine the correlation between optical proxies  $\gamma$  and  $S_{vis}$ , and variables linked to PSD and chemical composition of SPM.

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 larger than  $0.2 \mu\text{m}$ ) are calculated at different regions 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, relationships between mass-specific optical coefficients of different SPM size fractions and parameters related to PSD and mineral-content of suspended particulates are investigated. Lastly in the third section, relationships between optical proxies  $\gamma$  and  $S_{vis}$  and 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 diffuse light attenuation of SLE waters (Nieke et al., 1997). This is 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. Nieke et al. (1997) reported high values (up to  $3 \text{ m}^{-1}$ ) of particulate beam attenuation coefficients ( $c_{SPM}$ ) and inverse relationships between salinity,  $c_{SPM}$ , and CDOM absorption coefficients ( $a_{CDOM}$ ) based on measurements done during summer of 1990.

Larouche and Boyer-Villemare (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  $5.8 \text{ m}^{-1}$  at  $\lambda = 412 \text{ nm}$ ) along the Saguenay Fjord.

Historical studies performed during summer of 1975 suggest that size distribution of SPM differs between UE, LE and SF sub-regions (Poulet et al., 1986). Based on surface samples, Poulet et al. (1986) found a dominance of relatively 'small-sized' (i.e., mode diameter < 10  $\mu\text{m}$ ) and relatively 'large-sized' (i.e., mode diameter > 30  $\mu\text{m}$ ) particulates over the UE and the mouth of the SLE, respectively. Conversely, particulates having an intermediate size were characteristic of sampling locations situated between the mouth of the Saguenay Fjord and the mouth of the SLE. In the surface waters of SF and during spring, Chanut and Poulet (1982) found that SPM is commonly composed of very small particles (i.e., 2-3  $\mu\text{m}$ ). Several investigations point out that suspended particulates in the SLE-SF regions are principally composed of inorganic matter (D'Anglejan and Smith, 1973; Larouche and Boyer-Villemare, 2010; Mohammadpour et al., 2015). This mineral contribution may vary between 60 and 95% of dry weight depending on the geographic location and period of the year (Yeats, 1988; Larouche and Boyer-Villemare, 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 attributes.

## 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 except for site 6 where 2 measurements were made during June 3 and 6 of 2013. Surface samples (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 study location, optically-derived PSDs of unfractionated water samples, and optical properties of different size fractions of SPM were determined onboard of the ship.

## 2.3 Biogeochemical analysis

Size fractionation of SPM was done after sequentially filtering the original samples (i.e., volume = 12 L) through pre-weighted membranes having a diameter of 47 mm and a pore size of 10  $\mu\text{m}$  (Whatman, polycarbonate), 0.7  $\mu\text{m}$  (GF/F, Whatman, glass fiber), 0.4  $\mu\text{m}$  (Whatman, polycarbonate), and 0.2  $\mu\text{m}$  (Nucleopore, polycarbonate). The contribution of size fraction  $i$  to the total mass of SPM ( $F_{\text{SPM}}^i$ ,  $i = 0.2\text{-}0.4 \mu\text{m}$ ,  $0.4\text{-}0.7 \mu\text{m}$ ,  $0.7\text{-}10 \mu\text{m}$ , and  $>10 \mu\text{m}$ ) was computed by normalizing the weight of the fraction  $i$  by the sum of weights derived from each size fraction. The contribution of PIM to total mass of SPM ( $F_{\text{SPM}}^{\text{PIM}}$ ) was only computed for particulates with a grain size greater than 0.7  $\mu\text{m}$  (i.e., after filtering the original unfractionated sample through a GF/F filter membrane). In this case, the mass of PIM and particulate organic matter (POM) was assumed to be negligible for particulates with a diameter smaller than 0.7  $\mu\text{m}$ . 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  $\mu\text{m}$ ) to PIM and POM. The mass of different SPM fractions was calculated based on pre-weighted

filters. At the end of each filtration, sample filters were rinsed with deionized water to remove sea salts. PIM was obtained after removing the organic mass 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 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  $\pm 1$  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. Notice that error in POM mass estimates was slightly greater than that associated with PIM mass estimates (18.2%).

#### 2.4 Optical measurements

The absorption and beam attenuation of unfractionated and size-fractionated water samples were measured by using an absorption-beam attenuation meter (ac-s, WetLabs,  $\lambda = 400.3-747.5$  nm, average spectral resolution = 4 nm, path-length = 10 cm, precision  $\pm 0.001$  m<sup>-1</sup>). In order to minimize the presence of bubbles, a pump (ISMATEC MCP-Z) was used to gently circulate the samples during the measurements. Spikes on the raw signal associated with bubbles were removed by visual inspection. The effect of scattering on the absorption measurements was minimized by applying a flat baseline at a reference wavelength of 715 nm (Bricaud and Stramski, 1990). This approximation implies no absorption at 715 nm and may result in anomalous low absorption values within the red and near-Infrared (NIR) spectral range when optical measurements are done in relatively turbid waters (i.e., absorption coefficient  $> 0.2$  m<sup>-1</sup>) (McKee et al., 2013). Also, these deviations are present when the proportional correction method (i.e., scattering correction directly related to magnitude of spectral attenuation coefficient) is applied (Zaneveld et al., 1994; Röttgers et al., 2013). Lastly, in situ calibrations were performed by using deionized water (Barnstead NANO purewater purification unit) as a reference (Twardowski et al., 1999). Pure water contribution was subtracted from absorption and beam attenuation measurements and resulting values were corrected for water temperature and salinity variations (Sullivan et al., 2013). Spectral values of  $a_{SPM}$  in m<sup>-1</sup> were derived from unfractionated samples by subtracting the contribution of CDOM to the absorption measurements. The absorption due to CDOM was determined after pre-filtration of size-fractionated samples through a membrane having a pore size of 0.2  $\mu$ m (nucleopore, Whatman). Similar to  $a_{SPM}$  calculations,  $c_{SPM}$  values were computed based on unfractionated samples after subtracting CDOM contributions to beam attenuation measurements. Lastly, particulate scattering coefficients ( $b_{SPM}$ ) in m<sup>-1</sup> were derived by subtracting  $a_{SPM}$  from  $c_{SPM}$  values.

Bench determinations of PSD were made by using a red laser (wavelength = 670 nm) diffractometer (LISST-100X, type B, Sequoia Scientifics) (Agrawal et al. 1991). 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 has 32 size ranges logarithmically placed from 1.25 to 250  $\mu\text{m}$  in diameter (the upper size in each bin is 1.18 times the lower), with the width of individual size classes varying from 0.2 to 35  $\mu\text{m}$ . Scattered light in the near forward angles is measured on concentric detector rings and inversion modeling based on Mie theory yields the particle volume concentration,  $V(D)$ , in the 32 size classes (Agrawal and Pottsmith, 2000). Despite this, only the interval 3-170  $\mu\text{m}$  was analyzed due to stray light effects and variability of particle shape and refractive index in the first bins (i.e.,  $< 3.2 \mu\text{m}$ ) (Agrawal et al., 2008; Andrews et al., 2010; Reynolds et al. 2010), and bias related to particle sinking in the last bins (i.e., 170-250  $\mu\text{m}$ ) (Reynolds et al. 2010). The Hampel filter algorithm was applied to the original measurements in order to eliminate outliers (Pearson, 2005). Lastly, each final PSD estimate was computed as the average of measurements made during 3 minutes at a 1 Hz sampling rate.

The number of particles per unit of volume within each size class ( $N(D)$ ) was computed by dividing  $V(D)$  by the diameter ( $D$ ) of a volume-equivalent sphere corresponding to the midpoint of each individual class:

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

Estimates of  $N(D)$  corresponding to 25 different size bins were calculated from inverting the measured volume scattering functions using an inversion based on Mie theory. The differential particle size distribution ( $N'(D)$ ) was defined as the average number of particles within a given size class of width  $\Delta D$  and per unit of volume (Reynolds et al., 2010):

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

The power-law fit to the differential PSD was computed as follows:

$$N'(D) = N'(D_0) (D/D_0)^{-\xi} \quad (3)$$

where  $\xi$  is the slope of the PSD,  $D_0$  is the reference particle diameter and was set to the midpoint of the size logarithmic size range (i.e., geometric mean = 35.17  $\mu\text{m}$ ). Calculations of  $\xi$  were done by least square minimization of log-transformed data (Reynolds et al., 2010). This method implicitly assumes that the relative error in particle counts is constant (e.g. a fixed percent). However, a more realistic error model should use a similar uncertainty for the area size distribution in each bin.

The uncertainty of  $\xi$  calculations, as estimated from 2 standard errors, varied between 1.6 and 10.2% with smaller errors in samples obtained in LE locations. Although PSD in natural waters may not follow the model proposed in equation (3), its use here was justified as our main interest was to have a first-order assessment of size effects of particulates on optical coefficient's variability. Also, the definition of  $\xi$  based on LISST measurements applies for particulates greater than 2  $\mu\text{m}$ . 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  $\xi$  and optical coefficients in this study are local and should not be generalized to other littoral environments.

## 2.5 Optical proxies and characteristics of particle assemblages

Another size proxy of suspended particulates is the power law exponential fit to the particulate beam attenuation spectra ( $\gamma$ ) (Boss et al., 2001). For a power-law PSD,  $\gamma$  is related to the power-law exponent fit to the particle number size distribution ( $\xi$ ) ( $\xi = \gamma + 3 - 0.5 e^{-6\gamma}$ , Boss et al., 2001) and negatively related to the mean particle size.

5 The parameter  $\gamma$  was derived as follows:

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

where  $\lambda_r$  is the reference wavelength at 488 nm (Boss et al., 2001; Boss et al., 2013).

The uncertainty of  $\gamma$  determinations varied between 2.2% and 6.4% with largest errors being computed in samples obtained in LE waters. The spectral slope of mass-specific particulate absorption coefficients ( $S_{\text{vis}}$ ) was calculated by nonlinear fitting of a single-exponential decay function over the visible range 400-700 nm:

$$a_x^*(\lambda) = A e^{-S_{\text{vis}}(\lambda-400)} + B \quad (5)$$

10 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). In our case,  $B$  is not different from zero due the initial correction of  $a$  by scattering effects (see section 2.4).  $S_{\text{vis}}$  is a proxy for dithionite-extractable iron and organic carbon-content of particulates of marine samples (Estapa et al., 2012).  
15 The uncertainty of  $S_{\text{vis}}$  estimates varied between 0.5 and 21.5% with largest errors associated to samples obtained in LE locations. The equation (5) is only valid in waters where NAP is the main optical component contributing to light absorption coefficient of SPM.

## 2.6 Mass-specific optical coefficients

20 The spectral mass-specific absorption ( $a_i^*(\lambda)$ ) and scattering ( $b_i^*(\lambda)$ ) coefficients in  $\text{m}^2 \text{g}^{-1}$  and for different size fractions of SPM are defined as follows:

$$a_i^*(\lambda) = a_i(\lambda) (\text{wp}_i)^{-1} \quad (6)$$

$$b_i^*(\lambda) = b_i(\lambda) (\text{wp}_i)^{-1} \quad (7)$$

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

25 No measurements of  $F_{\text{SPM}}^{\text{PIM}}$  and  $\xi$  were done in size fractions of SPM, thus it is difficult to compare 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 size fraction was verified by comparing the sum of weights of 0.7-10  $\mu\text{m}$  and >10  $\mu\text{m}$  fractions with the



weight of an independent sample after filtering it through a GF/F membrane (i.e., 0.7  $\mu\text{m}$  nominal pore size). In this case, the arithmetic average (median) of the relative bias for the whole dataset was 29.7% (24.9%) or a 29.7% (24.9%) overestimation with respect to samples without a previous size fractionation.

## 2.7 Statistical analysis

5 Relationships between PSD, particle chemical composition, optical proxies ( $\gamma$  and  $S_{vis}$ ) and mass-specific optical coefficients for different size fractions (i.e.,  $a_i^*$  and  $b_i^*$ ) of SPM were investigated based on correlations with respect to  $\xi$  and  $F_{SPM}^{PIM}$  variables. In all cases, the intensity and sign of correlations were quantified based on the non-parametric Spearman rank coefficient ( $\rho_s$ ) (Spearman, 1904). Notice that correlations of  $\xi$  and  $F_{SPM}^{PIM}$  with mass-specific optical coefficients of size fractions 0.2-0.4  $\mu\text{m}$  and 0.4-0.7  $\mu\text{m}$  may only reflect dependencies between mass-normalized optical coefficients of different size classes since size spectra of  $\xi$  and  $F_{SPM}^{PIM}$  calculations correspond to particles with a diameter greater than 2  $\mu\text{m}$  and 0.7  $\mu\text{m}$ , respectively.

## 3 Results

### 3.1 Spatial variability of physical and chemical characteristics of SPM

15 The size distribution of particulates varied among different sub-regions of the study area. In general, particulates with a diameter larger than 10  $\mu\text{m}$  had a relatively large contribution to the total SPM mass in UE locations ( $F_{SPM}^{>10 \mu\text{m}}$  as percentage up to 17%). This proportion was lower in the LE (up to 11%) and SF (up to 15%) sub-regions. The largest mass contribution of smallest-sized particulates (i.e., diameter  $< 0.4 \mu\text{m}$ ) was calculated in the lower estuary (up to 27%). Lastly, the intermediate size classes 0.4-0.7  $\mu\text{m}$  and 0.7-10  $\mu\text{m}$  were on average the fractions having the largest mass contributions to SPM in SF locations (up to 14 and 87%, respectively). The arithmetic average of  $\xi$  was not significantly different between the LE, (3.28  $\pm$  0.10 (1 standard error), N = 15), UE (3.46  $\pm$  0.21, N = 3), and SF (3.42  $\pm$  0.17, N = 5) sub-regions. Unlike PSD, the mineral content of SPM was less variable throughout the study area ( $F_{SPM}^{PIM}$  range = 20 to 87 %). On average, particle chemical composition in the UE, SF and LE sub-regions was dominated by minerals ( $F_{SPM}^{PIM} = 0.57 \pm 0.34$ ,  $0.43 \pm 0.07$ , and  $0.33 \pm 0.09$  for UE, SF and LE, respectively).

### 3.2 Mass-specific optical coefficients of particulates

25 In general for the entire visible spectrum, the sub-regional average of mass-specific absorption particulate coefficients was higher in SF (e.g.,  $a_{SPM}^*(440) = 0.100 \pm 0.033 \text{ m}^2 \text{ g}^{-1}$ , arithmetic average  $\pm 2$  standard errors) with respect to UE ( $0.030 \pm 0.020 \text{ m}^2 \text{ g}^{-1}$ ) and LE ( $0.011 \pm 0.004 \text{ m}^2 \text{ g}^{-1}$ ) locations (Fig. 2a). These differences were less pronounced within the red spectral range. In contrast, the sub-regional average of mass-specific particulate scattering coefficients was comparable between different spatial domains of the SLE (Fig. 2b). However, the highest and lowest values of the sub-regional averages

of  $b_{SPM}^*$  tended to be associated with SF (e.g.,  $b_{SPM}^*(440) = 0.356 \pm 0.092 \text{ m}^2 \text{ g}^{-1}$ ) and LE ( $0.117 \pm 0.033 \text{ m}^2 \text{ g}^{-1}$ ) locations, respectively. In general for all size fractions of SPM, mass-specific absorption coefficients were usually higher in SF (e.g.,  $a_i^*(440)$  up to  $0.281 \text{ m}^2 \text{ g}^{-1}$  for size range  $>10 \mu\text{m}$ ) with respect to UE and LE sub-regions (up to  $0.211 \text{ m}^2 \text{ g}^{-1}$ ) (Fig. 3). However, this pattern was reversed when the grain size of particulates was smaller than  $0.4 \mu\text{m}$  (Fig. 3a). Indeed, the highest  $a_{0.2-0.4 \mu\text{m}}^*$  estimates in this study corresponded to UE waters (Fig. 3a).

In general, very high  $a_i^*$  values (e.g., up to  $0.4 \text{ m}^2 \text{ g}^{-1}$  at  $\lambda = 400 \text{ nm}$ ) were associated with the size fraction of SPM having particulates with a diameter greater than  $10 \mu\text{m}$  (Fig. 3d). These values were up to 8 and 5 times higher than those characteristic of size fractions  $0.4-0.7 \mu\text{m}$  and  $0.7-10 \mu\text{m}$ , respectively (Fig. 3b-c). In general,  $\xi$  and  $F_{SPM}^{PIM}$  correlations with mass-specific absorption coefficients of different size fractions of SPM suggest that particle composition has a larger influence on  $a_i^*(440)$  ( $\rho_s$  up to 0.50,  $P = 0.0009$ ) with respect to PSD ( $\rho_s$  up to 0.32,  $P = 0.0033$ ) (Table 2).

Similar to  $a_i^*$ , highest  $b_i^*$  values (up to  $5.70 \text{ m}^2 \text{ g}^{-1}$  at  $\lambda = 400 \text{ nm}$ ) were associated with particulates within two size ranges,  $0.2-0.4 \mu\text{m}$  and  $>10 \mu\text{m}$  (Fig. 4). Notice that mass-specific optical coefficients in the NIR spectral range are not shown due to the presence of negative values at some wavelengths. For the same size range of particulates, the highest  $b_i^*$  values were not always measured in the same region. Indeed, maximum  $b_i^*$  values for the size fractions  $0.7-10 \mu\text{m}$  (up to  $1.25 \text{ m}^2 \text{ g}^{-1}$  at  $\lambda = 556 \text{ nm}$ ) and  $>10 \mu\text{m}$  (up to  $4.58 \text{ m}^2 \text{ g}^{-1}$ ) were obtained in UE and LE domains, respectively. Unlike  $a_i^*(440)$ ,  $b_i^*(550)$  variability was less influenced by changes on particle composition ( $\rho_s$  up to 0.42,  $P = 0.0015$ ) (Table 2). Conversely, the impact of changing particle dimensions, as inferred from  $\rho_s$  correlations, had a larger effect on  $b_i^*(550)$  ( $\rho_s$  up to 0.37,  $P = 0.006$ ) with respect to  $a_i^*(440)$  ( $\rho_s$  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, and optical proxies are presented in Table 3. Over the whole study area, there was not a clear relationship between  $\gamma$  and  $F_{SPM}^{PIM}$  values ( $\rho_s = -0.34$ ,  $P = 0.11$ ). However,  $\gamma$  changes were associated with variations of size-fractionated mass contributions of particulates within the range  $0.2-10 \mu\text{m}$  ( $\rho_s$  up to 0.53,  $P = 0.01$ ). The sign of this correlation varied depending on the size class under investigation (e.g., positive and negative  $\rho_s$  values for small-sized and intermediate-sized particulates, respectively). There was no clear relationship between  $\gamma$  and  $\xi$  values for samples obtained over the whole study area ( $\rho_s = 0.15$ ,  $P = 0.49$ ,  $N = 23$ ). The range of  $\gamma$  values was 0.759-3.282, 1.389-1.534, 2.873-3.282 and 0.759-1.802 for the SLE, UE, SF and UE domains, respectively. The spectra slope of  $a_{SPM}^*$  was not statistically related to  $F_{SPM}^{PIM}$  changes ( $\rho_s = -0.06$ ,  $P = 0.78$ ,  $N = 23$ ). However  $S_{vis}$  variability was strongly connected with changes on mass contribution of different size classes of SPM, and in particular those associated with small-sized particulates (i.e.,  $0.2-0.7 \mu\text{m}$ ) (Table 3). This pattern was consistent with a positive correlation between  $\gamma$  and  $S_{vis}$  ( $\rho_s = -0.489$ ,  $P = 0.018$ ,  $N = 23$ ). However, there was no clear relationship between  $S_{vis}$  and  $\xi$  values ( $\rho_s = 0.123$ ,  $P = 0.57$ ,  $N = 23$ ).

The range of  $S_{vis}$  values 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  $\text{nm}^{-1}$ , respectively. Over the whole study area, the range of  $S_{vis}$  values for SPM size fractions 0.2-0.4  $\mu\text{m}$ , 0.4-0.7  $\mu\text{m}$ , 0.7-10  $\mu\text{m}$  and  $> 10 \mu\text{m}$  was 0.004-0.026, 0.007-0.052, 0.004-0.109 and 0.001-0.028  $\text{nm}^{-1}$ , respectively. In general,  $S_{vis}$  slopes were not correlated with size fractions even though the variation of  $S_{vis}$  for unfractionated samples was strongly linked to changes on  $S_{vis}$  estimates associated with particulates within the size range 0.7-10  $\mu\text{m}$  ( $\rho_s = 0.66$ ,  $P = 0.004$ ).

## 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 for 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  $\sim 0.9^\circ$  and much larger than that corresponding to the LISST-100X diffractometer ( $\sim 0.027^\circ$ ), thus, a larger underestimation of the theoretical particulate beam attenuation is expected in the ac-s with respect to LISST-100X measurements due to a larger contribution of forward-scattered photons arriving at the detector of the ac-s (Boss et al., 2009). Unfortunately,  $c$  deviations due to acceptance angle variations were not corrected in this study due to the lack of  $c$  values as obtained by using an integrating cavity absorption meter (e.g., PSICAM) (Röttgers et al., 2005). Notice that these differences are much greater with respect to the standard deviation of each sample determination in this study and computed based on ac-s measurements (e.g.,  $< 1\%$  at  $\lambda = 532 \text{ nm}$ ).

In this investigation, the 'flat' baseline correction was selected for correcting the scattering effects on absorption coefficient estimates as derived from ac-s measurements. This technique was chosen due to the lack of PSICAM measurements or ancillary optical information (e.g., particle backscattering efficiency) to tune up a Monte Carlo scattering correction approach (McKee et al., 2008). Since NAP is an important component of SLE-SF environments, an underestimation of ac-s absorption measurements is expected due to a non-zero absorption at 715 nm (McKee et al., 2013; Röttgers et al., 2013). This deviation is amplified at wavelengths greater than 600 nm, is more remarkable at higher turbidities and decreases when phytoplankton contribution to total particulate absorption increases. To minimize this residual scattering, an empirical correction linking PSICAM and ac-9 absorption measurements at 715 nm has been proposed (Röttgers et al., 2013). Although practical, it is uncertain the use of this correction in our study area due to optical differences between particles assemblages of the SLS-SF and those studied by Röttgers et al. (2013). Thus, the magnitude of optical coefficients and mass-specific optical coefficients of particulates measured in SLE-SF waters may present large errors (i.e.,  $> 50\%$ ) with respect to PSICAM measurements and at wavelengths longer than 550 nm. This bias is anticipated to be maximum (minimum) in UE (LE) locations due to the greater contribution of NAP to particulate absorption of the former sub-region.

## 4.2 Variability of physical and chemical characteristics of SPM

A striking finding in this study was the important weight contribution of relatively large particulates (i.e.,  $>10\ \mu\text{m}$ ) 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). The chemical composition of size-fractionated SPM was not analyzed in this study. However, the correlation between  $F_{\text{SPM}}^{\text{PIM}}$  and  $F_{\text{SPM}}^{0.2-0.7\ \mu\text{m}}$  values suggest that mineral content of SPM increases as the contribution of particulates with a diameter smaller than  $0.7\ \mu\text{m}$  becomes larger ( $\rho_s = 0.30$ ,  $P = 0.035$ ,  $N = 23$ ). This finding is consistent with previous studies in the SLE showing that relatively small (i.e., diameter  $\sim 2\ \mu\text{m}$ ) particulates are mainly composed by inorganic matter (Yeats, 1988; Gagné et al., 2009). A large proportion of particulates with a diameter above  $50\ \mu\text{m}$  and lower  $\xi$  values were typically found in LE locations. These results go along with historical datasets and showing a greater proportion of relatively large particulates (i.e.,  $> 5$  and  $< 50\ \mu\text{m}$ ) over the LE locations and during the same period of the year (Chanut and Poulet, 1982).

## 4.3 Spatial variability of mass-normalized optical coefficients

$a_{\text{SPM}}^*$  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, Elbe Estuary, Gironde Estuary) (Snyder et al., 2008; Doxaran et al., 2009; Röttgers et al., 2014) (Table 4). Also, our values in the blue spectral range are within the interval of variation (e.g.,  $0.024-0.031\ \text{g}^{-1}\ \text{m}^2$ ,  $\lambda = 440\ \text{nm}$ ) of the linear regression slope between NAP absorption coefficient and SPM concentration values measured in mineral-rich waters (i.e.,  $a_{\text{SPM}}^* \cong a_{\text{NAP}}^*$ ) (Bowers et al., 1996; Babin et al., 2003). This is remarkable given the large diversity of methodologies used by different research teams for estimating  $a_{\text{SPM}}^*$  values (e.g., pad-technique, ac-s, integrating sphere). In general, the lowest  $a_{\text{SPM}}^*$  values (i.e.,  $0.01-0.02\ \text{m}^2\ \text{g}^{-1}$  at  $\lambda = 440\ \text{nm}$ ) commonly corresponded with samples obtained in very turbid environments (i.e.,  $> 100\ \text{g}\ \text{m}^{-3}$ , Mississippi River and Delta, Gironde River) (Bowers and Binding, 2006; D'Sa et al. 2006; Doxaran et al., 2009). These low values could be overestimated due to an increase on particulate absorption associated to an incomplete removal of multiple scattering effects. Relative low  $a_{\text{SPM}}^*$  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, dimensionless chl/SPM ratios varied between  $3.9 \cdot 10^{-5}$  and  $1.8 \cdot 10^{-3}$  with a median of  $1.1 \cdot 10^{-4}$  and an arithmetic mean of  $2.7 \cdot 10^{-4}$ . These values are commonly lower than those reported in coastal waters of the Gulf of Mexico by D'Sa et al. (2006) ( $\sim 10^{-3}$ ), and is consistent with the relatively high  $a_{\text{SPM}}^*$  values obtained in SLS-SF waters.

A well-known mechanism explaining the general decrease of  $a_{\text{SPM}}^*$  in very turbid waters is related to the packaging effects (Duysens, 1956; Morel, 1974). At higher turbidities, larger particulates contribute to PSD variations, thus as mean diameter of particles increases, the light absorption efficiency per mass decreases (i.e., the interior of larger particles has a greater

'shading'). This could also explain the spatial differences of  $a_{\text{SPM}}^*(440)$  in our study area where larger values corresponded with surface waters dominated by particles assemblages having a smaller mean diameter (e.g., UE and SF). In nearshore waters of California, Wozniak et al. (2010) demonstrated inverse relationships between  $a_{\text{SPM}}^*(440)$  and the median particle diameter of inorganic- and organic-dominated assemblages.

5 | Indirect size effects on  $a_{\text{SPM}}^*(440)$  due to 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 particulates are expected to have an enhancement of  $a_{\text{SPM}}^*(440)$  due to relatively high iron concentrations. This phenomenon could probably explain part of the  $a_{\text{SPM}}^*(440)$  variability in some locations of our study area where  
10 | relatively high concentrations of iron bound to particulates have been measured (e.g., SF)(Yeats and Bewers, 1976; Tremblay and Gagné, 2009).

Similar to  $a_{\text{SPM}}^*$ ,  $b_{\text{SPM}}^*$  values were highly variable between locations but within the range reported in other littoral environments (e.g., Irish Sea, Coast off Europe and French Guyana)(Bowers and Binding, 2006; Neukermans et al., 2012)(Table 4). In this study, the spectral variation  $b_{\text{SPM}}^*$  between regions showed a spectral flattening as particle  
15 | assemblages become dominated by organic matter (i.e., LE). This finding is consistent with Wozniak et al. (2010) determinations made at Imperial Beach, California.

#### 4.4 Relationships between PSD, particle chemical composition and mass-specific optical coefficients

For all size fractions of SPM,  $\xi$  was positively correlated with  $a_i^*(440)$  ( $\rho_s$  up to 0.32,  $P = 0.006$ ). This pattern suggests a higher absorption efficiency of relatively small-sized particulates. Since particle aggregates were altered during our  
20 | 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).  
Change on PSD due to aggregation with substantial reduction of absorption (i.e., 50%) due to packaging effect is expected to be important at  $d \sim 0.25 \lambda/n'$ , where  $d$  is the diameter of the particle and  $n'$  is the imaginary part of the index of refraction (Stemann and Boss, 2014). By assuming  $n' = 0.0025$  for a mixed particle assemblage of clays (i.e., kaolinite +  
25 | montmorillonite) and  $\lambda = 300$  nm, the resulting  $d$  is 30  $\mu\text{m}$ . Based on simulations, the formation of clay-derived aggregates may cause a change in  $a_{\text{SPM}}^*$  of approximately 10% (Estapa et al., 2012). This effect will be larger or smaller depending on aggregate size, solid mass fraction and primary particle size.

In general,  $\xi$  was positively correlated with  $b_i^*(550)$  ( $\rho_s$  up to 0.37,  $P = 0.008$ ) and suggests an increase of scattering efficiency as particulates become smaller. Unlike  $a_i^*(440)$ ,  $b_i^*(550)$  was preferentially correlated with  $\xi$ , and this relation was  
30 | more remarkable when particulates were large-sized. 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 PSDs. Although no



particulate backscattering measurements were available in this study, Reynolds et al. (2016) highlight the importance of PSD for driving variations on mass-specific optical coefficients linked to scattering processes.

A common pattern in all size fractions of SPM was the stronger correlation of  $F_{SPM}^{PIM}$  with  $a_i^*$ (440) compared with  $b_i^*$ (550) values. The enrichment of suspended particulates in inorganic matter and the concomitant variations in  $a_i^*$ (440) may be attributed to mineral-associated iron (Babin and Strasmki, 2004; Estapa et al., 2012) or/and organic-associated iron (Estapa et al., 2012). More studies are needed to test this hypothesis, however, it is interesting to notice that high  $a_{SPM}^*$  values in our study were commonly associated with SF locations where reduced iron associated with particulates is typically high (Deflandre et al., 2002).

#### 4.5 Optical proxies of SPM characteristics

10 The variability of  $\gamma$  was related to mass contribution changes of specific size fractions of SPM ( $\rho_s$  up to 0.53,  $P = 0.004$ ,  $i = 0.2-0.4 \mu m$ ). Conversely,  $\gamma$  was not correlated with the mass contribution of minerals to SPM. Despite the major effects of particle size classes on  $\gamma$ ,  $\gamma$  was not clearly correlated with  $\xi$ . In oceanic waters,  $\xi$  and  $\gamma$  values covary in a linear way for a specific range of refractive index and  $\xi$  (Boss et al., 2001; Twardowski et al., 2001). These covariations were observed for  $\xi$  values derived from LISST and Coulter Counter measurements (Boss et al., 2001; Slade and Boss, 2015). Our range of  $\xi$

15 values was within the natural variability reported in coastal and oceanic environments ( $\xi = 2-4.5$ ) (Reynolds et al., 2010; Neukermans et al., 2012; Xi et al., 2014). Also, the magnitude of  $\gamma$  in our samples ( $0.29-2.22 \text{ nm}^{-1}$ ) 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  $\xi$  and  $\gamma$  values in this study is linked to the finite acceptance angle of the ac-meter (Slade and Boss, 2015).

20 The variability of  $S_{vis}$  values in this study was relatively high (~10-fold) with respect to other littoral environments (1.3-fold,  $S_{vis} = 0.009-0.0113 \text{ nm}^{-1}$ ) (Estapa et al., 2012).  $S_{vis}$  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) ( $\rho_s = -0.55$ ,  $P = 0.04$ ,  $N = 14$ ). This pattern was previously detected in coastal waters of the Gulf of Mexico (Estapa et al., 2012).

#### 5 Conclusions

25 The measure of mass-specific optical coefficients of SPM is essential for developing optical inversions for mapping biogeochemical components in surface waters and improving our understanding regarding the origin of optical signatures in remote sensing studies. In this contribution, we presented for the first time, mass-specific scattering and absorption coefficients of size-fractionated 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

30 properties of particle assemblages, the following patterns were identified: 1). the mass-specific absorption coefficient of different size fractions of SPM was preferentially related to changes on particle chemical composition as inferred from



changes on  $F_{SPM}^{PIM}$  and at a wavelength of 440 nm, 2) the magnitude of  $\zeta$  had a stronger correlation with  $b_1^*$  (550) compared to  $a_1^*$  (440), and 3) the magnitude of  $Svis$  was inversely correlated with  $a_{SPM}^*$  (440) in areas having a larger marine influence (i.e., lower estuary). In summary, these relationships will be useful for investigating local and regionally-limited biogeo-optical properties of SPM. Thus, additional research based on true optical properties of PSD will be needed in order to propose more general relationships that can be applied to other littoral environments.

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Table 1. Summary of acronyms

Abbreviation	Definition	Unit
SLE	St. Lawrence Estuary	
UE	Upper estuary	
SF	Saguenay Fjord	
LE	Lower estuary	
<u>SPM</u>	<u>Suspended particulate matter</u>	
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	
$\lambda$	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	$m^{-1}$

$a_{\text{SPM}}^*$	Mass-specific absorption coefficient of total SPM	$\text{m}^2 \text{g}^{-1}$
$b_{\text{SPM}}^*$	Mass-specific scattering coefficient of total SPM	$\text{m}^2 \text{g}^{-1}$
$a_i^*$	<u>Mass-specific absorption coefficient of particle size fraction i</u>	<u><math>\text{m}^2 \text{g}^{-1}</math></u>
$b_i^*$	<u>Mass-specific scattering coefficient of particle size fraction i</u>	<u><math>\text{m}^2 \text{g}^{-1}</math></u>
$\xi$	<u>Slope of differential PSD</u>	<u>dimensionless</u>
D	Diameter of a volume-equivalent sphere at mid-point of size class	$\mu\text{m}$
V(D)	Volume concentration at size class D	$\mu\text{L L}^{-1}$
N(D)	Particle number concentration at size class D	$\text{m}^{-3}$
N'(D)	Particle number density at size class D	$\text{m}^{-3} \mu\text{m}^{-1}$
$\gamma$	Spectral slope of particulate beam attenuation coefficient	<u>dimensionless</u>
$S_{\text{vis}}$	Spectral slope of mass-specific particulate absorption coefficient within the visible spectral range	$\text{nm}^{-1}$

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

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

Mass fraction	$\gamma$	<i>Svis</i>
$F_{SPM}^{PIM}$	-0.34	-0.06
$F_{SPM}^{0.2-0.4 \mu m}$	0.53*	0.49**
$F_{SPM}^{0.4-0.7 \mu m}$	-0.43*	-0.49**
$F_{SPM}^{0.7-10 \mu m}$	-0.38*	-0.30*
$F_{SPM}^{>10 \mu m}$	0.13	0.19

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

<u>Location</u>	<u><math>\lambda</math></u>	<u><math>a_{SPM}^*</math></u>	<u><math>b_{SPM}^*</math></u>	<u><math>[SPM]^k</math></u>	<u>References</u>
<u>SLE-SF</u>	<u>440</u>	<u>0.001-0.073<sup>a</sup></u>	<u>0.1-1.06<sup>a</sup></u>	<u>2.28 – 30.6</u>	<u>This study</u>
	<u>488</u>	<u>0.001-0.040</u>	<u>0.1-0.97</u>		
	<u>556</u>	<u>0.001-0.017</u>	<u>0.1 -0.86</u>		
	<u>665</u>	<u>0.001-0.004</u>	<u>0.1-0.73</u>		
	<u>708</u>	<u>0.001-0.002</u>	<u>0.1-0.68</u>		
<u>Elbe River,</u>	<u>650</u>	<u>0.001 – 0.020<sup>b</sup></u>		<u>0.5-10</u>	<u>Röttgers et al.</u> <u>(2014)</u>
<u>German Bight,</u>	<u>750</u>	<u>0.001 – 0.019</u>			
<u>Baltic Sea, New</u> <u>Caledonia lagoon</u>	<u>850</u>	<u>0.001 – 0.014</u>			
<u>Monterey Bay,</u> <u>US</u>	<u>532</u>		<u>0.46 – 2.54<sup>c</sup></u>	<u>0.11 – 2.37</u>	<u>Zhang et al.</u> <u>(2014)</u>
<u>Mobile Bay, US</u>	<u>532</u>		<u>0.40 – 1.78</u>	<u>0.26 – 7.36</u>	
<u>Mobile Bay,</u>	<u>440</u>		<u>0.44 – 1.95<sup>d</sup></u>	<u>0.23-25.32</u>	<u>Stavn and Richter</u> <u>(2008)</u>
<u>Southwest Pass,</u> <u>US</u>	<u>488</u>		<u>0.41 – 1.89</u>		
	<u>550</u>		<u>0.40 – 1.80</u>		
	<u>676</u>		<u>0.36 – 1.63</u>		
	<u>715</u>		<u>0.34 – 1.61</u>		
<u>Coast of New</u> <u>Jersey,</u>	<u>440</u>			<u>0.44 – 6.6</u>	<u>Snyder et al.</u> <u>(2008)</u>



<u>Monterey Bay,</u>	<u>488</u>				
<u>Great Bay</u>	<u>556</u>				
<u>Mobile Bay</u>	<u>665</u>	<u>0.05 ± 0.01<sup>d</sup></u> ( <u>arithmetic mean</u> <u>± standard</u> <u>deviation</u> )			
<u>Irish sea, UK</u>	<u>665</u>		<u>0.08 – 0.45<sup>e</sup></u>	<u>1.9 – 26.5</u>	<u>Binding et al.</u> <u>(2005)</u>
<u>Irish sea, UK</u>	<u>443</u>	<u>0.062 ± 0.013<sup>f</sup></u>	<u>0.17 – 0.19</u>	<u>1.6 – 50</u>	<u>Bowers and</u> <u>Binding (2006)</u>
	<u>490</u>		<u>0.20 – 0.22</u>		
	<u>555</u>		<u>0.20 – 0.24</u>		
	<u>665</u>		<u>0.14 – 0.15</u>		
<u>Coast off Europe</u> <u>and French</u> <u>Guyana</u>	<u>676</u>		<u>0.63 – 2.07<sup>g</sup></u>	<u>1.2 – 82.4</u>	<u>Neukermans et al.</u> <u>(2012)</u>
<u>Elbe Estuary,</u> <u>Germany</u>	<u>555</u>	<u>0.05 – 0.07<sup>d</sup></u>	<u>0.35 – 0.47</u>	<u>73.5 – 294.2</u>	<u>Doxaran et al.</u> <u>(2009)</u>
	<u>715</u>	<u>0.01 – 0.03</u>	<u>0.32 – 0.44</u>		
<u>Gironde Estuary,</u> <u>France</u>	<u>555</u>	<u>0.02 – 0.06</u>	<u>0.28 – 0.50</u>	<u>21.9 – 344.1</u>	
	<u>715</u>	<u>0.01 – 0.02</u>	<u>0.27 – 0.45</u>		
<u>Coastal Louisiana</u> <u>and lower</u> <u>Atchafalaya and</u> <u>Mississippi</u>	<u>440</u>	<u>0.056 ± 0.012<sup>g</sup></u> <u>(0.05 - 0.065)</u>			<u>Estapa et al.</u> <u>(2012)</u>

<u>Rivers</u>					
	<u>488</u>	<u>0.035 - 0.05</u>			
	<u>556</u>	<u>0.25 - 0.35</u>			
	<u>665</u>	<u>0.125 - 0.02</u>			
<u>West of Mississippi Delta</u>	<u>443</u>	<u>0.012 - 0.079<sup>d</sup></u>			<u>D'Sa et al. (2006)</u>
<u>Imperial Beach, California</u>	<u>440</u>	<u>0.03 - 0.1<sup>h</sup></u>	<u>0.1 - 1.2</u>	<u>3-90</u>	<u>Wozniak et al. (2010)</u>
	<u>488</u>	<u>0.02 - 0.08</u>	<u>0.18 - 0.9</u>		
	<u>556</u>	<u>0.01 - 0.03</u>	<u>0.2 - 0.9</u>		
	<u>665</u>	<u>0.004 - 0.02</u>	<u>0.2 - 0.8</u>		
	<u>708</u>	<u>0.001 - 0.02</u>	<u>0.2 - 0.8</u>		

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



## Figure captions

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

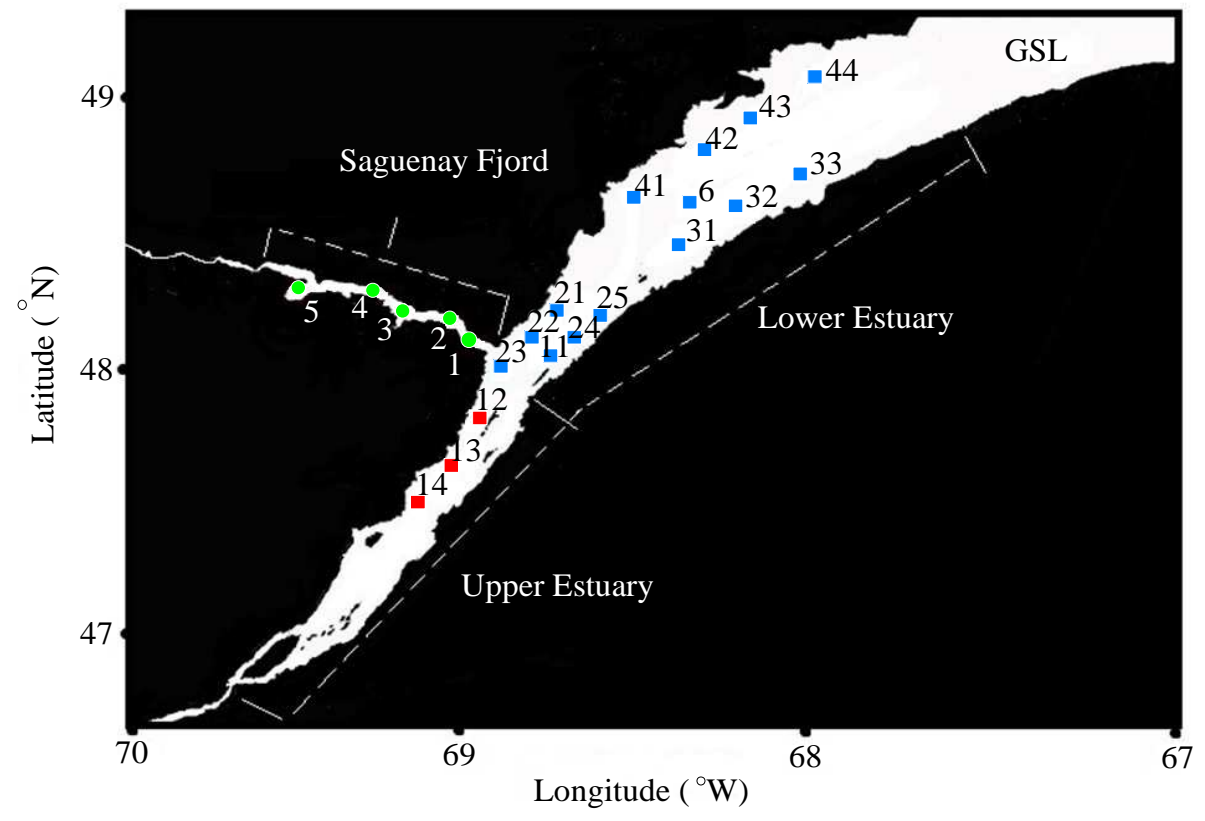
5  
Figure 2. Spectral variation of mass-specific optical coefficients for total SPM. (a)  $a_{\text{SPM}}^*$  (left axis SF, right axis UE, LE and SLE-SF) and (b)  $b_{\text{SPM}}^*$  (left axis SF and SLE-SF, right axis LE and UE). Each bar is the arithmetic average  $\pm 2$  standard errors, as computed for SLE-SF (black circles), UE (red circles), SF (green circles) and LE (blue circles) sub-regions. The number of observations for UE, SF and LE sub-regions are 3, 5 and 15 respectively.

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Figure 3. Spectral variation of mass-specific absorption coefficients for different size classes of suspended particulates. (a) 0.2-0.4  $\mu\text{m}$ , (b) 0.4-0.7  $\mu\text{m}$ , (c) 0.7-10  $\mu\text{m}$  and (d)  $>10 \mu\text{m}$ . 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.

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5  
fig. 1

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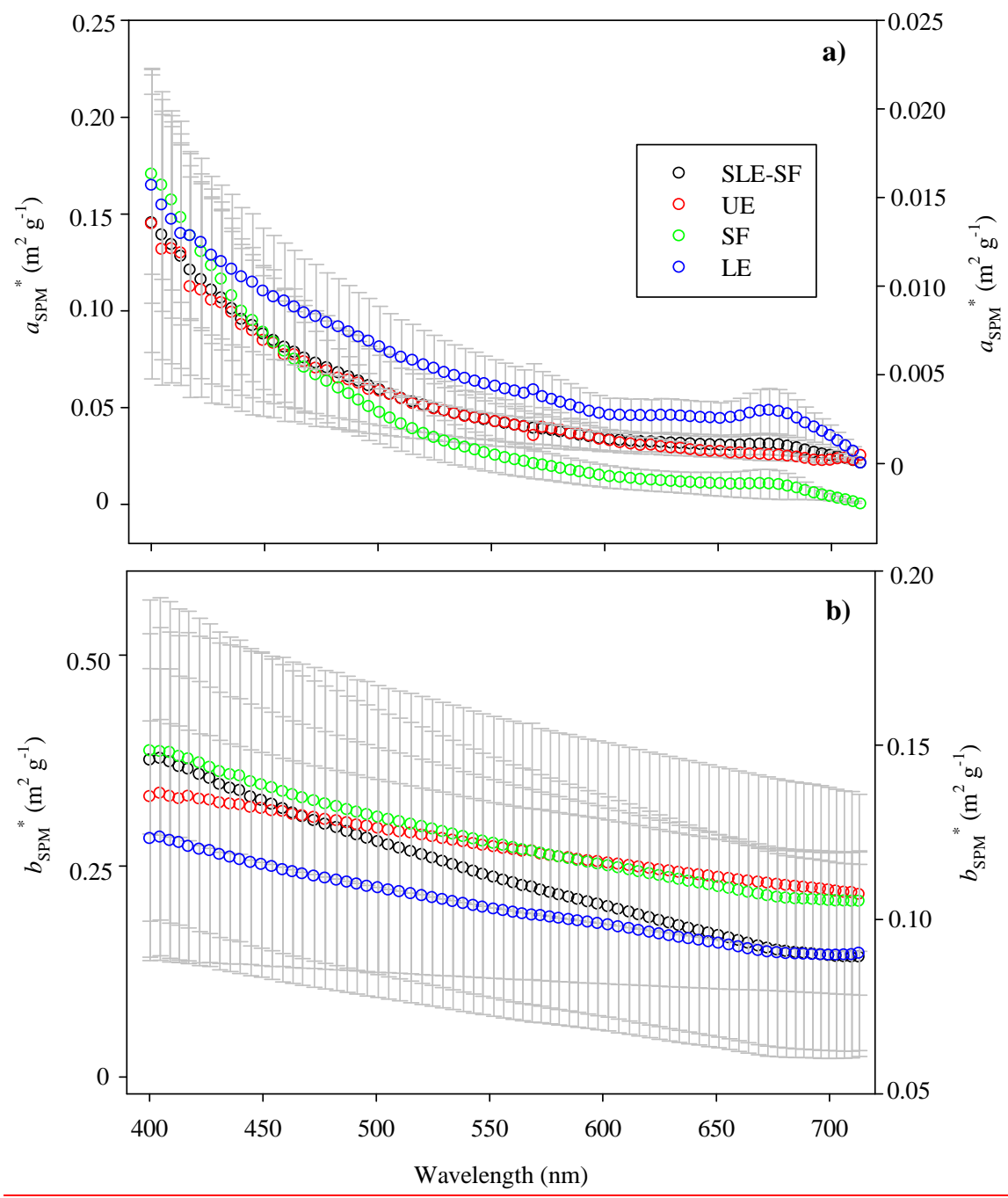


Fig. 2

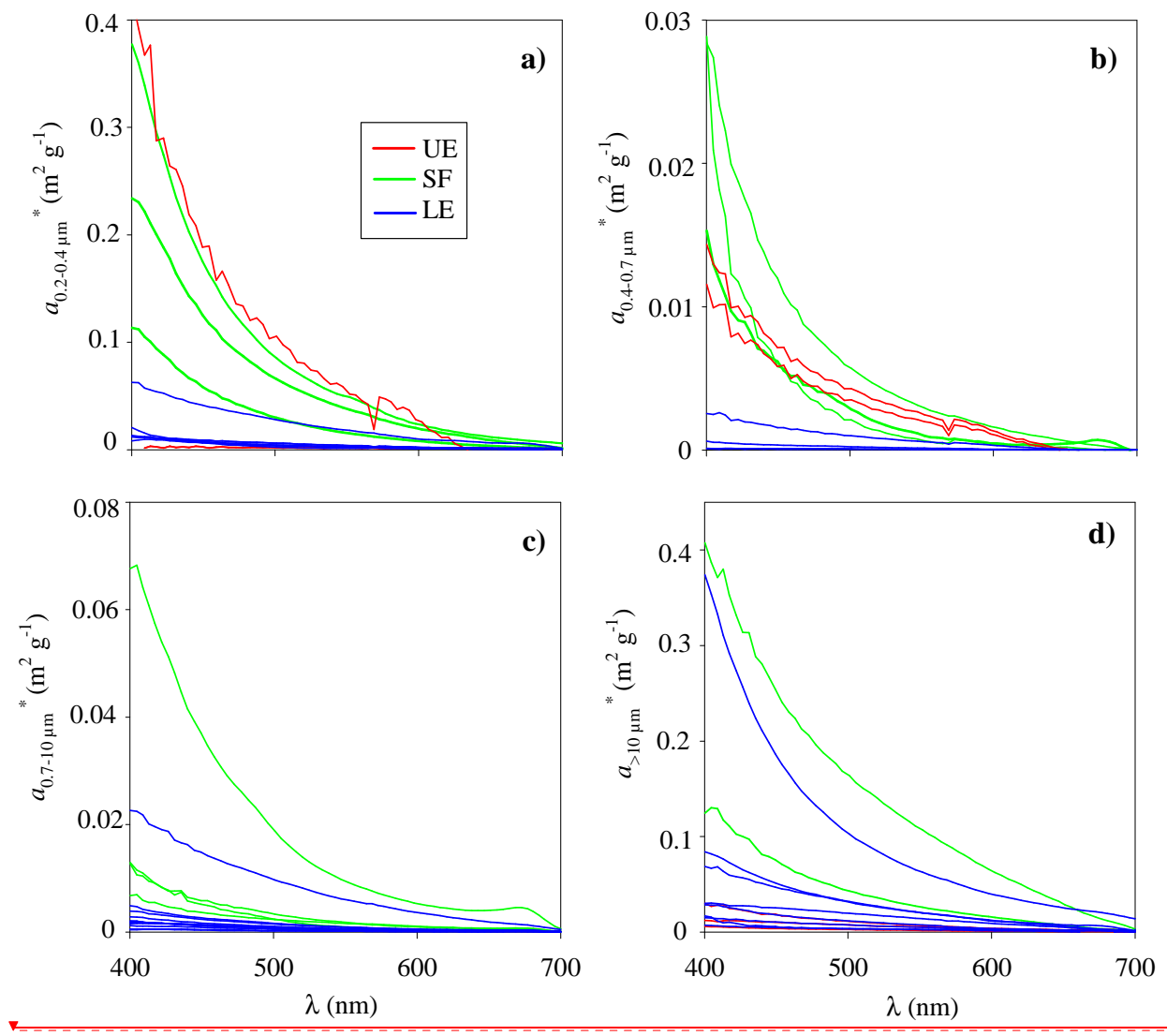
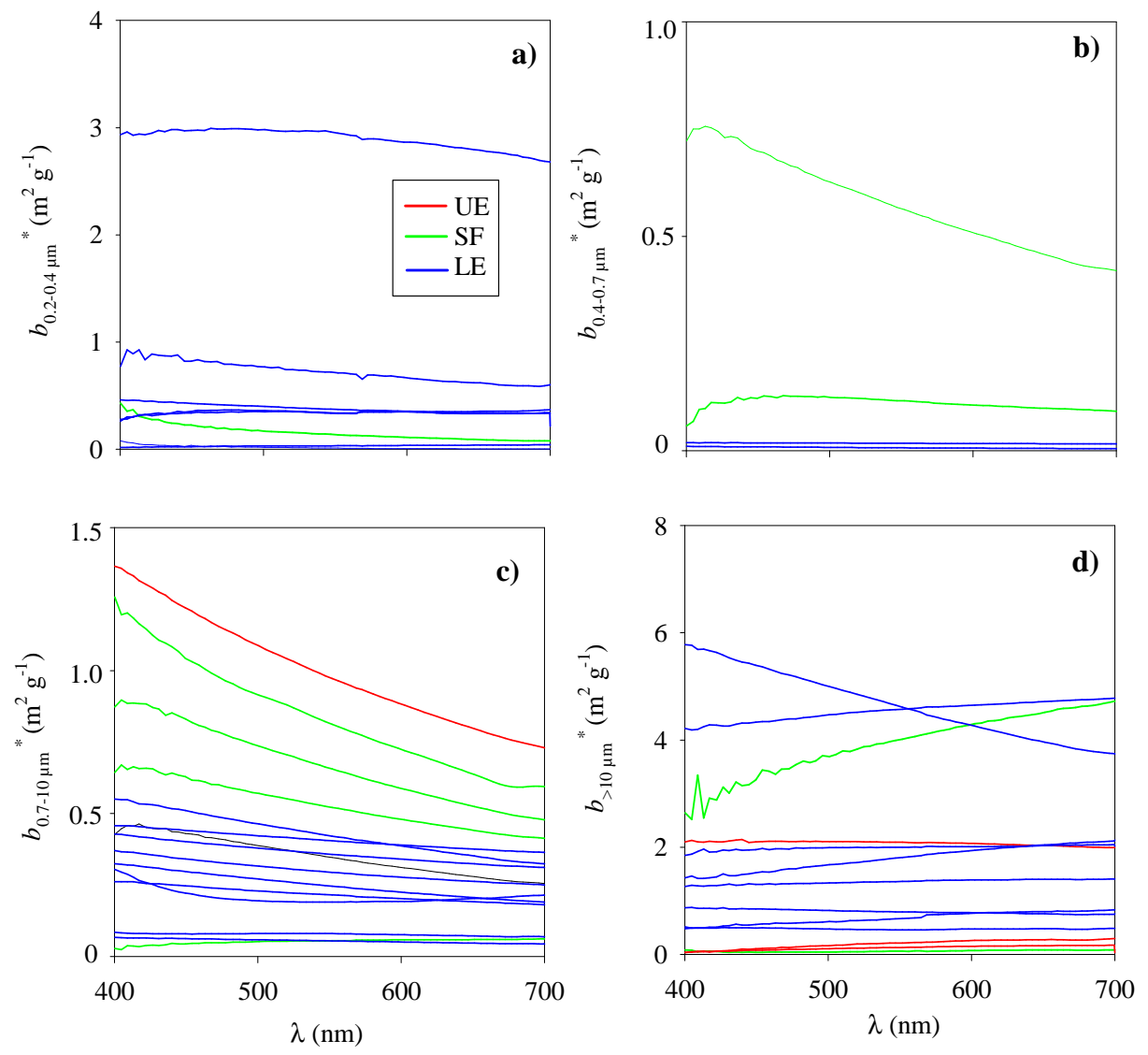


Fig. 3



10 | Fig. 4



**Page 5: [1] Supprimé** **Martin Montes** **2017-10-12 18:11:00**

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).

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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.,  $a > 0.2 \text{ m}^{-1}$ ) 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) (McKnee et al., 2013). Th

**Page 13: [3] Supprimé** **Martin Montes** **2017-10-15 18:50:00**

An important objection to correlations of  $\xi$  and  $F_{\text{SPM}}^{\text{PIM}}$  with mass-specific optical coefficients of SPM for different size fractions was related to differences in terms of particle size range used to compute  $\xi$  and  $F_{\text{SPM}}^{\text{PIM}}$  and particle size classes derived by sequential filtration of water samples. More specifically,  $\xi$  is not representative of submicron particles less than  $2 \mu\text{m}$ . Also,  $F_{\text{SPM}}^{\text{PIM}}$  is only a valid parameter for particles mostly larger than  $0.7 \mu\text{m}$ . Thus, correlations  $\xi$  and  $F_{\text{SPM}}^{\text{PIM}}$  with mass-specific optical coefficients of  $0.2\text{-}0.4 \mu\text{m}$  and  $0.4\text{-}0.7 \mu\text{m}$  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 subsequent impact on correlations with respect to  $F_{\text{SPM}}^{\text{PIM}}$  and  $\xi$  values. No measurements of  $F_{\text{SPM}}^{\text{PIM}}$  and  $\xi$  were done in size fractions of SPM, thus it is difficult to compare 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 size fraction was verified by comparing the sum of weights of 0.7-10  $\mu\text{m}$  and  $>10 \mu\text{m}$  fractions with the weight of an independent sample after filtering it through a GF/F membrane (i.e., 0.7  $\mu\text{m}$  nominal pore size). In this case, the arithmetic average (median) of the relative bias for the whole dataset was 29.7% (24.9%) or a 29.7% (24.9%) overestimation with respect to samples without a previous size fractionation.. An optimization scheme to adjust the mass for each size fractions (i.e. adjusting the various weights to sum up to the total mass filtered) was not attempted since we didn't filter unfractionated samples through 0.2 or 0.4  $\mu\text{m}$  membranes due to the sequential mode of our filtration. Thus, 'filtration weighting factors' for size fractions  $> 0.2 \mu\text{m}$  or  $> 0.4 \mu\text{m}$  could not be calculated.

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In terms of fractioned mass,

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the size of particulates was the dominant variable driving changes on

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content of SPM did not have a statistically detectable impact on  $\gamma$  at 95% confidence level

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In particular, the strongest relationship between  $\gamma$  and  $F_{\text{SPM}}^i$  was associated to the fraction having the smallest particles (i.e., 0.2-0.4  $\mu\text{m}$ ).

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different relationships between  $\gamma$ ,  $\xi$  and changes of two non-covarying optical contributions: minerals and phytoplankton. Also, the reduced number of sampling locations and the geographic variability of  $\xi$ - $\gamma$  relationships were additional factors likely explaining the lack of correlation for the study area. Lastly,  $\xi$  and  $\gamma$  were not substantially correlated in our samples due to deviations on Mie-based models (e.g, absorbing spheres) of  $\gamma$  as a function of  $\xi$  (Twardowski et al., 2001). Indeed during our surveys, high absorbing particulates were present in SLE-SF waters.

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found that  $a_{\text{SPM}}^*(440)$  ( $S_{\text{vis}}$ ) 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.

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Location	$\lambda$	$a_{\text{SPM}}^*$	$b_{\text{SPM}}^*$	$[\text{SPM}]^k$	References
UE	440	0.01 – 0.25 <sup>a</sup>	0.01 – 1.06 <sup>a</sup>	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 <sup>b</sup>	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 <sup>c</sup> 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 <sup>d</sup>		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		0.05 ± 0.01 <sup>d</sup>			
		(arithmetic			
	665	mean ±			
		standard			
		deviation)			
Irish sea, UK	665		0.08 – 0.45 <sup>e</sup>	1.9 – 26.5	Binding et al. (2005)
Irish sea, UK	443	0.062 ± 0.013 <sup>f</sup>	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	676		0.63 – 2.07 <sup>g</sup>	1.2 – 82.4	Neukermans et al. (2012)

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French Guyana

Elbe Estuary, Germany	555	0.05 – 0.07 <sup>d</sup>	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 Mississippi Rivers					Estapa et al. (2012)
	440	0.056 ± 0.012 <sup>g</sup> (0.05 - 0.065)			
	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 <sup>d</sup>			D'Sa et al. (2006)
Imperial Beach, California	440	0.03 – 0.1 <sup>h</sup>	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		

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