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Variability in the light absorption coefficients of phytoplankton, non-algal particles, and colored dissolved organic matter in a subtropical bay (Brazil)

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ABSTRACT

This study characterized the variability in magnitudes and spectral shapes of the absorption coefficients of phytoplankton, detritus, and colored dissolved organic matter (CDOM) in a dynamic bay (Santos Bay) in southeastern Brazil in response to the contributions of the main estuarine channel and large tide variations, therefore in different time scales. Two strategies were adopted: (1) monthly year-round sampling in the estuarine channel and Santos Bay and (2) sampling in Santos Bay during spring/neap tides and cold/warm months. Chlorophyll-*a* concentration and CDOM absorption were higher during warm (wet) months, while the relative contribution of organic and inorganic particles was driven by neap/spring tide cycles. Salinity partially accounted for changes in optical variables, especially for CDOM absorption and total suspended matter (TSM) during cold months and neap tides, respectively. The spectral shapes of detritus and CDOM absorption showed relatively little variability for the entire dataset and were not considered feasible for monitoring purposes. The spectral shape of phytoplankton absorption (index of cell size) varied broadly, with no remarkable dependence on the sampling conditions. Comparison of absorption coefficients measured by the Quantitative Filter Technique (QFT) and Transmittance Reflectance (TR) method showed higher phytoplankton coefficients toward longer visible wavelengths (flatter spectra) and shallower slopes of detritus absorption yielded by the TR method. Our results also suggest that measurements at the near red spectral region result from not only scattering signals but also non-algal particle absorption.

1. Introduction

Coastal waters receive dissolved and particulate materials from several sources that make them optically complex (IOCCG, 2000), and the use of optical properties of the water and bio-optical model parameterizations remains challenging because phytoplankton rarely dominate the optical signal (Siegel et al., 2002; Schofield et al., 2004), except during blooms (e.g., Lucas et al., 1999). Thus, the successful use of optical instruments for monitoring water quality (Bukata, 2005) depends on having a robust characterization of the optical properties of the region. Current global bio-optical models (e.g., Lee et al., 2002; Maritorena et al., 2002) discriminate two main categories of constituents in the open ocean, excluding water molecules themselves: phytoplankton and colored detrital material, which includes the combined signals of colored dissolved organic matter (CDOM) and non-algal (organic and inorganic) particles.

Especially near estuaries, the light-attenuating constituents will display variability driven by freshwater input fluctuations, sediments resuspension due to coastal circulation (e.g. tidal currents, coastal fronts, turbulence) (Gallegos, 2005; Sasaki et al., 2005; Vantrepotte et al., 2007) and the nature of this material, algal blooms (of varying species composition) caused by excess terrigenous nutrients (Anderson and Garrison, 1997) and higher or more variable concentrations of CDOM (Blough and Del Vecchio, 2002; Coble et al., 2004). Both the magnitudes and spectral shapes of CDOM absorption coefficients have been linked to their composition and sources (Chen et al., 2004; Twardowski et al., 2004), and are mainly driven by continental sources (Siegel et al., 2002; Schofield et al., 2004). Substantial disposal of sewage can also affect the CDOM absorption parameters and the proportion of non-algal particles in the water column (Abril et al., 2002; Callahan et al., 2004; Spencer et al., 2007). Tidal oscillation and biogeochemical interactions may be also important in driving an area optically (e.g., Shi et al., 2011).

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Parameterizations of spectral light absorption coefficients (Inherent Optical Properties, IOPs) in the oceans are generally developed using *in situ* IOP measurements as functions of chlorophyll-*a* concentration (IOCCG, 2000), which show robust general trends over orders of magnitude (Morel and Maritorena, 2001). These central trends seem to hold in open ocean and coastal waters for absorption coefficients (Babin et al., 2003), but there are few bio-optical datasets from coastal regions (e.g., Babin et al., 2003; Stæhr and Markager, 2004) and they lack seasonal characterizations (Sathyendranath et al., 1999; Stuart et al., 2004). Deviations from relationships between IOPs and chlorophyll-*a* are expected in coastal waters (Ciotti et al., 1999), driven by distinct proportions among the optical constituents (Morel and Gentili, 2009), and their spectral characteristics can also be the result of changes in phytoplankton assemblages (Ciotti et al., 2002; Bricaud et al., 2004).

Our study was conducted in the Santos Estuarine System, located in southeastern Brazil. The objective of our work was to investigate the influences of seasonal and shorter time scale variability on bio-optical properties in a costal urbanized area. Specifically, we describe the magnitudes and spectral characteristics of light absorption by particles and CDOM to test the hypothesis that the parameterization of light absorption coefficients of detritus, phytoplankton, and CDOM as a function of chlorophyll-*a* concentration and salinity is not robust in Santos Bay over different time scales of observation. We parameterize the absorption coefficients of detritus, phytoplankton, and CDOM using the following sampling design: (1) monthly sampling in Santos Bay (SB) and Santos Estuarine Channel (SEC) to investigate seasonal variability and the influence of continental runoff into SB and (2) sampling in SB on specific dates during warm (wet) and cold (dry) months and during spring and neap tides. Because of the high particle load expected in these waters, we also investigated differences in the magnitudes and spectral shapes of absorption coefficients obtained from the Quantitative Filter Technique, QFT (Kishino et al., 1985), and the Transmittance Reflectance method, TR (Tassan and Ferrari, 1995).

2. Materials and methods

2.1. Study area

The Santos Estuarine System is a region with substantial tourist and fishing activities (Fig. 1) and includes the Port of Santos, the busiest container port in Latin America, located in the Santos Estuary Channel. Our sampling was conducted in the Santos Estuary Channel and Santos Bay, a semi-enclosed area approximately 7.0 km long and 7.3 km wide at its widest point, with an average depth of 15 m (DHN, 2003). Tides are semi-diurnal with less than a meter in amplitude, but in association with mesoscale winds influences the dynamics of local water masses, and vertical mixing (Alfredini et al., 2008). Because of its shallow bathymetry and significant tidal mixing (Harari and Camargo, 2003), the plume formed in the bay is a mixture of intermittent continental sources and oceanic water masses. These waters include the Coastal Water (CW) and Tropical Water (TW) that vary seasonally, and the South Atlantic Central Water during coastal upwelling events farther north that are most intense during spring and summer (Castro Filho et al., 1987). Local climate resolves moderate variability in annual air temperatures and intense precipitation during warmer months (CPTEC/INPE, 2000).

In Santos Bay, waters are influenced by semi-diurnal tidal currents, wind-driven currents, coastal fronts (Harari et al., 2006), and freshwater from two main channels (São Vicente and Santos). The resuspension of bottom sediments can occur episodically during strong tidal currents (Alfredini et al., 2008). Surveys have shown high ammonium, phosphate and chlorophyll concentrations in the

Fig. 1. Sampling stations during the ECOSAN monthly sampling (circles) and CIRSAN tidal sampling (triangles) in the Santos Estuarine Channel (SEC) and Santos Bay (SB).

Santos estuarine complex year round (Gianesella et al., 2000; Aguiar and Braga, 2007), and changes in the phytoplankton species composition and size structure (mainly diatoms, dinoflagellates and mixotrophic dinofalgellates) have been related to freshwater input, tides and wave action (Moser et al., 2012).

The Santos Estuary Channel contains organic and inorganic materials from a variety of sources, including a submarine sewage outlet that releases treated sewage effluent in the center of the Santos Bay, but also other sources of sewage *in natura*. The channel is continuously dredged for harbor operations, which creates turbidity and releases inorganic materials (Abessa et al., 2005). Thus, the variability of organic and inorganic materials entering Santos Bay from several sources may be distinguishable by their optical properties.

2.2. Sampling designs and data collection

2.2.1. Description of the monthly and tidal sampling designs

A total of 205 samples were gathered monthly from November 2004 to September 2005 during the ECOSAN Project[1] (Fig. 1) at 4 fixed stations in the Santos Bay (SB) and 3 stations in the Santos Estuarine Channel (SEC), which corresponded to the monthly approach. Unfavorable weather conditions prevented sampling inside SB in April 2005. In January, June and July 2005, sampling at the central station of the SEC (Fig. 1) was canceled. Niskin bottles were used to collect samples for the determination of chlorophyll-*a* concentration and light absorption coefficients of particles and CDOM at the surface, middle depth (3–8 m) and near the bottom (8–20 m), depending on the local depth. The sampling process itself caused resuspension of bottom sediments, thus in these conditions ($N = 71$) the samples were discarded for the purpose of general optical characterization but were used for comparison between the QFT and TR methods. The ECOSAN survey will be hereafter referred to as monthly sampling.

[1] ECOSAN was a multidisciplinary project that aimed to evaluate the influence of continental sources from the Santos Estuarine System on the adjacent inner continental shelf (Fig. 1).

Table 1
Summary for the ECOSAN surveys with sampling in the Santos Estuarine Channel (SEC) and Santos Bay (SB) and the Tidal surveys with sampling in Santos Bay. See the text for details and Fig. 1.

Project	Sampling design	Sampling date	Sampling area	Objectives	Collected data
ECOSAN	Once in each month	(Eleven cruises) 2004 Nov to 2005 Sept	Seven fixed stations: 3 in SEC and 4 in SB	- To characterize the variability in optical parameters in the SEC and SB in warm (wet) and cold (dry) months - To compare the phytoplankton absorption coefficients and spectral shapes of phytoplankton and detritus absorption coefficients derived from the QFT and TR methods	- CTD casts - [Chl *a*] - Particulate (detritus plus phytoplankton) absorption coefficients using the QFT and TR methods - CDOM absorption coefficients - Spectral shapes of phytoplankton, detritus and CDOM absorption coefficients
CIRSAN	Once in each neap and spring tide in two warm and cold months	(Eight cruises) 2006 Mar 07 2006 Mar 15 2006 Aug 16 2006 Aug 25 2007 Mar 13 2007 Mar 20 2007 Sept 04 2007 Sept 1	Sixteen fixed stations in SB	- To characterize the variability in optical parameters for neap and spring tides and warm and cold months	- CTD casts - [Chl *a*] - TSM - %OM - Particulate (detritus plus phytoplankton) absorption coefficients using the TR methods - CDOM absorption coefficients - Spectral shapes of phytoplankton, detritus and CDOM absorption coefficients

For the tidal approach, a total of 256 samples were collected during the CIRSAN project[2] at 16 fixed oceanographic stations distributed uniformly in SB (Fig. 1). Eight cruises were carried out overall during March 2006 and March 2007 and August 2006 and September 2007, thus in the end of summer and winter, respectively. Two small vessels were used simultaneously, one sampling the inner and the other sampling the outer portion of SB. In each selected month, two dates were chosen to correspond to spring tide (ST) and neap tide (NT) conditions.

Water samples were collected with clean plastic 20-L bucket at the surface and with horizontal 5-L Van Dorn bottles at 1–2 m above the bottom (8–20 m, depending on local depth) for determination of the same variables as during the monthly sampling, and additionally for total suspended material and the percentage of particulate organic matter. The CIRSAN survey will be hereafter referred to as tidal sampling. A summary of both sampling surveys (ECOSAN and CIRSAN) is shown in Table 1.

2.2.2. Salinity and precipitation

Vertical salinity profiles were measured with a CTD Falmouth 2DACM during the ECOSAN samplings. In the CIRSAN surveys, CTD casts (Seabird, Seacat) were performed only at stations in the outer SB. At the laboratory, salinity for the inner SB stations was measured using an Autosal salinometer (BECKMAN RS10) in samples previously stored in sealed glass amber bottles. Precipitation data for the both datasets were provided by a gauge station located at 23°57′ S and 46°18′ W. No precipitation data were available for September 2007 at this station or near the study region.

2.2.3. Chlorophyll-a concentration

Sample volumes of 250–500 ml were concentrated on GF/F filters under low pressure and immediately stored in liquid nitrogen. The samples were extracted for 24–30 h at about −10 °C in a solution of pre-cooled 90% acetone:DMSO (6:4 by volume; Shoaf and Lium, 1976). Chlorophyll-*a* concentration [Chl *a*], in mg m^{-3}, was determined using a Hitachi U3010 spectrophotometer for monthly sampling and a spectral-radiometer USB4000 Ocean Optics for tidal sampling, following the procedure of SCOR/UNESCO (1966). No chlorophyll-*a* samples from near the bottom were collected during the NT sampling in September 2007.

2.2.4. Particulate absorption coefficients

A volume of 300–1000 ml of water was concentrated on GF/F filters and immediately preserved in liquid nitrogen. Absorption of particulate material was determined using the TR method of Tassan and Ferrari (1995) with a few modifications. A Hitachi U3010 dual-beam spectrophotometer was used with an integration sphere, and the correction of path length amplification described in Tassan et al. (2000) was applied. Sample and blank filters were first scanned against air from 350 to 750 nm at the entrance of the sphere and then placed directly against the exit of the integrating sphere, backed with a light trap, for a second scan. Blanks and all ECOSAN filters were treated with a few drops of 0.5% NaClO for 10–15 min and then carefully washed with 0.2-μm filtered seawater. The extracted filters were measured as described above, and the spectral absorption coefficients of phytoplankton, $a_{ph}(\lambda)$ in m^{-1}, were computed as the difference between scans before (total particulate, $a_p(\lambda)$ in m^{-1}) and after (detritus, $a_{det}(\lambda)$ in m^{-1}) the NaClO extraction, corrected for the volume filtered and the clearance area of the filtration. Values between 740 and 750 nm were considered as $a_{det}(\lambda)$ (see Tassan et al., 2000). No measurements were carried out in March 2006 (first sampling of the tidal survey) due to instrumental unavailability. To obtain the spectral slope of detritus absorption (S_{det} in nm^{-1}), and an exponential function was adjusted to $a_{det}(\lambda)$ from 350 to 700 nm (Bricaud et al., 1981).

For the CIRSAN sampling, $a_{det}(\lambda)$ was modeled based on the decomposition method proposed by Bricaud and Stramski (1990). A strong agreement between the modeled $a_{det}(\lambda)$ coefficients and those measured after the NaClO extraction was observed for 18 samples randomly extracted with NaClO (slope of 1.02, intercept of 0.07, and R^2 of 0.95 at 443 nm). When near-bottom samples were suspected of being contaminated by resuspension during the monthly sampling, the absorbance after extraction noticeably increased toward blue wavelengths compared to measurements before extraction, even after several rinses with filtered seawater. In these cases, the numerical correction was also applied. For few samples ($N = 12$), however, there was no solution for the numerical

[2] CIRSAN is a multidisciplinary project with the overall objective of characterizing the seasonal variability in the tide current system in Santos Bay (Fig. 1), emphasizing the contrast between winter and summer.

decomposition of $a_p(\lambda)$ in $a_{det}(\lambda)$ and $a_{ph}(\lambda)$, and these samples were discarded for all analyses.

For the ECOSAN samples, $a_p(\lambda)$ was also determined using the QFT method (Kishino et al., 1985). Each scan was corrected for scattering errors by offsetting the spectra with the mean absorption between 740 and 750 nm. A path length amplification correction was determined for monospecific cultures according to Mitchell (1990). These data were used to compare the magnitudes and spectral shapes of absorption coefficients obtained from the QFT and TR methods.

2.2.5. Parameterization of phytoplankton absorption

A size parameter (S_f, no unit) was computed from each phytoplankton-normalized absorption spectrum, following Ciotti et al. (2002). Each spectrum was previously normalized to its mean value computed on the basis of all spectral values between 400 and 700 nm, denoted as $<a_{ph}>$, which is considered the magnitude of the phytoplankton absorption. A Levenberg–Marquardt regression was used to fit the observed normalized phytoplankton absorption spectrum to a linear model (see Eq. (3) in Ciotti et al., 2002) by adjusting the values of the derived cell size parameter, S_f. The values of S_f are constrained to vary from 0 to 1. S_f tends to 0 when large cells of phytoplankton (>20 μm) are dominant, and 1 when small cells (<2 μm) dominate. Adjustments with R^2 <0.9 were considered unsatisfactory. The S_f values computed for these cases were not considered ($N = 11$).

2.2.6. CDOM absorption

GF/F filtrates were collected in amber Qorpak bottles that were previously acid cleaned and sterilized and kept in the dark at 4 °C until analysis, and the mean storage time was 5 days. The spectral absorbance of the filtrates was measured between 300 and 750 nm on a Hitachi U3010 spectrophotometer for the monthly sampling and on a spectral-radiometer USB4000 Ocean Optics for the tidal sampling. Freshly produced Milli-Q water was used as a reference. After converting the optical density values into absorption coefficients, $a_{cdom}(\lambda)$ in m^{-1}, an exponential function was applied to the 350–600 nm spectral absorption range (Babin et al., 2003) to describe the magnitude, $a_{cdom}(443)$ in m^{-1}, and spectral shape, S_{cdom} in nm^{-1}, of CDOM absorption.

2.2.7. Total suspended material

For the CIRSAN sampling, total suspended material (TSM), mg m^{-3}, was measured following gravimetric methods (APHA, 1985). Sample volumes of 100–500 ml were filtered through pre-weighted GF/F filters, which were stored in sealed containers with silica gel pellets. At laboratory, the filters were dried at 60 °C for 24 h and re-weighted using an analytical scale (0.001 g precision). The filters were then combusted for 6 h at 500 °C and re-weighted. TSM is assumed as the difference between the weight of the dried material and the initial weight of the unused filter, whereas the percentage of particulate organic matter (%OM) was computed from the ratio of the combusted and dried weight.

2.2.8. Statistical analyses

A three-way analysis of variance (ANOVA) was applied ($\alpha = 95\%$) on the monthly and tidal datasets to investigate the effects of fixed driving factors as well as interactions among them. Specifically for the monthly data, the following fixed factors were considered: (1) samples from warm months (WM – November 2004–March 2005) or cold months (CM – April–September 2005), (2) sampling in Santos Bay, SB, or Santos Estuarine Channel, SEC, and (3) samples from surface or middle depth. For the tidal sampling, the fixed factors were (1) samples from warm, WM, or cold, CM, months, (2) samples from Neap Tide, NT, or Spring Tide, ST, and (3) samples from surface or near the bottom. The ANOVA results were tested a posteriori with a Tukey test (Zar, 1999).

Spearman correlation tests were applied to detect significant relationships ($p < 0.05$) among absorption parameters as well as relationships between absorption parameters and salinity, [Chl *a*], and TSM. The correlation between $a_{cdom}(443)$ and S_{cdom} was tested using log-transformed data because of the well-known non-linear dependence between these parameters (Twardowski et al., 2004 and references therein). Differences between the magnitudes and the spectral behavior of the phytoplankton and detritus absorption parameters retrieved from the QFT and TR methods were evaluated using a weighted linear regression model to minimize the effect of outliers.

3. Results

3.1. Precipitation and salinity

Precipitation followed the seasonal pattern expected for the study area, although extreme unpredicted events were observed (e.g., April 2005). Rainfall was significantly higher (t-value = 1.97, $N = 183$, $p = 0.02$) during WM (November 2004–March 2005) than CM (April–September 2005); therefore the monthly data were grouped into these two periods to provide replicates for the statistical analyses. The best correlation among precipitation and surface salinity in the SEC was found using the mean daily rainfall of 20 days preceding the sampling ($N = 11$, $R = -0.62$, $p = 0.04$). During the tidal sampling, the surface salinity in SB varied from 23.3 to 35.6, and the low salinity observed during September 2007 was not related to precipitation.

3.2. Chlorophyll-a, total suspended matter and percentage of organic matter

Regardless of sampling areas and depths, [Chl *a*] was significantly higher in WM than CM, with averages of 16.43 and 7.09 mg m^{-3} at surface (Table 2). Lower [Chl *a*] was observed in January probably as a result of high precipitation preceding the sampling (not shown). During the tidal sampling, [Chl *a*] was higher at the surface than near the bottom (means of 10.54 and 5.63 mg m^{-3}), but this difference was significant only for NT (Table 3). The opposite was observed for TSM, which was higher near the bottom during ST. ST samples also contained significantly lower %OM, probably as a result of resuspension of inorganic sediments driven by spring tides in SB.

3.3. Magnitudes and spectral shapes of absorption coefficients

Monthly, $a_p(443)$ in SB showed little variation (mean of 0.55 ± 0.14 m^{-1}) and much higher variability in SEC (mean of 0.72 ± 0.40 m^{-1}), and was also higher in the middle-depth samples during CM (Table 2). The variability in $a_p(443)$ seemed to be controlled by phytoplankton absorption, as $a_{det}(443)$ varied largely only during April and June in middle-depth samples (1.54 and 0.97 m^{-1}, respectively), likely as a result of bottom resuspension. Values of $<a_{ph}>$ followed along with [Chl *a*], with surface values higher during WM (mean of 0.16 ± 0.06 m^{-1}). $a_{cdom}(443)$ was higher in SEC (mean of 0.37 ± 0.16) than in SB (mean of 0.25 ± 0.08 m^{-1}), but this difference was significant only during WM. Higher $a_{cdom}(443)$ was found at the surface than at middle depth.

The most variable spectral parameter during the monthly sampling was S_f, which ranged from 0.005 to 0.70 (mean of 0.31), and no statistical differences were observed (Table 2). S_{det} varied from 0.006 to 0.014 nm^{-1} and was lower during WM (mean of

Table 2
Statistical results ($\alpha = 95\%$) from three-way ANOVA analysis for the ECOSAN sampling design ($N = 183$) with the following chosen fixed factors: (1) sampling in wet or dry period, (2) sampling in bay or estuary and (3) sampling at the surface or middle-water. Significant cases ($p < 0.05$) are indicated.

Factor	Salinity	[Chl *a*]	$a_p(443)$	$a_{ph}(443)$	$a_{det}(443)$	$a_{cdom}(443)$	$a_{ph}(443)/a_{t-w}(443)$	$a_{det}(443)/a_{t-w}(443)$	$a_{cdom}(443)/a_{t-w}(443)$	S_f	S_{det}	S_{cdom}
Period	–	0.0005	–	0.03	–	0.003	0.01	0.0001	–	–	<0.0001	0.03
Sampled area	<0.0001	–	0.04	–	–	0.0001	–	–	–	–	0.0006	–
Depth	<0.0001	–	0.03	0.04	0.0008	0.0002	–	<0.0001	0.0002	–	–	–
Period × sampled area	0.03	–	–	–	–	0.01	–	–	–	–	–	–
Period × depth	–	–	0.005	0.02	0.04	–	–	0.02	0.04	–	–	–
Sampled area × depth	–	–	–	–	–	–	–	–	–	–	–	–
Period × sampled area × depth	–	–	–	–	–	–	–	–	–	–	–	–

0.011 nm^{-1}) than CM (mean of 0.012 nm^{-1}) and was also significantly higher in SB (mean of 0.012 nm^{-1}) than in SEC (mean of 0.011 nm^{-1}). S_{cdom} was less variable (0.011–0.019 nm^{-1}) than S_{det}, however, S_{cdom} was statistically lower during WM (mean of 0.015 nm^{-1}) compared to CM (0.016 nm^{-1}).

Overall, $a_p(443)$ was more variable during the tidal sampling (0.09–1.17 m^{-1} for NT and from 0.18 to 3.94 m^{-1} for ST). ANOVA showed a significant interaction among factors for $a_p(443)$ during the tidal surveys as well, which was statistically higher in ST during CM (Table 3). Both factors depended on the sampling depth as showed higher values near the bottom. Values for $a_{det}(443)$ varied between 0.02 and 0.38 m^{-1} for NT and between 0.03 and 2.32 m^{-1} for ST and showed more complex interactions in the ANOVA involving all three factors investigated. Both $<a_{ph}>$ and [Chl *a*] showed the same interactions, as expected, with higher $<a_{ph}>$ at surface (mean of 0.14 m^{-1}) than near the bottom (mean of 0.07 m^{-1}) during NT (Table 3).

During the tidal sampling, differences in $a_{cdom}(443)$ were detected by interactions between the sampling month and tide, probably caused by the extremely high $a_{cdom}(443)$ observed during NT in September 2007 (Table 3). It is noteworthy that low salinity was not related to high precipitation during this survey. The average value of S_{det} was 0.012 nm^{-1} for all tidal datasets and considerably higher S_{cdom} values were found in March 2007 during both NT and ST (average of 0.026 nm^{-1}).

3.4. Parameterization of absorption coefficients

In this section, we investigate the dependence of variations of TSM, %MO, $a_p(443)$, $<a_{ph}>$, $a_{det}(443)$, $a_{cdom}(443)$, S_f, S_{det}, and S_{cdom} on salinity and [Chl *a*] in SB for different time scales: (1) WM vs. CM for the monthly sampling and (2) NT vs. ST for the tidal sampling. Samples from surface and middle depth and from surface and near the bottom were considered for monthly and tidal sampling analyses, respectively. The correlations are expressed in terms of the correlation coefficient, *R*.

[Chl *a*] partially accounted for the variability in $a_p(443)$ and $a_{cdom}(443)$ during WM ($R = 0.51$ and 0.45), and in both $a_p(443)$ and TSM during NT ($R = 0.80$ and 0.44). [Chl *a*] also explained variations in the cell size index of phytoplankton, S_f, and S_{det}, during CM to some extent ($R = 0.48$ and 0.42). Except for some weak dependence of $a_{cdom}(443)$ on [Chl *a*] during WM ($R = 0.45$), neither $a_{cdom}(443)$ nor $a_{det}(443)$ was correlated with [Chl *a*].

Salinity was more important than [Chl *a*] in explaining variations in the investigated variables. Although $a_{cdom}(443)$ showed a significant negative dependence on salinity during all conditions, as generally reported for coastal regions, the correlation was only robust ($R = -0.94$) for CM (lower precipitation). This is consistent with recent findings on the contribution of inner shelf waters with low salinity to SB during winter (Carvalho et al., 2014). The expected inverse dependence of S_{cdom} (index of CDOM composition) on $a_{cdom}(443)$ was not observed during the monthly sampling, but was robust for the tidal sampling ($R = -0.86$ in NT and $R = -0.63$ in ST).

On a monthly scale, $a_{det}(443)$ was inversely related to salinity during CM, suggesting that part of the non-algal particles has a terrestrial origin in this period, but a positive weak relationship was also observed during ST ($R = 0.33$). On a tide time scale, a direct dependence was observed for TSM on salinity during NT ($R = 0.71$) and ST ($R = 0.53$) surveys, whereas negative but significant correlation was obtained between salinity and %OM ($R = -0.34$ and 0.30 for NT and ST), which were more robust once only the surface means of TSM and %OM were considered, with direct ($R = 0.85$) and inverse ($R = -0.92$) dependences on salinity, respectively (not shown).

3.5. Parameterization of phytoplankton absorption coefficients using chlorophyll-a

The dependence of $a_{ph}(\lambda)$ on [Chl *a*] was investigated at selected wavelengths (443, 490 and 676 nm) as illustrated in Fig. 2, separating WM from CM and NT from ST data. No significant differences were observed among sampling designs, so unique statistical adjustments were performed for both monthly and tidal surveys. A power function in the form $a_{ph}(\lambda) = A(\lambda)\,[\text{Chl } a]^{B(\lambda)}$ was appropriate to describe the dependence of $a_{ph}(\lambda)$ on [Chl *a*], as

Table 3
Statistical results ($\alpha = 95\%$) from three-way ANOVA analysis for the CIRSAN sampling design ($N = 239$) with the following chosen fixed factors: (1) sampling in wet or dry period, (2) sampling during neap or spring tide and (3) sampling at the surface or near bottom. Significant cases ($p < 0.05$) are indicated.

Factor	Salinity	[Chl *a*]	TSM	%MO	$a_p(443)$	$a_{ph}(443)$	$a_{det}(443)$	$a_{cdom}(443)$	$a_{ph}(443)/a_{t-w}(443)$	$a_{det}(443)/a_{t-w}(443)$	$a_{cdom}(443)/a_{t-w}(443)$	S_f	S_{det}	S_{cdom}
Period	<0.0001	–	–	–	–	0.02	0.006	–	0.0005	–	0.001	0.0003	–	<0.0001
Tide	–	<0.0001	0.04	0.002	0.0005	0.0001	0.0001	–	0.003	–	–	–	–	
Depth	<0.0001	<0.0001	0.04	<0.0001	–	<0.0001	–	–	0.05	–	–	<0.0001	–	
Period × tide	–	–	–	–	0.002	0.006	0.004	0.0001	<0.0001	–	0.003		–	0.03
Period × depth	–	–	–	–	0.001	0.03	0.001	–	–	–	–	0.003	–	
Tide × depth	–	0.001	0.02	–	<0.0001	0.0001	0.01	–	0.03	0.01	–		–	
Period × tide × depth	–	–	–	–	–	–	–	–	–	–	–		–	

commonly found in literature (Bricaud et al., 2004 and references therein).

A large dispersion of $a_{ph}(\lambda)$ as a function of [Chl *a*] was verified at 443 nm, although our data generally agreed with empirical relationships established by Bricaud et al. (1995) – B95 – and Bricaud et al. (2004) – B04 for oceanic and coastal waters (Fig. 2a). The scattering of data at the blue spectral region (Fig. 2b) is similar for 443 and 490 nm (R^2 of 0.63 and 0.68, respectively), suggesting that pigments other than [Chl *a*] contributed to $a_{ph}(\lambda)$ variability. This result is reinforced by a remarkable decrease in the dispersion of $a_{ph}(676)$ as a function of [Chl *a*] (note the difference in *y* scales, Fig. 2c), as variations in this spectral region is attributable solely to [Chl *a*] and the package effect (Bricaud et al., 1995). Moreover, our data at 676 nm are in very good agreement with the B95 regression. However, some points appear to deviate greatly from the central empirical relationship of $a_{ph}(676)$ vs. [Chl *a*] (Fig. 2c), which may indicate the occurrence of distinct phytoplankton communities, especially during warm months for monthly sampling.

3.6. The QFT and TR methods for light absorption of particles

Although documentation on the TR method for particle light absorption has been available for more than 15 years, the traditional QFT method remains widely used and assumed to provide satisfactory results in waters where phytoplankton dominates the particle pool. Investigations of the extent to which the TR method improves measurements in waters with high-suspended sediment content (e.g., Tassan and Ferrari, 2002, 2003; Moate et al., 2012; Röttgers and Gehnke, 2012) have yet to include the possible effects on the spectral shape of the phytoplankton coefficients.

Differences in $a_{det}(\lambda)$ provided by both QFT and TR methods are undoubtedly expected, as the former assumes a null absorption near 750 nm, while the TR method attributes the absorption measured at this wavelength exclusively to detritus (but see Babin and Stramski, 2002). Nonetheless, when $a_{det}(443)$ measurements from both methods are compared, TR-derived values were 1.20 times higher for very low values to about 0.5 m^{-1}, trending toward larger differences above this value, which indicates a non-linear effect. It is noteworthy that $a_p(750)$ derived by the TR method varied about 9-fold (0–0.94 m^{-1}) and showed a dependence ($R^2 = 0.30$, $p < 0.001$) on TSM (Fig. 3a), which varied about 13-fold.

Linear regressions showed good agreement between the magnitudes of phytoplankton absorption spectra measured with the QFT and TR methods (Fig. 3b–d), whereas the TR-derived S_f was systematically lower than QFT-derived S_f (slope = 0.86, Fig. 3e). The TR method thus yielded slightly flatter phytoplankton absorption spectra, although the comparison was dispersed ($R^2 = 0.75$) probably because of differences in the amplification factor beta applied for each method, which can also spectrally affect $a_{ph}(\lambda)$ (Röttgers and Gehnke, 2012). Lastly, S_{det} computed for the $a_{det}(\lambda)$ spectra measured by the TR method was also substantially lower, with large discrepancies for very high QFT-S_{det} (Fig. 3f).

4. Discussion

4.1. Time variability of optical parameters

The characterization of optical properties and their temporal and spatial scales of variability has been a successful tool for coastal water research and management (Orrico et al., 2007; Reuter et al., 2009). Our results strongly suggest that continuous observation of optical properties can provide information on the concentration and distribution of suspended and dissolved materials, as well as their main characteristics and sources in Santos Bay, similarly to other optically complex environments (e.g., Garel and Ferreira, 2011). Moreover, we investigate whether parameterizations of

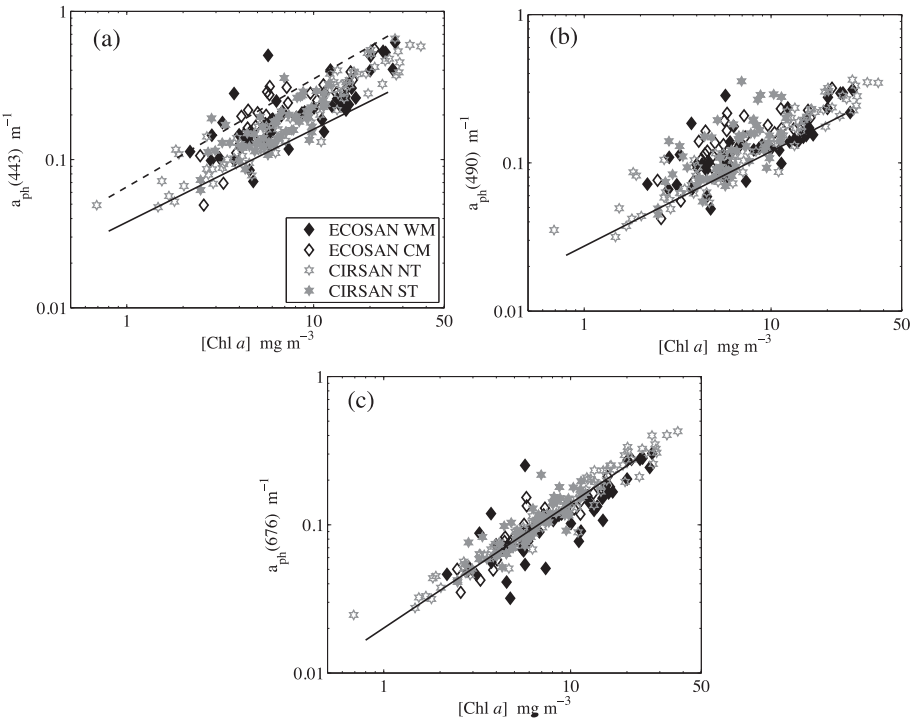

Fig. 2. Phytoplankton absorption coefficients at 440, 490 and 676 nm, as a function of chlorophyll-*a* concentration [Chl *a*], considering the ECOSAN and CIRSAN data. The equations that describe the best fit between [Chl *a*] and $a_{ph}(\lambda)$ were $a_{ph}(440) = 0.047\ [\text{Chl } a]^{0.707}$, $R^2 = 0.63$; $a_{ph}(490) = 0.038\ [\text{Chl } a]^{0.598}$, $R^2 = 0.68$; $a_{ph}(676) = 0.021\ [\text{Chl } a]^{0.793}$, $R^2 = 0.84$ ($N = 268$, $p < 0.001$). R^2 corresponds to the determination coefficients computed between log-transformed data of [Chl *a*] and $a_{ph}(\lambda)$. The solid line and dashed line represent the relationships obtained by Bricaud et al. (1995, 2004), respectively. The latter work only provided the equation for 440 m.

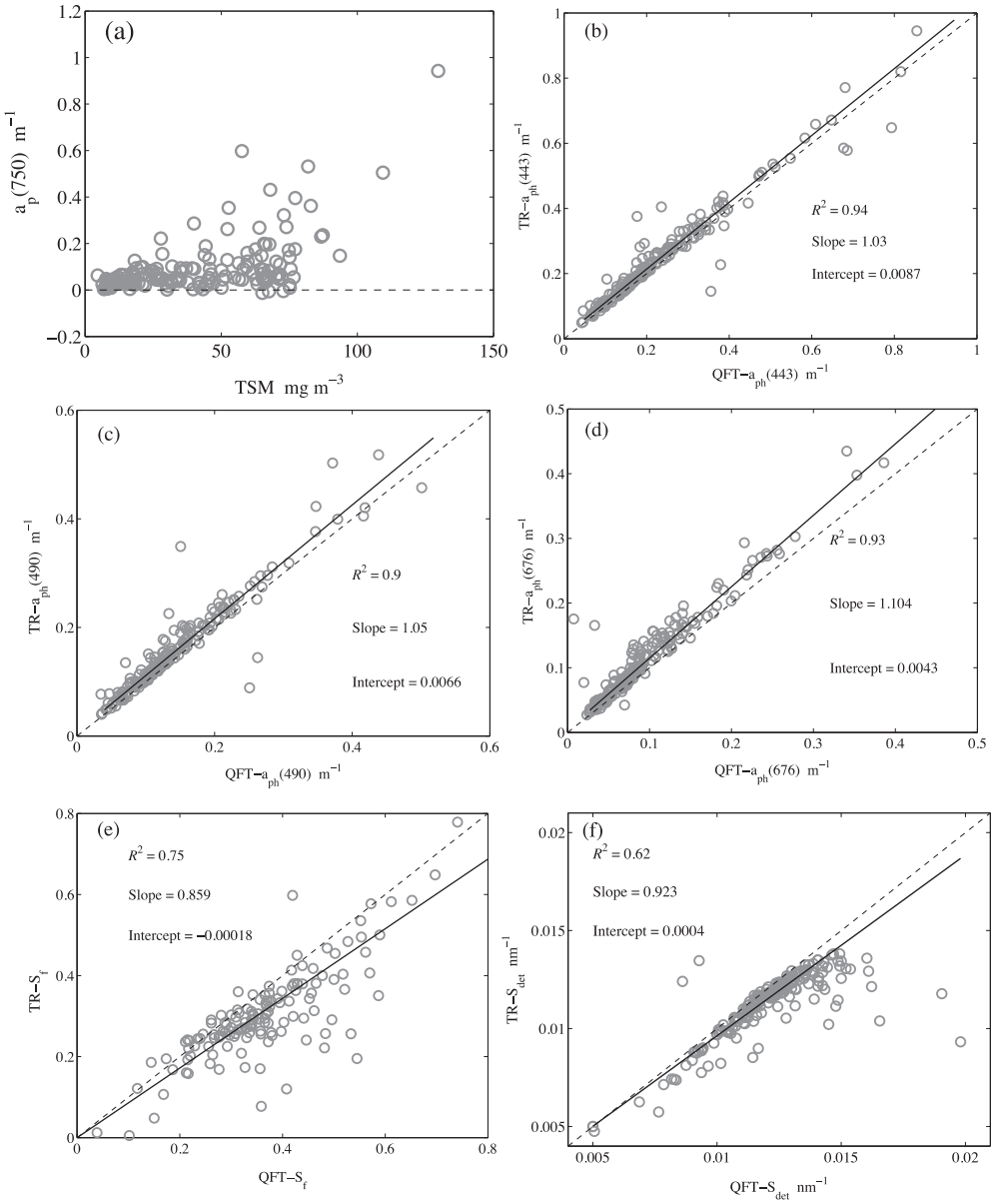

Fig. 3. (a) Particulate absorption coefficient at 750 nm, $a_p(750)$, as a function of total suspended material, TSM. (b–d) Comparison between phytoplankton absorption coefficients, $a_{ph}(\lambda)$, at 443, 490 and 676 nm. (e) Spectral shape of phytoplankton absorption, S_f, and (f) spectral shape of detritus absorption, S_{det}, derived from the QFT and TR methods.

these optical components as a function of chlorophyll-*a* and salinity are robust in this site regardless of the time scale.

Our data suggest that rainfall controls salinity in Santos Bay only partially on a monthly scale and that both [Chl *a*] and phytoplankton absorption are higher during warm months when terrestrial freshwater inputs are more intense in the Santos Estuarine System. Although during tidal cycles salinity and precipitation did not correlate, TSM varied positively with salinity, and [Chl *a*] and phytoplankton absorptions were consistently lower during spring than neap tides. Enhanced mixture during spring tides can suspend bottom sediments, which increase light attenuation (e.g., Shibata et al., 2010) and dilute Santos Bay with inner continental shelf water masses. As TSM increased and %OM decreased during spring tides, turbidity has been suggested to limit phytoplankton development due to resuspension of bottom sediments. During neap tides, the higher proportion of OM to TSM suggests that phytoplankton benefits from light availability.

With regard to the relative contribution to light absorption, when $a_p(\lambda)$, $a_{det}(\lambda)$ and $<a_{ph}>$ are compared, the particle load in Santos Bay is controlled by phytoplankton on a monthly scale and by the inorganic fraction of particles (detritus) on a shorter scale (tides). These data partially contradict previous observations of organic material export from the estuarine channels (Moser et al., 2005; Schmiegelow et al., 2008). Moreover, no robust relationship was found between salinity and $a_p(\lambda)$, or $a_{det}(\lambda)$, supporting the hypothesis that the Santos Estuarine Channel is not a significant source of particles for Santos Bay.

S_{det} was higher in Santos Bay than in the Santos Estuarine Channel on a monthly scale and was higher during cold (dry) months compared with warm (wet) months. Although this difference is small for any hypothesis regarding detritus origin, it suggests the predominance of inorganic particles in Santos Bay due to higher S_{det} values (Bukata et al., 1995). No difference was observed for S_{det} when comparing neap and spring tide conditions and its

average (0.012 nm^{-1}) was nearly identical to the average found for mineral particles by Bowers et al. (1996). The generally narrow range of variation in S_{det} and the lack of dependence on the variables considered discourage the use of this parameter for monitoring purposes. Scattering and backscattering coefficients and backscattering ratios may be more applicable (Twardowski et al., 2001; Boss et al., 2004).

The absorption coefficients of CDOM did not correlate with [Chl *a*] as observed in other coastal regions (Blough and Del Vecchio, 2002), which may reflect a lag time between algal and CDOM production (Bricaud et al., 1981; Nelson et al., 1998; Sasaki et al., 2005) or CDOM inputs unrelated to local productivity (Del Vecchio and Subramaniam, 2004). This lack of correlation was also verified in the São Vicente Estuarine Channel, which is connected to Santos Bay as well (Bucci et al., 2012).

In estuarine areas, the relationships between CDOM absorption and salinity are generally robust (Boss et al., 2001; Blough and Del Vecchio, 2002; Berto et al., 2010). In Santos Bay, the inverse dependence of $a_{cdom}(443)$ on salinity during all conditions investigated indicates terrestrial runoff as a source of CDOM to Santos Bay. Nevertheless, the most robust relationship ($R = -0.94$) was found during cold months suggesting the influence of the adjacent inner shelf waters (Carvalho et al., 2014). A contribution to CDOM by sediment resuspension (e.g., Menon et al., 2011) was ruled out, as no correlation was found between TSM and $a_{cdom}(443)$. Local CDOM produced by the degradation of algal estuarine species, and bacteria consumption will likely modify the characteristics of CDOM. Very high $a_{cdom}(443)$ was observed during the neap tide survey in September 2007, probably reflecting the susceptibility of the Santos Bay to periodic external contributions of CDOM (Moser et al., 2012). One possible source of this anomalous increase in CDOM could be freshwater released from the Henry Borden hydroelectric power plant (Gasparro et al., 2008) located in the city of Cubatão, 14 km uphill from Santos. This hypothesis is supported by the low salinity not related to the precipitation for the same period.

Similar to the description of the spectral shape of detritus absorption, S_{det}, the shape of CDOM absorption, S_{cdom}, was much less variable in Santos Bay than in the Santos Estuarine Channel on a monthly scale, which may suggest small differences in the CDOM composition of the system, as S_{cdom} reveals information about its sources and composition, including the ratio of humic to fulvic acids (Twardowski et al., 2004). Most S_{cdom} values in Santos Bay were within the range reported by Blough and Del Vecchio (2002) for coastal waters influenced by river input (0.013–0.018 nm^{-1}) and were similar to the common assumed value for CDOM in coastal waters (0.015 nm^{-1}; see Babin et al., 2003). However, episodic changes in S_{cdom}, such as the high values observed in March 2007 (mean of 0.026 nm^{-1}) also suggest important external and peculiar CDOM contributions to the system. No dependence of S_{cdom} on salinity was observed and a relatively stable spectral shape of CDOM absorption (for instance, the average value of 0.015 nm^{-1} found in this study) could be considered in bio-optical monitoring and modeling exercises for the region, excepting episodic inputs from anthropogenic sources. In turn, as both S_{cdom} and S_{det} showed relatively small variations, $a_{ph}(\lambda)$ may be obtained from the deconvolution of total absorption coefficient minus the absorption of the water itself.

Our values of $a_{ph}(\lambda)$ are in general in agreement to what is typically found at similar [Chl *a*] in Case 1 waters (Bricaud et al., 1995, 2004). No systematic differences were found for $a_{ph}(\lambda)$ vs. [Chl *a*] among the different conditions investigated here, indicating that this parameterization would be invariable regardless of the time scale of observation. Nevertheless, the scattering of this dependence is noticeable at the blue spectral region, where the contributions of other pigments are more important, so the prediction of phytoplankton biomass (chlorophyll-*a* concentration) from the phytoplankton absorption coefficients (or the inverse) would be more applicable when considering red wavelengths.

The size factor retrieved from the spectral shape of the absorption coefficients of phytoplankton, S_f, was highly variable on a monthly scale and not dependent on the variables investigated here, except for weak but significant correlations with [Chl *a*] and salinity during cold months. The size structure of phytoplankton, therefore, seems to be weakly dependent on precipitation and continental runoff to Santos Bay. This parameter was somewhat related to sampling month and depth but not to salinity. This indicates that mixing conditions (e.g., spring tides) tend to benefit the development of larger cells in Santos Bay. In fact, Moser et al. (2012) showed the predominance of chain-forming diatoms with large cell sizes in association with spring tides and the consequent resuspension processes.

The lack of an inverse [Chl *a*]-S_f dependence in our data indicates that chlorophyll-*a* concentration is a weak indicator of phytoplankton cell size in Santos Bay. Moreover, it indicates the infeasibility of using an average S_f for further bio-optical models applied to monitoring programs but provides usable information on the response of the phytoplankton community to physical forces, especially during large tidal variations. It is important to observe the time scale of physical forcing effects, because some changes may not be exactly in phase with the causal phenomenon (e.g., Shi et al., 2011).

4.2. Retrieval of light absorption parameters by different methods

The QFT method for determining particulate absorption (Kishino et al., 1985) assumes a null absorption at 750 nm on the premise that the absorption of marine particles is negligible in the near-IR (e.g., Babin and Stramski, 2002), which is not assumed in the TR method (Tassan and Ferrari, 1995). The computed $a_p(750)$ values for the TR method in our dataset were only weakly explained by TSM (~30%), suggesting that absorption measurements around the infrared region might not be exclusively attributed to particle load. Indeed, this result suggests that most of $a_p(750)$ is a result of a non-negligible absorption by particles around the infrared region, reinforcing the model proposed by Tassan and Ferrari (1995). On the other hand, Babin and Stramski (2002), using special geometry measurements and different types of particles, concluded that absorption by various aquatic particles in this spectral region is indeed negligible. It is worth noting, however, that both processes are interconnected, as an absorption enhancement may be consequently promoted by multiple scattering. Further field analyses are needed to investigate several categories of particles, specifically coastal and atmospheric ones, which may not present neglected absorption around the near-infrared region (D. Stramski, personal communication, 2011), in order to continue this discussion.

However, our analysis suggested that there were not only changes in the magnitudes but also changes in both S_{det} and S_f estimated from spectra derived by both methods, in contrast to the report by Lohrenz et al. (2003), which also showed that differences in the magnitude of both detrital and phytoplankton absorption coefficients depended on salinity and algal cell size. No clear trends were found in TR-$a_{ph}(\lambda)$:QFT-$a_{ph}(\lambda)$ and [Chl *a*], TR-$a_p(\lambda)$ or TR-offset (absorption in the red wavebands attributed to detritus by the TR method). Both the correction for scattering errors and the amplification of particulate signal (correction beta), however, impose wavelength-dependent effects (Röttgers and Gehnke, 2012), potentially affecting the retrievals of S_{det} and S_f. In general, the TR-derived spectra were flatter than those derived by the QFT method.

5. Conclusions

Our study demonstrated the effect of estuarine waters in increasing the phytoplankton biomass and CDOM in Santos Bay in a monthly scale. On a shorter time scale, however, vertical mixing and resuspension of bottom sediments caused by spring tides might suppress the effect of terrestrial sources. Moreover, strong tidal variations play a role in the distribution of suspended material and the relative contribution of organic and inorganic components in Santos Bay. Phytoplankton biomass is higher during neap tides especially during wet months, while non-algal particles dominate spring tide conditions.

Despite the influence of terrestrial sources in Santos Bay, salinity explained fairly weakly the absorption magnitudes and spectral shapes of CDOM, detritus, and phytoplankton. Actually, the most robust dependence of the absorption coefficient of CDOM on salinity was positive and observed when the influence of estuarine waters was reduced, in a sense that the total suspended material was associated with higher salinity during spring tides, likely as a result of bottom resuspension. The absorption coefficient of phytoplankton was the only optical variable well explained by chlorophyll-*a* concentration, regardless the conditions investigated here, but an important contribution of accessory pigments relative to chlorophyll was suggested and deserves further quantification. Because the spectral slopes of both detritus and CDOM absorption varied in a relatively narrow range, the use of these parameters does not seem to be feasible for monitoring variations in the nature of materials, and average shapes can be used to describe their spectral behaviors in bio-optical models. In turn, the spectral shape of phytoplankton absorption was highly variable and may be usable for monitoring phytoplankton cell size. Scattering and backscattering coefficients deserve further research in the studied region to access the nature of non-algal (organic and inorganic) particles.

The comparison between the use of the QFT and TR methods in measuring particulate absorption coefficients indicated considerable spectral differences in deriving the absorption coefficients of phytoplankton and detritus and suggested the contribution of non-algal particles to near-infrared absorption.

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