

Analyze of the inherent optical properties of French Guiana coastal waters for remote sensing applications.

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ABSTRACT

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The development of bio-optical algorithms to assess the spatio-temporal variability of Inherent Optical Properties (IOPs) and biogeochemical related components from space, is conditioned by our knowledge on these IOPs. The objective of this study is to characterize the IOPs and their relationships with biogeochemical parameters for the development of a future algorithm dedicated to the observation of the nearshore and offshore waters of the French Guiana from usual ocean color remote sensors. For that purpose, a set of IOPs and biogeochemical parameters was gathered from field measurements performed during a cruise achieved in the coastal waters of Cayenne in July 2006. The mean values of the mass specific non-algal absorption, ($a_{\text{nap}}(443)/\text{SPM} = 0.023 \pm 0.018 \text{ m}^2\text{g}^{-1}$), particulate scattering ($b_p(650)/\text{SPM} = 0.36 \pm 0.23 \text{ m}^2\text{g}^{-1}$) and backscattering ($b_{\text{bp}}(532)/\text{SPM} = 0.0065 \pm 0.0025 \text{ m}^2\text{g}^{-1}$) coefficients, as well as the $a_{\text{nap}}(\lambda)$ spectral behaviors, are in good agreement with the fact the investigated waters are dominated by mineral particles. The relatively low particulate backscattering to scattering ratio value for such waters (0.014 ± 0.004) could be explained by the presence of relatively large particles or aggregates with lower refractive index than pure mineral particles. This study shows that the chlorophyll concentration is largely overestimated with the standard OC4v4 algorithm.

ADDITIONAL INDEX WORDS: *scattering, absorption, remote sensing reflectance, ocean color*

INTRODUCTION

In situ measurements as well as remote sensing estimations of the water Inherent Optical Properties (IOPs) provide relevant qualitative and quantitative information on the suspended and dissolved material in water. While the variation of the concentration of optically significant material in water drives the IOPs variability to first order, the size and chemical composition of this material are responsible to the second order variability. Numerous studies were dedicated to the detailed examination of the relationships between IOPs and the chlorophyll *a* concentration (Chl, in $\text{mg}\cdot\text{m}^{-3}$) commonly used to specify the bio-optical state of open ocean waters. For instance, robust relationships were built between the particulate (a_p , in m^{-1}) or phytoplankton (a_{phy} , in m^{-1}) absorption coefficients and Chl over a large range of trophic conditions (BRICAUD et al., 1995; 1998). In the same way, the evolution of the particulate scattering coefficient, b_p (in m^{-1}), with Chl, but also with the particulate organic carbon (POC, in $\text{mg}\cdot\text{m}^{-3}$) were examined from *in situ* data collected in open ocean (LOISEL and MOREL, 1998). The recent development of *in situ* sensors to estimate the particulate backscattering coefficient (b_{bp} , in m^{-1}) allowed to develop regional parameterizations between b_{bp} , Chl, and POC, and to test semi-analytical ocean color algorithms. Mean general parameterization between IOPs and biogeochemical parameters are now available for open ocean waters, with however a relatively large scatter around the general trends.

More and more researches are now dedicated to the study of IOPs in coastal waters, which play a fundamental ecological and economical role, despite their limited geographical coverage. These areas are optically extremely complex, due to the numerous uncorrelated optically significant components

responsible for the IOPs variability. Among these different components, one may cite the phytoplankton, the colored dissolved matter from terrestrial and marine sources, and the non-algal particles originating from resuspended bottom sediments, river discharges, or coastal runoff. Based on a homogeneous and relatively large data set of IOPs and biogeochemical measurements collected in European coastal waters, the origin of the variations of b_p , a_p , and a_{ph} are now better understood (BABIN et al. 2003a; 2003b). These studies also allowed to develop relationships between b_p , a_p , and SPM for coastal waters and over a relatively large dynamic range. Similar studies were recently dedicated to the examination of the behavior of b_{bp} and b_{bp}/b_p in optically complex areas (SNIDER et al., 2008 and refs therein).

The development of bio-optical algorithms to assess the spatio-temporal variability of IOPs and biogeochemical related components from space, is conditioned by our understanding of the remote sensing reflectance, R_{rs} , variability, and our knowledge of the IOPs spectral behavior, as well as by the relationships between IOPs and the biogeochemical components. The objective of this study is to characterize the IOPs and their relationships with biogeochemical parameters for the development of a future algorithm dedicated to the observation of the French Guiana coastal waters from ocean color remote sensors. For that purpose, a set of IOPs, biogeochemical parameters, and R_{rs} was gathered from field measurements performed during a cruise in the coastal waters on French Guiana's continental shelf in July 2006. These waters, which are under the Amazon river influence, have never been optically characterized to our knowledge. A previous study based on *in situ* measurements of Chl, SPM and R_{rs} , showed that the standard OC2 algorithm (O'REILLY et al., 1998) performs poorly in retrieving Chl from R_{rs} due to the relatively high SPM

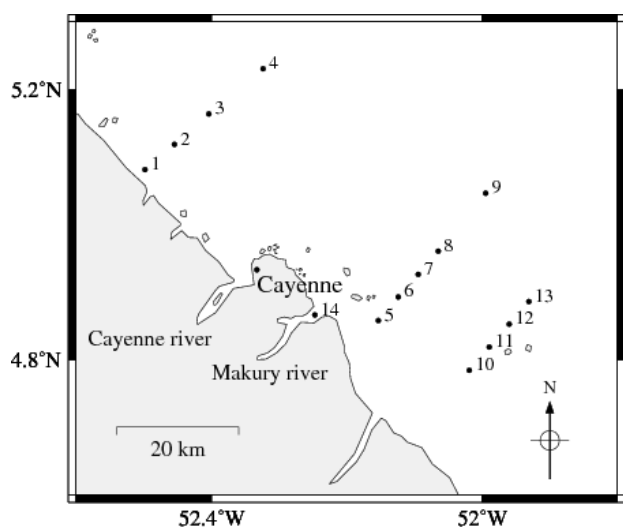


Figure 1. Location of the stations sampled on 7-11 July 2006.

concentration (FROIDEFOND et al., 2002). In the present study, the relationships between IOPs and biogeochemical components are first investigated. These results are then compared with general relationships usually used to assess the IOPs variability. Finally, different empirical algorithms dedicated to the retrieval of Chl and SPM from R_{rs} are tested, and new paths are proposed.

MATERIAL AND METHOD

The location of the sampled stations is indicated in Figure 1. The studied area is characterized by relatively shallow water, and by a coastal morphology with a series of mud banks which migrate along the coast towards the NW. At each station, a conductivity-temperature and depth (CTD) profiler and an optical package were deployed from surface down to 7 m. The optical package included a chlorophyll fluorometer, a 10-cm-pathlength beam transmissometer (at wavelength $\lambda = 650$ nm), and two ECO-VSF (at $\lambda = 532$ and 650 nm, respectively). All instruments were calibrated by their manufacturer. A detailed description of the procedure used to obtain the particulate attenuation coefficient, $c_p(650)$, from the beam transmissometer, as well as the particulate backscattering coefficients $b_{bp}(532)$ and $b_{bp}(650)$ from the two ECO-VSF is provided in LOISEL et al. (2007).

On each station, surface water samples were collected just below the surface simultaneously with the in situ optical measurements described above. Filtrations were performed immediately onboard at low vacuum pressure onto 25-mm glass-fiber filters (Whatman GF/F) for subsequent determination of the concentrations of total suspended matter (SPM; $g\ m^{-3}$), particulate organic and inorganic carbon (POC and PIC; $mg\ m^{-3}$), chlorophyll a (Chl; $mg\ m^{-3}$), absorption coefficients of phytoplankton ($a_{phy}(\lambda)$, m^{-1}), and non-algal particles ($a_{nap}(\lambda)$, m^{-1}). Each filter was immediately put in polycarbonate Petri dishes and stored in liquid nitrogen until laboratory analyses. Water samples were also filtered under low vacuum onto 0.22 μm Millipore membranes for the determination of the absorption by colored dissolved organic matter ($a_{cdom}(\lambda)$, m^{-1}). The methodology described in LOISEL et al. (2007) is used for the determination of all parameters, except for $a_{phy}(\lambda)$ and $a_{nap}(\lambda)$, for which the protocol described in BABIN et al. (2003a) is adopted.

Remote sensing reflectance, $R_{rs}(\lambda)$, measurements are performed at each station using two Trios hyperspectral (every 3 nm) radiometers: one measuring the downwelling irradiance on

the deck, $E_d(0^+, \lambda)$, and one measuring the in water upwelling radiance just below the sea surface, $L_u(0^-, \lambda)$. The immersion factors, as well as the impact of the self-shading are accounted for as in LUBAC and LOISEL (2007). These measurements were performed from a very small flat bottomed boat, far away from any perturbations of the main boat. $R_{rs}(\lambda)$ is calculated as follows: $R_{rs}(\lambda) = 0.543 L_u(0^-, \lambda)/E_d(0^+, \lambda)$.

RESULTS AND DISCUSSION

Biogeochemical parameters and inherent optical properties of surface waters

SPM includes all organic and mineral material above approximately 0.5–0.7 μm of diameter, POC encompasses autotrophic organisms, heterotrophic bacteria, and detritus (non-living organic particles), and PIC is mainly carbon carbonate. The ratios of these biogeochemical parameters are used to characterize the nature of the particulate assemblage measured by the optical sensors: POC/SPM is used as a rough indicator of the organic fraction of the suspended particulate matter, POC/Chl is related to the carbon mass of both living and nonliving material with respect to that of autotrophic organisms, and the POC/PIC ratio gives the proportion of particulate organic versus inorganic carbon. The mean values of SPM, Chl, POC, and PIC are $24.0 \pm 24.2\ g\ m^{-3}$, $4.2 \pm 3.7\ mg\ m^{-3}$, $0.27 \pm 0.22\ mg\ l^{-1}$, and $0.95 \pm 0.46\ mg\ l^{-1}$, respectively. The Chl and SPM values are in good agreement with a previous study performed in this area (FROIDEFOND et al., 2002). The low POC/SPM mean value (0.013 ± 0.011) indicates that, even for relatively high concentrations of Chl, particulate matter is mostly dominated by mineral particles. This is consistent with the conclusions of FROIDEFOND et al. (2002). Note that such low POC/SPM values are of the same order as those measured at the most mineral dominated stations sampled by LOISEL et al. (2007) along the eastern English Channel coast. The mean POC/PIC value (0.33 ± 0.35) is rather low, compared to other measurements performed in coastal areas (VANTREPOTE et al., 2008). However, the proportion between POC and PIC is in the range measured in the same area between suspended organic and inorganic particulate matter (FROIDEFOND et al., 2002). The statistically significant correlation between Chl and PIC ($r^2 = 0.55$) may have a direct (formation of PIC by calcareous phytoplankton and microzooplankton) or indirect (re-suspension of sediments) origin. The indirect link is much more probable in this environment. By removing one peculiar station which presents a POC/Chl value of 1356, the mean POC/Chl value is 76 ± 29 . This value is about 2-3 times lower than measurements performed in the eastern English Channel for a similar Chl. This indicates that POC is meanly dominated by autotrophic organisms, and that the contribution of non-living matter and heterotrophic bacteria to POC is minor, as stated in previous studies in littoral and coastal Guianese waters (ARTIGAS et al., 2007).

The relationships between IOPs and biogeochemical parameters are assessed only from surface measurements where water samples are collected. For that purpose full-resolution optical profiles were averaged over the first meter. The absorption coefficient at 443 nm from which the pure sea water absorption has been subtracted, $a_w(443)$, is dominated by non-algal particles absorption ($61 \pm 25\ %$), then by the colored dissolved organic matter absorption ($25 \pm 19\ %$), and at last by phytoplankton absorption ($14 \pm 15\ %$). This result indicates that the absorption process is here controlled by mineral particles, non-living particles, as well as by heterotrophic bacteria.

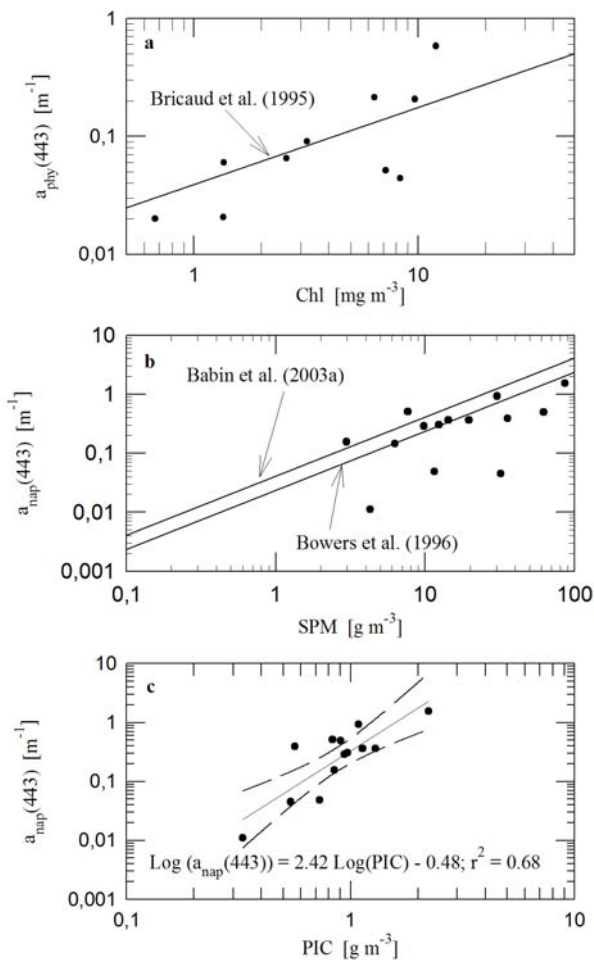


Figure 2. a) Scatter plots of a_{phy} versus Chl, b) a_{nap} versus SPM, and c) $a_{nap}(443)$ versus PIC. Previous relationships developed by different authors are plotted in panels a-b. In panel c the solid black line is the corresponding linear regression, and the long dashed lines delimit the 95% confidence interval.

The relationships between a_{phy} and Chl (Figure 2a) as well as between a_{nap} and SPM (Figure 2b), are coherent with previous studies performed in coastal areas (BABIN et al., 2003a). The good correlation between $a_{nap}(443)$ and PIC (Figure 2c) suggests a permanent influence of inorganic sediments on the NAP absorption signal, and confirms the dominant role of inorganic matter in the SPM composition (as already suggested by the low POC/SPM mean value). In contrast, $a_{nap}(443)$ is weakly correlated with POC ($r^2=0.2$). The overall average $a_{nap}(443)/SPM$ ratio is $0.023 \pm 0.018 \text{ m}^2 \text{ g}^{-1}$, which is not far from the value measured in turbid coastal areas of the North Sea ($0.033 \pm 0.016 \text{ m}^2 \text{ g}^{-1}$), but nearly three times ($0.067 \pm 0.022 \text{ m}^2 \text{ g}^{-1}$) as low as that measured in the Baltic Sea (BABIN et al., 2003a). This result reinforces the statement made by BABIN et al. (2003a) that inorganic particles, which largely dominate our data set, have a lower $a_{nap}(443)/SPM$ ratio than organic particles. A significant decrease of both $\log(a_{nap}(443))$ ($r^2=0.43$) and $\log(a_{cdom}(443))$ ($r^2=0.36$) with salinity, not observed for $a_{phy}(443)$, denotes a net influence of mixing and dilution processes on the absorption properties of surface waters.

Based on the relationship developed by LOISEL AND MOREL (1998) between the particulate scattering coefficient, $b_p(650)$, and Chl, one may emphasize that the investigated waters belong to turbid Case 2 waters, for which IOPs are not only controlled by phytoplankton and their associated and derivative products, but rather by all other optically significant un-covariate components (Figure 3a). This is coherent with the fact that $a_{t-w}(443)$ is dominated by $a_{nap}(443)$ which is here mostly driven by mineral particles. The $b_p(650)$ vs. SPM relationship falls within the range of variability established from measurements performed in European coastal waters (Figure 3b). The overall average $b_p(650)/SPM$ ratio is $0.36 \pm 0.23 \text{ m}^2 \text{ g}^{-1}$, which slightly increases when this value is extrapolated at 550 nm ($=0.42 \text{ m}^2 \text{ g}^{-1}$) by assuming an hyperbolic spectral shape for $b_p(\lambda)$ with a slope of -1. The value of this ratio is close to the average value adopted for turbid water at 550 nm, which is $0.5 \text{ m}^2 \text{ g}^{-1}$ (BABIN et al., 2003b). Indeed, due to their low water content mineral particles have a lower specific scattering coefficient than living particles. This low $b_p(650)/SPM$ value again confirms the unique and extreme character of the investigated area in terms of IOPs. While almost no correlation is observed between $b_p(650)$ and POC, significant co-variations of $b_p(650)$ with both Chl, and PIC are highlighted (Figures 3a,c).

The behaviour of the particulate backscattering coefficients, $b_{bp}(\lambda)$, at 532 and 650 nm with the different biogeochemical components is roughly similar to that described for $b_p(\lambda)$. Significant statistical correlations are found between $b_{bp}(\lambda)$, Chl and PIC, as stated by the following relationships:

$$\text{Log}(b_{bp}(532)) = 2.8 \text{ Log (PIC)} - 0.99 \quad (r^2=0.59) \quad (1)$$

$$\text{Log}(b_{bp}(532)) = 1.00 \text{ Log (Chl)} - 1.69 \quad (r^2=0.56) \quad (2)$$

The average value of the mass specific ratio $b_{bp}(532)/SPM$ is $0.0065 \pm 0.0025 \text{ m}^2 \text{ g}^{-1}$. While not fully comparable, the value of this ratio is of the same order as the value of the b_{bp}/PIM ratio measured by SNYDER et al. (2008) at different coastal sites (PIM stands for particulate inorganic matter). It is interesting to note that b_{bp} ($r^2=0.55$) and b_p ($r^2=0.9$) both co-vary with $a_{nap}(443)$. While absorbing non-algal particles largely contribute to the particulate scattering ($r^2=0.9$), they only explain half of the backscattering signal. The nature of the optically significant bulk particulate assemblage does not show a large variability, as emphasized by the relatively low coefficient of variation (28%) of the particulate backscattering coefficient. The mean $b_{bp}/b_p(650)$ value (0.014 ± 0.004), is lower than expected for such waters (LOISEL et al., 2007). This could be explained by the presence of relatively large particles or aggregates with lower refractive index than pure mineral particles.

The spectral behavior of b_{bp} , a_{nap} , and a_{cdom}

The spectral values of both $a_{nap}(\lambda)$ and $a_{cdom}(\lambda)$ can be fitted by exponential models driven by different slopes, S_{nap} and S_{cdom} , respectively: $a(\lambda) = a(\lambda_{ref}) \exp(-S(\lambda - \lambda_{ref}))$. The spectral shape of $b_{bp}(\lambda)$ is derived from the measurements of $b_{bp}(532)$ and $b_{bp}(650)$ assuming that $b_{bp}(\lambda)$ follows a hyperbolic law: $b_{bp}(\lambda) = b_{bp}(\lambda_0) (\lambda/\lambda_0)^{-\gamma}$, which is reasonable in this part of the spectrum where $a_{t-w}(\lambda)$ is relatively low. The mean values of S_{nap} , S_{cdom} , and γ are 0.0084 ± 0.002 , 0.028 ± 0.007 , and 1.06 ± 0.35 , respectively. These values are close to the minimum and maximum values of S_{nap} and S_{cdom} measured by BABIN et al. (2003a), respectively. Our low S_{nap} value reinforced the assumption made by these authors on the fact that S_{nap} may be related to the proportion of mineral and

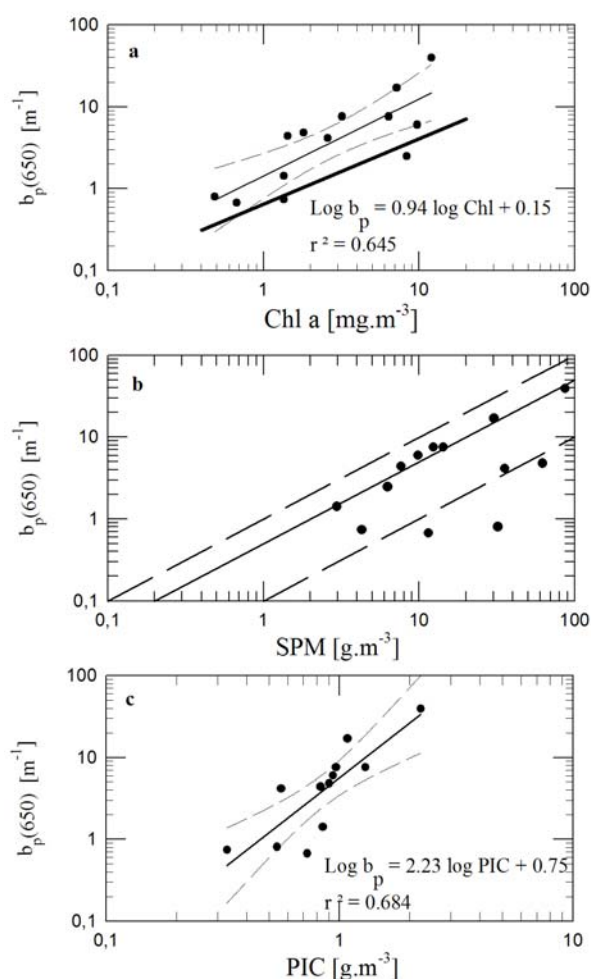


Figure 3. a) Scatter plots of $b_p(650)$ versus Chl. The solid black line is the corresponding linear regression, the long dashed lines delimit the 95% confidence interval, and the bold one the case1/case2 delimitation of LOISEL and MOREL (1998). b) $b_p(650)$ versus SPM. The 1/1, 1/2, and 1/10 lines are shown. The 1/10 line gives the limit of the BABIN et al. (2003b)'s data set. c) $b_p(650)$ versus PIC. The solid black line is the corresponding linear regression, and the long dashed lines delimit the 95% confidence interval.

organic matter, with low values generally found in mineral dominated waters. The high mean S_{cdom} values reported here, which are consistent with other previous studies performed in coastal areas (see Table 1 in TWARDOWSKI et al., 2004), suggest that CDOM is here mainly marine-derived and then dominated by fulvic acid, which is surprising. Because samples were collected at surface, and under high irradiance levels, this high slope value may also partly be due to photobleaching which could tend to increase the slope (TWARDOWSKI et al., 2004). The quality of the CDOM data set is reinforced by the net decreasing trend between S_{cdom} and $a_{cdom}(443)$ which is consistent with the CARDER et al. (1989)'s study (Figure 4). The mean value of the spectral slope of the b_{bp} (1.06 ± 0.35) is in good agreement with the conclusion of SNYDER et al. (2008) who showed from a large coastal data set that "all the spectra, except possibly the very

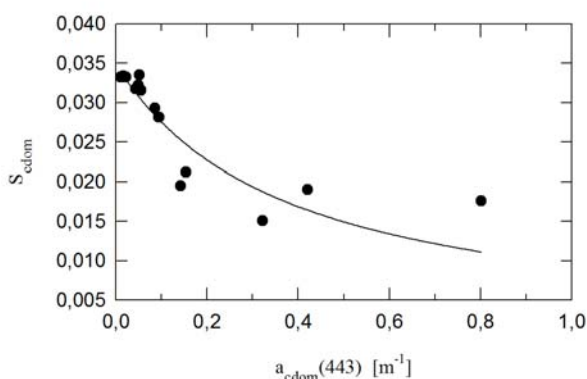


Figure 4. a) scatter plots of S_{cdom} versus $a_{cdom}(443)$.

clearest waters, cluster around a single wavelength power-law exponent of -0.94 ".

The remote sensing reflectance variability and inverse algorithms evaluations

The remote sensing reflectance spectra exhibit a great variability in shape and amplitude (Figure 5). However, all these $R_{rs}(\lambda)$ spectra fall into the five classes defined by LUBAC and LOISEL (2007). The greatest spectral variation is observed in the green and red part of the spectrum. This variability, which is coherent with the measurements of FROIDEFOND et al. (2002), is directly related to the various and un-correlated optically significant components, as described above. A regression analysis performed between the $R_{rs}(\lambda)$ spectra and the different measured bio-optical components reveals that the $R_{rs}(412)$ variability is equally driven by dissolved and non-algal particles absorption ($r^2=0.42$) and particulate backscattering ($r^2=0.5$). In the green (532 nm), and red (650 nm) part of the spectrum, R_{rs} is mainly driven by the nature of the suspended particles (i.e. b_{bp}/b_p , $r^2=0.58$), and the concentration of suspended particles (i.e. b_{bp} , $r^2=0.56$), respectively.

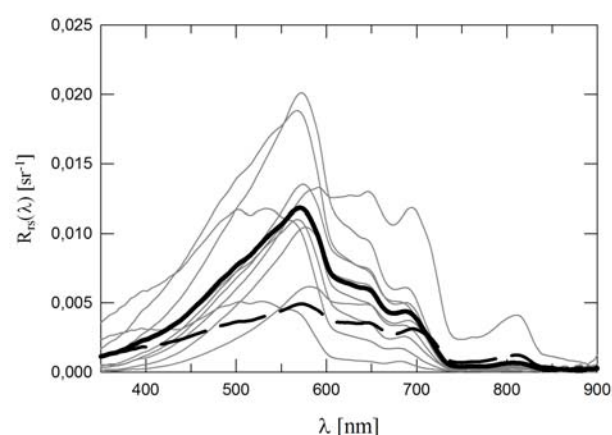


Figure 5. R_{rs} spectra measured on July 2006 in grey, and their mean (solid black line) and standard deviation (long dashed line) spectra.

The performance of the standard empirical SeaWiFS OC4v4 algorithm (O'REILLY et al., 1998) developed to inverse Chl from $R_{rs}(\lambda)$ is evaluated from our data set. The chlorophyll concentration is estimated with a root mean square (RMS) log

error of 39%, and a low coefficient of determination (r^2) of 0.24. This RMS value is only slightly larger than the one obtained by GREGG and CASEY (2004) for open ocean waters (31%). The value of the Chl_{inversed}/Chl_{measured} ratio is 2.16 ± 1.43 , denoting a net overestimation of Chl by OC4v4 in this area. This expected result is due to the presence of mineral particles. Due to the relatively low variability of $R_{rs}(850)$, SPM can not be retrieved from the $R_{rs}(850)/R_{rs}(550)$ ratio generally used for estuarine waters (DOXARAN et al., 2005).

CONCLUSIONS AND PERSPECTIVES

These IOPs measurements represent the first ones performed in this region. The mean a_{nap}/SPM , b_p/SPM , b_{bp}/SPM values are in good agreement with the fact the investigated waters are dominated by mineral particles (relatively low POC/SPM and POC/PIC ratios). The low mean $b_p(650)/SPM$ and a_{nap}/SPM values confirm that mineral dominated waters have lower specific particulate scattering and absorption properties than organic ones. In the same way, the relatively low values of the spectral slope of non algal absorption is conformed with the fact that S_{nap} is related to the proportion of mineral and organic matter, with low values generally found in mineral dominated waters.

This study shows that Chl is overestimated by a factor of 2 from the OC4v4 algorithm. The present data set shows that this region presents very specific IOPs properties, and that the adoption of standard specific IOPs values in semi-analytical algorithms for the inversion of biogeochemical parameters would fail. The fact that the present $R_{rs}(\lambda)$ spectra all belong to some predefined classes is very encouraging for the development of inverse class specific algorithms. However, prior to any inverse algorithm development the present data set should be extended. In future cruises the origin of the relatively high PIC concentration in the suspended particulate matter should be investigated.

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