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Empirical and semi-analytical chlorophyll algorithms in the south-western Atlantic coastal region (25–40°S and 60–45°W)

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Global ocean colour algorithms, used to extract chlorophyll concentration in the ocean surface, normally overestimate pigment values in coastal regions, due to optical interference of water components. The objective of the present investigation was to test the performance of both empirical (SeaWiFS OC4v4) and semi-analytical (GSM01 and CARDER) algorithms in the south-western Atlantic. *In situ* pigment and optical data have been collected in waters influenced by continental discharge from La Plata River and Patos Lagoon. The data was used to develop a regional version of the empirical SeaWiFS OC2v4 algorithm (termed OC2-LP). The relative percentage difference (RPD) between *in situ* and algorithm-derived chlorophyll was 11% in the regional version as compared to the global OC4v4 (RPD=27%). The GSM01 and CARDER showed RPD of 14% and 31%, respectively. We have also tested the accuracy of the four algorithms (OC4v4, OC2-LP, GSM01 and CARDER) on SeaWiFS images taken over two cruise periods in the study region (winter of 2003 and summer of 2004). A seasonal difference was observed, where both OC4v4 and OC2-LP overestimate chlorophyll in summer at a higher magnitude than in winter, and the GSM01 algorithm showed a marked underestimation of chlorophyll in winter. The CARDER model showed a good performance both in winter and summer, when applied to satellite-retrieved radiances. Our results show that the use of semi-analytical models does not improve significantly the accuracy of chlorophyll retrievals in coastal areas when not properly tuned with regional inherent optical properties measurements.

1. Introduction

Over the past decades, remote sensing of ocean colour has provided valuable data on the distribution of phytoplankton biomass (as chlorophyll-a) in the oceans surface. However, in coastal waters, especially under influence of continental discharge, the available global algorithms for chlorophyll-a retrieval do not show an acceptable performance (Darecki and Stramski 2004, Jorgensen 2004, Magnuson *et al.* 2004). In these case II waters, non-specific algorithms normally overestimate chlorophyll levels, due to the optical interference of both suspended inorganic material and dissolved organic matter (Carder *et al.* 1991, Gordon and Morel 1983, Hu *et al.* 2000). On the other hand, waters under strong continental influence are

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normally very productive coastal ecosystems, where high phytoplankton biomass and productivity sustains substantial fisheries yield. In the south-western Atlantic, the region between 23°S and 43°S (which includes most of the study region) has a fishery production that represents ca. 75% of the total catches in the entire eastern South American coast (FAO region 41) (Odebrecht and Castello 2001).

The shelf waters within the study area (figure 1) are highly influenced by the continental discharges from the La Plata River (~35°S), Patos Lagoon (~32°S) and further north by summer up-welling events of South Atlantic Central Water (~29°S). In addition, offshore areas south of 37°S are affected by the confluence of two western boundary currents: Brazil and Malvinas currents.

The La Plata river (figure 1), with a 230 km wide mouth, has a basin of $3.1 \times 10^6\,\mathrm{km}^2$ and a mean annual discharge of 20,000 to 23,000 $\mathrm{m}^3\,\mathrm{s}^{-1}$ (Berbery and Barros 2002, Nagy *et al.* 1997). This runoff is a significant source of fertilization to the adjacent sea. Out of the river mouth, low salinity waters are associated with relatively high levels of nitrate (maximum approximately 15 μmol l^{-1}) and especially silicate (maximum approximately 160 μmol^{-1}), and these levels decrease steadily with increasing salinity, due to mixing and redox changes (Nagy *et al.*, 1997). Phytoplankton growth and production can be greatly enhanced in the haline frontal

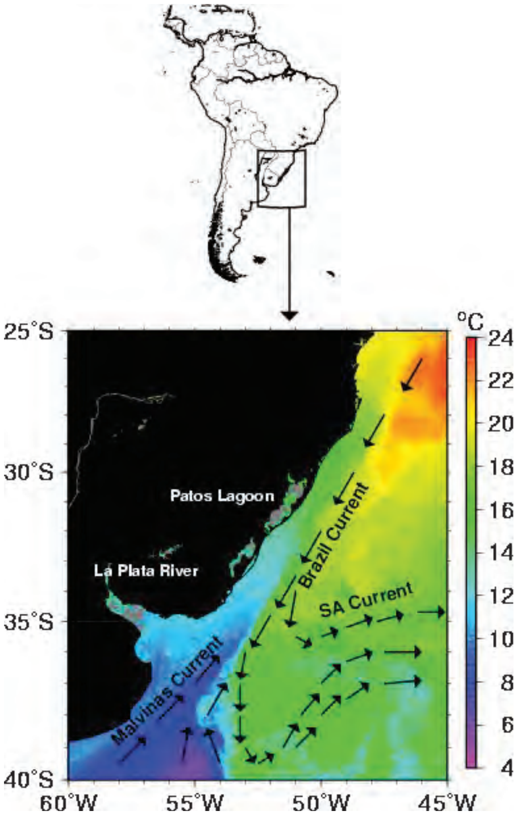

Figure 1. Study region, on an Aqua-MODIS August 2003 sea surface temperature image, with the main ocean circulation features. Note the convergence of Brazil and Malvinas Currents south of 35°S.

system between La Plata plume and shelf waters (Carreto *et al.* 1995, Negri *et al.* 1992). A climatology based on historical salinity and silicate data showed that in the winter the La Plata river plume extends north in the Brazilian coast to ~28°S, while in summer it is more confined to latitudes south of ~33°S (Piola *et al.* 2000).

Further north in the study region, the Patos Lagoon (at 32°S) has a mean annual freshwater runoff between 700 and 3000 $m^3 s^{-1}$, with the maximum in the winter/spring (Moller *et al.* 1991). The estuarine plume of Patos Lagoon extends to circa 50 km off the coast (Hartman *et al.*, 1986) and also has a significant influence on the biological production of the adjacent coastal water (Abreu *et al.* 1995). During high precipitation periods, in El Niño years, the low salinity coastal waters in south Brazil can reach up to 130 km offshore and these are related with higher chlorophyll levels (Ciotti *et al.* 1995b).

Despite the importance in terms of productivity and fisheries potential of the study area, ocean colour studies are very scarce in the coastal region encompassing La Plata river and Patos Lagoon. Garcia *et al.* (2005) have recently shown that the global SeaWiFS OC4v4 algorithm overestimates chlorophyll concentration in coastal areas affected by La Plata plume and emphasized that more detailed and region-specific approaches are necessary to study surface phytoplankton variability by remote sensing techniques in this region.

Remote sensing of chlorophyll in the ocean has been studied using two main approaches: empirical and semi-analytical algorithms. The empirical type is based on statistical relationships between either normalized water leaving radiance (nLw) or remote sensing reflectance (Rrs) ratios at two or more bands and *in situ* chlorophyll, e.g. the SeaWiFS OC4v4 and OC2v4 algorithms (O'Reilly *et al.* 1998, O'Reilly 2000). The semi-analytical models, on the other hand, relate Rrs to inherent optical properties (IOPs) of the aquatic medium, such as absorption and backscattering coefficients. Absorption can be described by the absorption due to phytoplankton, a_{ph}, to coloured dissolved organic matter, a_{cdom}, and by detrital material, a_d, while backscattering, b_{bp}, is mainly due to particles (Carder *et al.* 1999, Maritorena *et al.* 2002, Roesler and Perry 1995, Sathyendranath and Platt 1997).

In the present study, we evaluate a few algorithms to extract chlorophyll-a in the region influenced by La Plata River and Patos Lagoon, including empirical and semi-analytical approaches. *In situ* normalized water-leaving radiances, in conjunction with a chlorophyll dataset, are used to evaluate the accuracy of existing algorithms and to develop a modified version of an empirical model.

2. Methodology

2.1 *Bio-optical data set and measurements*

The bio-optical dataset (figure 2) has been collected during six cruises on Brazilian and Argentinean ships in the study region (table 1) and from the UK Atlantic Meridional Transect (AMT) cruises, available in the SeaWiFS bio-optical data archive and storage system (SEABASS, Werdell *et al.*, 2003). In-water radiometric measurements (in the regionally sponsored cruises 1 to 6) were made using a Satlantic Inc. Tethered Spectral Radiometer Buoy (TSRB). The Satlantic buoy collects spectral upwelling radiance, $L_u(\lambda,z_0)$ at $z_0 = 50$ cm depth, at 412, 443, 490, 510, 555, 670 and 683 nm, and downwelling irradiance, $E_d(490)$ at sea surface at 490 nm.

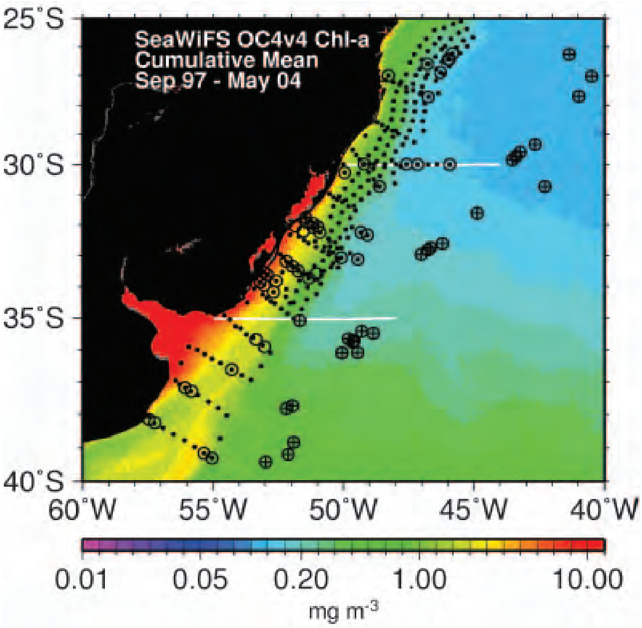

Figure 2. Mean SeaWiFS image from September 1997 to May 2004. Black dots show stations where chlorophyll climatology was taken, during cruises 1–6 in table 1. The circled points indicate sites where radiometric measurements were also made. Crosses show AMT-Atlantic Meridional Transect−data points (cruises 7–12 in table 1), mainly in the offshore area.

Table 1. Cruises to the study region, where bio-optical (chlorophyll and radiometric) data were collected.

Cruise no.	Cruise name	Period	Research ship	Chlorophyll	Radiometry
1	COROAS 3	10/17–10/23/1997	RV Atlantico Sul	X	X
2	REVIZEE 4	04/23–05/01/2000	RV Astro Garoupa	X	
3	SAFARI	05/22–05/26/2002	RV Atlantico Sul	X	X
4	DPA	02/15–03/10/2002	RV Atlantico Sul	X	X
5	LA PLATA 1	08/20–08/31/2003	RV Puerto Deseado	X	X
6	LA PLATA 2	01/30–02/19/2004	RV Antares	X	
7–12	*AMT 3–8	1996–1999	RV James C. Ross	X	X

*AMT data was taken from SEABASS.

In the AMT cruises (7–12, table 1), which sampled mostly the low-chlorophyll deep water region of the study area, a series of profiling instruments were used to measure the spectral upwelling radiance, $L_u(\lambda)$ and downward irradiance, $E_d(\lambda)$ as documented by Aiken *et al.* (1998), Hooker and Lazin (2000), Robins and Aiken (1996). Intercalibration exercises and assessment of uncertainties in the measurements have been carried out (Hooker *et al.* 2002). Upward irrandiance, $E_u(\lambda)$, was also measured in some cases.

In situ chlorophyll measurements for cruises 1–6 were made by collecting surface water (200 to 1000 ml) and filtering through 25 mm Whatman GF/F filters. These were kept frozen until laboratory analyses, within 1 to 8 weeks after collection. The pigment was extracted with 90% acetone solution for 24 h at −20°C and the fluorescence was determined with a Turner Designs TD-700 fluorometer, previously calibrated with Sigma chlorophyll-a. The non-acidification method (Welschmeyer 1994) was used, where errors associated with phaeopigments are avoided by appropriate excitation and emission filters. In the AMT cruises, chlorophyll concentration was determined by HPLC, as total chlorophyll *a* (chlorophyllide *a* + divinyl chlorophyll *a* + chlorophyll *a*) (Gibb *et al.* 2000).

2.2 *Computation of the spectral water leaving radiances and reflectances in cruises 1–6*

The upwelling radiances measured with the Satlantic buoy at z_0=0.5 m were converted to values just beneath the surface, $L_u(\lambda,0^-)$, using the formulation for spectral attenuation coefficients, $K(\lambda)$, given in Morel and Maritorena (2001). This formulation is mainly based on the downward attenuation by water and biogenic substances (including phytoplankton), but a source of error can be introduced in very turbid waters, where other suspended particles play a major role in the magnitude of $K(\lambda)$. In this work, turbid waters were detected in a few points, using a turbidity flag, where Rrs(670)>0.012 sr^{-1} (Robinson *et al.* 2003). These have been appropriately marked in the respective plots. The spectral water-leaving radiances, L_w (λ), were then computed from the upwelling radiances using the Fresnel reflectance at the sea-air interface, ρ_f, and the refractive index of the seawater, n_w, as 0.0215 and 1.345, respectively. The reflectance values were corrected for instrument self-shading, using a specific correction procedure for the TSRB buoy described by Leathers and Downes (2001). The spectral downwelling irradiance at sea surface, $E_d(\lambda)$, was estimated by using a combination of measured E_d(490) and Bird and Riordan (1986) model values as detailed in (Garcia *et al.* 2005). We assumed that the ratio between modelled and measured E_d(490) holds for the remaining spectral bands. The spectral remote sensing reflectance, $R_{rs}(\lambda)$, was then calculated from

$$R_{rs}(\lambda)=\frac{L_w(\lambda)}{E_d(\lambda)} \tag{1}$$

2.3 *Algorithm characteristics*

The empirical algorithms used in this work relate chlorophyll-a to ratios between remote sensing reflectance ($R^{\lambda_1}_{\lambda_2}=R_{rs}(\lambda_1)/R_{rs}(\lambda_2)$) in the blue and green bands. While OC2v4 uses R^{490}_{555} ratio, OC4v4 uses the greatest among R^{412}_{555}, R^{443}_{555} or R^{490}_{555} (O'Reilly *et al.*, 1998, 2000).

The semi-analytical algorithms tested in this work were the Garvel, Siegel and Maritorena (GSM01) algorithm (Maritorena *et al.* 2002) and the CARDER semi-analytical ocean colour algorithm for MODIS (Carder *et al.* 1999, 2004). The GSM01 employs model parameters which are derived through a 'statistical optimization procedure' to maximize the algorithm performance for the global ocean. The remote sensing reflectance (Rrs(λ)) values at the six SeaWiFS wavebands are used as model input, combined with IOP parameters that vary depending on water optical characteristics: spectral phytoplankton specific absorption coefficients, $a^*_{ph}(\lambda)$, the spectral slopes of coloured dissolved + detrital material (a_{cdm}), normalized by a_{cdm} at 443 nm (S_{cdm}) and the power law exponents for spectral variability of particle backscattering, b_{bp} (η).

The CARDER algorithm employs a more complex approach, where pigment absorption components are separated from those due to degradation products (e.g. gelbstoff and detritus, $a_g^*(\lambda)$) and the chlorophyll-specific phytoplankton absorption coefficient, $a_{ph}^*(\lambda)$ is adjusted, on the basis of chlorophyll-a concentration and nutrient and light sufficiency (Carder *et al.* 1999). The separation of the effects of the major components is achieved by using the spectral differences between $a_{ph}^*(\lambda)$ and $a_g^*(\lambda)$. By comparing the sea-surface temperature to nitrate-depletion temperature (NDT) (Kamykowski 1987, Kamykowski *et al.* 2002), the presence of large, chlorophyll-rich cells and small, chlorophyll-poor cells are then deduced from space (Carder *et al.* 1999). Chlorophyll-rich cells with low $a_{ph}^*(\lambda)$ values (packaged pigments) are generally present in photon-poor, nutrient-replete environments whereas chlorophyll-poor cells with high $a_{ph}^*(\lambda)$ values (unpackaged pigments) are present in photon-rich, nutrient deplete environments. The NDT for any region of the ocean is the temperature above which nitrate is negligible. In developing and evaluating the algorithm, global *in situ* data sets were partitioned into two regions, one where little pigment packaging is to be expected and one where more packaging might be expected. These two subsets were labelled 'unpackaged' and 'packaged', respectively. The 'unpackaged' data set corresponds to high-light, non-upwelling regions in warm, tropical and sub-tropical waters. The 'packaged' data set originates from eastern boundary upwelling and high latitude regions at non-summer times. Furthermore, a 'global' average algorithm was also developed for use in conditions where pigment packaging is unknown or transitional. The algorithm was tested on a global data set combining the 'packaged', 'unpackaged', and other mixed data sets from SeaBAM. Furthermore, one data set originating from the Bering Sea and the Antarctic Polar Frontal Zone was used to define a 'highly packaged' condition. The algorithm has an NDT-dependent weighting function to blend transitional zones falling between 'unpackaged' and 'highly packaged' situations. The algorithm has also many switches (flags) to transition from empirical (default) to semi-analytical formulations (and blended combination), plus different coefficients for various levels of pigment packaging. The blend of empirical and semi-analytical algorithms occurs when $a_{ph}^*(672)$ falls within the range of 0.015–0.03 m^{-1}. For values below 0.015 m^{-1} the algorithm is fully semi-analytical, while for values above 0.03 m^{-1} the algorithm is fully empirical.

2.4 *Algorithms evaluation*

The performance of both empirical and semi-analytical algorithms was made through linear regression analyses between the observed (*in situ*) chlorophyll-a concentration and those estimated by the algorithms (*alg*). The statistical parameters (besides log-derived r^2, slope and intercept) used for these evaluations were the linear-transformed root mean square error (*rmse-L*) (Carder *et al.* 2004), the mean relative percentage difference (RPD) and the mean absolute percentage difference (APD) between algorithm-derived and *in situ* chlorophyll. The rmse-L has been proposed to represent reasonably well the errors over a large range of chlorophyll values (Carder *et al.* 2004). These parameters are defined as:

$$rmse\text{-}L = 0.5[(10^{+rmse} - 1) + (1 - 10^{-rmse})] \tag{2}$$

where

$$rmse = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left[\log_{10}\left(\frac{Chla_{a\lg}}{Chla_{insitu}}\right)^2\right]} \tag{3}$$

$$RPD = \sum_{n=1}^{N}\left(\frac{Chla_{a\lg} - Chla_{insitu}}{Chla_{insitu}}\right)\frac{1}{N} \times 100\% \tag{4}$$

$$APD = \sum_{n=1}^{N}\left(\frac{Chla_{a\lg} - Chla_{insitu}}{Chla_{insitu}}\right)\frac{1}{N} \times 100\% \tag{5}$$

2.5 *Match-up analysis*

A match-up exercise was carried out to compare *in situ* chlorophyll measurements with remote sensed values according to the SeaWiFS Project procedure (Hooker and McClain 2000, McClain *et al.* 1992, McClain *et al.* 2004). The exclusion criterion in the procedure discards invalid or redundant data, based on temporal windows and quality control masks and flags (Bailey *et al.* 2000). The satellite time window used for match-ups was 12 hours. A dataset of 380 measurements (all points in figure 2, except crosses) was submitted and 68 points became final valid matches.

3. Results and discussion

3.1 *Regional variability*

A mean chlorophyll image from September 1997 to May 2004 was produced for the study region using SeaWiFS SMI 9km × 9 km images (OC4v4 algorithm) and compared with a chlorophyll data base from 1997 to 2004 (380 points) in the shelf area (figure 2). Pixel values were extracted from the mean image at each data point location and averaged over three sub-regions: South (⩾35°S and <40°S), under direct influence of La Plata river mouth; Middle (<35°S and >30°S), influenced by Patos Lagoon runoff and the north displacement of La Plata plume; and North (⩽30°S and ⩾25°S), where coastal waters are affected by summer upwelling around 29°S. As shown in table 2, mean values from the OC4v4 satellite images compare

Table 2. Results of comparison between the mean SeaWiFS OC4v4 chlorophyll image (September 2003 to May 2004) and climatology of chlorophyll values in the study region. North: ⩽30 and ⩾25°S, Middle: <35 and >30°S, South: ⩾35°S and <40°S.

Region	Chlorophyll	Mean (mg/m^3)	Standard deviation (mg/m^3)	Median (mg/m^3)	Number of data
North	Mean OC4v4	0.42	0.40	0.26	109
	Climatology	0.40	0.45	0.28	109
Middle	Mean OC4v4	2.00	5.24	0.80	185
	Climatology	1.02	1.67	0.35	185
South	Mean OC4v4	3.23	3.00	1.91	86
	Climatology	1.60	2.94	0.97	86
All	Mean OC4v4	1.83	4.68	0.78	380
	Climatology	0.98	2.17	0.38	380

well with the mean *in situ* data in the north region, but overestimate on average by 100% both in the middle and southern regions. However, the standard deviations are very large in these two regions, reflecting the high degree of variability associated with the freshwater runoff influence. Apparently, the OC4v4 algorithm can be used with confidence in coastal areas of the north region. However, south of 30°S the influence of dissolved organic matter and suspended sediments from continental runoff require a more regional approach and/or the use of semi-analytical models for improving accuracy in chlorophyll estimates. In the next section we use our bio-optical dataset to evaluate algorithm performances in the region.

3.2 *Comparison between algorithms*

The bio-optical dataset (73 points) was used to evaluate some existing algorithms and to generate a modified empirical algorithm for the study area. A third order, 2-band R_{555}^{490} empirical algorithm (termed OC2-LP) was generated for the study region. Figure 3 shows a plot of the bio-optical relationship, where NASA's OC2v4 is also plotted for comparison. Both models are very similar at the lower chlorophyll range ($<$ approximately $0.5\,\mathrm{mg\,m^{-3}}$) but the regional version shows a certain deviation at higher chlorophyll, compensating to some extent the overestimation by OC2v4.

An evaluation of other algorithms performances, using the same data set has been made, where the following models were tested: SeaWiFS OC4v4, the Garvel, Siegel and Maritorena (GSM01) algorithm and the CARDER semi-analytical ocean colour algorithm for MODIS. For the latter model, in addition to the radiometric data, *in situ* temperature values at the sampling sites were also used. These, in conjunction with the nitrate depletion temperature (NDT) (Kamykowski *et al.* 2002) can be used as a proxy for nutrients and to determine the degree of pigment packaging (see the Methodology section).

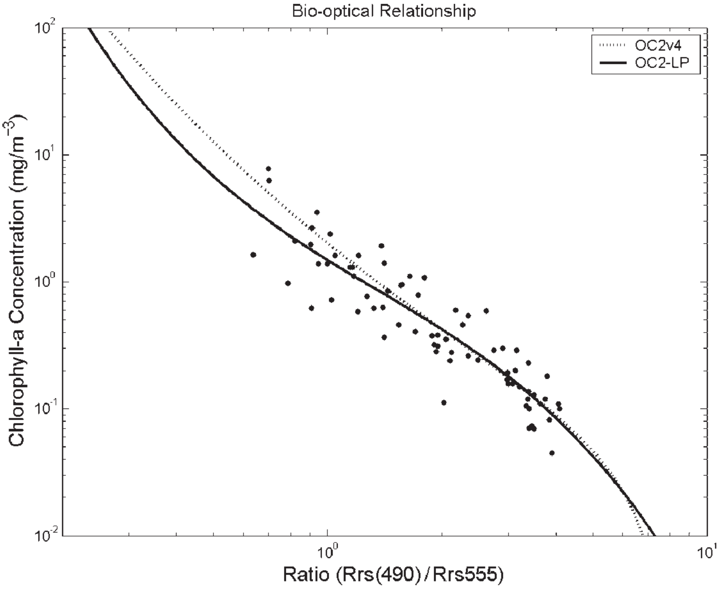

Figure 3. Bio-optical relationship of the empirical 2-band algorithm (OC2-LP) generated for La Plata–Patos Lagoon region (thick line). The NASA OC2v4 algorithm is also plotted for comparison (dotted line).

The evaluation was made by applying the spectral remote sensing reflectance values, $R_{rs}(\lambda)$, calculated from our measured $L_u(\lambda, z_0)$ (see Methodology) to the respective algorithm. Then, the extracted chlorophyll values from each model were compared with the *in situ* chlorophyll, which was measured simultaneously with $L_u(\lambda, z_0)$. Figure 4 shows plots of *in situ* chlorophyll versus algorithm-derived data from OC4v4, OC2-LP, GSM01 and CARDER. The circled points are associated with turbid waters, where Rrs(670)>0.012 sr^{-1} (turbidity flag, Robinson *et al.* 2003), but these points have been included in the statistical analyses. Parameters of these statistical relationships can be seen in table 3. Both OC4v4 and OC2-LP show a fairly good agreement with *in situ* values (*rmse-L* of 0.56 and 0.50, respectively). However, OC4v4 shows an overestimation of chlorophyll values, reflected in the positive bias (RPD) of 30.4%, which was reduced to 12.5% using OC2-LP.

In general, the GSM01 conforms well to *in situ* chlorophyll values (figure 4C), except in highly turbid waters, where chlorophyll is spuriously overestimated. This is not unexpected, as it is mainly a Case I algorithm. For instance, a value

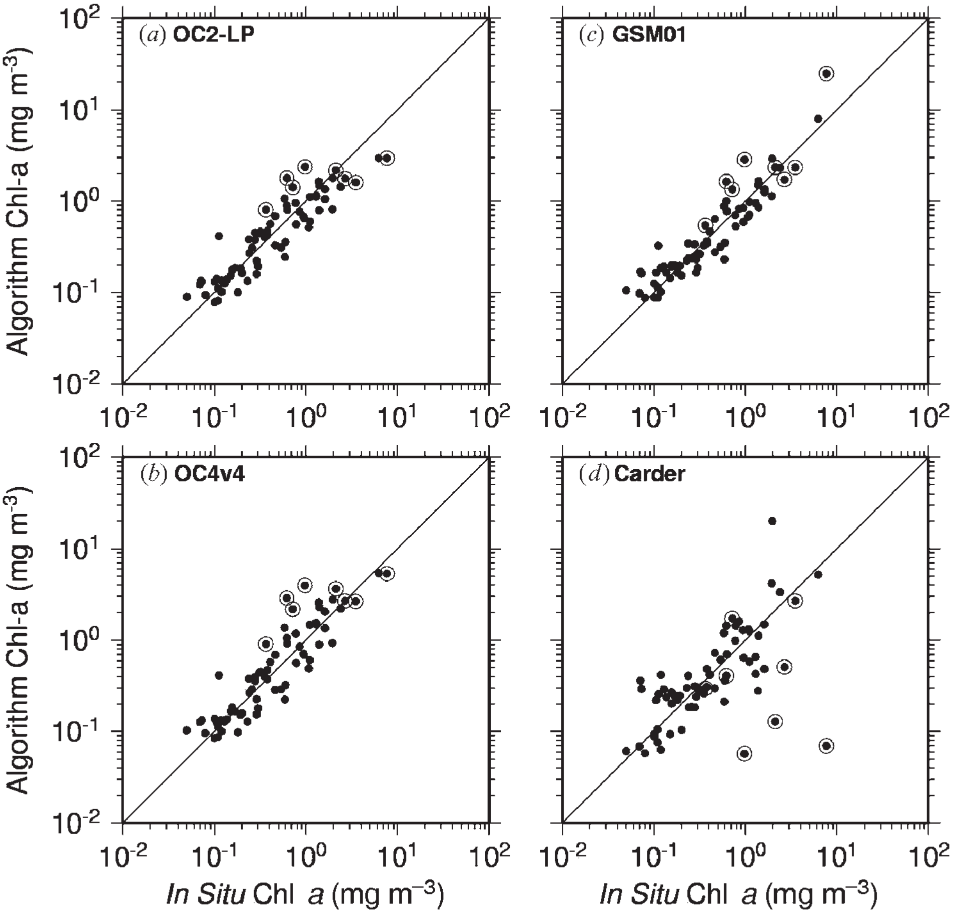

Figure 4. Plots of in-situ chlorophyll and algorithm-derived values from OC2-LP (*a*), OC4v4 (*b*), GSM01 (*c*) and CARDER (*d*). Circled points correspond to turbid waters, where Rrs(670)>0.0012 sr^{-1}.

Table 3. Comparison of algorithm performances on our *in-situ* bio-optical dataset.

Algorithm	Type	Coefficients/parameters a_n, $n=0, 1, 2, \ldots, M$	rmse-L	RPD (%)	APD (%)	r^2	Slope	Interc	N
NASA OC4v4	4th-order	0.366 −3.067 1.930 0.649 −1.532]	0.54	26.9	50.4	0.82	0.93	−0.004	72
OC2-LP	3rd-order	[−1.6266 0.6372 −1.8562 0.1691]	0.49	11.0	41.1	0.83	0.79	−0.093	72
GSM01	Semi-analytical	Original/global	0.44	14.4	38.9	0.86	0.90	−0.062	72
CARDER	Semi-analytical	Original	1.17	31.1	69.7	0.39	0.91	−0.035	72

rmse-L, RPD and APD are defined in equations (2) through (5).

of 22 mg m^{-3} was estimated by GSM01, where the in-situ value was 7.72 mg m^{-3} (figure 4C). In this case, Rrs(670) was 0.00297 sr^{-1}, which is much higher than the value of 0.0012 (used as a threshold for turbid waters). However, even including this point in the statistical analysis, an APD of 38.9% seems reasonable (table 3). We have to point out that the original version of the algorithm has been used here. A better regional tuning of GSM01 using region and season-specific IOP parameters, could improve the performance of this model in the region, as was done for the Chesapeake Bay region (Magnuson *et al.* 2004). The CARDER model (table 3, figure 4D) shows the highest error magnitude (*rmse-L*=1.2), although the slope and intercept are fairly good. It could be argued that the low chlorophyll estimates (negative outliers) would be associated with spurious radiance measurements; however, the same data set was used for GSM01, which was not affected to that extent (figure 4C). The CARDER model has been developed for case II waters (*Carder et al.*, 1999) and uses a switching mechanism between empirical and semi-analytical approaches (see Methodology section). The three negative outliers seen in figure 4D have been extracted using the automatic semi-analytical mode. Therefore, it seems that even the semi-analytical models (at least the global version) present problems in coastal waters with high suspended sediment loads and/or high CDOM concentration.

Figure 5 shows images of the study area, on 27 April 2004, using the four algorithms. The GSM01 shows many black dots (negative retrievals) along the coast, around and north of the La Plata river mouth, which are associated with low reflectance values in the blue bands (mainly 412 and 443 nm). Underestimation of reflectance in coastal regions by ocean colour sensors is often associated with absorbing aerosols which are not accurately accounted for in the atmosphere correction algorithms (Schollaert *et al.* 2003). The CARDER algorithm chlorophyll image also has a few negative values in the same region. These are associated with a tongue of very low radiance magnitudes at 412 nm (not shown). A proper use of these algorithms depends upon good quality reflectance (or radiance) data. However, this is less critical in the case of the empirical models, since they use ratios between reflectance values, which partially compensates for small errors or inaccuracy in radiometric data (*in situ* and satellite). Other works have shown the applicability of SeaWiFS chlorophyll images in coastal areas under estuarine influence (e.g. Harding *et al.* 2005, Magnuson *et al.* 2004). The authors point out that problems of chlorophyll overestimation by the operational SeaWiFS algorithm (OC4v4) is related with its inability to account for the effects of dissolved organic matter absorption. In addition, this is further complicated by the underestimation of reflectance in the blue region by the satellite sensor due to atmospheric correction problems. Despite these drawbacks, the authors demonstrate the usefulness of SeaWiFS retrievals in applications that require short time and space scales variability in phytoplankton biomass.

3.3 *La Plata cruises*

Chlorophyll data from two recent cruises to the study region are used to evaluate the application of the tested algorithms to satellite retrieved radiance data. The difference from plots in figure 6 is that here we have applied the SeaWiFS-retrieved reflectances to each of the four algorithms to extract chlorophyll values, while in

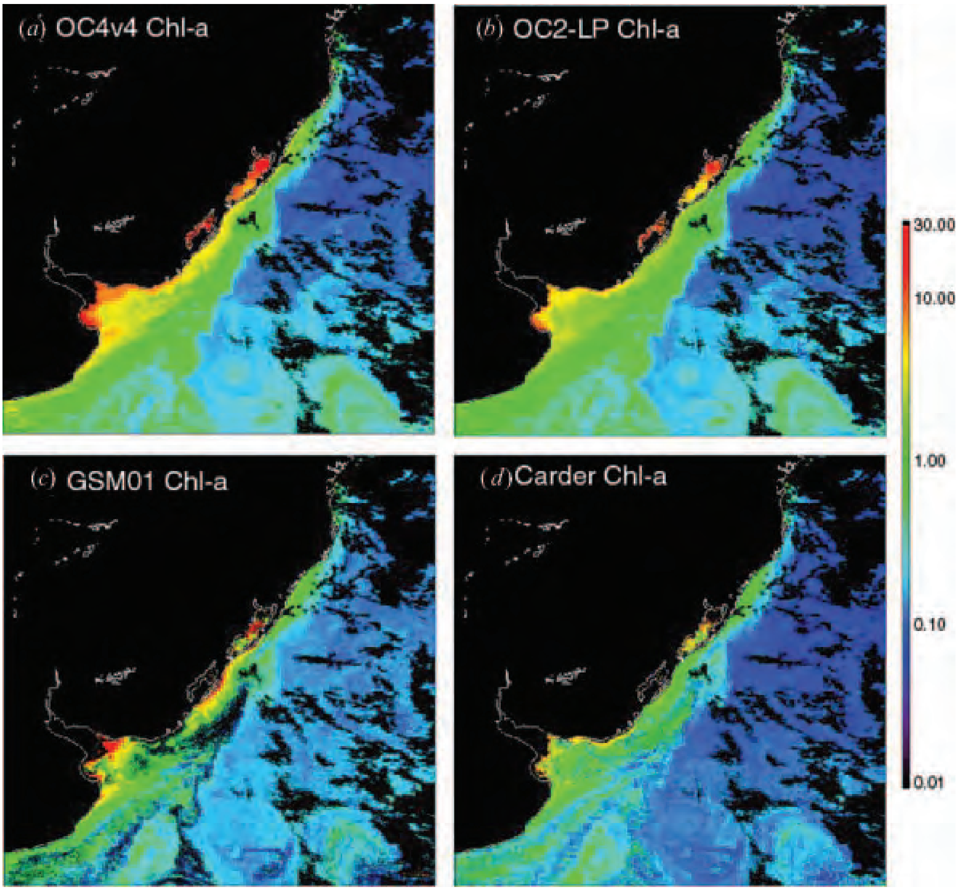

Figure 5. SeaWiFS image on 27 April 2004, where chlorophyll-a has been calculated using the algorithms: OC4v4 (*a*), OC2-LP (*b*), GSM01 (*c*) and CARDER (*d*). Black points are either clouds (mainly in the right half portion of the image) or negative retrieved chlorophyll values.

figure 4 we applied our measured and computed reflectance values. The cruises were carried out in the austral winter of 2003 (La Plata I) and austral summer of 2004 (La Plata II). For this analysis, daily SeaWiFS merged local area coverage (MLAC) images (1 km resolution) of the region from the period 20 August to 2 September 2003 (winter) and 1–19 February 2004 (summer) have been processed using the four algorithms. A stray light flag was used to detect and discard those pixels which were contaminated from land effects. Chlorophyll data extracted from daily images were averaged for the respective cruise periods. Pixel values corresponding with each sampling point were then retrieved for comparison with in-situ values (see figure 9 for sampling points location and the generated mean images). A number of uncertainties and errors are associated with this type of analysis, including space and time mismatch, since the measurements were made at one point and at a certain time, while pixel sizes are approximately 1 km^2, and pixel values were averaged over the cruise period. However, through this exercise we intend to make a comparative analysis of the performances of the four models and also detect possible differences associated with seasonal variations.

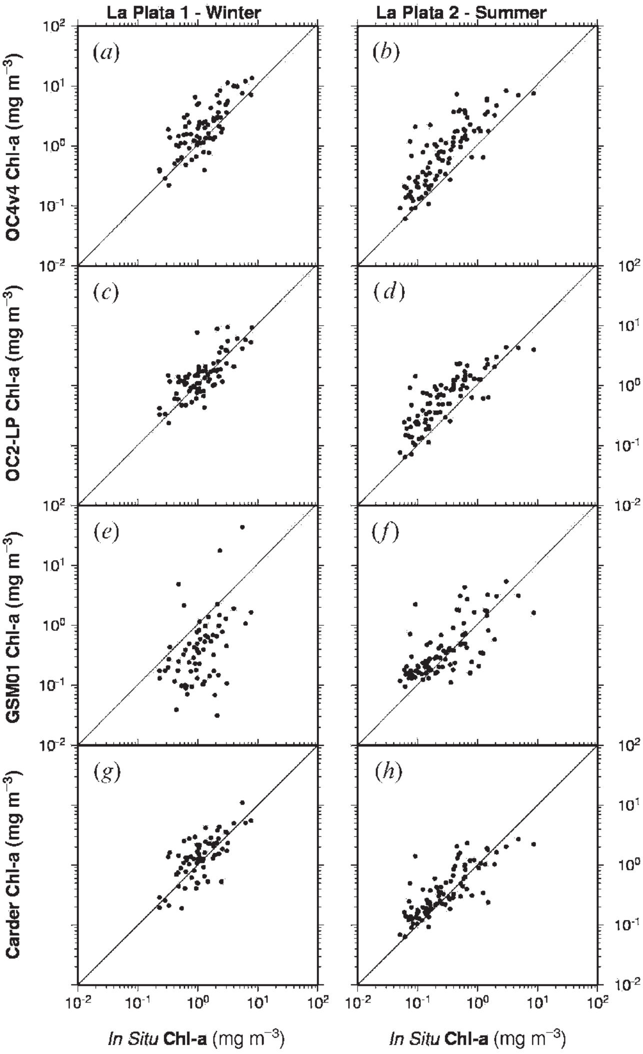

Figure 6. Plots of in-situ chlorophyll values (mg/m^3) during both winter (left column) and summer (right column) La Plata cruises and derived values from the following algorithms: OC4v4 (*a*,*b*), OC2-LP (*c*,*d*), GSMO1 (*e*,*f*), CARDER (*g*,*h*). Winter period: 20 August to 2 September 2003. Summer period: 1–19 February 2004.

Many of the daily images were partially covered by clouds; therefore the mean chlorophyll value for each sampling location was calculated using different number of data points. In addition, the GSM01 and CARDER algorithms retrieve negative chlorophyll values when Rrs at the blue bands (412 and 443 nm) are negative or very low. These negative values have been discarded in the mean calculation. For processing the CARDER algorithm, daily temperature data were extracted from MODIS-Aqua 4-km images over the respective periods.

Figure 6 and table 4 present results of chlorophyll extracted from the four tested algorithms and *in situ* data for both La Plata I and La Plata II cruises. An interesting seasonal difference can be seen in the algorithms performance. In winter (figure 6, left column) both empirical OC4v4 and OC2-LP (figures 6A and 6C), and the semi-analytical CARDER (figure 6G) show very good agreement with the data, whereas in summer, OC4v4 and OC2-LP mostly overestimate chlorophyll (RPD of 246% and 156%, respectively). GSM01 (figure 6E and 6F) generally underestimated chlorophyll values in winter, but showed a better agreement in summer. The CARDER algorithm showed good performance in both seasons (*rmse-L* of 0.69 and 0.77, for winter and summer, respectively), although this was not observed when applying this algorithm to the radiometric *in situ* data (see figure 4D). This result is puzzling and will remain elusive until additional *in situ* data collection and analyses are conducted, including nutrient and CDOM sampling, concurrent with chlorophyll and radiometric observations.

The differences in performance of the empirical OC4v4 and OC2-LP algorithms in winter (June-July-August) and summer (December-January-February) (figure 6A through 6D) could be due to either atmospheric correction problems or to higher incidence of optically interfering components in the water in summer. Problems in the atmospheric correction are related with two main issues: absorbing aerosols and finite reflectance of coastal water. If the shelf waters are primarily absorbing with little particulate backscatter and high CDOM concentration, the second issue is not critical. This is usually the case in winter in the study area, when the La Plata plume with high CDOM content is spread over the shelf region. In summer, however, this can be a problem. In addition, in summer there is a great incidence of fires in the region, contributing to aerosol optical thickness interference. It has been demonstrated that, despite a generally good matching between SeaWiFS-derived and *in situ* reflectance measurements near the Chesapeake Bay, there is an underestimation by SeaWiFS in the blue region of the spectrum (412 and 443 nm), which was attributed to atmospheric correction uncertainties (Harding *et al.* 2005). On the other hand, a very good relationship was found between satellite-retrieved and *in situ* water-leaving radiances (Garcia *et al.* 2005), despite a few negative retrievals at 412 nm. In the winter, after passage of the frequent cold atmospheric fronts in the region, there is great prevalence of clear sky days, therefore we expect less aerosol influence. The same pattern of overestimation in summer is seen in the chlorophyll match-up results (circled points in figure 10). Intra-pixel variation can contribute to mismatch between *in situ* and remote sensing chlorophyll estimation, especially in highly dynamic coastal areas. In the study region, the freshwater discharge flows, particularly from La Plata River, could be an important source of small scale chlorophyll variation, although its influence over the studied coastal area is much stronger in winter due to southerly winds influence and rainfall over the basin (Piola *et al.* 2000). Still, we see a better matching between *in situ* and satellite chlorophyll in this season than in summer. Another source of error, mainly in shallow water stations could be an overtestimation of water-leaving radiances due to bottom reflectance. During the La Plata cruises, 14 of the approximately 85 stations were in water depths less than 30 m both in summer and winter. However, the coastal waters of the study region are normally highly turbid due to sediment re-suspension and freshwater discharge from both La Plata river and Patos lagoon. Light attenuation in the PAR-visible range at depths less than 30 m in the region have been shown to be between 0.1 and 0.4 m^{-1} (V.M.T. Garcia, unpublished data); thus bottom contamination in most shallow sites are unlikely to have occurred during our samplings. However, it is possible that in a few cases this may have been

Table 4. Comparison of algorithm performances on data from cruises La Plata I (winter) and La Plata II (summer).

		rmse-L		RPD (%)		APD (%)		r^2		Slope		Interc		N		Neg		Spu	
Algorithm	Type	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S
NASA OC4v4	4th-order	0.86	1.48	95.8	246.3	106.4	249.2	0.57	0.68	0.93	1.03	0.19	0.39	77	91	0	0	0	0
OC2-LP	4th-order	0.63	1.11	46.0	155.6	66.4	161.3	0.57	0.68	0.75	0.82	0.07	0.22	75	90	2	1	0	0
GSM01	Semi-analytical	2.34	0.99	−19.4	100.0	96.2	121.5	0.20	0.49	0.72	0.67	−0.42	−0.07	67	91	8	0	2	0
CARDER	Semi-analytical	0.69	0.77	46.0	67.5	69.3	85.5	0.50	0.63	0.77	0.75	0.12	−0.05	69	89	8	2	1	0

W=winter; S=summer; Neg=Number of negative retrievals; Spu=number of spuriously high values in turbid waters, which were discarded and not considered in the statistical analysis.

a problem, although it can hardly be ascertained with our available data. This is still a matter to be further investigated.

The low chlorophyll values of GSM01 in winter (figures 6E and 6F) are probably related with the seasonal differences in the spectral shape of the reflectance (or normalized water-leaving radiances). Figure 7 shows the radiance spectra retrieved from the SeaWiFS images, for both La Plata I (A) and La Plata II (B) cruises, where the thick line represents the mean radiance values at each wavelength. In winter, the blue bands (412 and 443 nm) tend to be much lower, including many values approaching zero, whereas in summer the mean radiances at these bands are considerably higher (over 100% at 412 nm). This is consistent with the chlorophyll values in each season. However, these low radiances in the blue part of the spectrum may also be caused by high CDOM absorption, associated with the La Plata river plume. In winter, the influence of La Plata plume is higher over the coastal region of

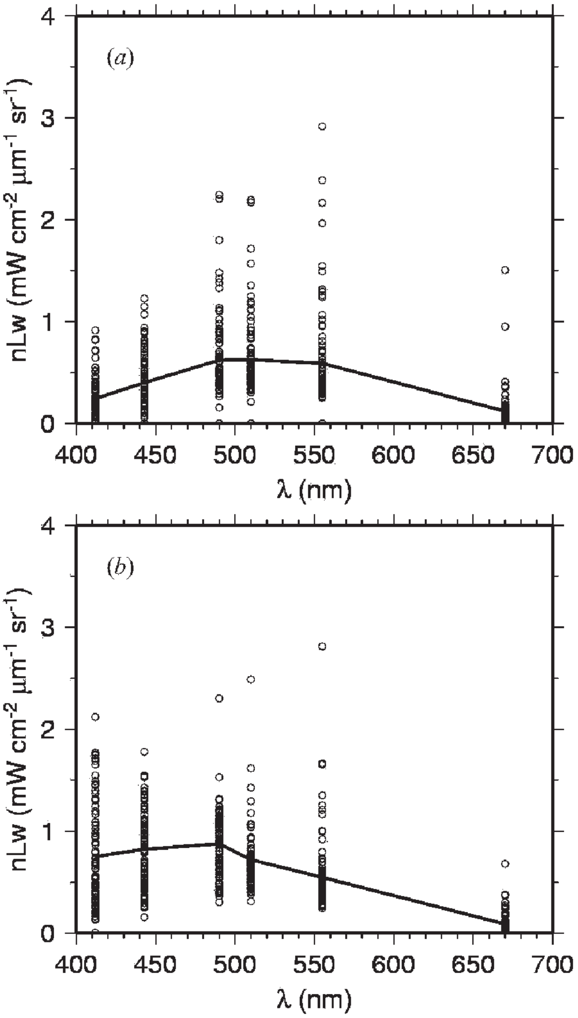

Figure 7. Spectral variation of normalized water-leaving radiances (nLw) from SeaWiFS images during both La Plata cruises: winter (*a*) and summer (*b*). The thick lines represent the mean spectra taken from values at the six bands.

the study area (*Piola et al.* 2000), due to predominance of stronger southerly alongshore wind stress.

The GSM01 output of coloured dissolved and detrital material [$a_{cdm}(443)$] shows no correlation with chlorophyll in winter, as opposed to summer, where a marked correlation exists between the two parameters (figures 8A and 8B). Therefore, the general underestimation of chlorophyll by GSM01 for La Plata I cruise (figure 6E) is associated with the lack of co-variation of pigment with other optically interfering components in the water, such as detritus and CDOM, as observed in case II waters (*Morel and Maritorena* 2001). In fact, the GSM01 model was proposed for global applications (*Maritorena et al.* 2002) and has been shown to reproduce well the IOPs and chlorophyll-a in clear waters. However, for application to satellite retrieved radiance, especially in turbid waters, a proper tuning of the model will be necessary from *in situ* IOP's measurements. The CARDER algorithm, on the other hand, did show a good match with the La Plata cruises chlorophyll, both in winter and

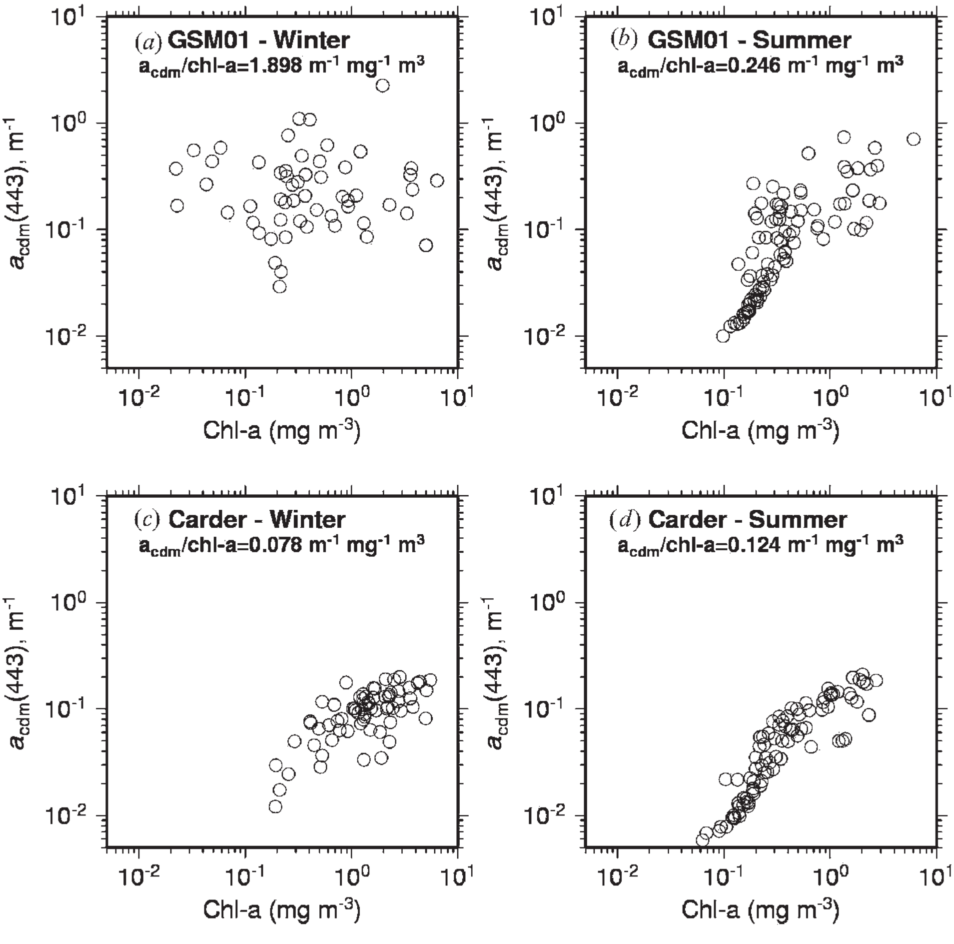

Figure 8. Comparison between absorption coefficients for dissolved and detrital materials—$a_{cdm}(443)$—and chlorophyll, both retrieved from GSM01 (*a* and *b*) and CARDER (*c* and *d*) models for La Plata I (winter) and La Plata II (summer) cruises, respectively. The parameter $a_{cdm}(443)$ for the CARDER model has been calculated from $a_{cdm}(443) = a_{cdm}(400).e^{-0.0225(443-400)}$.

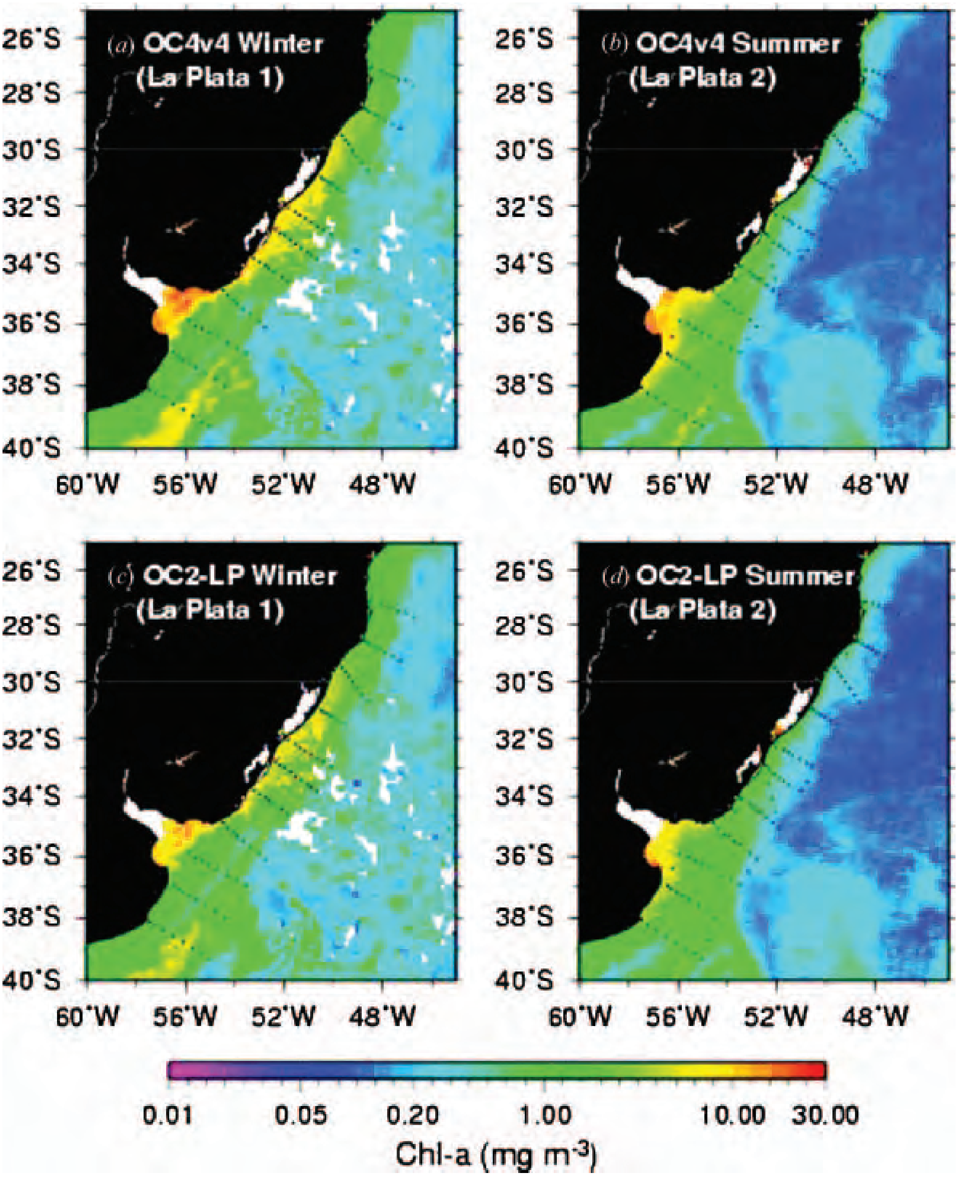

Figure 9. Mean composite images for the cruise periods of La Plata I (left column, winter) and La Plata II (right column, summer) using the four studied algorithms. The white areas correspond to either lack of valid pixels due to clouds or negative chlorophyll retrievals. Winter period: 20 August to 2 September 2003. Summer period: 1–19 February 2004.

summer (figures 6G and 6H), and this is reflected in the coherent correlation of retrieved a_{cdm} (converted to $a_{cdm}(443)$) and chlorophyll, seen in figures 8C and 8D. This algorithm automatically selected the empirical mode in 33% of the points in the winter cruise (La Plata I) and 68% in the summer cruise (La Plata II). Apparently, the CARDER algorithm does operate reasonably well with satellite-based radiance, despite a few outliers, common to both semi-analytical models, in very turbid regions. In this respect, it is recommended that turbid pixels (where $\mathrm{Rrs}(670)>0.012\,\mathrm{sr}^{-1}$) be flagged when processing SeaWiFS images using this

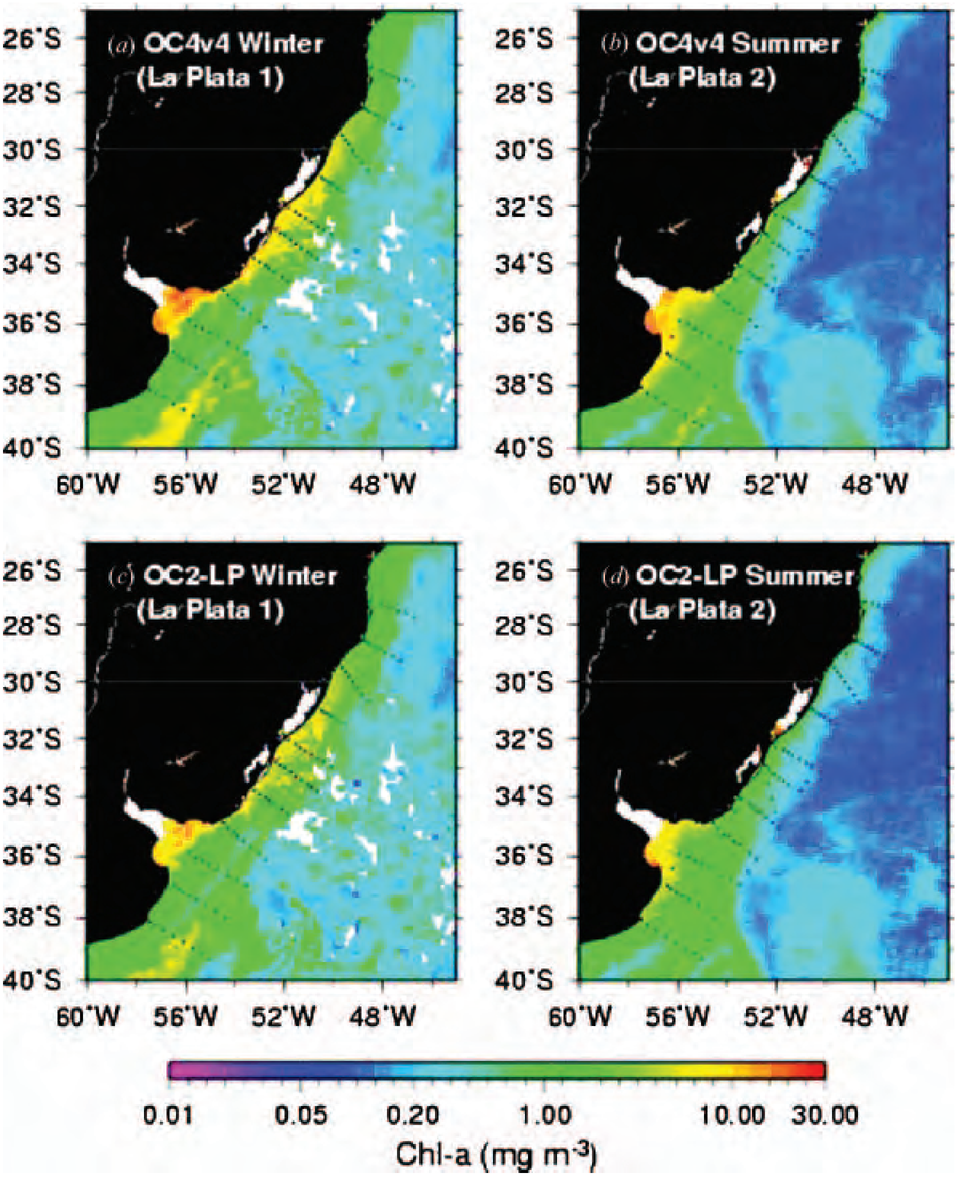

Figure 9. (*Continued.*)

algorithm, until a better characterization of particle backscattering is made in these waters.

Figure 9 shows a mean composite of chlorophyll images, during La Plata I and La Plata II cruise periods, using OC4v4, OC2-LP, GSM01 and CARDER algorithms. These images represent the results of Figure 6 (plots of *in situ* and model-derived chlorophyll), at least in the coastal, inner shelf area, where the cruise tracks are shown as black dots. In winter (left side images), a high chlorophyll signal can be seen associated with the La Plata river mouth and in the southern Brazilian coast, from 34°S to ~30°S. All winter images (except 9E) show relatively high chlorophyll

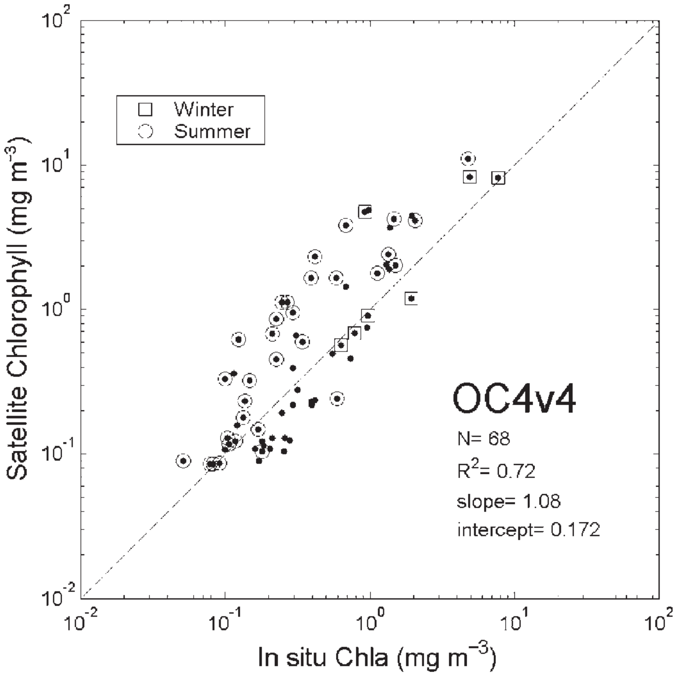

Figure 10. Match-up between *in-situ* chlorophyll and SeaWiFS OC4v4 derived values, within a 12 hours window of the satellite passing. Points surrounded by circles were sampled in summer and by squares were taken in winter. Statistical parameters describing this relationship (including all 68 data points) are: rmse-L=0.89; RPD=81%; APD=106%.

levels along the coast (shown as green patches), up to the northern end. This is an influence of the nutrient rich, freshwater discharge from La Plata river, specially high in silicate levels (Piola *et al.* 2000). This pattern of high phytoplankton biomass associated with the rivers plumes has been previously observed in the region (Ciotti *et al.* 1995b). However, the GSM01 image (figure 9E) does not show this feature, as it mainly underestimated chlorophyll in this period (see figure 6E for comparison with *in situ* values). Note that GSM01 (figures 9E and 9F) retrieved many negative chl-a values, seen as white dots near the La Plata mouth (~36°S). In summer (images on the right column, figure 9), high chlorophyll ($>10\,\mathrm{mg/m^3}$) is mainly associated with coastal areas near the river mouth, while large areas of low values offshore (blue areas) are associated with the oligotrophic Brazil current. This low nutrient warmer current has been shown to dominate the south Brazilian shelf region in summer, determining low phytoplankton biomass and primary production rates (Ciotti *et al.* 1995a, Odebrecht and Castello 2001). In this season, the CARDER algorithm represented well the *in situ* values (see figure 6H). Overall, the CARDER model provided the best chlorophyll retrievals results both in summer in winter. This is expected to be further improved by feeding the model with regional *in situ* optical data.

3.4 *OC4v4 match-ups*

The OC4v4 chlorophyll match-up results, within 12 hours of the satellite passing, can be seen in figure 10. This match-up was conducted in order to compare with results from La Plata cruises, where image data was averaged over the cruises periods. The procedure was only adopted with the OC4v4 algorithm for simplicity and to avoid redundancy. The points surrounded by a circle in figure 10 were taken in summer and by a square, in the winter. As reflected in the RPD of 81%, a general overestimation in chlorophyll values can be seen, especially the summer retrievals. This corroborates the results from La Plata cruises, where overestimation is more severe in this season, due to predominant days with higher aerosol thickness, not accounted for in the standard atmospheric correction procedure. Note that the APD of 106% in this match-up is similar to the value found for winter La Plata cruise (see table 4).

4. Summary and conclusions

We have investigated the performances of ocean colour algorithms (empirical and semi-analytical) for chlorophyll retrievals in the south-western Atlantic, between 25°S and 40°S and 60°W to 45°W. Coastal waters within this region are subject to large optical interference by continental runoff from La Plata river and Patos lagoon. Based on *in situ* pigment and optical measurements we have developed an empirical regional 2-band algorithm (termed OC2-LP), which reduces chlorophyll positive bias (RPD=11%), as compared to the global SeaWiFS OC4v4 algorithm (RPD=27%), but remains with an overall inaccuracy of over 40% (APD=41.1%). Other models tested were the semi-analytical GSM01 (Maritorena *et al.* 2002) and CARDER (Carder *et al.* 1999), with APDs of 39% and 70%, respectively. Because of reliance on the 412 nm band, the semi- analytical models are very sensitive to unrealistically low or negative values of Rrs (412).

In situ chlorophyll data from two cruises to the study region (La Plata I, winter of 2003, and La Plata II, summer of 2004) have been used to test the accuracy of the four algorithms (OC4v4, OC2v4-LP, GSM01 and CARDER) on SeaWiFS images over the cruise periods. A marked seasonal difference was found in the performance of the tested models. Both OC4v4 and OC2-LP overestimate chlorophyll in summer at a higher magnitude than in the winter, due to the inability to compensate for absorbing aerosol influences on reflectances. This trend was also observed in the chlorophyll match-up (within 12 hours) using OC4v4. The GSM01 algorithm, on the other hand, shows a marked negative bias in winter, which is not seen in summer. This can be associated with the lack of co-variation between chlorophyll and the other absorbing components (detritus and CDOM), which was shown to be much more severe in winter. The CARDER algorithm showed a good performance both in winter and summer, when applied to satellite-retrieved radiances, during both La Plata cruises.

No single algorithm tested showed a consistent reproduction of *in situ* chlorophyll values over the study region. Using *in situ* radiometric measurements, both OC2-LP and GSM01 show the best performances. When applying to satellite-retrieved radiometry, the CARDER model reproduces reasonably well chlorophyll values both in winter and summer. However, the CARDER algorithm showed many outliers when *in situ* reflectances were used. This is an unexpected result that requires further analysis. The complex nature of this hybrid algorithm (empirical and semi-analytical), which includes pigment packaging and turbid waters sensitivity, will require more regional tuning based on an expanded observational data base of concurrent measurements of nutrients, chlorophyll, CDOM, backscattering, SST, and reflectances.

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