Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Remote Sensing of Environment 95 (2005) 125–137

Remote Sensing of Environment

www.elsevier.com/locate/rse

Evaluation of SeaWiFS chlorophyll algorithms in the Southwestern Atlantic and Southern Oceans

Carlos Alberto Eiras Garcia[a,1], Virginia Maria Tavano Garcia[b,*], Charles R. McClain[c]

[a]*Department of Physics, Federal University of Rio Grande, Brazil*
[b]*Department of Oceanography, Federal University of Rio Grande, Brazil*
[c]*NASA Goddard Space Flight Center, United States*

Received 9 June 2004; received in revised form 1 December 2004; accepted 8 December 2004

Abstract

Bio-optical measurements of spectral upwelling radiance and surface chlorophyll-*a* concentration have been conducted during 15 cruises between 1995 and 2004. The bio-optical data were divided into two sub-sets: the Southwestern Atlantic Ocean (SwAO), comprising a variety of biogeochemical provinces, from the oligotrophic waters in the South Atlantic gyre to the coastal waters influenced by La Plata River and Patos Lagoon discharge, and the Southern Ocean (SO) data set, comprising sampling stations south of the mean position of the Polar Front, with most stations being located in the vicinity of the Antarctic Peninsula. We derived regional chlorophyll algorithms for both regions and comparisons were made with the NASA's OC4v4 (operational algorithm) and OC2v4. For the Southwestern Atlantic region, the NASA OC4v4 algorithm presented a reasonable performance (r^2=0.87, rmse-L=0.475, N=136) as compared to the revised algorithm for SwAO data (r^2=0.89, rmse-L=0.426, N=136). A few stations under strong river plume influence were not considered in the analyses. These were detected by a higher reflectance at 670 nm, at low in situ chlorophyll concentration (<2 mg m^{-3}). These results show that empirical algorithms applied to in-situ radiance data have a limited ability to extract accurate chlorophyll estimates below a 30% uncertainty level. For Southern Ocean stations, a 2-band linear-type model was generated (r^2=0.64, rmse-L=0.347, N=77), which significantly improved the bias (6.4%) as compared to NASA's OC4v4 algorithm (bias=−21.7%). An evaluation of some published high-latitude algorithms on our data set has shown a better performance by taxon-specific models, even from distant regions. A validation experiment of the normalized spectral water-leaving radiances and chlorophyll-*a* SeaWiFS products was also conducted using the FURG-SwAO/SO data set, through a match-up exercise. Despite the relatively low number of pairs of radiometric measurements, SeaWiFS estimations compare well with in situ data ($0.77<r^2<0.98$, N=21), although the satellite estimate show a marked bias (−35.6%) in the blue band nL_w (412). Regarding the chlorophyll-*a* concentration, an overall agreement was observed (r^2=0.77, rmse-L=0.66, N=28), with a mean absolute percentage difference of 66%, which is above the goal generally accepted of 35% for satellite ocean color chlorophyll estimates. For the studied Southern Ocean area (mainly the Bransfield Strait), NASA's OC4v4 algorithm systematically underestimates chlorophyll above 0.2 mg m^{-3}, as previously demonstrated by other researchers.

Keywords: Ocean color; SeaWiFS; Chlorophyll; Southwestern Atlantic Ocean; Southern Ocean

1. Introduction

Remote sensing techniques have been successfully used to provide a synoptic coverage of surface patterns of phytoplankton biomass distribution at a global scale. Several algorithm types have been proposed for retrieving chlorophyll-*a* from ocean color data, including empirical (e.g. Gordon et al., 1983) and semi-analytical (e.g. Maritorena et al., 2002) models. O'Reilly et al. (2000)

---

[*] Corresponding author.

E-mail addresses: dfsgar@furg.br (C.A.E. Garcia), docvmtg@furg.br (V.M.T. Garcia), Charles.R.McClain@nasa.gov (C.R. McClain).

[1] University of Maryland Baltimore County, Goddard Earth Sciences and Technology Center (GEST), Goddard Space Flight Center/NASA Code 970.2, Greenbelt, MD 20771, USA.

0034-4257/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.rse.2004.12.006

presented an update of NASA's OC2 and OC4 SeaWiFS algorithms, based on a large in situ data set, including measurements in oligotrophic and eutrophic waters around the world oceans. Over the past few years, there have been increasing efforts to gather in situ spectral optical properties data for remote sensing data validation (Hooker & McClain, 2000). Recently, regions like the Mediterranean Sea (D'Ortenzio et al., 2002) and high latitude areas in the North Atlantic (Cota et al., 2003; Stramska et al., 2003) have been sampled for algorithm development and evaluation.

Bio-optical properties of seawater in the South Atlantic Ocean are poorly known, despite the works of some investigators (Aiken & Hooker, 1997; Omachi & Garcia, 2000). A significant contribution has been made during the Atlantic Meridional Transect (AMT) program (Aiken et al., 2000). Data from this program have been used to examine and characterize the properties of the biogeochemical provinces and their boundaries over the Atlantic Ocean (Hooker et al., 2000). A more detailed classification of biogeographical regions was generated for the Southwestern Atlantic region using CZCS and SeaWiFS derived pigment variability (Gonzalez-Silvera et al., 2004). A recent report, focused on the distribution of phytoplankton pigments and bio-optical properties of a section of the AMT data from the South Atlantic Ocean (0–40°S), is given by Signorini et al. (2003).

In the Southwestern Atlantic, the presence of La Plata River mouth (at 35°S), and to a lesser extent the Patos Lagoon mouth (at 32°S), originate a low salinity plume along the shelf that can extend northward up to approximately 28°S during the austral winter (Piola et al., 2000). In some cases, coastal waters influenced by the plume may show a sharp increase in chlorophyll-*a* concentration (Negri et al., 1992), particularly in El Niño years, when high chlorophyll events (>15 mg m^{-3}) are related to anomalous large freshwater outflow (Ciotti et al., 1995). Concerning ocean color pigment retrievals, the presence of these plumes cause the optical properties of the water in the region to be affected by both inorganic and organic matter from the continental runoff. Indeed, it has been shown that SeaWiFS-derived chlorophyll values can be highly overestimated in coastal waters influenced by the La Plata River plume (Armstrong et al., 2004). Based on SeaWiFS chlorophyll time-series analyses, Garcia et al. (2004) reported that near La Plata River (where values are probably contaminated by plume waters) chlorophyll variability present no detectable seasonal cycle, as opposed to the adjacent areas, where a marked annual cycle is observed.

In the Southern Ocean, in situ sampling is limited by severe weather conditions and isolation from land based institutions. These difficulties have restricted the studies predominantly to areas close to the Antarctic coastal zone. Data from investigations in the western Antarctic Peninsula have shown that NASA's algorithms underestimate pigment concentration in the area (Dierssen & Smith, 2000; Mitchell & Holm-Hansen, 1991; Mitchell et al., 2001). Both low concentrations of detritus and large pigment packaging of the dominant phytoplankton species have been suggested as causes for the failure of global algorithms in the region (Mitchell & Holm-Hansen, 1991). Mitchell (1992) has already suggested the need for a specific ocean color pigment algorithm for polar regions. In the Australian sector of the Southern Ocean, Clementson et al. (2001) have also found that the NASA OC4v4 algorithm generally underestimates chlorophyll-*a* concentration but overestimates in low pigment (<0.15 mg m^{-3}) areas. On the other hand, in the southwestern Ross Sea, the bio-optical relationship is strongly dependent on the phytoplankton species present and in some cases they resemble those of temperate waters (Arrigo et al., 1998).

The main goal of this work is to present an independent bio-optical data set consisting of spectral upwelling radiance measurements and chlorophyll-*a* concentration in the Southwestern Atlantic and adjacent sectors of the Southern Ocean, collected during 15 cruises between 1995 and 2004. These regions have been considered relevant in terms of the global ocean carbon cycle, as important CO_2 sink areas (Feely et al., 2001; Sarmiento & Sundquist, 1992; Takahashi et al., 1997). The Southwestern Atlantic and Southern Oceans data set of Federal University of Rio Grande (FURG-SwA/SO) are used to generate regional algorithms and compare their performances with NASA's SeaWiFS operational algorithms. We also compare our bio-optical data to both other data sets from the Atlantic and Antarctic waters and to SeaWiFS-retrieved values (match-up analyses).

2. Methods and data set

Fifteen cruises (Table 1) have been conducted in the Southwestern Atlantic and Southern Oceans, between 1995 and 2004, resulting in 218 sampling stations covering a very wide region (0–80°S and 15–60°W). Fig. 1 shows the geographical extent of the study region and sampling stations on a SeaWiFS binned (9 km×9 km resolution) mean image for the October 1997–September 2003 period, after the 4th data reprocessing (Feldman & Patt, 2003).

2.1. Bio-optical measurements

In-water radiometric measurements were made using a Tethered Spectral Radiometer Buoy (TSRB) manufactured by Satlantic Inc. (Cullen et al., 1994). The instrument collects spectral upwelling radiance, $L_u(\lambda, z_0)$, at z_o=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. The instrument was always kept 30–70 m away from research vessels to avoid shadowing. The distance depended on the length of the ship used to collect the optical data. Time interval for measurements varied from

Table 1
The 15 cruises in the Southwestern Atlantic and Southern Oceans: WOCE-A23 (World Ocean Circulation Experiment—Leg A23), PROANTAR 14, 15, 21, and 22 (Brazilian Antarctic Program—Operations 14, 15, 21, and 22), COROAS 3 (Regional Oceanic Circulation in the South Atlantic—Leg 3), SAMBA 3 (SubAntarctic Motions in the Brazil Basin—Leg 3), MAC IV (Coastal Environment Monitoring, Leg IV) REVIZEE (Living Resources in the Economic Exclusive Zone), DEPROAS (Ecosystem Dynamics of the Southwestern Atlantic Shelf Region), DOVETAIL (Deep Ocean Ventilation Through Antarctic Intermediate Levels), SAFARI (Southwestern Atlantic Fresh Water Assimilation and River Input), DPA (Department of Fishery and Aquaculture), LA PLATA 1 (La Plata Project /SACC—Leg 1)

No.	Cruise	Period	Research vessel
1	WOCE-A23	03/31–05/05/1995	RV James Clark Ross
2	PROANTAR 14	11/14–11/16/1995	RV Ary Rongel
3	PROANTAR 15	03/18–03/15/1997	RV Ary Rongel
4	COROAS 3	10/17–10/23/1997	RV Atlantico Sul
5	SAMBA 3	11/27–12/13/1997	RV Nadir
6	MAC 4	08/19–08/04/1998	RV Astro Garoupa
7	REVIZEE 4	04/23–05/01/2000	RV Astro Garoupa
8	DOVETAIL	01/22–02/25/2001	RV Ary Rongel
9	DEPROAS	07/14–07/18/2002	RV Prof. Besnard
10	SAFARI	05/22–05/26/2002	RV Atlantico Sul
11	DPA	02/15–03/10/2002	RV Atlantico Sul
12	PROANTAR 21a	11/13–11/17/2002	RV Ary Rongel
13	PROANTAR 21b	01/23–01/29/2003	RV Ary Rongel
14	LA PLATA 1	08/20–08/31/2003	RV Puerto Deseado
15	PROANTAR 22	01/15–02/13/2004	RV Ary Rongel

10 to 30 min and at 1 Hz sample frequency. Spikes were removed prior to radiometric analysis. A 5-s running mean was applied to the radiometric measurements to smooth out any residual spikes in the time series. The median spectral upwelling radiances at 50-cm depth were calculated to characterize the spectral signature of the surface waters for all stations.

At each station, surface water samples (200 to 2000 ml, depending on water type) for chlorophyll determinations were filtered onto 25 mm Whatman GF/F filters. These were kept dry and frozen until laboratory analyses (within 1–8 weeks after collection) with Turner 111 or Turner Design TD-700 fluorometers were performed. Pigments were extracted in 90% acetone solution and fluorescence readings were made using two approaches. For cruises 1, 4, 5, 6, 7, and 9, the readings before and after acidification were taken to correct for phaeopigments interference (Holm-Hansen et al., 1965). For all other cruises, the non-acidification approach was used (Welschmeyer, 1994), where errors associated with phaeopigments are avoided by using appropriate excitation and emission filters.

Although the chlorophyll measurements were made in water collected from surface waters, it would be desirable to relate remote sensing reflectance (R_{rs}) to the weighted mean pigment concentration within the surface layer (Morel & Berthon, 1989). In this study, vertical profiles of pigments were only available from a few sites, due to logistical issues in various cruise samplings. However, the Global SeaWiFS algorithm (OC4v4) has also been built using mostly surface chlorophyll values and, therefore, it largely represents the relationship between reflectance

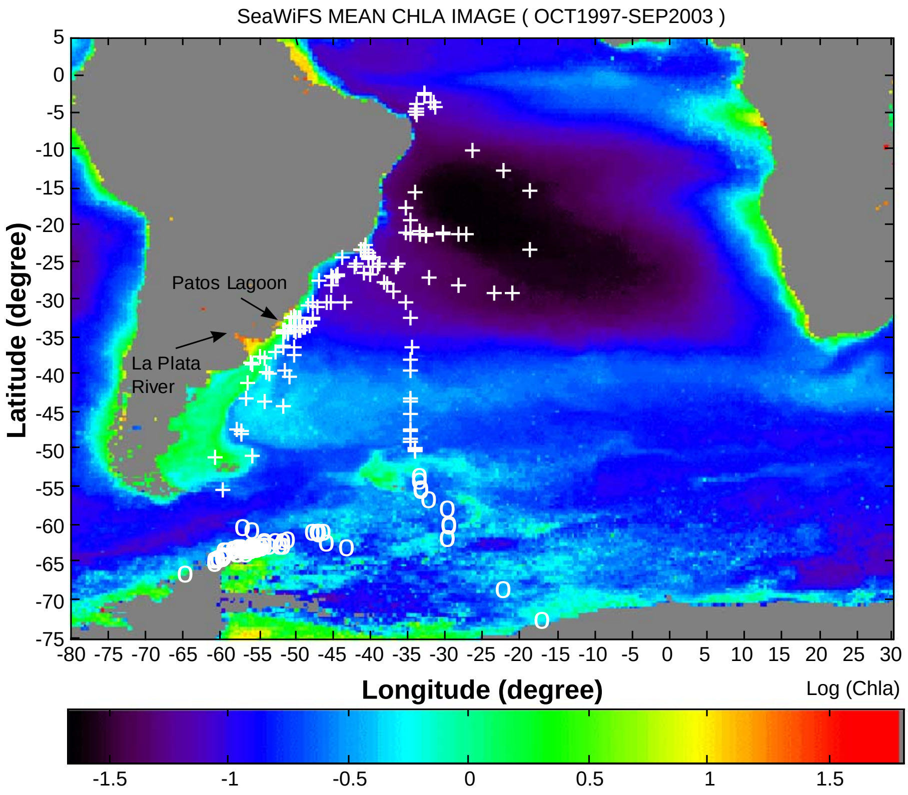


Fig. 1. Mean SeaWiFS chlorophyll image showing the study region and position of the sampling stations: Southwestern Atlantic waters (+), Southern Ocean waters (o) are marked on the image.

ratios and chlorophyll concentration in the surface layer. Furthermore, Clark (1981) found no significant difference in the values calculated both ways when developing the CZCS algorithm.

2.2. Computation of the spectral water leaving radiances and reflectances

The spectral water-leaving radiances, $L_w(\lambda)$, were computed from the upwelling radiance at z_0=0.5 m, which was converted to values just beneath the sea surface, $L_u(\lambda, 0^-)$, and then through the sea–air interface. The spectral attenuation coefficients, $K(\lambda)$, used here were estimated using Morel and Maritorena (2001) relationships, where chlorophyll-*a* concentrations are previously known. The spectral water leaving radiance was calculated by

$$L_w(\lambda) = \frac{1-\rho_w}{n_w^2} L_u(\lambda, z_0)\exp(K(\lambda)z_0) \qquad (1)$$

Where ρ_w and n_w stand for the Fresnel reflectance at the sea–air interface and the refractive index of the seawater, respectively. These parameters depend weakly on wavelength for low solar zenith angle and calm sea surface. In this work, ρ_w was set to 0.0215 and n_w to 1.345. The spectral remote sensing reflectance, $R_{rs}(\lambda)$, was then calculated from

$$R_{rs}(\lambda) = \frac{L_w(\lambda)}{E_d(\lambda)} \qquad (2)$$

Where 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. The modeled spectral incident irradiance on the sea surface, E_d^{BR}, was computed for cloudless sky and standard atmosphere conditions for all stations. $E_d(\lambda)$ was then calculated assuming that the ratio between modeled and measured $E_d(490)$ holds for the remaining spectral bands:

$$E_d(\lambda) = \frac{E_d^{BR}(\lambda)}{E_d^{BR}(490)} E_d(490) \qquad (3)$$

An evaluation of E_d values computed this way was made by comparing the calculated $E_d(\lambda)$ with other irradiance data set from the region (AMT cruises), available in the SeaWiFS bio-optical data archive and storage system (SEABASS, Werdell et al., 2003). The FURG/SwAO irradiance values are generally lower than the AMT data, due to the large number of cloudy days during FURG cruises sampling. The ratio SwAO/AMT values for $E_d(412)$, $E_d(443)$, $E_d(490)$, $E_d(510)$, and $E_d(555)$ are, respectively, 0.726, 0.757, 0.767, 0.779, and 0.843. Considering our $E_d(490)$ as a true, non-error value, the relative difference for the five wavelengths would be of the order of −5.3%, −1.3%, 0%, 1.6%, and 9.9%, respectively. These differences are not so large, considering that the AMT measurements were made mostly in offshore areas, whereas the FURG data were mainly from coastal regions and measurements were not time-coincident. Also, even simultaneous measurements of E_d, using different sensors, have shown a disagreement up to 7.1% (Hooker & Maritorena, 2000). Therefore, our method for calculating $E_d(\lambda)$ from modeled $E_d(490)$ can be considered acceptable.

2.3. Bio-optical relationships

Empirical algorithms for estimating chlorophyll-*a* concentration from space usually rely on blue to green ratios of the remote sensing reflectance or water-leaving radiance. The blue to green reflectance ratio, $R_{\lambda_2}^{\lambda_1}$=$R_{rs}(\lambda_1)/R_{rs}(\lambda_2)$, was computed for the following wavelengths: R_{555}^{412}, R_{555}^{443}, and R_{555}^{490}. The functional form of the empirical algorithms is given by

$$\log_{10}[\mathrm{Chla}] = \sum_{n=0}^{M} a_n R^n \qquad (4)$$

where R is the $\log_{10}$ of $R_{\lambda_2}^{\lambda_1}$. We performed a series of statistical analysis with M varying from 1 (first order) to 4 (fourth order). A third and fourth order polynomials were used for generating a revision of the OC2v4 and OC4v4 algorithms, for our data sets of the Southwestern Atlantic and Southern Ocean, respectively. These were then compared with NASA's respective algorithms (O'Reilly et al., 2000). In the case of the third order polynomial, R is $\log_{10}$ of R_{555}^{490} and, in the fourth order, M=4 and R is the $\log_{10}$ of the maximum value among R_{555}^{443}, R_{555}^{490}, and R_{555}^{510} (O'Reilly et al., 1998, 2000).

For the purpose of evaluating the algorithm performances, linear regression analyses were carried out 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. These parameters are defined as:

$$\mathrm{rmse{-}L} = 0.5[(10^{+\mathrm{rmse}} - 1) + (1 - 10^{-\mathrm{rmse}})] \qquad (5)$$

Where

$$\mathrm{rmse} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left[\log_{10}\left(\frac{\mathrm{Chla_{alg}}}{\mathrm{Chla_{in\ situ}}}\right)^2\right]} \qquad (6)$$

$$\mathrm{RPD} = \sum_{n=1}^{N}\left(\frac{\mathrm{Chla_{alg}} - \mathrm{Chla_{in\ situ}}}{\mathrm{Chla_{in\ situ}}}\right)\frac{1}{N} \times 100\% \qquad (7)$$

$$\mathrm{APD} = \sum_{n=1}^{N}\left|\frac{\mathrm{Chla_{alg}} - \mathrm{Chla_{in\ situ}}}{\mathrm{Chla_{in\ situ}}}\right|\frac{1}{N} \times 100\% \qquad (8)$$

3. Results and discussion

3.1. The FURG bio-optical data

The bio-optical data set collected by Federal University of Rio Grande (FURG) was classified into two sets: Southern Ocean data (SO), from stations located south of the mean position of the Polar Front (Moore et al., 1999), and Southwestern Atlantic Ocean data (SwAO), comprising the remaining stations (see Fig. 1). A frequency distribution of $\log_{10}$ surface chlorophyll concentration can be seen in Fig. 2A and B, for both sub-regions. In the Southwestern Atlantic, chlorophyll varied from 0.016 to 7.72 mg m^{-3} (median=0.23 mg m^{-3}) and, in the Southern Ocean, values were between 0.1 and 1.19 mg m^{-3} (median=0.37 mg m^{-3}). Table 2 shows some basic statistical parameters of the chlorophyll concentration over both study regions.

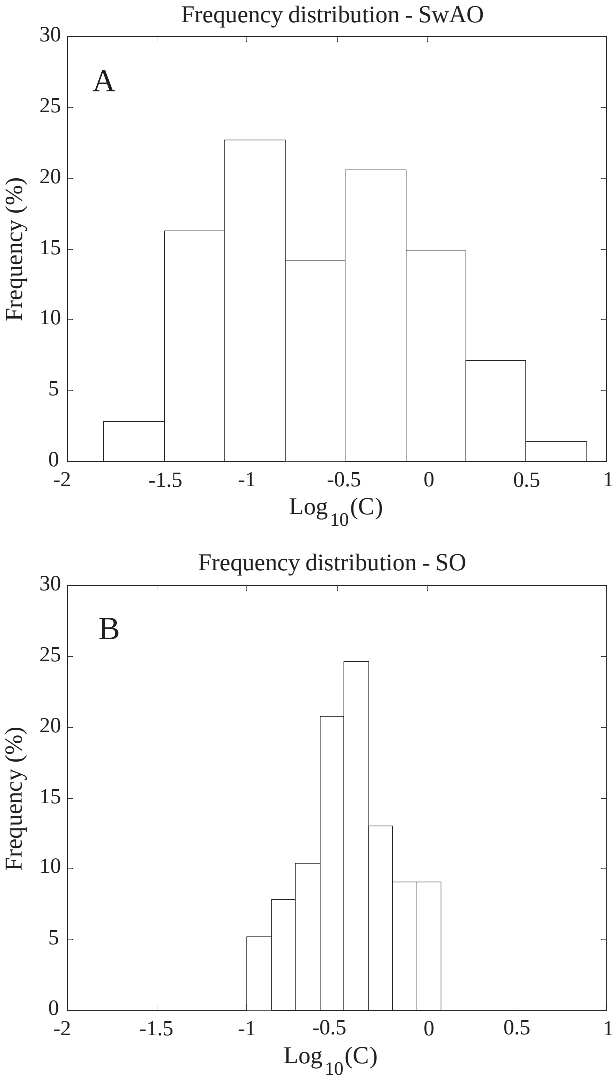


Fig. 2. Histograms showing the frequency distribution of the log chlorophyll values for the Southwestern Atlantic region (A) and the Southern Ocean (B).

Table 2
Statistical parameters of chlorophyll-a concentration for the two datasets: Southwestern Atlantic Ocean (SwAO) and Southern Ocean (SO) waters (see locations in Fig. 1 for both data sets)

Region	Mean (mg/m^3)	Standard deviation (mg/m^3)	Chl range (mg/m^3)	Median (mg/m^3)	Number of data
SwAO	0.61	0.99	0.016–7.72	0.23	141
SO	0.43	0.24	0.1–1.19	0.37	77
All	0.55	0.81	0.016–7.72	0.32	218

Fig. 3 shows reflectance values at 6 wavelengths for 5 classes of chlorophyll concentration for all the data (218 data points). As chlorophyll levels increase, reflectance values are lower at the blue and higher at green and especially at red (670 nm) bands. The typical inflection point can be seen at approximately 500 nm. In Fig. 4, the relationship between chlorophyll concentration and the reflectance ratios R_{555}^{412}, R_{555}^{443}, R_{555}^{490}, and R_{555}^{510} are shown. The R_{555}^{490}, which is also used in the NASA OC2v4 algorithm, shows the best correlation coefficient (r^2=0.79) with chlorophyll data, followed by R_{555}^{443} (r^2=0.76) and the remaining two ratios (Fig. 4A and B) had r^2=0.69.

3.2. Chlorophyll algorithms

A preliminary analysis of the Southwestern Atlantic (SwAO) data set showed a few locations (five stations) under strong influence of riverine discharge, detected by anomalously high reflectance signals in the red band. These have not been considered in the algorithm development analysis, because their optical properties must be strongly influenced by suspended inorganic matter (sediment load) and dissolved organic material from La Plata River, typical of case II waters. The criterion for flagging these points was the following: reflectance values at 670 nm greater than 0.0012 sr^{-1} (turbidity flag, Robinson et al., 2003) coincid-

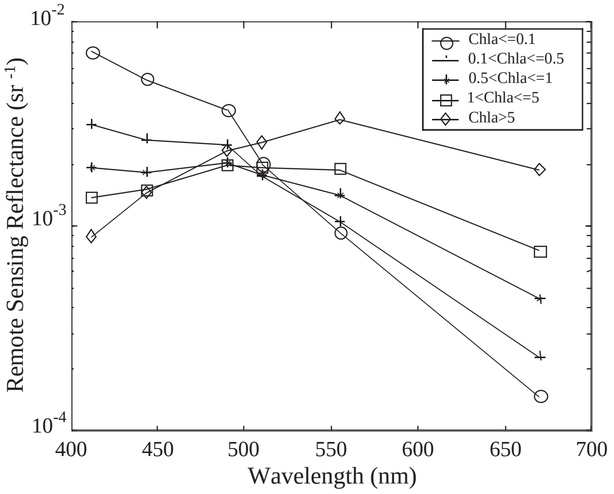


Fig. 3. Remote sensing reflectance at the 6 radiometer wavelength bands (412, 443, 490, 510, 555 and 670 nm) for 5 classes of chlorophyll concentration: $C \leq 0.1$, $0.1 < C \leq 0.5$, $0.5 < C \leq 1$, $1 < C \leq 5$ and $C > 5$ mg m^{-3}.

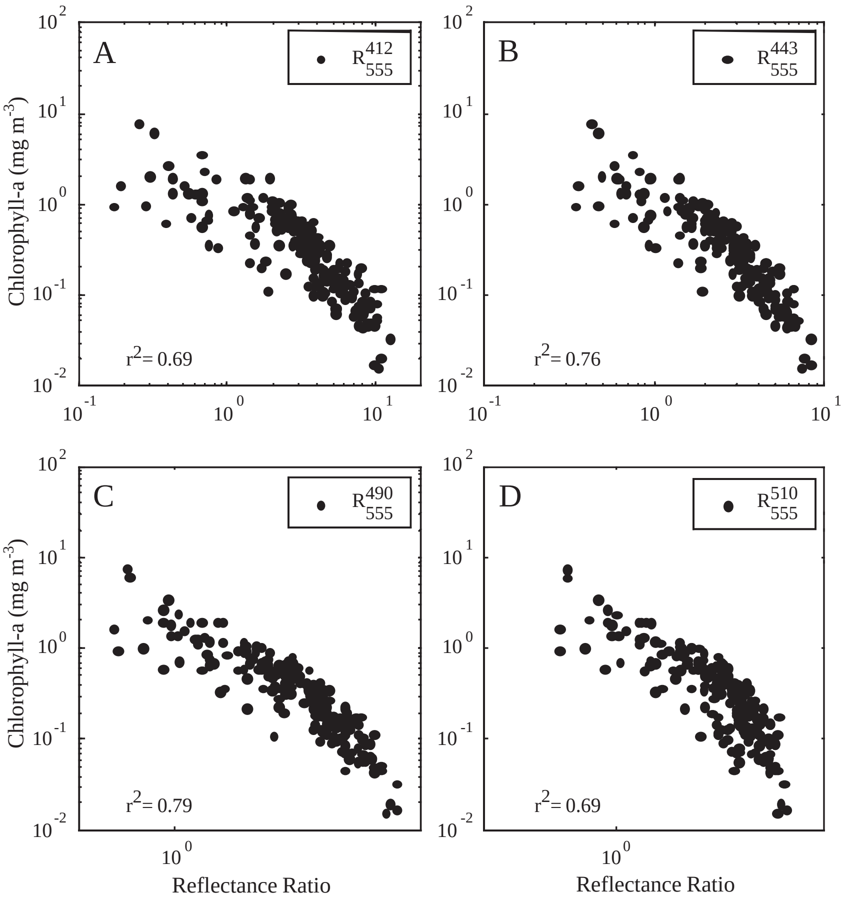


Fig. 4. Remote sensing reflectance ratios (A) R_{555}^{412}, (B) R_{555}^{443}, (C) R_{555}^{490}, (D) R_{555}^{510} and the corresponding chlorophyll concentration of the FURG-SwAO/SO dataset (N=218 data points).

ing with in situ chlorophyll values less than 2 mg m^{-3}, in latitudes between 38°S and 28°S. The latitude range (38°S to 28°S) was based on the climatological southern and northernmost reach, respectively, of the low salinity plume from La Plata River and Patos Lagoon systems, from historical data (Piola et al., 2000). Indeed, chlorophyll values in waters influenced by La Plata River plume in the continental shelf have been shown to be highly overestimated by SeaWiFS-retrieved values (Armstrong et al., 2004).

For the Southwestern Atlantic (SwAO) data a fourth-order polynomial (revision of NASA's OC4v4) was generated, while for the Southern Ocean (SO) data set, where we have a more limited range of chlorophyll values, a better performance was found with linear regression of a 2-band (R=R_{555}^{490}) algorithm. Table 3 shows the parameters of the fourth-order polynomial algorithm (excluding the five stations mentioned above) for the Southwestern Atlantic and the linear regression algorithm for the Southern Ocean data, respectively. For comparison, the performance of NASA's

Table 3

Performance of empirical bio-optical algorithms for chlorophyll derived from the FURG SwAO/SO data set. The FURG-OC4 algorithm (a revision of NASA's OC4v4) was derived for the Southwestern Atlantic Ocean (SwAO) using R=[max (R_{555}^{443}, R_{555}^{490}, and R_{555}^{510})] and FURG-OC2L was derived for the Southern Ocean (SO) using R=R_{555}^{490}. The performances of NASA OC4v4 (for both data sets) and OC2v4 (for the SO data set) are also shown

Algorithm	Data set (region)	Type	Coefficients a_n, n=0,1,2,. . .,M	rmse-L	RPD (%)	APD (%)	r^2	S	I	N
FURG OC4	SwAO	4th order	[0.277 −3.192 7.446 −12.035 5.811]	0.426	9.5	32.2	0.89	0.89	−0.061	136
NASA OC4v4	SwAO	4th order	[0.366 −3.067 1.930 0.649 −1.532]	0.475	14.5	41.7	0.87	0.84	−0.079	136
FURG OC2L	SO	linear	[0.4552 −2.2841]	0.347	6.4	30.0	0.64	0.64	−0.15	77
NASA OC2v4	SO	3th order	[0.319 −2.336 0.879 −0.135 −0.071]	0.475	−21.7	32.8	0.64	0.62	−0.30	77
NASA OC4v4	SO	4th order	[0.366 −3.067 1.930 0.649 −1.532]	0.512	−23.4	34.7	0.61	0.58	−0.33	77

Obs: rmse-L is the linear-transformed rmse (Eq. (5)). RPD and APD are mean relative and mean absolute percentage differences between algorithm-derived and in situ chlorophyll values (Eqs. (7) and (8)). S and I stand for slope and intercept of the linear regression between the log-transformed algorithm-derived and in situ chlorophyll values. N=number of data points. SO=Southern Ocean. SwAO=Southwestern Atlantic.

OC4v4 operational algorithm is presented for both data sets. In addition, the performance of OC2v4 in the Southern Ocean data is also presented, to compare with the 2-band model selected for this region. A plot of in-situ and NASA and FURG algorithm-retrieved chlorophyll for both regions can be seen in Fig. 5. In general, the SwAO chlorophyll data conforms well to NASA OC4v4 derived concentration (Fig. 5C). The rmse-L value of 0.475 for the NASA OC4v4 is not much greater than the regional FURG-OC4 model (rmse-L=0.426) (Table 3). Also, the slope and intercept values are fairly close to the regional model results. However, the mean relative percentage difference (RPD), which can be considered a measure of bias, is 14.5% for the NASA's algorithm and 9.5% for the FURG-OC4. The mean absolute percentage difference (APD) is 41.7% and 32.2%, respectively, for OC4v4 and our regional algorithm. These percentage differences are relatively large, considering that in-situ bio-optical data are being used and also that we have removed the outliers (case II points). A greater difference should then be expected when applied to satellite retrieved radiance data. Therefore, the goal of 35% accuracy for satellite chlorophyll retrieval (as for SeaWiFS, Hooker et al., 1992) seems to be hard to achieve by use of solely empirical algorithms.

The Southern Ocean data (Table 3) shows a consistent deviation from the NASA's OC4v4 algorithm, as can be detected by the relatively great and negative bias in chlorophyll values, as estimated by the RPD of −23.4%. Therefore, the use of NASA's OC4v4 model would result in a general underestimation of ca. 23% in chlorophyll values for this region, over ranges between 0.2 and 1 mg m^{-3}. A slightly better performance is seen when the 2-band OC2v4 is used (Table 3, Fig. 5D), resulting in a chlorophyll underestimation of 21.7% and a rmse-L of 0.475, compared to the OC4v4 rmse-L of 0.512. Therefore, in the studied area of the Southern Ocean, it seems that the simpler 2-band OC2v4 would be preferable to the more complex OC4v4. The bias in both NASA'a models is significantly improved with our linear algorithm (Fig. 5B, Table 3), where an RPD of 6.4% is achieved. However, in absolute terms, even our region-specific algorithm does not seem to do much better then both OC4v4 and OC2v4. Again, the empirical models reasonably solve the bias problem, but due to scattering in radiometric and/or

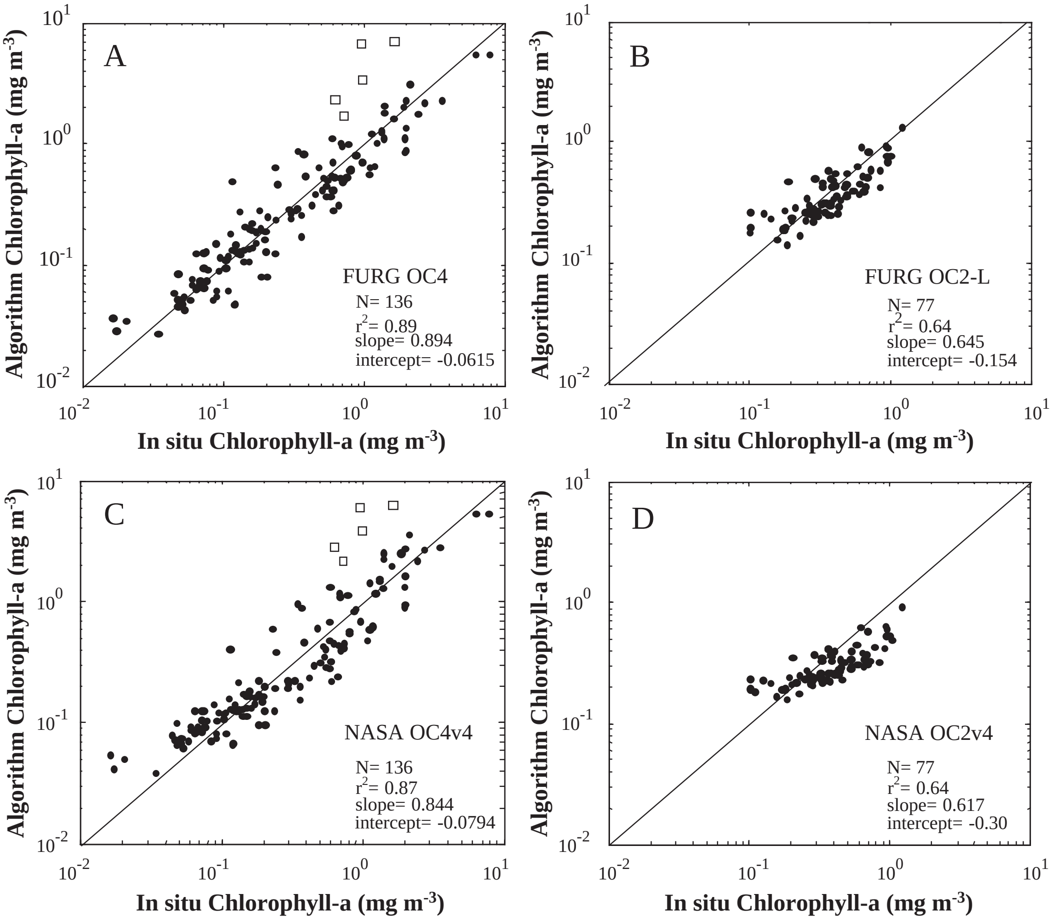


Fig. 5. Plot of chlorophyll data derived by FURG algorithms and in situ data, for (A) Southwestern Atlantic waters and (B) Southern Ocean waters. NASA algorithm derived data are also shown for both corresponding regions (C and D). The points marked with square symbols in (A) and (C) are the flagged locations under river plume influence and were excluded from the analysis (see text).

Table 4
Performance of empirical high-latitude chlorophyll algorithms using the FURG SO bio-optical data set (N=77)

Source	Algorithm-type	Region	rmse-L	RPD (%)	APD (%)	r^2	S	I
This study	OC2-Linear	Bransfield Strait (mostly)	0.347	6.45	30.0	0.64	0.64	−0.154
Arrigo et al. (1998)	OC2-L-*P. ant.*	Ross Sea	0.403	10.1	34.7	0.64	0.37	−0.267
Cota et al. (2003)	OC4-Linear-*Prym*	Arctic-Labrador Sea	0.434	−5.93	34.9	0.62	0.86	−0.124
Cota et al. (2003)	OC4-Linear	Arctic-Labrador Sea	0.451	−3.19	36.7	0.62	0.92	−0.088
Barbini et al. (2003)	OC2-Linear	Ross Sea	0.461	−20.1	32.3	0.64	0.64	−0.281
Dierssen and Smith (2000)	OC2-3rd order	West of Ant. Peninsula	0.471	43.2	48.4	0.65	0.82	0.047
Arrigo et al. (1998)	OC2-Linear	Ross Sea	0.760	92.2	93.9	0.64	0.29	−0.066

The OC2 and OC4 use R_{555}^{490} and max (R_{555}^{443}, R_{555}^{490}, R_{555}^{510}), respectively.

Obs: OC2-Linear-*Prym* and OC2-Linear-*P. ant.* are algorithms for waters dominated by *Prymnesiophytes* and *Phaeocystis antarctica*, respectively. RPD and APD are the mean relative and mean absolute percentage difference between algorithm-derived and in situ chlorophyll values (Eqs. (7) and (8)). S (slope) and I (intercept) result from a linear regression between log-transformed measured (x) and SeaWiFS derived chlorophyll (y).

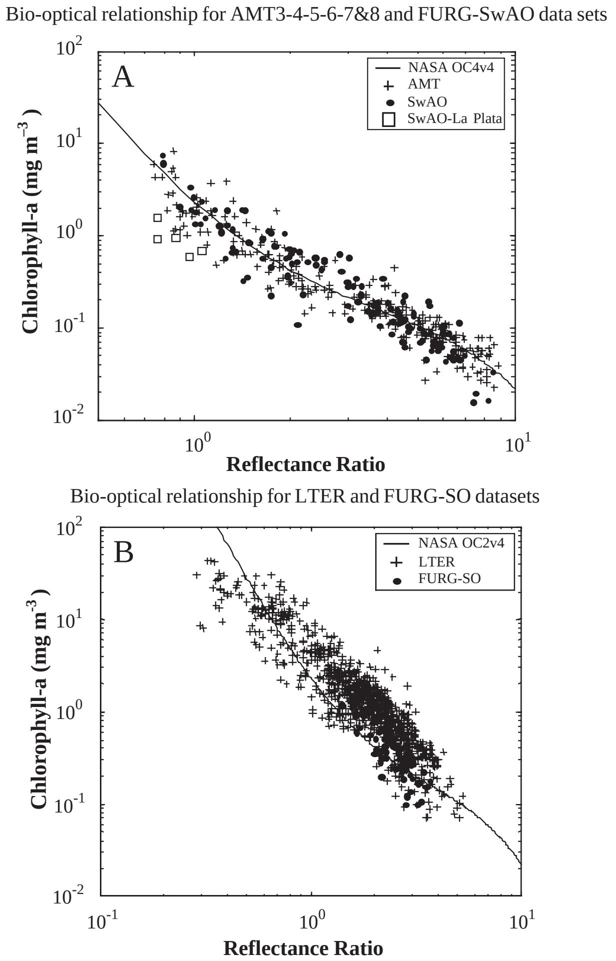
chlorophyll measurements, an absolute difference of less than 30% is hardly attainable.

The discrepancies found in this work for the Southern Ocean region are not so large as previously noted by Dierssen and Smith (2000), which reported an approximately 2–2.5-fold in chlorophyll underestimation by NASA OC2v2 in the western Antarctic Peninsula waters. Our results agree with other works from high latitudes in the southern and northern hemispheres. For instance, Cota et al. (2003) found approximately 1.5-fold underestimates for chlorophyll <10 mg m^{-3} using the OC4v4 algorithm in the Labrador Sea. Stramska et al. (2003) report underestimation magnitudes of 20% to 50% by OC4v4 and MODIS algorithms for chlorophyll ranges between 2 and 3 mg m^{-3} in the north polar region of the Atlantic Ocean.

We have evaluated the application of other high-latitude algorithms from the literature on our Southern Ocean bio-optical data set and results are shown in Table 4, where they are ranked from smallest to greatest rmse-L. The algorithm of Arrigo et al. (1998) for waters dominated by the Prymnesiophyte *Phaeocystis antarctica* in the Ross Sea shows the best performance (as evaluated by rmse-L, RPD and APD of 0.35%, 10.1%, and 34.7%, respectively), followed by a Prymnesiophyte-specific algorithm from the Labrador Sea, near the Arctic (Cota et al., 2003). The other general algorithm of Arrigo et al. (1998) including all data from the Ross Sea (Cryptophytes, diatoms and *P. antarctica* dominance) was the least adjusted to our data set. These results reveal that the taxon-specific algorithm approach seems to be very appropriate, irrespective of the region studied, since both the Arctic and Antarctic Prymnesiophyte models worked well to our bio-optical data. Indeed, *Phaeocystis* cf. *antarctica*, along with *Cryptomonas* and small flagellates, have been shown (Rodriguez et al., 2002) to dominate the summer phytoplankton assemblages in the Bransfield Strait (region mostly sampled in this work).

3.3. Comparisons between FURG-SwAO/SO and other bio-optical data sets

Bio-optical properties measured during the AMT cruises (Aiken et al., 2000) comprise approximately 11.3% of the global data compilation for NASA's operational algorithms generation (O'Reilly et al., 2000). We have plotted our FURG SwAO data, which do not include the Southern


Bio-optical relationship for AMT3-4-5-6-7&8 and FURG-SwAO data sets

Bio-optical relationship for LTER and FURG-SO datasets

Fig. 6. (A) Chlorophyll versus 4-band reflectance ratios R=[max (R_{555}^{443}, R_{555}^{490}, R_{555}^{510})] for the Southwestern Atlantic waters (FURG-SwAO) and from the AMT (Atlantic Meridional Transect) program. The dashed line is NASA OC4v4 algorithm. (B) Chlorophyll versus 2-band reflectance ratio R=R_{555}^{490} for Southern Ocean (SO) data and LTER (Long Term Ecological Research) program data set. The continuous line represents NASA's OC2v4 algorithm.

Ocean stations, combined with AMT data available at the SeaWiFS bio-optical data archive and storage system (SEABASS, Werdell et al., 2003) (Fig. 6A). Overall, there is a good agreement between the two data sets and the OC4v4 algorithm. Considering that one of the important goals of the AMT cruises is calibration and validation of satellite ocean color data (Aiken et al., 2000), the coherence in Fig. 6A supports the consistency of the FURG-SwAO/SO bio-optical data set.

Our high latitude FURG SO data (south of the Polar Front) are compared with other bio-optical data sources (from SEABASS) collected in the vicinities of the Antarctic Peninsula, and results can be seen in Fig. 6B, where NASA OC2v4 algorithm is also shown. Although it is clear that use of OC2v4 algorithm would result in an underestimation of chlorophyll values in Antarctic waters, our limited data suggest it may not be as critical as in the case of the Long Term Ecological Research (LTER) program data. The LTER large bio-optical data set was collected in waters west of the Antarctic Peninsula while most (ca. 71%) of the FURG-SO data are from the Bransfield Strait. From a hydrographic point of view, the Bransfield Strait is recognized as a transition zone between the Bellingshausen and the Weddell Sea. In both 2003 and 2004 cruises to the Bransfield Strait, Weddell Sea waters (C. Garcia, unpublished data), mostly influenced surface layers in the region. The phytoplankton communities in the western Antarctic Peninsula (LTER program) and Bransfield Strait regions probably differ in species composition, size and, consequently, in absorption and scattering properties. Dierssen and Smith (2000) emphasize that in the LTER region there is a dominance of large diatoms (and occasionally cryptophytes), with relatively low absorption coefficients, compared with diatoms from the Ross Sea, which are normally smaller. This may have contributed to the greater reflectance observed in the blue region, promoting a relatively high blue/green ratio for comparable chlorophyll concentrations. On the other hand, in the Bransfield Strait, where most stations in this work are located, phytoplankton assemblages in summer have been shown to be dominated by nannoplankton (*Cryptomonas* sp.), the haptophyte *Phaeocystis* cf. *antarctica* and small flagellates (Rodriguez et al., 2002). Therefore, some differences in bio-optical propertizes may be expected between both regions. It can be noticed, however, that the NASA OC2v4 algorithm underestimated chlorophyll above a threshold of approximately 0.2 mg m^{-3} (see also Fig. 5D). Values below this threshold in our work are not associated with a particular area within the study region, but may be associated with particular phytoplankton assemblages, with very high absorption in the blue region. For instance, the mean ratio of specific absorption of phytoplankton (490/555) in the Ross Sea was shown to vary from 2.4 m^2 mg Chl^{-1} for diatom-dominated to 5.2 m^2 mg Chl^{-1} for Prymnesiophytes-dominated assemblages (Arrigo et al., 1998). Differences of this magnitude may at least partially account for the shifts in the relationship of chlorophyll to reflectance ratios below chlorophyll levels of 0.2 mg m^{-3} in this work.

4. Satellite match-up analysis

In order to validate products derived from ocean color sensors, we need to compare in-situ measurements of bio-optical properties with remote sensed values. The SeaWiFS Project has established a match-up procedure which includes both Unix C-shell scripts and Interactive Data Language (IDL) to compare remotely sensed ocean and atmospheric properties to in situ measurements provided by ocean color researchers (Hooker & McClain, 2000; McClain et al., 1992, 2004).

Table 5

Comparison of SeaWiFS and in-situ measurements (match-up) of spectral normalized water-leaving radiance (nL_w) and of chlorophyll-*a* concentration. NASA OC4v4 algorithm was used to retrieve SeaWiFS chlorophyll-*a* concentration

	In situ range	Satellite range	r^2	rmse[a]	RPD (%)	APD (%)	*S*	*I*	*N*
nLw412	0.081–2.166	−0.116–2.310	0.98	0.146	−35.61	41.93	1.138	−0.1490	21
nLw443	0.127–1.779	0.039–1.910	0.97	0.126	−5.23	17.05	1.131	−0.082	21
nLw490	0.209–1.314	0.168–1.290	0.87	0.132	−2.32	11.51	0.946	0.021	21
nLw510	0.222–1.429	0.218–1.433	0.78	0.139	2.84	10.83	0.863	0.081	21
nLw555	0.202–1.664	0.244–1.903	0.78	0.201	1.24	13.05	0.948	0.013	21
nLw670	0.017–0.582	0.017–0.577	0.93	0.041	−3.64	25.19	0.896	−0.023	21
Chlorophyll	0.044–1.970	0.060–3.907	0.77	0.663[b]	31.19	65.75	1.033	0.041	28

Obs: RPD and APD are calculated by comparing the SeaWiFS-derived to the measured values. RPD and APD are mean relative and mean absolute percentage differences between algorithm-derived and in situ chlorophyll values. The *S* (slope) and *I* (intercept) result from a linear regression between measured (*x*) and SeaWiFS derived-properties (*y*), except for chlorophyll where the log-transformed values were used.

[a] rmse was calculated as

$$\mathrm{rmse} = \sqrt{\frac{1}{N}\sum_{1}^{N}\left(nLw_{\mathrm{SeaWiFS}} - nLw_{\mathrm{in\ situ}}\right)^2}$$

[b] For chlorophyll, rmse-L was calculated as in Eq. (5).

FURG SwAO and SO data sets were organized according to the SEABASS format and submitted to the match-up procedure. A match-up exclusion criterion in the procedure discards invalid or redundant data. It is based on temporal windows and certain quality control masks and flags (clouds, stray light on scenes, atmosphere correction failure, sun glint, total radiance above the knee value, high satellite zenith angle, coccolithophores, and low normalized water-leaving radiance at 555 nm; Bailey et al., 2000). The match-up approach used a 5×5 pixel-averaged box for spatial comparisons. Although the SwAO/SO data set contains 218 stations, only 176 could be considered candidates since 42 were sampled before the SeaWiFS launching. At the end of the match-up selection process, 12% of stations (*N*=21) became final valid matches for radiometric comparisons.

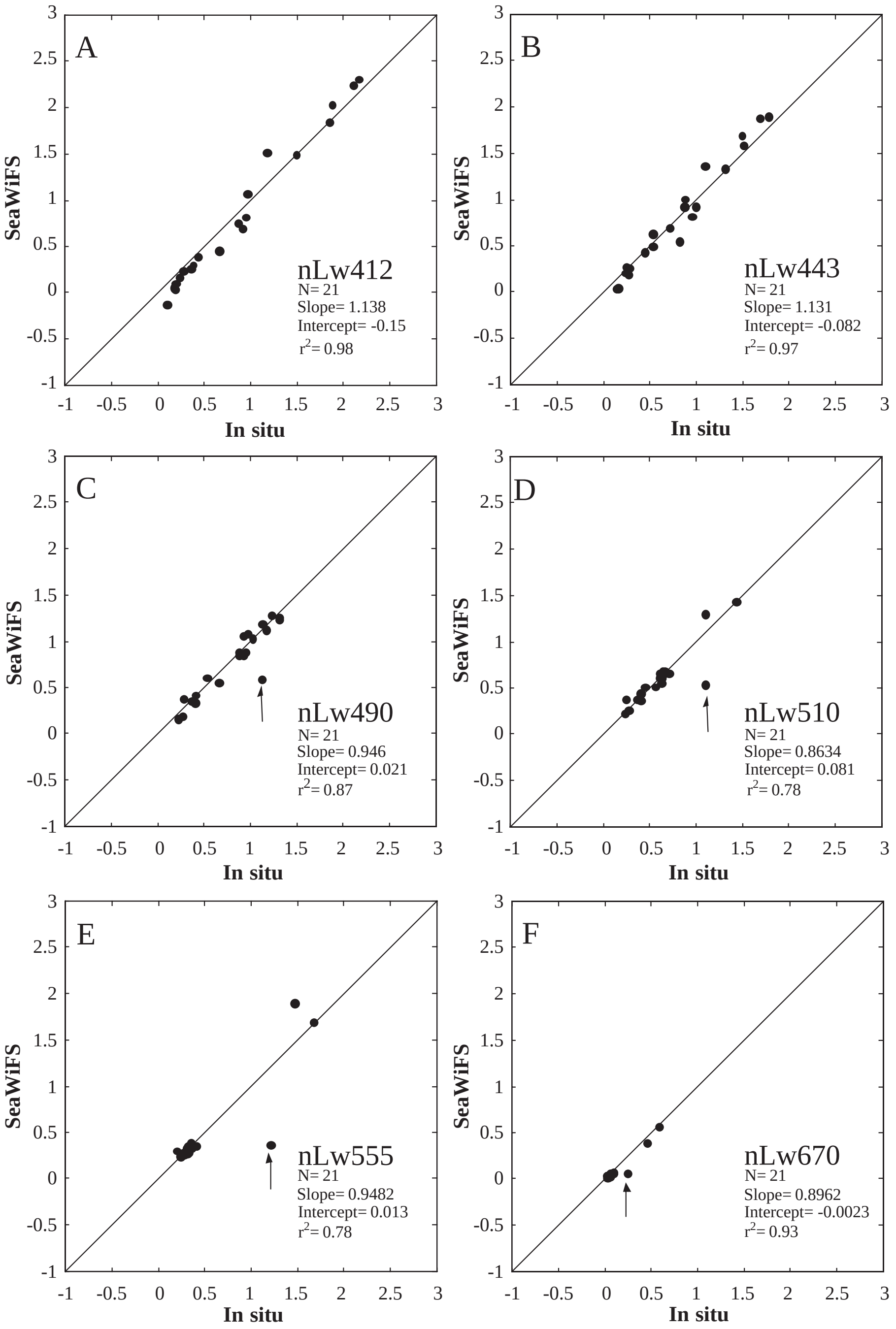


Fig. 7. Comparisons (match-up) between SeaWiFS and in situ measurements of normalized water-leaving radiances at (A) 412 nm, (B) 443 nm, (C) 490 nm, (D) 510 nm, (E) 555 nm and (F) 670 nm. Arrows indicate an outlier (see text for details), which has been included in the match-up statistical analysis. The dashed line represents the 1:1 relationship.

Table 5 and Fig. 7 show that the SeaWiFS-derived spectral water-leaving radiances are well-related ($0.77<r^2<0.98$) with in situ measurements, with higher correlation at lower wavelengths. However, the absolute percentage difference for the 6 bands varied from 10.8% for nL_w (510) to 41.9% for nL_w (412). The greatest error in SeaWiFS retrieved radiance in the blue band (412 nm) is associated with a bias of −35.6%, while the other bands showed no significant bias values (Table 5). Two slightly negative values of remote sensing nL_w (412) were extracted in May 2002 in the southern Brazilian coastal area (Fig. 7A), which were probably caused by overestimation of aerosol radiances in coastal stations. In addition, at one station (shown by the arrows in Fig. 7), SeaWiFS-derived reflectance values were underestimated, especially in the green spectral region. A closer inspection of the chlorophyll image for that site (not shown) revealed a small patch of high chlorophyll (detected also by our in-situ sampling) which was probably displaced at the time of the satellite overpass (nearly 3 h later). This point, however, has been included in the statistical analyses.

For chlorophyll-*a* match-ups (Fig. 8), a greater data set was submitted, since many stations have been sampled for pigment alone without simultaneous optical measurements. After the exclusion criteria, 32 stations remained for the match-up exercise, by accepting ±3 h time difference between sampling data and satellite overpass. Fig. 8 shows the result of satellite derived (match-up) versus in situ chlorophyll values. The arrow shows the spurious value associated with the lower nL_w's in the green bands (shown in Fig. 7), which resulted in a lower estimate by SeaWiFS. The three circled points in Fig. 8 are associated with stations close to La Plata River (where reflectance values at 670 nm are greater than 0.0012 sr^{-1}) and were excluded from the analysis. A good relationship can be seen between in situ and satellite-derived chlorophyll concentration (r^2=0.77), but the uncertainty as estimated by the APD and rmse-L is approximately 66% (Table 5).

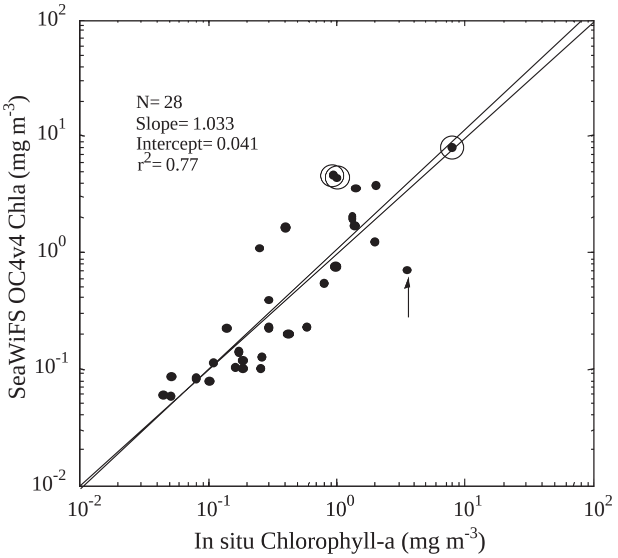


Fig. 8. Comparison (match-up) between SeaWiFS estimates (by the NASA OC4v4 algorithm) and in situ measurements of chlorophyll-*a* concentration. The circled points represent the turbidity flagged stations ($R_{rs}(670)>0.0012$ sr^{-1}), which were not considered in the regression analysis. The arrow indicates an outlier, which results from the spurious values in reflectance (see Fig. 7 and text) and was also not included. The dashed line represents the 1:1 relationship.

5. Conclusions

Bio-optical properties have been measured in the surface waters in the Southwestern Atlantic and Southern Ocean (mostly Bransfield Strait) for chlorophyll algorithm generation and validation of remote sensing oceanic properties provided by ocean color sensors. The bio-optical data set comprises several bio-geographic provinces, ranging from oligotrophic waters in the South Atlantic tropical gyre to highly productive coastal waters influenced by the La Plata River and Patos Lagoon.

Our analysis show that the NASA's OC4v4 algorithm for extracting chlorophyll-*a* data in the Southwestern Atlantic would result in an error margin of at least 42% (or a rmse-L of 47%) in waters without strong influence of continental discharge (from La Plata River or Patos Lagoon). Our derived algorithm for this region improves the error margin to some extent (32% error margin or rmse-L of 43%), but significantly reduces bias. In coastal waters affected by river runoff, the OC4v4 algorithm highly overestimates chlorophyll values. These waters have been masked in our work using $R_{rs}(670)>0.0012$ sr^{-1} combined with in situ chlorophyll values less than 2 mg m^{-3} in regions under potential freshwater plume influence.

In the Southern Ocean, comprising mainly the Bransfield Strait, the NASA OC4v4 algorithm underestimates pigment concentration but not to the same magnitude as previously reported (Dierssen and Smith, 2000; Mitchell & Holm-Hansen, 1991). A linear relationship has been proposed between R_{555}^{490} and chlorophyll ranges from 0.1 to 1 mg m^{-3}, which yields a significant improvement in bias, as compared with both NASA's OC4v4 and OC2v4. An evaluation of other high-latitude algorithms from the literature showed variable performances when applied to our data. The best adjustment (following our linear model) was found for the Ross Sea, Prymnesiophyte-specific algorithm (Arrigo et al., 1998).

The spectral water-leaving radiance and chlorophyll-*a* concentration derived from SeaWiFS were compared with FURG-SwAO/SO bio-optical measurements through a match-up procedure. There is a good agreement between in-situ and sensor-derived optical data (APD between 10.8% and 41.9%; rmse between 0.04 and 0.20). For chlorophyll match-ups, the concentration estimated by SeaWiFS imagery (OC4v4 algorithm) show a positive bias of 32% and values are comparable with in-situ data, within a 66% error, which is above the accuracy goal of 35% for satellite-retrieved chlorophyll estimates.

Acknowledgements

We acknowledge the help of C. Omachi, A. Gonzalez, A. Belem, A. Ciotti, Y. Sarma, V. Duarte, C. Flores, and B. Franco in the collection of the bio-optical data at sea. The help provided by the crews of R.V. James Clark Ross, R.V. Ary Rongel, R.V. Astro Garopa, R.V. Prof. Besnard, and R.V. Atlântico Sul during the oceanographic cruises are equally appreciated. We also thank P. J. Werdell and S. Bailey for the match-up processing at NASA/GSFC facilities. The helpful comments of S. Signorini on the manuscript are greatly appreciated. The authors thank the constructive comments and suggestions of two anonymous reviewers. S. Hooker, S. Maritorena, G. Moore, and J. Aiken collected the AMT program bio-optical data in the SEABASS. The LTER data were obtained by R. Smith and H. Dierssen. The Goddard Earth Sciences and Technology (GEST) visitor fellowship program supports the authors. This research work has been funded by the Brazilian Antarctic Program (PROANTAR) and by the Brazilian National Council for Scientific and Technological Development (CNPq).

References

Aiken, J., & Hooker, S. B. (1997). The Atlantic Meridional Transect: Spatially extensive calibration and validation of optical properties and remotely-sensed measurements of ocean color. *Backscatter*, *8*, 8–11.

Aiken, J., Rees, N., Hooker, S. B., Holligan, P., Bale, A. J., Robins, D. B., et al. (2000). The Atlantic Meridional Transect: Overview and synthesis of data. *Progress in Oceanography*, *45*(3–4), 257–312.

Armstrong, R. A., Gilbes, F., Guerrero, R., Lasta, C., Benavidez, H., & Mianzan, H. (2004). Validation of SeaWiFS-derived chlorophyll for the Rio de la Plata Estuary and adjacent waters. *International Journal of Remote Sensing*, *25*(7–8), 1501–1505.

Arrigo, K. R., Robinson, D. H., Lizotte, M. P., Worthen, D. L., & Schieber, B. (1998). Bio-optical properties of the southwestern Ross Sea. *Journal of Geophysical Research*, *103*, 21683–21695.

Bailey, S. W., McClain, C. R., Werdell, P. J., & Schieber, B. D. (2000). Normalized water-leaving radiance and chlorophyll a match-up analyses. In C. R. McClain, R. A. Barnes, R. E. Eplee Jr., B. A. Franz, N. C. Hsu, F. S. Patt, C. M. Pietras, W. D. Robinson, B. D. Schieber, G. M. Schmidt, M. Wang, S. W. Bailey, & P. J. Werdell (Eds.), *SeaWiFS Postlaunch Calibration and Validation Analyses*: Part 2. NASA Tech. Memo. 2000-206892, vol. 10. In S.B. Hooker and E.R. Firestone (Eds.), NASA Goddard Space Flight Center, Greenbel, Maryland (pp. 45–52).

Bird, R. E., & Riordan, C. J. (1986). Simple solar spectral model for direct and diffuse irradiance on horizontal and tilted planes at the earth's surface for cloudless atmospheres. *Journal of Climate and Applied Meteorology*, *25*(1), 87–97.

Carder, K. L., Chen, F. R., Cannizzaro, J. P., Campbell, J. W., & Mitchell, B. G. (1986). Performance of the MODIS semi-analytical ocean color algorithm for chlorophyll-*a*. *Climate change processes in the stratosphere, earth–atmosphere–ocean systems, and oceanographic processes from satellite data*. *Advances in Space Research*, *vol. 33 (7)*. (pp. 1152–1159).

Clark, D. K. (1981). Phytoplankton pigment algorithms for the Nimbus-7 CZCS. In: J. F. R. Gower (Ed.), *Oceanography from Space*, (pp. 227–237). New York: Plenum.

Clementson, L. A., Parslow, J. S., Turnbull, A. R., McKenzie, D. C., & Rathbone, C. E. (2001). Optical properties of waters in the Australian sector of the Southern Ocean. *Journal of Geophysical Research*, *106*(C12), 31,611–31,625.

Ciotti, A. M., Odebrecht, C., Fillmann, G., & Moller Jr., O. (1995). Freshwater outflow and Subtropical Convergence influence on the phytoplankton biomass in southern Brazilian continental shelf. *Continental Shelf Research*, *15*(14), 1737–1756.

Cota, G. F., Harrison, W. G., Platt, T. & Sathyendranath, S., (2003). Bio-optical properties of the Labrador Sea. Journal of Geophysical Research, 108 (C7), 3228, 21-1, 21-14.

Cullen, J. J., Ciotti, A. M., & Lewis, M. R. (2001). Observing biologically induced optical variability in coastal waters. *Proc. SPIE Ocean Optics XII*, *vol. 2258* (pp. 105–115).

Dierssen, H., & Smith, R. C. (2000). Bio-optical properties and remote sensing ocean color algorithms for Antarctic Peninsula waters. *Journal of Geophysical Research*, *105*(C11), 26,301–26,312.

D'Ortenzio, F., Marullo, S., Ragni, M., d'Alcalà, M. R., & Santoleri, R. (2002). Validation of empirical SeaWiFS algorithms for chlorophyll-*a* retrieval in the Mediterranean Sea: A case study for oligotrophic seas. *Remote Sensing of Environment*, *82*, 79–94.

Feely, R. A., Sabine, C. L., Takahashi, T., & Wanninkhof, R. (2001). Uptake and storage of carbon dioxide in the ocean: The global CO_2 survey. *Oceanography*, *14*(4), 18–32.

Feldman, G. C. & Patt, F. S. (2003). Introduction to the fourth SeaWiFS reprocessing. In F. S. Patt, R. A. Barnes, R. E. Eplee, B. A. Franz, W. D. Robinson, G. C. Feldman, S. W. Bailey, J. Gales, P. J. Werdell, M. Wang, R. Frouin, R. P. Stumpf, R. A. Arnone, R. W. Gould, Jr., P. M. Martinolich, V. Ransibrahmanakul, J. E. O'Reilly & J. A. Yoder (Eds.), *Algorithm updates for the fourth SeaWiFS data reprocessing*, SeaWiFS Postlaunch Technical Report Series, NASA Tech. Memo. 2003-206892, vol. 22. In S.B. Hooker and E.R. Firestone (Eds.), NASA Goddard Space Flight Center, Greenbelt, Maryland (pp. 4–11).

Garcia, C. A. E., Sarma, Y. V. B., Mata, M. M., & Garcia, V. M. T. (2004). Chlorophyll variability and eddies in the Brazil-Malvinas Confluence region. *Deep-Sea Research. Part 2. Topical Studies in Oceanography*, *51*(1–3), 159–172.

Gonzalez-Silvera, A., Santamaria-del-Angel, E., Garcia, V. M. T., Garcia, C. A. E., Millan-Nunez, R., & Muller-Karger, F. (2004). Biogeographical regions of the tropical and subtropical Atlantic Ocean off South America: Classification based on pigment (CZCS) and chlorophyll-*a* (SeaWiFS) variability. *Continental Shelf Research*, *24*(9), 983–1000.

Gordon, H. R., Clark, D. K., Brown, J. W., Brown, O. B., Evans, R. H., & Broenkow, W. W. (1983). Phytoplankton pigment concentrations in the Middle Atlantic Bight: Comparison of ship determinations and CZCS estimates. *Applied Optics*, *22*(1), 20–36.

Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W., & Strickland, J. D. H. (1965). Fluorometric determination of chlorophyll. *Journal du Conseil-Conseil International Pour L'Exploration de la Mer*, *30*, 3–15.

Hooker, S. B., Esaias, W. E., Feldman, G. C., Gregg, W. W., & McClain, C. R. (1992). An Overview of SeaWiFS and Ocean Color. NASA Tech. Memo. 104566, vol. 1. In S. B. Hooker & E. R. Firestone (Eds.), NASA Goddard Space Flight Center, Greenbelt, Maryland. 24 pp.

Hooker, S. B., & Maritorena, S. (2000). An evaluation of oceanographic radiometers and deployment methodologies. *Journal of Atmospheric and Oceanic Technology*, *17*(6), 811–830.

Hooker, S. B., & McClain, C. R. (2000). The calibration and validation of SeaWiFS data. *Progress in Oceanography*, *45*, 427–465.

Hooker, S. B., Rees, N., & Aiken, J. (2000). An objective methodology for identifying oceanic provinces. *Progress in Oceanography*, *45*(3–4), 313–338.

Maritorena, S., Siegel, D. A., & Peterson, A. R. (2002). Optimization of a semi-analytical ocean color model for global-scale applications. *Applied Optics*, *41*(15), 2705–2714.

McClain, C. R., Esaias, W. E., Barnes, W., Guenther, B., Endres, D., Hooker, S., et al. (1992). SeaWiFS calibration and validation plan. *NASA Technical Memorandum*, *3*, 1–41.

McClain, C. R., Feldman, G. C., & Hooker, S. B. (2004). An overview of the SeaWiFS project and strategies for producing a climate research quality global ocean bio-optical time series. *Deep-Sea Research. Part 2. Topical Studies in Oceanography*, *51*(1–3), 5 – 42.

Mitchell, B. G. (1992). Predictive bio-optical relationships for polar oceans and marginal ice zones. *Journal of Marine Systems*, *3*, 91 – 105.

Mitchell, B. G., & Holm-Hansen, O. (1991). Bio-optical properties of Antarctic Peninsula waters: Differentiation from temperate ocean models. *Deep-Sea Research. Part 1. Oceanographic Research Papers*, *38*, 1009 – 1028.

Mitchell, B. G., Kahru, M., Reynolds, R., Wieland, J., Stramski, D., Hewes, C., et al. (1999). Evaluation of chlorophyll-*a* ocean color algorithms for the Southern Ocean. American Geophysical Union, San Francisco, 10–14 December, 2001.

Moore, J. K., Abbott, M. R., & Richman, G. (1999). Location and dynamics of the Antarctic Polar Front from satellite sea surface temperature data. *Journal of Geophysical Research*, *104*, 3059 – 3073.

Morel, A., & Berthon, J. F. (1989). Surface pigments, algal biomass profiles, and potential production of the euphotic layer: Relationships reinvestigated in view of remote-sensing applications. *Limnology and Oceanography*, *34*(8), 1545 – 1562.

Morel, A., & Maritorena, S. (2001). Bio-optical properties of oceanic waters: A reappraisal. *Journal of Geophysical Research*, *106*, 7163 – 7180.

Negri, R. M., Carreto, J. I., Benavides, H. R., Akselman, R., & Lutz, V. A. (1992). An unusual bloom of *Gyrodinium cf-aureolum* in the Argentine Sea—community structure and conditioning factors. *Journal of Plankton Research*, *14*, 261 – 269.

Omachi, C. Y., & Garcia, C. A. E. (2000). Analysis of empirical algorithms of surface chlorophyll a for SeaWiFS in the Southwestern Atlantic Ocean. *Proceedings of the XV Conference on Ocean Optics, Monaco*.

O'Reilly, J. E., Maritorena, S., Mitchell, B. G., Siegel, D. A., Cardel, K. L., Garver, S. A., et al. (1998). Ocean color chlorophyll algorithms for SeaWiFS. *Journal of Geophysical Research-Oceans*, *103*(C11), 24937 – 24953.

O'Reilly, J. E., Maritorena, S., Siegel, D., O'Brien, M. C., Toole, D., Mitchell, B. G., et al. (2000). Ocean color chlorophyll a algorithms for SeaWiFS, OC2, and OC4: Version 4. In S. B. Hooker, & E. R. Firestone (Eds.), *SeaWiFS postlaunch technical report series*. *SeaWiFS post-launch calibration and validation analyses: Part 3, vol. 11* (pp. 9 – 23) NASA/GSFC.

Piola, A. R., Campos, E. J. D., Möller Jr., O. O., Charo, J., & Martinez, C. (2000). Subtropical shelf front off eastern South America. *Journal of Geophysical Research*, *105*(C3), 6565 – 6578.

Robinson, W. D., Franz, B. A., Patt, F. S., Bailey, S. W., & Werdell, P. J. (2003). Masks and flags updates. In Hooker, S.B. & Firestone, E.R. (Eds.), *SeaWiFS Postlaunch Technical Report Series, Vol 22, Algorithm updates for the fourth SeaWiFS data reprocessing*. NASA Technical Memorandum 2003-206892 (pp. 34–40).

Rodriguez, F., Varela, M., & Zapata, M. (2002). Phytoplankton assemblages in the Gerlache and Bransfield Straits (Antarctic Peninsula) determined by light microscopy and CHEMTAX analysis of HPLC pigment data. *Deep-Sea Research. Part 2. Topical Studies in Oceanography*, *49*, 723 – 747.

Sarmiento, J. L., & Sundquist, E. T. (1992). Revised budget for the oceanic uptake of anthropogenic carbon dioxide. *Nature*, *356*, 589 – 593.

Signorini, S. R., Hooker, S. B., & McClain, C. R., (2003). Bio-optical and geochemical properties of the South Atlantic Subtropical Gyre. *NASA/TM-2003-212253, Goddard Space Flight Center*, Greenbelt, Maryland. 43 p.

Stramska, M., Stramski, D., Hapter, R., Kaczmarek, S., & Ston, J. (2003). Bio-optical relationships and ocean color algorithms for the north polar region of the Atlantic. *Journal of Geophysical Research*, *108*, 3143.

Takahashi, T., Feely, R. A., Weiss, R. F., Wanninkhof, R. H., Chipman, D. W., Sutherland, S. C., et al. (1997). Global air–sea flux of CO_2: An estimate based on measurements of sea–air pCO_2 difference. *Proceedings of the National Academy of Sciences of the United States of America*, *94*(16), 8292 – 8299.

Welschmeyer, N. A. (1994). Fluorometric analysis of chlorophyll *a* in the presence of chlorophyll *b* and phaeopigments. *Limnology and Oceanography*, *39*, 1985 – 1992.

Werdell, P. J., Bailey, S. W., Fargion, G. S., Pietras, C., Knobelspiesse, K. D., Feldman, G. C., et al. (2003). Unique data repository facilitates for ocean color satellite validation. *EOS, Transactions, AGU*, *84*(38), 377.