Available online at www.sciencedirect.com
ScienceDirect
Remote Sensing of Environment 105 (2006) 367–375
Remote Sensing of Environment
www.elsevier.com/locate/rse

Validation of SeaWiFS chlorophyll *a* concentrations in the Southern Ocean: A revisit

Marina Marrari *, Chuanmin Hu, Kendra Daly

College of Marine Science, University of South Florida, 140 Seventh Avenue South, St. Petersburg, FL 33701, USA

Received 25 April 2006; received in revised form 12 July 2006; accepted 15 July 2006

Abstract

Surface chlorophyll *a* concentrations (C_a, mg m^{-3}) in the Southern Ocean estimated from SeaWiFS satellite data have been reported in the literature to be significantly lower than those measured from *in situ* water samples using fluorometric methods. However, we found that high-resolution (~1 km^2/pixel) daily SeaWiFS C_a (C_a^{SWF}) data (SeaDAS4.8, OC4v4 algorithm) was an accurate measure of *in situ* C_a during January–February of 1998–2002 if concurrent *in situ* data measured by HPLC (C_a^{HPLC}) instead of fluorometric (C_a^{Fluor}) measurements were used as ground truth. Our analyses indicate that C_a^{Fluor} is 2.48±2.23 (n=647) times greater than C_a^{HPLC} between 0.05 and 1.5 mg m^{-3} and that the percentage overestimation of *in situ* C_a by fluorometric measurements increases with decreasing concentrations. The ratio of C_a^{SWF}/C_a^{HPLC} is 1.12±0.91 (n=96), whereas the ratio of C_a^{SWF}/C_a^{Fluor} is 0.55±0.63 (n=307). Furthermore, there is no significant bias in C_a^{SWF} (12% and −0.07 in linear and log-transformed C_a, respectively) when C_a^{HPLC} is used as ground truth instead of C_a^{Fluor}. The high C_a^{Fluor}/C_a^{HPLC} ratio may be attributed to the relatively low concentrations of chlorophyll *b* (C_b/C_a=0.023±0.034, n=482) and relatively high concentrations of chlorophyll *c* (C_c/C_a=0.25±0.59, n=482) in the phytoplankton pigment composition when compared to values from other regions. Because more than 90% of the waters in the study area, as well as in the entire Southern Ocean (south of 60° S), have C_a^{SWF} between 0.05 and 1.5 mg m^{-3}, we consider that the SeaWiFS performance of C_a retrieval is satisfactory and for this C_a range there is no need to further develop a "regional" bio-optical algorithm to account for the previous SeaWiFS "underestimation".

Keywords: Remote sensing; Ocean color; Algorithm; Chlorophyll; HPLC; Fluorometric; Southern Ocean

1. Introduction

Since the launch of the Sea-viewing Wide Field-of-view Sensor (SeaWiFS, McClain et al., 1998) onboard the Orbview-II satellite in August 1997, ocean color data products, in particular concentrations of chlorophyll *a* (C_a, mg m^{-3}) in the surface ocean, have been used to investigate a wide variety of fundamental topics including ocean primary productivity, biogeochemistry, coastal upwelling, eutrophication, and harmful algal blooms (e.g., Hu et al., 2005; Muller-Karger et al., 2004). Other ocean color missions, such as the ongoing MODerate-resolution Imaging Spectroradiometer (MODIS, Esaias et al., 1998; Terra satellite for morning pass since 1999 and Aqua satellite for afternoon pass since 2002) or the future National Polar-Orbiting Operational Environmental Satellite System (NPOESS), assure the continuity of remotely sensed ocean color in assessing the long-term global change in several key environmental parameters, including C_a. Quantitative use of ocean color data products requires a high level of accuracy. During algorithm development, the errors in the C_a data products after logarithmic transformation were about 0.2 or less (O'Reilly et al., 2000), which corresponds to roughly 60% root mean square (RMS) relative error. Global validation efforts show that in most ocean basins C_a errors are about 0.3 (Gregg & Casey, 2004), although in regions such as the Southern Ocean, reported errors are significantly larger.

The Southern Ocean (SO) was defined by the International Hydrographic Organization in 2000 to encompass waters between the northern coast of Antarctica and 60°S. Oceanographers, however, traditionally have defined the northern limit of the SO as the Subtropical Front (at approximately 40°S) (Orsi

* Corresponding author. Tel.: +1 727 553 1207; fax: +1 727 553 1186.
E-mail address: mmarrari@marine.usf.edu (M. Marrari).

0034-4257/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.rse.2006.07.008

et al., 1995). Typical chlorophyll concentrations in the SO range between 0.05 and 1.5 mg m^{-3} (Arrigo et al., 1998; El-Sayed, 2005). It is believed that the interaction of light and deep mixing, iron, and grazing limit phytoplankton growth throughout the SO, in addition to low silicate concentrations which can limit diatom production north of the Polar Front (Boyd, 2002; Daly et al., 2001; Moline & Prézelin, 1996). However, elevated chlorophyll concentrations (1 to >30 mg m^{-3}) are characteristic of many regions, including continental shelf and ice edge areas (El-Sayed, 2005; Holm-Hansen et al., 1989; Moore & Abbott, 2000), and even values of up to 190 mg m^{-3} have been reported (El-Sayed, 1971). The Antarctic Peninsula region, in particular, supports large concentrations of phytoplankton, zooplankton, seabirds, seals, and whales, and is considered one of the most productive areas of the Southern Ocean, for reasons that are not fully understood (Deibel & Daly, in press).

Several studies have relied on ocean color data to investigate phytoplankton spatial patterns (Holm-Hansen et al., 2004; Moore & Abbott, 2000), interannual variability during summer (Korb et al., 2004; Smith et al., 1998), and primary productivity (Dierssen et al., 2000; Smith et al., 2001) west of the Antarctic Peninsula and in the adjoining Scotia Sea. These studies used *in situ* C_a determined from water samples using fluorometric methods (C_a^{Fluor}) to validate monthly/weekly averages of SeaWiFS C_a (C_a^{SWF}) data product at ~9×9 km^2 or ~4×4 km^2 resolution and concluded that, in the Southern Ocean, C_a^{SWF} values are significantly lower than those estimated from *in situ* water samples. For example, Dierssen and Smith (2000) applied *in situ* bio-optical data measured between 1991 and 1998 to the OC2v2 algorithm to test its applicability west of the Antarctic Peninsula in the Southern Ocean. They concluded that C_a derived from the OC2v2 algorithm using *in situ* reflectance was 60% lower than *in situ* C_a (C_a between 0.7 and 43 mg m^{-3}, median ~1 mg m^{-3}). Korb et al. (2004) reported that C_a^{SWF} values were only 87% of C_a^{Fluor} for concentrations lower than 1 mg m^{-3} and only 30% for concentrations above 5 mg m^{-3} in the South Georgia area (54.5°S, 37°W). In addition, Moore et al. (1999) found a strong linear relationship between C_a^{SWF} and C_a^{Fluor} ($R^2=0.72$, $n=84$) in the Ross Sea, although they noted that SeaWiFS tended to underestimate C_a values between 0.1 and 1.5 mg m^{-3}.

The previous validation methods may present several limitations. First, *in situ* samples are point measurements while satellite pixels cover a larger area (up to 9×9 km^2). Patchiness within a pixel will affect the comparison of results between areas and over time (e.g., Hu et al., 2004). Second, the *in situ* and satellite measurements are not strictly concurrent and the time differences can be large (up to a month). Finally, and most

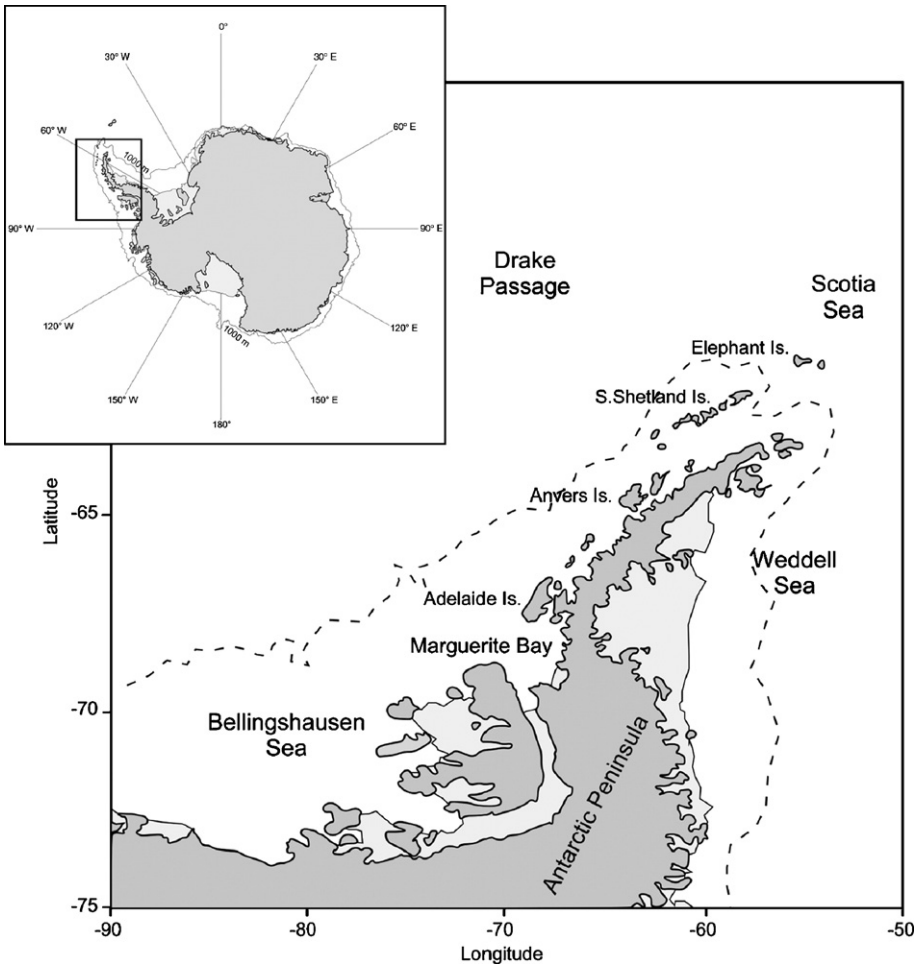

Fig. 1. Study area and geographic locations. The dotted line indicates the 1000 m isobath.

importantly, previous validation studies used *in situ* C_a from fluorometric measurements, while it is now widely recognized that high performance liquid chromatography (HPLC) may yield more accurate results in determining C_a from water samples. Fluorometric methods may result in biased results, particularly in the presence of certain accessory pigments (Lorenzen, 1981; Welschmeyer, 1994).

In a study that included three different areas of the world's oceans, Trees et al. (1985) reported that errors in the C_a^{Fluor} ranged between −68% and 53% with a mean of 39%. In addition, Bianchi et al. (1995) found that C_a^{Fluor} in the northern Gulf of Mexico was approximately 30% lower than C_a^{HPLC}, except in near coastal areas. It is believed that the presence of significant amounts of chlorophyll *b* (C_b), characteristic of chlorophytes, prochlorophytes, and cryptophytes, causes fluorometric techniques to underestimate C_a. On the other hand, high concentrations of chlorophyll *c* (C_c), typically found in diatoms, dinoflagellates, prasinophytes, and haptophytes, lead to an overestimation of C_a with respect to fluorometric measurements. The fluorescence emission spectra of degradation products (phaeopigments) of C_a and C_b overlap considerably, causing an overestimation of C_a phaeopigments and, thus, an underestimation of C_a. On the other hand, C_a and C_c have partially overlapping fluorescence spectra, causing an overestimation of C_a and subsequent underestimation of phaeopigments *a* (Gibbs, 1979; Jeffrey et al., 1997). The filters used in the standard fluorometric method (Lorenzen, 1981) cannot effectively discriminate between C_a, C_b, C_c, and their degradation products; thus, depending on the type of phytoplankton present and their associated pigments, C_a may be overestimated or underestimated by fluorometric methods.

Herein, we use concurrent HPLC and fluorometric data collected between 1998 and 2002 in waters west of the Antarctic Peninsula, as well as high-resolution SeaWiFS data, to re-examine whether SeaWiFS C_a is underestimated in the Southern Ocean as reported in previous studies. We also discuss possible explanations for the observed results and investigate the effects of different accessory pigments on C_a estimations.

2. Methods

SeaWiFS daily Level 2 data between December 1997 and December 2004 were obtained from NASA Goddard Space Flight Center (http://oceancolor.gsfc.nasa.gov). These data were

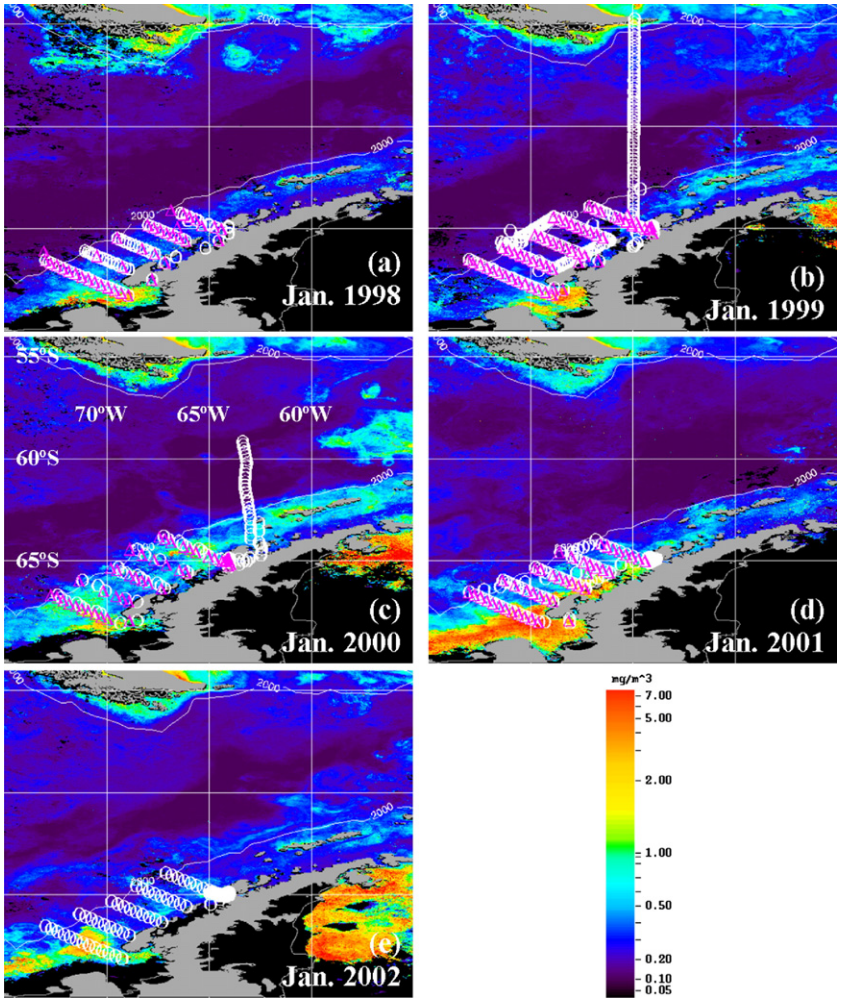

Fig. 2. Sampling stations overlaid on SeaWiFS images of mean C_a for January (a) 1998, (b) 1999, (c) 2000, (d) 2001, and (e) 2002. White circles: fluorometric samples, pink triangles: HPLC samples, white line: 2000 m isobath.

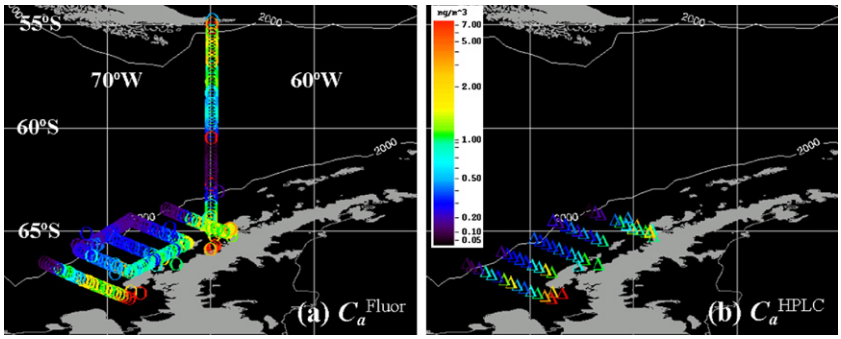

Fig. 3. Distribution of *in situ* depth-weighted (a) C_a^{Fluor} and (b) C_a^{HPLC} during January–February 1999. White line: 2000 m isobath.

derived from the high-resolution (~1 km/pixel near nadir) Level 1 data collected by ground stations, as well as occasional satellite onboard recording over the area using the most current algorithms and software package (SeaDAS4.8). A total of 6606 data files were obtained and mapped to a rectangular projection with approximately 1 km^2/pixel for the area between 45–75°S and 50–80°W west of the Antarctic Peninsula (Fig. 1). The data product used in this study is the surface C_a estimated with the OC4v4 empirical algorithm (O'Reilly et al., 2000):

$$C_a = 10^{0.366-3.067R+1.93R^2+0.649R^3-1.532R^4} \quad (1)$$

where $R=\log_{10}[(\max(R_{rs443}, R_{rs490}, R_{rs510}))/R_{rs555}]$ and R_{rs} is the remote sensing reflectance, a data product after atmospheric correction.

Chlorophyll fluorescence and HPLC pigment data were collected and analyzed by Drs Raymond Smith (University of California Santa Barbara) and Maria Vernet (University of California San Diego) as part of the Palmer Long Term Ecological Research (LTER) program during cruises west of the Antarctic Peninsula (see http://pal.lternet.edu/data/ for detailed methods). The location of the LTER chlorophyll sampling stations between 1998 and 2002 are shown in Fig. 2. Most of the samples were collected within the 2000 m isobath, although two transects were conducted across Drake Passage in January–February 1999 and 2000 to measure C_a^{Fluor}. At each station, water column samples were collected at discrete depths for both fluorometric and HPLC measurements. C_a, C_b, and C_c were obtained by HPLC from samples collected at fixed stations during January–February 1998 and 1999 following the methods of Wright et al. (1991), and during January–February 2000 and 2001 following the methods of Zapata et al. (2000). C_a and phaeopigment concentrations also were obtained by fluorometric methods by measuring total fluorescence and subtracting phaeopigments after acidification from samples collected during January–February 1998, 1999, 2000, 2001, and 2002 following Smith et al. (1981, 1996, 1998). Welschmeyer's (1994) method, which effectively measures fluorescence from C_a only and reduces interference from C_b or its phaeoderivatives, was not applied (M. Vernet, pers. comm.).

Because the signal detected by the satellite sensor is an optically weighted function of signals at all depths (up to 50–60 m for clear waters), we used the method of Gordon (1992) to calculate a depth-weighted chlorophyll concentration, $\langle C\rangle$, to compare with satellite estimates:

$$\langle C\rangle = \frac{\int_0^z g(z')C(z')dz'}{\int_0^z g(z')dz'} \quad (2)$$

where $g(z) = \exp[-2\int_0^z K(z')dz']$ and z is the depth. K is the diffuse attenuation coefficient that is approximated by $K(z)\approx 0.121C(z)^{0.428}$ (Morel, 1988). The integration was from 0 to 50 m and included 5 or 6 vertical samples at most stations, although in some cases only 3–4 samples were available for the calculations. A total of 189 HPLC and 775 fluorometric C_a

Table 1
Statistics for the comparisons between C_a^{SWF} and *in situ* C_a (C_a^{Fluor}, C_a^{HPLC})

Parameter	C_a^{SWF} vs. C_a^{Fluor}	C_a^{SWF} vs. C_a^{HPLC}
n	307	96
Ratio±S.D.	0.55±0.63	1.12±0.91
RMS	77.2%	91.4%
Bias	−45.2%	12%
Log_RMS	0.44	0.34
Log_bias	−0.36	−0.07

n is the number of matching pairs, RMS is root mean square error, and S.D. is standard deviation.

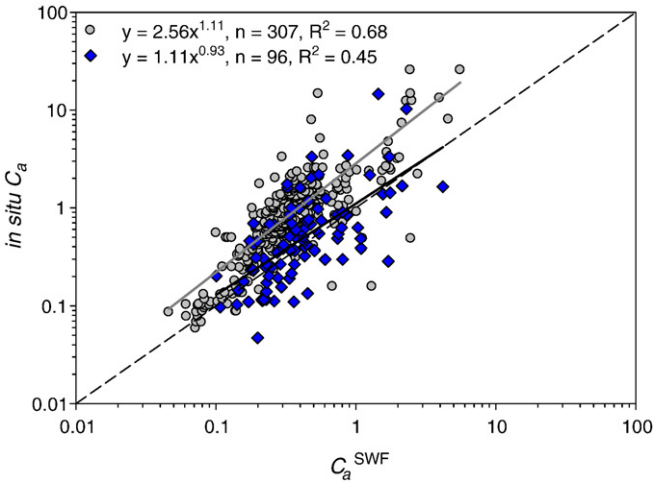

Fig. 4. Comparison between C_a^{SWF} (mg m^{-3}, SeaDAS4.8, OC4v4 algorithm) and *in situ* C_a (mg m^{-3}). Grey circles and line: C_a^{Fluor}, blue diamonds and black solid line: C_a^{HPLC}. The dashed line shows the 1:1 relationship. The statistics of the comparisons are listed in Table 1.

values were used in our analyses. Because the weighting function, $g(z)$, decreases exponentially with increasing depth, $\langle C \rangle$ is not very different from the surface value, at least for fluorometric C_a (ratio = 1.02 ± 0.15, p = 0.841). For the HPLC samples, the differences between $\langle C \rangle$ and surface C_a are significant (ratio = 1.05 ± 0.99, p = 0.022). The daily, high-resolution SeaWiFS C_a data were queried to compare with the *in situ* data in the following manner. To reduce errors caused by digitization and random noise, for each *in situ* data point, all valid satellite data from a 5×5 pixel box covering the *in situ* location (except those cloud and land adjacent pixels) were used to compute the median value (Hu et al., 2001). A rigorous comparison between satellite and *in situ* data should limit the time difference between the two measurements to within ±2–3 h. Due to extended cloud coverage and the occasional presence of sea ice, however, only a small number of HPLC data points were obtained under such rigorous criteria, leading to statistically meaningless results. Therefore, the time difference between satellite and *in situ* measurements was relaxed to ±3 days.

Estimating uncertainty in a satellite-derived parameter with log-normal distribution is not trivial, as discussed in Campbell (submitted for publication). Here, two estimates were used to assess the differences between the *in situ* and satellite-derived data. First, the root mean square (RMS) and the mean difference (bias) in percentage were defined as:

$$\mathrm{RMS} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i)^2} \times 100$$

$$\mathrm{bias} = \bar{x} = \left(\frac{1}{n}\sum_{i=1}^{n} x_i\right) \times 100$$

$$x = \frac{S-I}{I} \tag{3}$$

where S is satellite data, I is *in situ* data, and n is the number of data pairs. For a normally distributed x, RMS should equal the standard deviation. Further, because the natural distribution of C_a is lognormal (Campbell, 1995), error estimates were also made on the logarithmically transformed (base 10) data:

$$\log\_\mathrm{RMS} = \sqrt{\frac{\sum[(\log(S)-\log(I)]^2}{n}}$$

$$\log\_\mathrm{bias} = \frac{\sum[\log(S)-\log(I)]}{n} \tag{4}$$

These error estimates have been used in recent publications to describe the performance of the ocean color algorithms (O'Reilly et al., 2000) and to validate SeaWiFS global and regional estimates of C_a (Darecki & Stramski, 2004; Gregg & Casey, 2004; Zhang et al., 2006). Note that these latter error estimates cannot be expressed as percentages because they are logarithmically transformed (Campbell, submitted for publication).

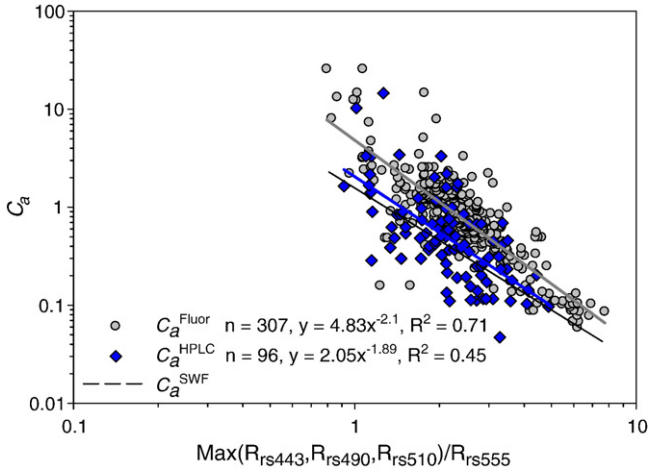

Fig. 5. Comparison between C_a predicted by the OC4v4 algorithm (using SeaWiFS-derived R_{rs} as input) and measured *in situ* C_a (mg m^{-3}). Black broken line: OC4v4 prediction (C_a^{SWF}), grey circles and solid line: C_a^{Fluor}, blue diamonds and thick line: C_a^{HPLC}.

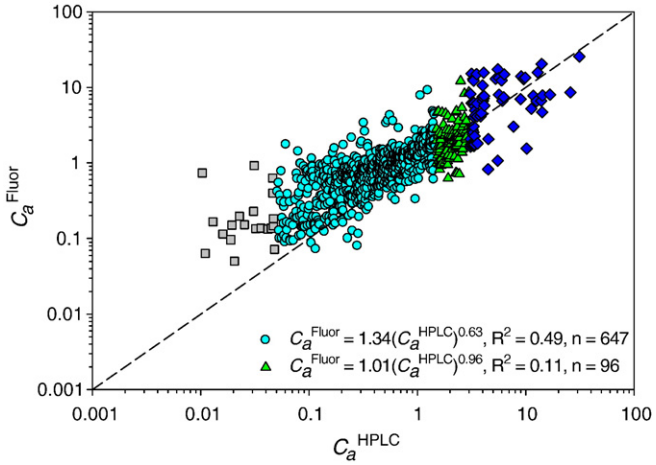

Fig. 6. Comparison between C_a^{HPLC} and C_a^{Fluor} (mg m^{-3}) between January and February 1998–2001 (n = 832). Grey squares: C_a < 0.05 mg m^{-3}, cyan circles: C_a between 0.05 and 1.5 mg m^{-3}, green triangles: C_a between 1.5 and 3 mg m^{-3}, blue diamonds circles: C_a > 3 mg m^{-3}. The dashed line shows the 1:1 relationship. Statistics for the comparison are listed in Table 2.

Table 2
Statistics for the comparisons between C_a^{Fluor} and C_a^{HPLC} (mg m^{-3}) for data shown in Fig. 6

C_a^{HPLC} range	0.01–15	<0.05	0.05–1.5	1.5–3.0	>3.0
n	832	21	647	96	68
a_0, a_1	1.40, 0.66	0.28, 0.14	1.34, 0.63	1.01, 0.96	2.15, 0.55
R^2	0.67	0.01	0.49	0.11	0.14
C_a^{Fluor}/C_a^{HPLC} ±	2.43 ±	10.06 ±	2.48 ±	1.15 ±	1.37 ±
S.D.	3.37	15.21	2.23	0.73	1.04
RMS	366%	1739%	268%	74%	110%
Bias	143%	905%	148%	15%	37%
Log_RMS	0.40	0.87	0.40	0.23	0.34
Log_bias	0.25	0.79	0.29	−0.01	0.02

a_0 and a_1 are the power fitting coefficients in the form of $C_a^{Fluor} = a_0 \times (C_a^{HPLC})^{a1}$, R^2 is the corresponding coefficient of determination, n is the number of matching pairs, RMS is root mean square error, and S.D. is standard deviation.

3. Results

Typical C_a^{Fluor} and C_a^{HPLC} distributions during austral summer are presented for January–February 1999 (Fig. 3). In all years, C_a^{Fluor} ranged from 0.052 to 27.6 mg m^{-3}, with a median of 0.86 mg m^{-3}. C_a^{HPLC} was typically lower and ranged from 0.017 to 14.6 mg m^{-3} with a median of 1.04 mg m^{-3}. In general, the lowest C_a values (<0.1 mg m^{-3}) were consistently found off-shelf in Drake Passage. Elevated C_a values (>1 mg m^{-3}) were detected throughout the continental shelf, with the highest values (>10 mg m^{-3}) always observed in Marguerite Bay.

A total of 96 $C_a^{\mathrm{SWF}}-C_a^{\mathrm{HPLC}}$ matching pairs and 307 $C_a^{\mathrm{SWF}}-C_a^{\mathrm{Fluor}}$ matching pairs were obtained using the method described above. Table 1 lists the statistics of these comparisons. In general, C_a^{SWF} is significantly lower than C_a^{Fluor} (Fig. 4), with a ratio of 0.55±0.63 between the two (Table 1). The inverse ratio, i.e., the ratio of $C_a^{\mathrm{Fluor}}/C_a^{\mathrm{SWF}}$, is 2.73±2.19, consistent with previous observations in the Southern Ocean where C_a^{Fluor} was used to validate C_a^{SWF} and the same pattern of underestimation was observed (Dierssen & Smith, 2000; Korb et al., 2004; Moore et al., 1999). In contrast, C_a^{HPLC} showed a more satisfactory agreement with C_a^{SWF} over a wide dynamic range (0.1–4 mg m^{-3}) (Fig. 4). The mean ratio of $C_a^{\mathrm{SWF}}/C_a^{\mathrm{HPLC}}$ is close to 1 (i.e., 1.12), in contrast to the lower ratio of 0.55 for $C_a^{\mathrm{SWF}}/C_a^{\mathrm{Fluor}}$.

Although the RMS errors for the two comparisons are comparable (Table 1), C_a^{HPLC} is nearly equally scattered around the 1:1 line (Fig. 4), suggesting that the bias errors in $C_a^{\mathrm{SWF}}/C_a^{\mathrm{HPLC}}$ are significantly smaller than those in $C_a^{\mathrm{SWF}}/C_a^{\mathrm{Fluor}}$. Clearly, the agreement between C_a^{SWF} and C_a^{HPLC} is much improved over that between C_a^{SWF} and C_a^{Fluor}.

Similar results were also obtained from the algorithm perspective. By using the spectral remote sensing reflectance data (R_{rs}) derived from satellite measurements (Fig. 5), the OC4v4 algorithm yielded comparable results to those obtained from HPLC measurements. In contrast, C_a^{Fluor} values are significantly higher than those predicted by the OC4v4 algorithm for the entire range considered.

Are these results representative of the entire Southern Ocean? Due to cloud cover, satellite data were not available for all pixels every day. This reduced the number of C_a^{SWF} data points, which resulted in a limited number of matching pairs for comparing satellite and *in situ* data (307 for fluorometric and 96 for HPLC). However, the *in situ* data itself comprised a much larger dataset that included 832 concurrent fluorometric and HPLC measurements. When this *in situ* dataset was used to compare C_a^{Fluor} and C_a^{HPLC}, similar results were obtained, i.e., the ratio of $C_a^{\mathrm{Fluor}}/C_a^{\mathrm{HPLC}}$ is 2.43±3.37 (Fig. 6). The ratio of $C_a^{\mathrm{Fluor}}/C_a^{\mathrm{HPLC}}$ appears to decrease with increasing concentrations (Table 2), although for $C_a^{\mathrm{HPLC}}<0.05$ mg m^{-3} and $C_a^{\mathrm{HPLC}}>3.0$ mg m^{-3} the statistical results may not be reliable because of the few matching pairs available and the scatter of the data (Fig. 6). For C_a^{HPLC} between 1.5 and 3.0 mg m^{-3}, the bias is small (15%) and the ratio of $C_a^{\mathrm{Fluor}}/C_a^{\mathrm{HPLC}}$ is close to unity (1.15±0.73). Between 0.05 and 1.5 mg m^{-3}, however, C_a^{Fluor} is much higher than Ca^{HPLC} ($C_a^{\mathrm{Fluor}}/C_a^{\mathrm{HPLC}}=2.48\pm2.23$, $n=647$). This difference is believed to be due to errors in the C_a^{Fluor} measurements as described above. Because most (>90%) of the waters in the Southern Ocean have surface C_a^{SWF} values between 0.05 and

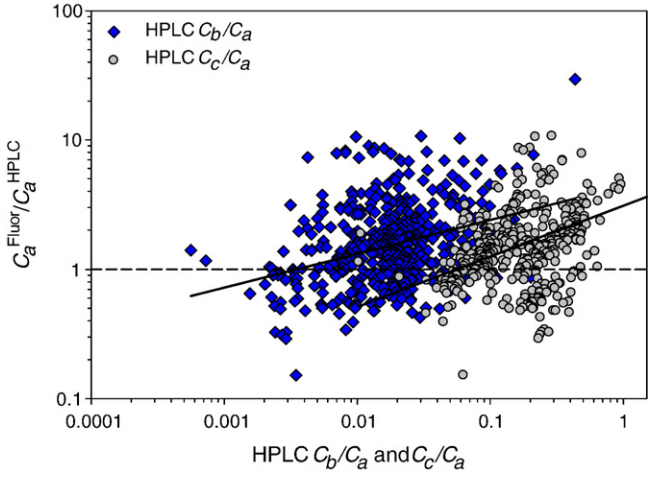

Fig. 8. Relationship between HPLC C_b/C_a and $C_a^{\mathrm{Fluor}}/C_a^{\mathrm{HPLC}}$ ($y=4.36x^{0.26}$, $R^2=0.11$, $n=482$), and between HPLC C_c/C_a and $C_a^{\mathrm{Fluor}}/C_a^{\mathrm{HPLC}}$ ($y=3.09x^{0.39}$, $R^2=0.19$, $n=482$). Note that the slope for the latter (0.39) is significantly larger than for the former (0.26). Here $C_b/C_a=0.023\pm0.034$ ($n=482$) and $C_c/C_a=0.25\pm0.59$ ($n=482$).

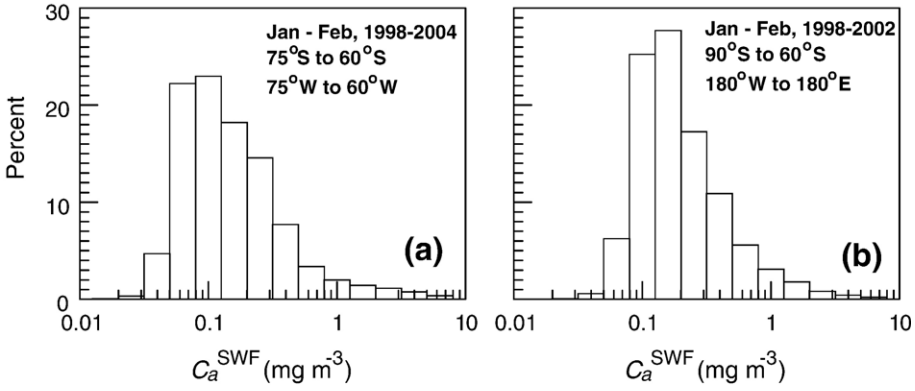

Fig. 7. Normalized histogram of C_a^{SWF} distributions (mg m^{-3}) in the Southern Ocean during austral summer. (a) For the study region (Fig. 1) bound by 75–60°S and 75–60°W; (b) for the entire Southern Ocean (south of 60°S). The *y*-axis shows the percentage surface area. 91% and 96% of the surface waters for (a) and (b), respectively, fall within the range of 0.05 to 1.5 mg m^{-3}.

1.5 mg m^{-3} (Fig. 7), this assessment can be generalized and applied to most regions.

4. Discussion

Although HPLC has been recommended as the most reliable method to determine C_a (e.g., Trees et al., 1985), most cruise surveys still use the fluorometric method because it is faster, requires less technical expertise, and is less expensive than HPLC. The C_a data originally used in the development of the OC4v4 algorithm (O'Reilly et al., 2000) included 2853 *in situ* measurements from a variety of oceanic environments (but not the Southern Ocean), of which 72% were fluorometric and 28% were HPLC measurements. Therefore, the predicted C_a satellite measurements should naturally lean toward the fluorometric values. However, this is not what we found, suggesting that the species composition and their associated pigment absorption characteristics in waters west of the Antarctic Peninsula region may be different from the "mean" composition and absorption on which the original algorithm was based.

The large difference observed between C_a^{Fluor} and C_a^{HPLC} from the same water samples was likely due, in part, to interference of the fluorescence signal by chlorophyll accessory pigments (C_b, C_c, and their degradation products). In our study, C_b only occurred in low concentrations compared to C_a (mean ratio $C_b/C_a=0.023$, $n=486$); however, C_c was relatively high (mean ratio $C_c/C_a=0.25$, $n=486$) (Fig. 8). The presence of significant amounts of C_c is known to cause an overestimation of C_a by the fluorometric method (Gibbs, 1979; Lorenzen, 1981).

C_b is an accessory pigment in prochlorophytes, chlorophytes, and prasinophytes, while C_c is generally present in diatoms, dinoflagellates, cryptophytes, and haptophytes (Parsons et al., 1984). Diatoms are the dominant phytoplankton in waters west of the Antarctic Peninsula, with dinoflagellates being very abundant at times (Prézelin et al., 2000, 2004). Prochlorophytes, a type of cyanobacteria first identified in the late 1980s (Chisholm et al., 1988), have not yet been observed in the Southern Ocean, while chlorophytes can be abundant (Prézelin et al., 2000, 2004). Similarly, cryptophytes are usually scarce in the water column, but can be very abundant in coastal surface melt water during spring and summer (Moline & Prézelin, 1996). Alloxanthin, the biomarker pigment for cryptophytes (Prézelin et al., 2000), occurred in 91% ($n=516$) of the pigment samples. Hence, chlorophytes were probably the dominant source of C_b during our study period, while the dominant sources of C_c appear to be diatoms, dinoflagellates and cryptophytes, identified by the presence of fucoxanthin, peridinin, and alloxanthin in 99.5%, 53%, and 91% of the samples, respectively.

C_b and C_c vary widely throughout the world's ocean (Bianchi et al., 1995; Bidigare et al., 1986; Goericke & Repeta, 1993; Jeffrey, 1976; Lorenzen, 1981; Trees et al., 1985). Overall, these studies found that C_b can cause an underestimation of C_a by the fluorometric method with ratios of C_b/C_a ranging from 0.15 to 0.51, while the presence of significant amount of C_c can lead to an overestimation of C_a. Typical ratios of C_c/C_a for assemblages dominated by phytoplankton containing chlorophyll *c* range from 0.15 to 0.44 (Bianchi et al., 1995; Bidigare et al., 1986; Lohrenz et al., 2003). Our results are consistent with these previous findings.

Can the presence of significant amount of C_c lead to overestimation of C_a when the latter is derived from remote sensing reflectance data? The inversion of remote sensing reflectance to C_a is an implicit (e.g., OC4v4) or explicit (e.g., Maritorena et al., 2002) function of phytoplankton pigment absorption. Lohrenz et al. (2003) reported that, even if the amount of accessory pigments (sum of carotenoids and C_b+C_c) is equal to C_a, the perturbation to the pigment absorption is <30%, suggesting a relatively small error in the satellite-retrieved C_a. Hence, the large differences between C_a^{SWF} and C_a^{Fluor} observed here cannot be explained by the additional absorption of accessory pigment, but can be explained by the interference of these accessory pigments to the fluorescence peak when C_a is determined using the fluorometric method.

5. Conclusion

In contrast to previous reports that estimates of C_a^{SWF} in the Southern Ocean were significantly lower than those measured *in situ*, we found that for January–February between 1998 and 2001, these satellite estimates agree with those determined from water samples for C_a between 0.05 and 1.5 mg m^{-3}. This is primarily because the *in situ* C_a data were determined by HPLC (C_a^{HPLC}) rather than by fluorometric methods (C_a^{Fluor}), which are known to introduce significant errors in C_a estimates in the presence of certain accessory pigments.

Because >90% of the Southern Ocean has C_a values in the 0.05–1.5 mg m^{-3} range, and there is no significant bias in C_a^{SWF} when C_a^{HPLC} is regarded as the ground truth (bias=12% and $C_a^{\mathrm{SWF}}/C_a^{\mathrm{HPLC}}$ ratio=1.12±0.91), it is not necessary to develop an alternative bio-optical algorithm for this C_a range. However, if computer models (e.g., to estimate primary production or eutrophic depth) have been developed using C_a^{Fluor} as input, the satellite estimates of C_a will need adjustment to be consistent with these models.

Acknowledgements

This study was supported by the US National Science Foundation (NSF) grants OPP-9910610 and OPP-196489, and by the US NASA grant NNS04AB59G. We are deeply indebted to the Palmer LTER Group and Drs. Maria Vernet and Raymond Smith for collecting and processing the *in situ* chlorophyll data, without which it would have been impossible to complete this study. Data from the Palmer LTER data archive were supported by Office of Polar Programs of NSF (OPP-9011927). We also thank Brock Murch of USF/IMaRS for his assistance in obtaining and processing the satellite data IMaRS contribution # 104.

References

Arrigo, K. R., Worthen, D., Schnell, A., & Lizotte, M. P. (1998). Primary production in Southern Ocean waters. *Journal of Geophysical Research*, *103*, 15587–15600.

Bianchi, T. S., Lambert, C., & Biggs, D. C. (1995). Distribution of chlorophyll *a* and phaeopigments in the northwestern Gulf of Mexico: A comparison between fluorometric and high-performance liquid chromatography measurements. *Bulletin of Marine Science*, *56*, 25−32.

Bidigare, R. R., Frank, T. J., Zastrow, C., & Brooks, J. M. (1986). The distribution of algal chlorophylls and their degradation products in the Southern Ocean. *Deep-Sea Research*, *33*, 923−937.

Boyd, P. W. (2002). Environmental factors controlling phytoplankton processes in the Southern Ocean. *Journal of Phycology*, *38*, 844−861.

Campbell, J. W. (1995). The lognormal distribution as a model for bio-optical variability in the sea. *Journal of Geophysical Research*, *100*, 13237−13254.

Campbell, J. W. (submitted for publication). Methods for quantifying the uncertainty in a chlorophyll algorithm as demonstrated for the SeaWiFS algorithm. *Remote Sensing of Environment*.

Chisholm, S. W., Olson, R. J., Zettler, E. R., Goericke, R., Waterbury, J., & Welschmeyer, N. (1988). A novel free living prochlorophyte abundant in the oceanic euphotic zone. *Nature*, *334*, 340−343.

Daly, K. L., Smith, W. O., Johnson, G. C., DiTullio, G. R., Jones, D. R., Mordy, C. W., et al. (2001). Hydrography, nutrients, and carbon pools in the Pacific sector of the Southern Ocean: Implications for carbon flux. *Journal of Geophysical Research*, *106*, 7107−7124.

Darecki, M., & Stramski, D. (2004). An evaluation of MODIS and SeaWiFS bio-optical algorithms in the Baltic Sea. *Remote Sensing of Environment*, *89*, 326−350.

Deibel, D., & Daly, K. L. (in press). Zooplankton processes. In W. O. Smith Jr., & D. Barber (Eds.), *Polynyas: Windows into Polar Oceans*. Elsevier Oceanography Series.

Dierssen, H. M., & Smith, R. (2000). Bio-optical properties and remote sensing ocean color algorithms for Antarctic Peninsula waters. *Journal of Geophysical Research*, *105*, 26301−26312.

Dierssen, H. M., Vernet, M., & Smith, R. C. (2000). Optimizing models for remotely estimating primary production in Antarctic coastal waters. *Antarctic Science*, *12*, 20−32.

El-Sayed, S. Z. (1971). Observations on phytoplankton bloom in the Weddell Sea. In G. A. Llano & I.E. Wallen (Eds.), *Biology of the Antarctic Seas* (pp. 301−312).Washington: American Geophysical Union.

El-Sayed, S. Z. (2005). History and evolution of primary productivity studies of the Southern Ocean. *Polar Biology*, *28*, 423−438.

Esaias, W. E., Abbott, M. R., Barton, I., Brown, O. B., Campbell, J. W., Carder, K. L., et al. (1998). An overview of MODIS capabilities for ocean science observations. *IEEE Transactions on Geoscience and Remote Sensing*, *36*, 1250−1265.

Gibbs, C. F. (1979). Chlorophyll *b* interference in the fluorometric determination of chlorophyll *a* and 'phaeo-pigments'. *Australian Journal of Marine and Freshwater Research*, *30*, 597−606.

Goericke, R., & Repeta, D. J. (1993). Chlorophylls *a* and *b* and divinyl chlorophylls *a* and *b* in the open subtropical North Atlantic Ocean. *Marine Ecology Progress Series*, *101*, 307−313.

Gordon, H. R. (1992). Diffuse reflectance of the ocean: Influence of nonuniform phytoplankton pigment profile. *Applied Optics*, *31*, 2116−2129.

Gregg, W. W., & Casey, N. W. (2004). Global and regional evaluation of the SeaWiFS chlorophyll dataset. *Remote Sensing of Environment*, *93*, 463−479.

Holm-Hansen, O., Mitchell, B. G., Hewes, C. D., & Karl, D. M. (1989). Phytoplankton blooms in the vicinity of Palmer Station, Antarctica. *Polar Biology*, *10*, 49−57.

Holm-Hansen, O., Kahru, M., Hewes, C. D., Kawaguchi, S., Kameda, T., Sushin, V. A., et al. (2004). Temporal and spatial distribution of chlorophyll *a* in surface waters of the Scotia Sea as determined by both shipboard measurements and satellite data. *Deep-Sea Research*, *51*, 1323−1331.

Hu, C., Carder, K. L., & Müller-Karger, F. E. (2001). How precise are SeaWiFS ocean color estimates? Implications of digitization-noise errors. *Remote Sensing of Environment*, *76*, 239−249.

Hu, C., Nababan, B., Biggs, D. C., & Müller-Karger, F. E. (2004). Variability of bio-optical properties at sampling stations and implications for remote sensing. A case study in the NE Gulf of Mexico. *International Journal of Remote Sensing*, *25*, 2111−2120.

Hu, C., Muller-Karger, F. E., Taylor, C., Carder, K. L., Kelble, C., Johns, E., et al. (2005). Red tide detection and tracing using MODIS fluorescence data: A regional example in SW Florida coastal waters. *Remote Sensing of Environment*, *97*, 311−321.

Jeffrey, S. W. (1976). A report of green algal pigments in the Central North Pacific Ocean. *Marine Biology*, *37*, 33−37.

Jeffrey, S. W., Mantoura, R. F. C., & Bjornland, T. (1997). Data for the identification of 47 key phytoplankton pigments. In S. W. Jeffrey, R. F. C. Mantoura, & S. W. Wright (Eds.), *Phytoplankton pigments in oceanography*. Paris UNESCO Publishing 661 pp.

Korb, R. E., Whitehouse, M. J., & Ward, P. (2004). SeaWiFS in the Southern Ocean: Spatial and temporal variability in phytoplankton biomass around South Georgia. *Deep-Sea Research*, *51*, 99−116.

Lohrenz, S. E., Weidemann, A. D., & Tuel, M. (2003). Phytoplankton spectral absorption as influenced by community size structure and pigment composition. *Journal of Plankton Research*, *25*, 35−61.

Lorenzen, C. J. (1981). Chlorophyll *b* in the eastern North Pacific Ocean. *Deep-Sea Research*, *28*, 1049−1056.

Maritorena, S., Siegel, D. A., & Peterson, A. R. (2002). Optimization of a semianalytical ocean color model for global-scale application. *Applied Optics*, *41*, 2705−2714.

McClain, C. R., Cleave, M. L., Feldman, G. C., Gregg, W. W., Hooker, S. B., & Kuring, N. (1998). Science quality SeaWiFS data for global biosphere research. *Sea Technology*, *39*, 10−16.

Moline, M., & Prézelin, B. B. (1996). Long-term monitoring and analyses of physical factors regulating variability in coastal Antarctic phytoplankton biomass, in situ productivity, and taxonomic composition over subseasonal, seasonal and interannual time scales. *Marine Ecology Progress Series*, *145*, 143−160.

Moore, J. K., & Abbott, M. R. (2000). Phytoplankton chlorophyll distributions and primary production in the Southern Ocean. *Journal of Geophysical Research*, *105*, 28709−28722.

Moore, J. K., Abbott, M. R., Richman, J. G., Smith, W. O., Cowles, T. J., Coale, K. H., et al. (1999). SeaWiFS satellite ocean color data from the Southern Ocean. *Geophysical Research Letters*, *26*, 1465−1468.

Morel, A. (1988). Optical modeling of the upper ocean in relation to its biogenous matter content (case 1 waters). *Journal of Geophysical Research*, *93*, 10749−10768.

Muller-Karger, F. E., Varela, R., Thunell, R., Astor, Y., Zhang, H., Luerssen, R., et al. (2004). Processes of coastal upwelling and carbon flux in the CARIACO basin. *Deep Sea Research*, *51*, 927−943.

O'Reilly, J. E., Maritorena, S., O'Brien, M. C., Siegel, D. A., Toole, D., Menzies, D., et al. (2000). SeaWiFS postlaunch calibration and validation analyses: Part 3. SeaWiFS postlaunch technical report series, 11. In S. B. Hooker, & E. R. Firestone (Eds.), NASA Technical Memorandum 2000-206892 49 pp.

Orsi, A. H., Whitworth III, H., & Nowlin, W. D. (1995). On the meridional extent and fronts of the Antarctic Circumpolar Current. *Deep-Sea Research*, *42*, 641−673.

Parsons, T. R., Takahashi, M., & Hargrave, B. (1984). Biological oceanographic processes. Oxford Pergamon Press 330 pp.

Prézelin, B. B., Hoffman, E. E., Mengelt, C., & Klinck, J. M. (2000). The linkage between Upper Circumpolar Deep Water (UCDW) and phytoplankton assemblages on the west Antarctic Peninsula continental shelf. *Journal of Marine Research*, *58*, 165−202.

Prézelin, B. B., Hoffman, E. E., Moline, M., & Klinck, J. M. (2004). Physical forcing of phytoplankton community structure and primary production in continental shelf waters of the western Antarctic Peninsula. *Journal of Marine Research*, *62*, 419−460.

Smith, R. C., Baker, K. S., Dierssen, H. M., Stammerjohn, S. E., & Vernet, M. (2001). Variability of primary production in an Antarctic marine ecosystem as estimated using a multi-scale sampling strategy. *American Zoologist*, *41*, 40−56.

Smith, R. C., Baker, K. S., & Dustan, P. (1981). Fluorometric techniques for the measurement of oceanic chlorophyll in the support of remote sensing. *SIO Reference*, 81-17.

Smith, R. C., Baker, K. S., & Vernet, M. (1998). Seasonal and interannual variability of phytoplankton biomass west of the Antarctic Peninsula. *Journal of Marine Systems*, *17*, 229−243.

Smith, R. C., Dierssen, H., & Vernet, M. (1996). Phytoplankton biomass and productivity in the western Antarctic Peninsula region. In R. M. Ross, E. E.

Hofmann, & L. B. Quetin (Eds.), *Foundations for Ecological Research West of the Antarctic Peninsula*, *Vol. 70* (pp. 233–256). AGU Antarctic Research Series.

Trees, C. C., Kennicutt, M. C., & Brooks, J. M. (1985). Errors associated with the standard fluorometric determination of chlorophylls and phaeopigments. *Marine Chemistry*, *17*, 1–12.

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

Wright, S. W., Jeffrey, S. W., Mantoura, R. F. C., Llewellyn, C. A., Bjorland, T., Repeta, D., et al. (1991). Improved HPLC method for the analysis of chlorophylls and carotenoids from marine phytoplankton. *Marine Ecology Progress Series*, *77*, 183–196.

Zapata, M., Rodriguez, F., & Garrido, J. L. (2000). Separation of chlorophylls and carotenoids from marine phytoplankton: A new HPLC method using a reversed phase C8 column and pyridine-containing mobile phases. *Marine Ecology Progress Series*, *195*, 29–45.

Zhang, C., Hu, C., Shang, S., Müller-Karger, F. E., Li, Y., Dai, M., et al. (2006). Bridging between SeaWiFS and MODIS for continuity of chlorophyll *a* concentration assessments off southeastern China. *Remote Sensing of Environment*, *102*, 250–263.