Validation of SeaWiFS chlorophyll \(a\) concentrations in the Southern Ocean: A revisit

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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 \(2.48 \pm 2.23\) (\(n=647\)) 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 \(1.12 \pm 0.91\) (\(n=96\)), whereas the ratio of \(C_a^{SWF}/C_a^{Fluor}\) is \(0.55 \pm 0.63\) (\(n=307\)). 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 \(b\) (\(C_b/C_a=0.023 \pm 0.034\), \(n=482\)) and relatively high concentrations of chlorophyll \(c\) (\(C_c/C_a=0.25 \pm 0.59\), \(n=482\)) 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”.

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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 et al., 2000).
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 $\geq$30 mg m$^{-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 ($C_a^{\text{Fluor}}$) to validate monthly/weekly averages of SeaWiFS $C_a$ ($C_a^{\text{SWF}}$) data product at $\sim 9 \times 9$ km$^2$ or $\sim 4 \times 4$ km$^2$ resolution and concluded that, in the Southern Ocean, $C_a^{\text{SWF}}$ 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 $\sim$1 mg m$^{-3}$). Korb et al. (2004) reported that $C_a^{\text{SWF}}$ values were only 87% of $C_a^{\text{Fluor}}$ 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 $C_a^{\text{SWF}}$ and $C_a^{\text{Fluor}}$ ($R^2 = 0.72, n = 84$) 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 $9 \times 9$ 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
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 $C_a^{\text{Fluor}}$ ranged between $-68\%$ and $53\%$ with a mean of $39\%$. In addition, Bianchi et al. (1995) found that $C_a^{\text{Fluor}}$ in the northern Gulf of Mexico was approximately $30\%$ lower than $C_a^{\text{HPLC}}$, 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 $C_c$ 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
Table 1
Statistics for the comparisons between \( C_{\text{a,SWF}} \) and \( C_{\text{a,Fluor}} \) and \( C_{\text{a,HPLC}} \) in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( C_{\text{a,SWF}} ) vs. ( C_{\text{a,Fluor}} )</th>
<th>( C_{\text{a,SWF}} ) vs. ( C_{\text{a,HPLC}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>307</td>
<td>96</td>
</tr>
<tr>
<td>Ratio±S.D.</td>
<td>0.55±0.63</td>
<td>1.12±0.91</td>
</tr>
<tr>
<td>RMS</td>
<td>77.2%</td>
<td>91.4%</td>
</tr>
<tr>
<td>Bias</td>
<td>-45.2%</td>
<td>12%</td>
</tr>
<tr>
<td>Log_RMS</td>
<td>0.44</td>
<td>0.34</td>
</tr>
<tr>
<td>Log_bias</td>
<td>-0.36</td>
<td>-0.07</td>
</tr>
</tbody>
</table>

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

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

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

\[ C_{\text{a}} = 10^{0.366–3.0678+1.938^2+0.6498^3–1.5128^4} \] (1)

where \( R = \log_{10}[(\max\{R_{\text{rs}443}, R_{\text{rs}490}, R_{\text{rs}510}\})/R_{\text{rs}555}] \) and \( R_{\text{rs}} \) 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) 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 \( C_{\text{a,Fluor}} \). At each station, water column samples were collected at discrete depths for both fluorometric and HPLC measurements. \( C_{\text{a,Fluor}} \), \( C_{\text{a,h}} \), and \( C_{\text{a,v}} \) 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). \( C_{\text{a}} \) and phaeopigment concentrations also were obtained by fluorometric methods by measuring total fluorescence and subtracting phaeopigment concentrations 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 \( C_{\text{a}} \) only and reduces interference from \( C_{\text{b}} \) or its phaeo-derivatives, 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:

\[
\langle C \rangle = \frac{\int_0^h g(z)C(z)dz}{\int_0^h g(z)dz}
\] (2)
values were used in our analyses. Because the weighting function, \( g(z) \), decreases exponentially with increasing depth, \( \langle \mathbf{C} \rangle \) 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 \( \langle \mathbf{C} \rangle \) 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 \textit{in situ} data in the following manner. To reduce errors caused by digitization and random noise, for each \textit{in situ} data point, all valid satellite data from a 5 × 5 pixel box covering the \textit{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 \textit{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 \textit{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 \textit{in situ} and satellite-derived data. First, the root mean square (RMS) and the mean difference (bias) in percentage were defined as:

\[
\text{RMS} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (x_i - I)^2} \times 100
\]

\[
\text{bias} = \bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \times 100
\]

\[
x = \frac{S - I}{T}
\]

where \( S \) is satellite data, \( I \) is \textit{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:

\[
\log_{-} \text{RMS} = \sqrt{\frac{\sum [\log(S) - \log(I)]^2}{n}}
\]

\[
\log_{-} \text{bias} = \frac{\sum [\log(S) - \log(I)]}{n}
\]

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. 6. Comparison between \( C_a^\text{HPLC} \) and \( C_a^\text{Fluor} \) (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

<table>
<thead>
<tr>
<th>( C_a^\text{HPLC} ) range</th>
<th>0.01–15</th>
<th>&lt;0.05</th>
<th>0.05–1.5</th>
<th>1.5–3.0</th>
<th>&gt;3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>832</td>
<td>21</td>
<td>647</td>
<td>96</td>
<td>68</td>
</tr>
<tr>
<td>( a_0 ) ( a_1 )</td>
<td>1.40, 0.66</td>
<td>0.28, 0.14</td>
<td>1.34, 0.63</td>
<td>1.01, 0.96</td>
<td>2.15, 0.55</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.67</td>
<td>0.01</td>
<td>0.49</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>( C_a^\text{Fluor} ) ( C_a^\text{HPLC} )</td>
<td>2.43±</td>
<td>10.06±</td>
<td>2.48±</td>
<td>1.15±</td>
<td>1.37±</td>
</tr>
<tr>
<td>S.D.</td>
<td>3.37</td>
<td>15.21</td>
<td>2.23</td>
<td>0.73</td>
<td>1.04</td>
</tr>
<tr>
<td>RMS</td>
<td>366%</td>
<td>1739%</td>
<td>268%</td>
<td>74%</td>
<td>110%</td>
</tr>
<tr>
<td>Bias</td>
<td>143%</td>
<td>905%</td>
<td>148%</td>
<td>15%</td>
<td>37%</td>
</tr>
<tr>
<td>Log₂RMS</td>
<td>0.40</td>
<td>0.87</td>
<td>0.40</td>
<td>0.23</td>
<td>0.34</td>
</tr>
<tr>
<td>Log₂bias</td>
<td>0.25</td>
<td>0.79</td>
<td>0.29</td>
<td>−0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

\( a_0 \) and \( a_1 \) are the power fitting coefficients in the form of \( C_a^\text{Fluor} = a_0 \times (C_a^\text{HPLC})^{a_1} \). \( R^2 \) 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.

Fig. 5. Comparison between \( C_a \) predicted by the OC4v4 algorithm (using SeaWiFS-derived \( R_{864} \) as input) and measured \textit{in situ} \( C_a \) (mg m\(^{-3}\)). (a) Black broken line: OC4v4 prediction \( (C_a^\text{OC4v4}) \), grey circles and thick line: \( C_a^\text{Fluor} \), blue diamonds and thick line: \( C_a^\text{HPLC} \).
3. Results

Typical $C_{a}^{\text{Fluor}}$ and $C_{a}^{\text{HPLC}}$ distributions during austral summer are presented for January–February 1999 (Fig. 3). In all years, $C_{a}^{\text{Fluor}}$ ranged from 0.052 to 27.6 mg m$^{-3}$, with a median of 0.86 mg m$^{-3}$. $C_{a}^{\text{HPLC}}$ 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 $C_{a}^{\text{SWF}}$–$C_{a}^{\text{Fluor}}$ matching pairs and 307 $C_{a}^{\text{SWF}}$–$C_{a}^{\text{HPLC}}$ matching pairs were obtained using the method described above. Table 1 lists the statistics of these comparisons. In general, $C_{a}^{\text{Fluor}}$ and $C_{a}^{\text{HPLC}}$ are significantly smaller than those in $C_{a}^{\text{SWF}}$ (Fig. 4), suggesting that the bias errors in $C_{a}^{\text{SWF}}$ are presented for January 1:1 line (Fig. 4), indicating that the bias errors in $C_{a}^{\text{SWF}}$ and the same pattern of underestimation was observed (Dierssen & Smith, 2000; Korb et al., 2004; Moore et al., 1999).

In contrast, $C_{a}^{\text{HPLC}}$ showed a more satisfactory agreement with $C_{a}^{\text{SWF}}$ over a wide dynamic range (0.1–4 mg m$^{-3}$) (Fig. 4). The mean ratio of $C_{a}^{\text{SWF}}/C_{a}^{\text{HPLC}}$ is close to 1 (i.e., 1.12), in contrast to the lower ratio of 0.55 for $C_{a}^{\text{SWF}}/C_{a}^{\text{Fluor}}$.

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

Similar results were also obtained from the algorithm perspective. By using the spectral remote sensing reflectance data ($R_{a}$) derived from satellite measurements (Fig. 5), the OC4v4 algorithm yielded comparable results to those obtained from HPLC measurements. In contrast, $C_{a}^{\text{Fluor}}$ 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 $C_{a}^{\text{SWF}}$ 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 $C_{a}^{\text{Fluor}}$ and $C_{a}^{\text{HPLC}}$, similar results were obtained, i.e., the ratio of $C_{a}^{\text{Fluor}}/C_{a}^{\text{HPLC}}$ is 2.43±3.37 (Fig. 6). The ratio of $C_{a}^{\text{Fluor}}/C_{a}^{\text{HPLC}}$ appears to decrease with increasing concentrations (Table 2), although for $C_{a}^{\text{HPLC}}<0.05$ mg m$^{-3}$ and $C_{a}^{\text{HPLC}}>3.0$ 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 $C_{a}^{\text{HPLC}}$ between 1.5 and 3.0 mg m$^{-3}$, the bias is small (15%) and the ratio of $C_{a}^{\text{Fluor}}/C_{a}^{\text{HPLC}}$ is close to unity (1.15±0.73). Between 0.05 and 1.5 mg m$^{-3}$, however, $C_{a}^{\text{Fluor}}$ is much higher than $C_{a}^{\text{HPLC}}$ ($C_{a}^{\text{Fluor}}/C_{a}^{\text{HPLC}} = 2.48±2.23, n = 647$). This difference is believed to be due to errors in the $C_{a}^{\text{Fluor}}$ measurements as described above. Because most (>90%) of the waters in the Southern Ocean have surface $C_{a}^{\text{SWF}}$ values between 0.05 and

![Fig. 7. Normalized histogram of $C_{a}^{\text{SWF}}$ 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$^{-3}$.

![Fig. 8. Relationship between HPLC $C_{a}$ and $C_{a}^{\text{Fluor}}$/$C_{a}^{\text{HPLC}}$ (y=4.36x0.26, R$^{2}$=0.11, n=482), and between HPLC $C_{a}$/$C_{a}^{\text{Fluor}}$ and $C_{a}^{\text{HPLC}}$ (y=3.09x0.39, 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 $C_{a}$/$C_{a}^{\text{Fluor}}=0.023±0.034 (n=482)$ and $C_{a}$/$C_{a}^{\text{HPLC}}=0.25±0.59 (n=482)$.


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 differ from the “mean” composition and absorption on which the original algorithm was based.

The large difference observed between \(C_a^{\text{Fluor}}\) and \(C_a^{\text{HPLC}}\) 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 \(C_b\) 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 \(C_c+C_b\)) 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 \(C_a^{\text{SWF}}\) and \(C_a^{\text{Fluor}}\) 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 \(C_a^{\text{SWF}}\) 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 (\(C_a^{\text{HPLC}}\)) rather than by fluorometric methods (\(C_a^{\text{Fluor}}\)), 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 \(C_a^{\text{SWF}}\) when \(C_a^{\text{HPLC}}\) is regarded as the ground truth (bias=12% and \(C_a^{\text{SWF}}/C_a^{\text{HPLC}}\) 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 \(C_a^{\text{Fluor}}\) as input, the satellite estimates of \(C_a\) will need adjustment to be consistent with these models.

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