# A locally tuned Cphyto algorithm for the Ross Sea, Antarctica

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### Abstract

To improve current estimates of phytoplankton specific carbon in the Ross Sea, we calculated a regionally specific algorithm from in situ particulate organic carbon (POC) concentrations and backscatter sensor data. These data come from three independent Seaglider deployments during the austral summer. Algal-specific POC (Cphyto) accounted for between 19.8-61.0% of total POC in the Ross Sea with an average Cphyto concentration of 84.2  $\mu$ g C L-1. As a result, Cphyto:chlorophyll a ratios were less than POC:chlorophyll a ratios and ranged from 9.00-257  $\mu$ g C ( $\mu$ g chlorophyll a) L-1. This regionally-specific method is substantially more accurate (average Cphyto concentrations are 10-78  $\mu$ g C L-1 greater) than estimates derived from published algorithms. Our findings highlight the value of regionally-specific algorithms for measuring inherent optical properties and how such approaches can inform our current understanding of particulate carbon partitioning and food web dynamics.

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#### 35 Abstract

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#### **Plain Language Summary** 48

49 Phytoplankton account for a substantial portion of the organic carbon in the ocean, but not all of it, and traditional sampling methods cannot differentiate between phytoplankton 50 51 (algal) carbon and non-algal carbon. This frequently leads to overestimates of the amount of 52 algal carbon within an ecosystem. New methods have been developed to measure algal 53 carbon alone, but they are calibrated to the global ocean, making them inaccurate in some 54 regions with specific ecosystem characteristics. Here, we modify one of those methods for 55 the Ross Sea, Antarctica, thus improving its accuracy substantially. Our method shows the importance of developing region specific algorithms in order to develop a better 56 57 understanding of carbon dynamics, globally.

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# 60 Key Points

- 61 1. When applied to data from the Ross Sea, current algorithms substantially
- 62 underestimate phytoplankton carbon ( $C_{phyto}$ ).
- 63 2. By modifying pre-existing algorithms with regionally specific data, we can develop64 regional algorithms to improve our estimates immensely.
- 65 3. Our method has potential to substantially improve satellite estimates of Cphyto in
  66 regions that have been traditionally difficult to measure.

## I. Introduction

69 Labor-intensive methods and substantial differences among species have made accurate measurements for phytoplankton-specific carbon on large scales a consistent and 70 71 elusive problem in oceanography for decades. Without this parameter, the accuracy of carbon 72 export, food web, and biogeochemical models remain constrained. Traditional proxies for phytoplankton biomass include chlorophyll *a* (Chl *a*) and particulate organic carbon (POC) 73 74 concentrations. However, both of these are influenced by factors independent of changes in 75 phytoplankton biomass, specifically phytoplankton physiology (variable chlorophyll a 76 concentrations per cell) and detrital carbon stocks (POC), making a quantitative assessment 77 of phytoplankton carbon uncertain.

The development of direct estimates of phytoplankton carbon (C<sub>phyto</sub>) from inherent 78 79 optical properties on autonomous assets and remote sensing retrievals has made it possible to 80 estimate C<sub>phyto</sub> on large spatiotemporal scales (Behrenfeld et al., 2005). Further advances in 81 the form of in situ calibration of C<sub>phyto</sub> measurements have enhanced confidence in the 82 parameter (Graff et al., 2015). However, due to logistical constraints and limited validation 83 efforts, C<sub>phyto</sub> algorithms substantially vary in accuracy and are regionally dependent 84 (Martinez-Vincente et al., 2013; Serra-Pompei et al., 2023). Specifically, the Graff et al. (2015) C<sub>phyto</sub> algorithm was developed using in situ samples from open-ocean regions of the 85 86 North and South Atlantic and appears to be less accurate in regions with large phytoplankton 87 standing stocks and higher concentrations of detrital and mineral particles, such as coastal, upwelling, and high latitude areas, including the Southern Ocean continental shelves. 88 Accurate estimates of phytoplankton carbon are critical in the latter, given its substantial role 89 90 in carbon cycling and the importance of the biological pump in that system (Le Quere et al., 2007; Gruber et al., 2019). 91

92 Analyses of how well the algorithm performs in various regions of the Southern 93 Ocean have been conducted (Thomalla et al., 2019 and references therein), but applications of the algorithm to specific regions of the Southern Ocean have not been completed. The 94 95 Ross Sea, which is responsible for approximately 28% of Southern Ocean net primary 96 production (Arrigo et al., 2008), is of particular importance to carbon dynamics. It is the most 97 productive shelf region of the Southern Ocean (Smith et al., 2014) and experiences an annual spring phytoplankton productive period where surface POC concentrations exceed 400 mg C 98 m<sup>-3</sup> and Chl *a* concentrations can be >15  $\mu$ g L<sup>-1</sup>; Smith et al., 2000, 2011; Meyer et al., 99 100 2022). During the productive period, the phytoplankton assemblage is dominated initially by colonies of the haptophyte Phaeocystis antarctica before transitioning to dominance by a 101 102 mixed assemblage of diatoms (Smith et al., 2000, 2011). This region also supports a 103 substantial amount of macrofaunal biodiversity, with 38% of the world's Adelie penguins, 104 25% of the world's emperor penguins, 70% of Antarctic petrels, and an abundance of marine 105 mammals (seals and whales; Ainley et al., 2015). However, studies on the non-algal organic 106 carbon dynamics in this region are lacking, leading to uncertainties in our understanding of 107 food web dynamics and carbon transformations.

108

109 II. Methods

We compiled POC-b<sub>bp</sub>(470) calibration samples from three glider surveys in the Ross
Sea. All gliders were launched from the fast ice near Ross Island and recovered by the *RVIB N.B. Palmer*. During glider recoveries CTD casts were completed as close to the glider dive
location as possible, and water samples collected from known depths for POC and
chlorophyll *a* calibration of the glider sensors. Kongsberg (formerly iRobot) Seagliders were
deployed in 2010-2011, 2012-2012, and 2022-2023 during austral spring/summer (Fig. 1).
POC-b<sub>bp</sub>(470) samples were measured by an Imagenex 853 Echo Sounder and counts were

converted to POC concentrations following Boss and Pegau (2001). POC samples were
processed according to Gardner et al. (2000). The Seagliders were also equipped with a Wet
Labs ECO Triplet Puck to measure in situ fluorescence. Fluorescence was converted to Chl *a*concentrations according to Kaufman et al. (2014) and calibrated against samples which were
analyzed fluorometrically on a Trilogy fluorometer (JGOFS, 1996). Full information on POC
samples and processing and glider deployments are provided in Kaufman et al. (2014) and
Meyer et al. (2022). All figures were made in Matlab (R2022b; The Mathworks, Inc.).





- 127 glider deployments occurred in the Ross Sea as indicated by the inset map.
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129 Because C_{phyto} has not been measured directly in the Ross Sea, we used our b_{bp}(470)-
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- 130 based POC concentrations (concentrations (n = 29) ranged from  $17.0 577 \ \mu g \ C \ L^{-1}$ ),
- assuming 95% algal carbon in the surface waters during the annual bloom. We chose 95% as

132 our assumption after a sensitivity analysis was performed for assumptions of 40, 85, and 100% algal POC with 95% yielding the most realistic results. POC:Chl a ratios vs. depth for 133 134 all three deployments showed no substantial decline with depth. Therefore, we applied our 135 95% algal carbon assumption uniformly through depth to all calibration samples. The data were then plotted, mimicking Graff et al. (2015), thus generating an equation for a C<sub>phyto</sub> 136 algorithm. We applied this algorithm to all three glider deployments, calculating  $C_{\text{phyto}}$  at 5 137 m. The 2012-2013 deployment was chosen as our case study to validate this regional tuning, 138 given that it has been analyzed in the greater detail relative to the 2010-2011 and 2022-2023 139 140 studies (Jones and Smith, 2017; Meyer et al., 2022). In addition to C<sub>phyto</sub>, the ratio of C<sub>phyto</sub> to optically derived POC and fluorometrically derived Chl a (Jones and Smith, 2017; Kaufman 141 et al., 2014) were calculated. All C<sub>phyto</sub> concentrations and ratios were confined to the mixed 142 143 layer to make them more closely comparable to satellite retrievals.

144

## 145 III. Results

146 Our calibration algorithm relating  $b_{bp}(470)$  (m<sup>-1</sup>) counts to  $C_{phyto}$  concentrations ( $\mu g L^{-1}$ 147 <sup>1</sup>) was (Supplemental Fig. S1):

148

$$C_{phvto} = 39474 * b_{bp}(470) + 46.1 \tag{3}$$

149 where 39474 is the slope of the linear relationship between the glider backscatter ( $b_{bp}(470)$ )

and the in situ POC modified to account for non-algal POC and 46.1 is the y-intercept.

151 Average C<sub>phyto</sub> concentrations for each glider deployment varied among the three

deployments, and each had substantial variability within each data set (Table 1). For all three

datasets, derived  $C_{phyto}$  concentrations were strongly correlated with POC concentrations ( $r^2 =$ 

- 154 0.50, 0.96, 1.00, respectively). In 2012-2013, C<sub>phyto</sub> increased from early to mid-December
- 155 with increased variability in late January to early February; maximum values occurred on
- 156 January 18<sup>th</sup> (Fig. 2a). The variability in  $C_{phyto}$  concentrations was small (mean = 84.2 ± 11.0

- 157  $\mu$ g C L<sup>-1</sup>; range from 63.0 150.0  $\mu$ g C L<sup>-1</sup>), whereas surface POC concentrations averaged 158 264 ± 81.4  $\mu$ g C L<sup>-1</sup> (104 to 756  $\mu$ g C L<sup>-1</sup>). The integrated mixed layer C<sub>phyto</sub> was 3.52 ± 2.17 159 g C m<sup>-2</sup> (Fig. 2b). However, due to substantial mixed layer variability, values were highly 160 variable, ranging from 0.67 – 13.9 g C m<sup>-2</sup> in the 2012-2013 study (Fig. 2b; for details on 161 mixed layer depth calculations, see Meyer et al., 2022).
- 162

Table 1. Surface (5 m) average, standard deviation, minimum, and maximum C<sub>phyto</sub>
 concentrations (μg C L<sup>-1</sup>) from three Ross Sea glider deployments.

167	Year	Average	Minimum	Maximum
168 169 170		C <sub>phyto</sub> (µg C L <sup>-1</sup> )	C <sub>phyto</sub> (µg C L <sup>-1</sup> )	C <sub>phyto</sub> (µg C L <sup>-1</sup> )
171 172 173	2010-2011	75.6 ± 17.8	37.4	281
174 175 176	2012-2013	84.1 ± 11.0	63.0	150
177 178 179	2022-2023	77.1 ± 14.2	57.8	123

180 All calculations use  $b_{bp}470$  data applied to the algorithm from this study. 181



Figure 2. a) Surface (5 m) C<sub>phyto</sub> concentrations from this study and previously published
algorithms, b) mixed layer integrated C<sub>phyto</sub> concentrations calculated according to this
study's algorithm, and c) ratios of surface C<sub>phyto</sub>:POC concentrations from this study and
previously published algorithms. All values are discrete and based on the 2012-2013
Seaglider deployment to the Ross Sea (Jones and Smith, 2017; Meyer et al., 2022). The black
line in b represents a 5-point running average of the data.

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191 C<sub>phyto</sub> concentrations were lower than anticipated, as exemplified by the ratios of
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192 C_{phyto}:POC, which averaged 0.34 \pm 0.07 over the survey period (Fig. 2c). However, our ratios
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- are within reported  $C_{phyto}$ :POC ratios (Behrenfeld et al., 2006), ranging from 0.20 0.61 and
- are substantially higher than those calculated from any previously published algorithm (Fig.
- 195 2c). Patterns of  $C_{phyto}$ :POC ratios exhibited a different pattern from that of  $C_{phyto}$
- 196 concentrations (Figs. 2c, 3a). Ratios declined in early to late December before increasing

197 slightly from early January through late January, and by early February, ratios begin to again 198 decline, perhaps due to enhanced viral lysis or bacterial remineralization following increases 199 in phytoplankton biomass. Because  $C_{phyto}$  concentrations remained consistent with those 200 observed in mid-December through early January, this would suggest detrital carbon (i.e., 201 POC –  $C_{phyto}$ ) increased in mid- to late January, coincident with the highest concentrations of



202 POC and the highest rates of net community production (Meyer et al., 2022).

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**Figure 3.** Surface (5 m) ratios of (a)  $C_{phyto}$ :POC and  $C_{phyto}$ :Chl *a* concentrations (µg C (µg Chl *a*)<sup>-1</sup>) and  $C_{phyto}$ :Chl *a* and POC:Chl *a* (µg C (µg Chl *a*)<sup>-1</sup>) from the 2012-2013 Seaglider deployment to the Ross Sea.

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Ratios of C<sub>phyto</sub>:Chl *a* exhibit the same general pattern as POC:Chl *a* ratios (Meyer et al., 2022), averaging  $85.3 \pm 53.3$  (average POC:Chl *a* ratios were  $266 \pm 179$ ; Fig. 3b). While

210	the patterns remain consistent, the difference between $C_{phyto}$ :Chl <i>a</i> and POC:Chl <i>a</i> can give
211	further indication of phytoplankton physiology by providing a more specific relative cellular
212	Chl content per unit carbon for <i>P. antarctica</i> vs. diatoms, i.e., the C <sub>phyto</sub> :Chl <i>a</i> ratio is more
213	comparable (differences between C <sub>phyto</sub> :Chl <i>a</i> and POC:Chl <i>a</i> ratios range ~ $< 70 - 564 \mu g C$
214	$L^{-1}$ ) in magnitude to POC:Chl <i>a</i> ratios during the period known to be dominated by diatoms
215	(early January to early February) than during the period known to be dominated by <i>P</i> .
216	antarctica (differences range $13 - 906 \ \mu g \ C \ L^{-1}$ ; early to late December; Figs. 3a,b). While
217	both exhibit large ranges, this would suggest that diatoms contribute more algal carbon to
218	total POC than <i>P. antarctica</i> , likely due to a higher overall cellular POC to Chl <i>a</i> content as
219	seen through the difference in C <sub>phyto</sub> :Chl <i>a</i> and POC:Chl <i>a</i> ratios.
220	The greatest degree of uncertainty in these estimates results from the assumption that
221	during the peak productive period 95% of the POC in the surface ocean is algal as well as
222	limited calibration samples. While average $C_{phyto}$ concentrations for the variety of
223	assumptions tested are within previously reported estimates, ranging 30.3 to 170 $\mu g \ C \ L^{\text{-1}}$
224	(Table 1; Table S1), given the lack of in situ $C_{phyto}$ samples for validation and the relatively
225	few number of calibration samples, we suspect our values are low. Another source of
226	uncertainty results from sampling and analysis biases that come from POC samples and
227	sensor precision. Early (2010-2011 and 2012-2013) calibration efforts collected single POC
228	samples, but the 2022-2023 study collected duplicate POC samples with a standard deviation
229	of 16.1 $\mu$ g C L <sup>-1</sup> . Additionally, the relatively few calibration samples and the highly dynamic
230	environment always presents some uncertainty associated with the Echo Sounder ( $r^2$ between
231	bbp470 and in situ POC samples were 0.85, 0.80, and 0.63, for 2010-2011, 2012-2013, and
232	2022-2023, respectively).

234 IV. Discussion

235 Our C<sub>phyto</sub> concentrations appear to be more accurate than those generated when 236 applying global algorithms, lending confidence in the ability to regionally tune pre-existing 237 algorithms to achieve a more realistic estimate of algal carbon. Our C<sub>phyto</sub> concentrations and C<sub>phyto</sub>:POC ratios are all greater than values calculated from previously reported algorithms 238 (Figs. 2a, 3). The substantial difference between our calculated C<sub>phyto</sub> concentrations and 239 POC concentrations, as represented by a low (<50) average C<sub>phyto</sub>:POC ratio in 2012-2013 240 (Arrigo et al., 2000, 2003; Meyer et al., 2022), is surprising and would suggest that C<sub>phyto</sub> is 241 242 still too low and is being limited by the lack of in situ data. Despite this, the C<sub>phyto</sub>:POC 243 ratios are within the range previously reported by Graff et al. (2015) and Burt et al. (2018) for 244 other regions. C<sub>phyto</sub>:POC ratios from the 2022-2023 deployment lend confidence to the method, producing higher but less variable values ranging from 0.50 to 0.53 (average = 0.51245 246  $\pm$  0.01), as 2022-2023 appeared to be more productive and with greater biomass relative to 2012-2013, supporting the notion of a higher C<sub>phyto</sub> concentration. Interestingly, C<sub>phyto</sub>:POC 247 ratios from the 2010-2011 deployment were all >1. This year had low POC concentrations 248 (mean mixed layer concentration  $< 110 \ \mu g \ C \ L^{-1}$ ; Kaufman et al., 2014), as well as the 249 weakest r<sup>2</sup> value between C<sub>phyto</sub> and POC, suggesting our algorithm is better tuned to higher 250 POC concentrations which are more characteristic of the Ross Sea during a typical productive 251 period. However, given concentrations calculated by our algorithm for all years are higher 252 253 than concentrations calculated by algorithms from other studies, it suggests our algorithm 254 provides more realistic estimates for this region. 255 When applied to  $b_{bp}(470)$  data from the Ross Sea, current global algorithms

underestimate  $C_{phyto}$  substantially (by approximately >80%; Table 2). This is evident from extremely low  $C_{phyto}$ :POC ratios through the productive period (Table 2). The one exception to this is the Chl-derived method of Sathyendranath et al. (2009) which overestimates  $C_{phyto}$ concentrations substantially (average  $C_{phyto}$ :POC ratios > 3).  $C_{phyto}$ :POC is useful to evaluate

260	the proportion of algal relative to total carbon concentrations in the surface ocean. Whereas
261	ratios of C <sub>phyto</sub> :Chl <i>a</i> ( $\mu$ g C L <sup>-1</sup> : $\mu$ g Chl <i>a</i> L <sup>-1</sup> ) can be used to broadly assess the phytoplankton
262	assemblage through pre-established relationships (Arrigo et al., 2000; Riemann et al., 1989)
263	and assessments of spatio-temporal transitions (Figs. 4a,b). Our algorithm produced
264	C <sub>phyto</sub> :Chl <i>a</i> ratios within previously reported values (Kauffman et al., 2014; Smith and
265	Kauffman, 2018), ranging from 9.01 in early December to >200 by mid-January.

#### Table 2. Previously published algorithms for optically derived phytoplankton-specific 267 carbon (C<sub>phyto</sub>). 268

Reference	Algorithm	C <sub>phyto</sub>	C <sub>phyto</sub> :
		(µg C L <sup>-1</sup> )	POC
Behrenfeld et al., 2005	$C_{\text{phyto}} = 13000 * (b_{\text{bp}}(470) - 3.5 \text{x} 10^{-4})$	8.00	0.03
Sathyendranath et al., 2009		851	3.62
	$C_{phyto} = 119 * (chl^{0.55})$		
Martinez-Vincente et al., 2013	$C_{\text{phyto}} = 30100 * (b_{\text{bp}}(470) - 7.6 \times 10^{-4})$	6.19	0.02
Graff et al., 2015	$C_{phyto} = 12129 * b_{bp}(470) + 0.59$	12.3	0.05
Arteaga et al., 2020	$C_{phyto} = 0.19 * POC$	50.1	0.19
This study	$C_{phyto} = 39474 * b_{bp}(470) + 46.13$	84.1	0.34

269

Algorithms, concentrations of  $C_{phyto}$ , and the ratio of  $C_{phyto}$ : particulate organic carbon (POC) 270 as calculated from a Ross Sea glider deployment when sed algorithms are applied to this

271 backscatter, chlorophyll a (chl), or POC datasets. 272

273

274	Despite the strong correlation between $C_{phyto}$ and POC in our analysis, temporal
275	patterns in the ratio of $C_{phyto}$ :POC can provide more information on the algal vs. non-algal
276	partitioning in the surface waters during the seasonal progression of the annual productive

POC concentrations rather than C<sub>phyto</sub>, i.e., ratios are highest when POC concentrations are 278 279 low in early December and lowest in late December when surface biomass is maximal (Figs. 3, 4a). The low degree of variability in ratios and  $C_{phyto}$  concentrations is noteworthy, given 280 281 the substantial variability in POC concentrations themselves (standard deviation for surface POC = 81.3  $\mu$ g C L<sup>-1</sup>; Meyer et al., 2022). C<sub>phyto</sub>:POC ratios increase slightly but significantly 282 (p <0.05) in late January - early February when bacterial remineralization has been 283 284 hypothesized to increase and could change the concentration of the detrital carbon pool 285 (Ducklow et al., 2001; Meyer et al., 2022). Whether this change results from a net decline in 286 POC concentrations or increased detrital carbon is impossible to tell, but studies which 287 capture the full decline in the productive period and final diatom reduction would resolve this. 288

289 One advantage of calculating C<sub>phyto</sub> relative to either POC or Chl a is the removal of 290 apparent changes in biomass related to physiological effects, such as irradiance impacts on 291 fluorescence (Chl *a*), and environmental effects, such as a high concentration of non-algal 292 carbon (POC). Changes in C<sub>phyto</sub> concentrations reflect actual biomass changes and therefore, should exhibit a different temporal trend from both POC and Chl a. Cphyto should be more 293 294 similar to POC, peaking later than Chl a in early to mid-January with a faster decline than POC. We hypothesize that POC concentrations would remain more elevated into mid- to late 295 296 January than C<sub>phyto</sub> because POC concentrations would likely be influenced by detrital POC 297 resulting from processes like sloppy feeding (Steinberg et al., 2008), bacterial 298 remineralization (Asper and Smith, 2019), and the generation of *Phaeocystis* ghost colonies 299 (Smith et al., 2017), all of which may increase the non-algal POC pool. Additionally, trends 300 in C<sub>phyto</sub> can be compared to trends in nonphotochemical quenching (NPQ; Ryan-Keogh and Smith, 2021) that would impact Chl a concentrations. Like POC, Cphyto exhibited similar 301 302 temporal patterns to NPQ, suggesting both are impacted by light and iron availability, but

that NPQ is not serving as a strong negative control on C<sub>phyto</sub> concentrations themselves
(Ryan-Keogh and Smith, 2021).

305 The phytoplankton assemblage experiences a predictable shift from being dominated 306 by P. antarctica to being diatom dominated in mid-December to early January (Smith et al., 307 2014; Meyer et al., 2022) - a pattern further confirmed by the increase in C<sub>phyto</sub>:Chl *a* ratios. 308 The varying degrees of difference in POC:Chl a and C<sub>phyto</sub>:Chl a during periods of P. 309 antarctica or diatom dominance would suggest that diatoms have less Chl a relative to cellular carbon than *Phaeocystis* (Fig. 3b). This notion is further supported by the 310 311 discrepancy in patterns between C<sub>phyto</sub>:POC and C<sub>phyto</sub>:Chl a in early December where the 312 greatest difference corresponds to the period of *Phaeocystis* dominance (Fig. 3a). These findings have implications for both remote sensing and carbon export dynamics and further 313 314 supports the argument for C<sub>phyto</sub> as a proxy for phytoplankton biomass in biogeochemical 315 models. Application of this algorithm to additional datasets may help elucidate physical 316 factors that impact the balance between algal and non-algal carbon (Arrigo et al., 2003). How 317 this impacts food web dynamics and the transfer of organic carbon to higher trophic levels is 318 uncertain but warrants further investigation.

319

320 V. Conclusion

We developed a locally-tuned Ross Sea  $C_{phyto}$ - $b_{bp}$  algorithm through in situ calibration POC samples and sensor measurements and knowledge of the region's bloom dynamics. Our analysis provides the most realistic constraint of  $C_{phyto}$  in this region to date. However,  $C_{phyto}$ concentrations in the surface appear low relative to what we would expect given extensive sampling in the Ross Sea. The accuracy of any  $C_{phyto}$  algorithm will be limited until in situ validation to generate direct  $C_{phyto}$  estimates is conducted. Further initiatives toward this goal and the overall development of regional algorithms are needed and would greatly improve

328	biogeochemical models of the region and our understanding of the mechanisms driving its
329	role in carbon fluxes (Le Quere et al., 2007; Casey et al., 2013).
330	
331	Data Availability
332	All data presented here are publicly available at the Biological and Chemical Oceanography
333	Data Management Office (Woods Hole, MA; Smith, 2014; Smith, 2015) and at the British
334	Oceanographic Data Centre (Southampton, UK; Heywood, 2023).
335	
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