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1 Seasonal depletion of the dissolved iron reservoirs in the sub-Antarctic zone of 2 the Southern Atlantic Ocean

3
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16 17 Key Points

- 18 • We report the first seasonal changes of the upper surface dissolved iron concentrations of
19 four occupations from late-winter to late-summer
- 20 • Euphotic zone dissolved iron decreases due to biological uptake, while aphotic iron
21 decreases due to colloidal aggregation and scavenging
- 22 • Recycling of nutrients might be responsible for sustaining the observed seasonal primary
23 production in late January to early February

24 25 Abstract

26 Seasonal progression of dissolved iron (DFe) concentrations in the upper water column were
27 examined during four occupations in the Atlantic sector of the Southern Ocean. DFe inventories
28 from euphotic and aphotic reservoirs decreased progressively from July to February, while
29 dissolved inorganic nitrogen (DIN) decreased from July to January with no significant change
30 between January and February. Results suggest that between July and January, DFe loss from both
31 euphotic and aphotic reservoirs were predominantly in support of phytoplankton growth (Iron to
32 carbon (Fe:C) uptake ratio of $16 \pm 3 \mu\text{mol mol}^{-1}$) highlighting the importance of the “winter DFe-
33 reservoir” for biological uptake. During January to February, excess loss of DFe relative to DIN
34 (Fe:C uptake ratio of $44 \pm 8 \mu\text{mol mol}^{-1}$ and aphotic DFe loss rate of $0.34 \pm 0.06 \mu\text{mol m}^{-2} \text{d}^{-1}$)
35 suggests that scavenging is the dominant removal mechanism of DFe from the aphotic, while
36 continued production is likely supported by recycled nutrients.

37 **Plain Language Summary:** Trace metal iron is one of the limiting nutrients for primary
38 productivity in the Southern Ocean; however the relative importance of seasonal iron supply and
39 sinks remains poorly understood, due to sparse data coverage across the seasonal cycle and lack
40 of high-resolution dissolved iron (DFe) measurements. Here, we present four “snap-shots” of DFe
41 measurements at a single station in the south-east Southern Atlantic Ocean (one in winter and three
42 in late spring-summer), to address the seasonal evolution of DFe and dissolved inorganic nitrogen
43 (DIN) concentrations within the biologically active sunlit and subsurface reservoirs. We observed
44 a seasonal depletion of DFe inventories from July-February, while DIN inventories decreases from
45 July-January with no concomitant changes between January-February. This suggests that, in
46 addition to biological uptake in the sunlit layer, the observed decrease in DFe inventories below
47 this (relative to DIN) is driven by aggregation and incorporation of iron particles into larger
48 "marine snow" sinking particles, while nutrient recycling is driving the observed continuation of
49 primary productivity during late summer. Our results provide insight into seasonal change of DFe
50 availability in different reservoirs where interplay between removal and supply processes are
51 controlling its distributions and bioavailability to support upper surface primary production.

52 53 **1. Introduction**

54 Iron availability in the Southern Ocean (SO) controls phytoplankton growth, plankton community
55 composition and carbon export to the deep ocean through the biological carbon pump (BCP)
56 (Tagliabue et al., 2014). Although the spatial distribution of SO blooms is known to be driven by
57 iron availability (Pollard et al., 2009), different seasonal expressions of these blooms, with both
58 high and low seasonal cycle reproducibility, implies distinct regulatory supply mechanisms
59 (Thomalla et al., 2011). Indeed, variability in iron supply can significantly impact maximum
60 potential primary production (PP) across the SO (by as much as 80%; Ryan-Keogh et al., 2017).
61 The iron supply across the seasonal cycle can be divided into three terms; new supply, recycled
62 supply and internal transport (Boyd et al., 2010, 2010a). The processes and sources responsible for
63 these different supply mechanisms include, but are not limited to, deep winter mixing (Tagliabue
64 et al., 2014), internal metal transformations (Boyd et al., 2010b; Boyd et al., 2017), aerosols
65 (Jickells et al., 2005), sediments (Planquette et al., 2007), sea-ice and icebergs (Lancelot et al.,
66 2009), hydrothermal vents (Tagliabue et al., 2010), upwelling (Klunder et al., 2011), eddy-
67 diffusion (Law et al., 2003) and horizontal and lateral advection (Chever et al., 2010a). The relative
68 importance of iron supply pathways remains poorly understood, primarily due to sparse data
69 coverage across the seasonal cycle in the SO (Tagliabue et al., 2012). This hampers our ability to
70 constrain the response of the BCP to climate change in this key region of the World's oceans. A
71 compilation study of dissolved iron (DFe) measurements concluded that even in regions where
72 many DFe measurements exist, the processes governing the seasonal evolution remain poorly
73 constrained, which suggests that biological consumption may not be the major driver of DFe
74 variability (Tagliabue et al., 2012). The number of in-situ DFe measurements available for the
75 Global Ocean is rapidly increasing, thanks to efforts made by programs such as GEOTRACES
76 (Intermediate Data Products; Schlitzer et al., 2018; Mawji et al., 2015). Nonetheless, missing
77 measurements during key seasonal transitions make it difficult to quantify and understand surface
78 water replenishment processes and the seasonal DFe cycle, especially in the SO (Tagliabue et al.,
79 2012).

80
81 Phytoplankton blooms in the sub-Antarctic Zone (SAZ) of the SO are characterized by high inter-
82 annual and intra-seasonal variability with an extended duration (e.g., ~16 weeks in Racault et al.,

83 2012) that sustains high chlorophyll concentrations late into summer (Thomalla et al., 2011, 2015;
84 Swart et al., 2015; Carranza and Gille, 2015). The longevity of these blooms is unusual as DFe
85 limitation at this time of year is expected to limit growth (Boyd and Doney, 2002). Deep winter
86 mixing entrains DFe and macronutrients from subsurface reservoirs, replenishing the mixed layer
87 to support springtime PP. However, upper ocean biota and abiotic scavenging onto settling
88 particles rapidly depletes this mixed layer inventory (Tagliabue et al., 2012, 2014). Although
89 diapycnal diffusion resupplies the mixed layer from late spring onwards, its low rates cannot be
90 reconciled with phytoplankton utilization. Instead, summertime blooms are sustained by this
91 “once-off” winter entrainment supply of nutrients through biologically mediated recycling
92 (Tagliabue et al., 2014; Strzepek et al., 2005; Boyd et al., 2012, 2017). However, there is now
93 growing evidence to suggest that in addition to the entrained supply, intermittent storm-driven
94 mixing may also play a role in extending the duration of summertime production through intra-
95 seasonal entrainment of DFe from a subsurface reservoir beneath the productive layer (Thomalla
96 et al., 2011; Fauchereau et al., 2011; Swart et al., 2015; Carranza and Gille, 2015; Nicholson et al.,
97 2016).

98
99 SO phytoplankton species can display a large degree of plasticity in their elemental stoichiometry,
100 as opposed to previous theory of canonical Redfield ratios. This is best demonstrated by the 100
101 fold difference measured in Fe to carbon ratios (Fe:C) from both in situ and laboratory studies
102 (ranging 0.29 - 25.00 $\mu\text{mol mol}^{-1}$, Strzepek et al., 2011, 2012; Fung et al., 2000; Abraham et al.,
103 2000; Sarthou et al., 2008; Twining et al., 2004a,b), which is a function of cell size, light and DFe
104 availability (Sunda and Huntsman, 1997; Geider and La Roche, 2002). Overall changes in DFe
105 include Fe-specific losses such as scavenging and colloidal aggregation (that could be captured by
106 total or particulate Fe measurements), such that seasonal changes in Fe:C ratios and their
107 comparison to known algal demands can be used to enhance our understanding of the drivers of
108 variability. This paper aims to understand the seasonal progression of DFe concentrations in the
109 upper 200 m of the water column by examining changes in stoichiometry and nutrient inventories
110 from different depth horizons at a single location in the SAZ of the south Atlantic SO.

111 112 **2. Materials and Methods**

113 Data presented here were obtained during two cruises on board the SA Agulhas II in winter (22
114 July – 15 August 2015) and summer (3 December 2015 – 11 February 2016) as part of SOSCEX
115 III (Swart et al., 2012). Results focus on a process station within the SAZ (Figure 1a), which was
116 sampled on 28 July 2015, 8 December 2015, 5 January 2016 and 8 February 2016; whilst a
117 Seaglider deployed in July (at 42.7°S, 8.7°E) in mooring mode sampled continuously for ~6
118 months for potential temperature, salinity and fluorescence derived chlorophyll and retrieved in
119 February (at 43.0°S, 8.5°E) (Supporting Information Figure S1).

120
121 Full methodology is presented in Supporting Information Text S1. Briefly, following a
122 GEOTRACES sampling protocol (Cutter et al., 2013), acidified DFe samples were analyzed using
123 Flow Injection Analysis with chemiluminescence detection (FIA-CL) (Obata et al., 1993; Sarthou
124 et al., 2003). Dissolved inorganic nitrogen (nitrate + nitrite; DIN) samples were measured using a
125 Lachat FIA (Egan, 2008; Wolters, 2002). The mixed layer depth (MLD) was defined as the depth
126 where density differs from surface (10 m) density by more than 0.03 kg m^{-3} (de Boyer Montégut
127 et al, 2004). The euphotic depth (Z_{eu}) was defined as the depth at which PAR is 1% of the surface
128 value. The isopycnal depth of deep winter mixing was identified at a density threshold of 26.70 kg m^{-3} .

129 m^{-3} and extended throughout summer to represent remnant winter waters. Depth-integrated PP
130 rates (PP_{wc} , $\text{mol C m}^{-2} \text{d}^{-1}$) were calculated from quenching corrected glider derived chlorophyll
131 (Thomalla et al., 2017a) and PAR according to Platt et al. (1980), Platt and Sathyendranath (1993),
132 and Thomalla et al. (2015). PP parameters were determined from a linear relationship with
133 chlorophyll using experimental values from both cruises (Supporting Information Figure S2,
134 Ryan-Keogh et al., 2018b). Seasonal variation in nutrient concentrations within the euphotic and
135 winter mixed layer isopycnals required three different methods to derive depth-integrated nutrient
136 inventories. Significant differences were calculated using a t-test of two samples assuming equal
137 variance and one-way ANOVA single factor, with significant results reported at the 95%
138 confidence level.

139

140 **3. Results**

141 **3.1. Station characterization**

142 **3.1.1. Hydrographic context**

143 Sea surface temperatures ranged from 7.0 - 10.8 °C with salinity ranging from 34.1 - 34.6. Surface
144 chlorophyll concentrations were low ($\sim 0.28 \mu\text{g L}^{-1}$) throughout winter (July-October), increasing
145 to a maximum of $1.40 \mu\text{g L}^{-1}$ in December (Supporting Information Figure S1c). The deepest MLD
146 from the glider dataset was observed in October (169 m) compared to July (157 m); suggesting
147 that July does not correspond to the timing of deepest winter convective mixing. Seasonal heating
148 of the upper water column in summer (December - February) resulted in a shoaling of the MLD to
149 a 16 - 43 m range. The extended isopycnal depth of the deepest winter ML during summer ranged
150 from 131 - 149 m, which was 89 - 119 m deeper than the summer MLD. Z_{eu} did not vary
151 significantly, with a mean value of 63 ± 7 m. Although, the station has the same geographical
152 location, it is also positioned within the larger eastward flowing ACC. Thus, the water sampled
153 during each occupation will be slightly different as the water is advected eastward. Nevertheless,
154 the water mass characterisation (Figure 1b) between each occupancy is relatively consistent.
155 However, the December occupation exhibited a TS signature of warmer (>9.0 °C), saltier (>34.5)
156 subtropical water (Chever et al., 2010b; Boye et al., 2012; Joubert et al., 2011); suggesting an
157 intrusion of Agulhas water. Due to the distinct water mass sampled in December, calculated
158 nutrient inventories do not form part of the budget calculations, profiles are nonetheless included
159 to explore seasonal changes in nutrient inventories.

160

161 **3.1.2. Vertical profiles of DFe and DIN concentrations**

162 DFe concentrations in July ranged between 0.14 - 0.70 nM, with two pronounced peaks above the
163 isopycnal layer of winter and summer MLD (50 m = 0.35 ± 0.01 nM, 100 m = 0.44 ± 0.01 nM)
164 (Figure 2a,b). During December and February, DFe concentrations showed a slight elevation in
165 near surface waters, decreasing to minimum values in the subsurface, followed by increasing
166 concentrations with depth, while concentrations in January increased with depth. December
167 concentrations ranged between 0.14 - 0.79 nM, with a peak at 100 m (0.27 ± 0.00 nM), whilst in
168 January and February concentrations ranged between 0.14 - 0.45 nM and 0.04 - 0.48 nM,
169 respectively. DFe profiles displayed two distinct features; i) variability in deep water
170 concentrations (elevated in July and December and lower in January and February) that are largely
171 influenced by inflow of different water masses into the SAZ (Klunder et al., 2011; Piola and
172 Gordon, 1989; Boye et al., 2012), and ii) upper water column (<200 m) concentrations that were
173 elevated in July and depleted in February. DIN profiles typically showed minimum concentrations
174 at the surface increasing with depth (Figure 2c), with higher surface concentrations in winter than

175 in summer, decreasing from 18.0 μM in July to 10.0 μM in December, followed by slight increases
176 to 12.9 and 12.1 μM in January and February, respectively (Figure 2d).

177 178 **3.2. Depth-integrated DFe inventories**

179 DFe concentrations in the upper water column were binned into 2 inventories; the euphotic
180 (integrated from surface to Z_{eu}) and aphotic inventories (integrated from Z_{eu} to depth of the winter
181 isopycnal layer), with the total upper water column inventory being the sum of these two reservoirs
182 (Supporting Information Table S1). DFe inventories were significantly lower throughout summer
183 relative to winter across all depth horizons (Figure 3a, ANOVA, $p < 0.05$). Between July and
184 February, total upper water column DFe inventories decreased from 46 ± 0 to 11 ± 2 $\mu\text{mol m}^{-2}$. A
185 similar trend was observed within the euphotic and aphotic reservoirs, which decreased from 14 ± 1
186 to 5 ± 0.1 $\mu\text{mol m}^{-2}$ and from 32 ± 1 to 7 ± 2 $\mu\text{mol m}^{-2}$, respectively. A decrease in the total upper water
187 column inventory, resulted in a DFe loss of 35 ± 2 $\mu\text{mol m}^{-2}$, of which $\sim 71\%$ was from the aphotic
188 reservoir. Between July and January, the observed decrease in euphotic and aphotic inventories,
189 resulted in DFe losses of 3 ± 1 and 13 ± 5 $\mu\text{mol m}^{-2}$, which equates to loss rates of 0.02 ± 0.01 and
190 0.08 ± 0.03 $\mu\text{mol m}^{-2} \text{ d}^{-1}$, respectively. From January to February, both euphotic and aphotic DFe
191 losses were 7 ± 0.3 and 12 ± 2 $\mu\text{mol m}^{-2}$ with loss rates of 0.20 ± 0.01 and 0.34 ± 0.06 $\mu\text{mol m}^{-2} \text{ d}^{-1}$.

192 193 **3.3. Depth-integrated DIN inventories**

194 Unlike the trends observed for DFe, DIN inventories decreased from July to January with no
195 significant changes observed between January and February across all depth horizons (Supporting
196 Information Table S1, Figure 3b, ANOVA, $p > 0.05$). Another notable difference is that total upper
197 water column inventories of DIN in December were lower than in January and February, indicative
198 of the intrusion of low macronutrient subtropical water. Henceforth this month is excluded from
199 budget calculations. Between July and January, the observed euphotic and aphotic DIN losses were
200 283 ± 90 mmol m^{-2} (loss rate of 1.8 ± 0.6 $\text{mmol m}^{-2} \text{ d}^{-1}$) and 689 ± 431 mmol m^{-2} (loss rate of 4 ± 3
201 $\text{mmol m}^{-2} \text{ d}^{-1}$), while between January and February there was euphotic accumulation of 24 ± 0.8
202 mmol m^{-2} and aphotic loss of 22 ± 14 mmol m^{-2} . A similar seasonal decrease was observed in DIN
203 inventories, and again $\sim 73\%$ of the total upper water column loss could be accounted for from the
204 aphotic layer.

205 206 **3.4. Primary productivity estimates and iron to carbon ratios**

207 Mean PP_{wc} rates (Figure 4a) were low between July and October (2.1 ± 0.05 $\text{mmol C m}^{-2} \text{ d}^{-1}$)
208 alongside deep MLD and low average light intensity (mean MLD and PAR = 119.1 m and 480.4
209 $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$; Supporting Information Figure S3). Between October and January the MLD
210 shoaled and light availability increased (mean MLD and PAR = 71.6 m and 708.8 $\mu\text{mol photons}$
211 $\text{m}^{-2} \text{ s}^{-1}$), driving increased mean PP_{wc} (10.5 ± 0.2 $\text{mmol C m}^{-2} \text{ d}^{-1}$) that reached maximum between
212 December and January, remaining similar between January and February (12.3 ± 2.1 mmol C m^{-2}
213 d^{-1}). Phytoplankton Fe:C uptake ratios were calculated based upon the DFe loss between
214 occupations and the cumulative sum of carbon gained via PP_{wc} (corrected for the number of days
215 between occupations) (Figure 4b, Supporting Information Table S1). Between July and January,
216 the total upper water column Fe:C ratio was 16 ± 3 $\mu\text{mol mol}^{-1}$, with a euphotic ratio of 3 ± 1 μmol
217 mol^{-1} . Whereas between January and February, the total upper water column ratio was 44 ± 8 μmol
218 mol^{-1} , with a euphotic ratio of 17 ± 3 $\mu\text{mol mol}^{-1}$. Between July and February, the total upper water
219 column ratio was 24 ± 2 $\mu\text{mol mol}^{-1}$, with a euphotic ratio of 7 ± 1 $\mu\text{mol mol}^{-1}$.

220

221 4. Discussion

222 The importance of iron in the SO is well established, however the relative importance of seasonal
223 iron supply and removal pathways remains poorly understood. This is primarily due to sparse data
224 coverage across the seasonal cycle and a lack of high resolution DFe profiles, which limits our
225 understanding of seasonal drivers of upper ocean Fe supply (Tagliabue et al., 2012). In this study,
226 the seasonal progression of DFe concentrations at four occupations in the SAZ (spanning multiple
227 seasons from winter through to late summer) were examined to understand processes that control
228 DFe supply/removal and demand. Vertical DFe concentrations were typically <1.0 nM, with lower
229 surface concentrations that increased with depth (Figure 2a). The winter profile was different from
230 summer in that DFe concentrations were elevated within the MLD (Figure 2b), suggesting typical
231 winter DFe supply from a deep water source (Sohrin et al., 2000; Ellwood et al., 2008). To our
232 knowledge, there is only one other winter DFe dataset reported for the Indian sector of the SO
233 (Ellwood et al., 2008), where winter values were significantly lower (42.27°S, 159.99°E; range:
234 0.08 - 0.41 nM, upper 500 m; $p < 0.05$), highlighting differences in DFe concentration between
235 ocean basins (Tagliabue et al., 2012). DFe concentrations in summer, particularly in February, are
236 in good agreement with previous values reported for the SAZ (Chever et al., 2010b, range: 0.09 -
237 0.44 nM upper 1029 m; Klunder et al., 2011, range: 0.18 - 0.46 nM upper 1253 m; Abadie et al.,
238 2017, range: 0.09 - 0.60 nM upper 1468 m). The observed seasonal changes in nutrient availability
239 within the total upper water column and the distribution of nutrient inventories within different
240 depth horizons were used to investigate possible supply and removal processes responsible for
241 observed seasonal variability.

242
243 Depth-integrated nutrient inventories from all depth horizons show that both DFe and DIN in July
244 were high, due to deep winter mixing (Figure 3a,b). Between July and February, both DFe and
245 DIN inventories in the total upper water column showed a substantial decrease that was driven
246 mainly by losses from the aphotic layer (~70%), suggesting losses through a combination of
247 vertical supply of both nutrients (through rapid recycling) in support of surface production,
248 bacterial uptake and/or DIN losses through denitrification and iron losses through scavenging. The
249 added value of multiple occupations however becomes clear when changes in inventories are
250 investigated during interim occupations (i.e., between July and January), when both nutrient
251 inventories decrease, compared to between January and February, when little change is observed
252 in DIN, but DFe is depleted in all inventories.

253
254 Focusing on changes in the euphotic nutrient inventory losses during the winter-early summer
255 transition (July to January) results in a DFe:DIN loss ratio of $9 \pm 2 \mu\text{mol mol}^{-1}$, which when
256 assuming a Redfield C:N ratio of 6.6, equates to an Fe:C uptake ratio of $1.4 \pm 0.4 \mu\text{mol mol}^{-1}$, which
257 is similar to the euphotic zone PP estimated Fe:C ratio of $2.8 \pm 1 \mu\text{mol mol}^{-1}$. Assuming an average
258 Chl:C ratio $0.02 \text{ mg Chl mg C}^{-1}$ (Thomalla et al., 2017b), converting and integrating the colocated
259 glider derived chlorophyll into phytoplankton carbon (C_{phyto}), the calculated euphotic Fe:C ratio
260 of $0.4 \pm 0.2 \mu\text{mol mol}^{-1}$ is lower than the estimated ratios above (Supporting Information Figures
261 S4 and S5, Table S3). However, all of these values agree well with ratios reported in the literature
262 (mean = $4.6 \pm 4.6 \mu\text{mol mol}^{-1}$, range = 0.29 - 25.00; Supporting Information Table S2). Furthermore,
263 within the total upper water column, the estimated Fe:C ratio ($16 \pm 3 \mu\text{mol mol}^{-1}$) from PP falls
264 within the range reported in literature, suggesting that the observed DFe loss (from "winter reserve
265 stock") during the first half of growing season is predominantly in support of phytoplankton

266 growth. However since the ratio falls above the mean literature value, other loss processes (i.e.
267 scavenging) may also be at play.

268
269 In contrast, progressing further into late summer (January to February), a continual decrease in
270 DFe inventories from both reservoirs was observed, with little change observed in DIN, despite
271 continued PP (Figures 3a,b). An absence of change in DIN inventories suggests a re-supply of DIN
272 through remineralization processes, which would imply a similar DFe supply, to sustain the
273 observed production (Boyd et al., 2017; Bowie et al., 2001). Although Fe:C uptake ratios of 17 ± 3
274 $\mu\text{mol mol}^{-1}$ from the euphotic zone fall within the reported literature range, loss from the total
275 upper water column results in Fe:C ratio of $44 \pm 8 \mu\text{mol mol}^{-1}$, that is outside the likely range of
276 biological uptake in the presence of only 0.1 - 0.2 nM DFe concentrations. These results suggest
277 that in addition to biological Fe consumption within the euphotic zone, colloidal Fe aggregation
278 and scavenging onto sinking particles are most likely driving the observed loss of DFe from the
279 aphotic. To examine if colloidal aggregation and scavenging are the primary loss mechanisms
280 between January and February, aphotic DFe loss rates were used as a proxy for scavenging, in the
281 absence of particulate iron (PFe) flux rates. The observed euphotic and aphotic DFe loss rates of
282 0.20 ± 0.01 and $0.34 \pm 0.06 \mu\text{mol m}^{-2} \text{d}^{-1}$ are consistent with other scavenging rates that are better
283 defined by downward PFe export fluxes (Bowie et al., 2009, 0.17 ± 0.09 and $0.21 \pm 0.05 \mu\text{mol m}^{-2}$
284 d^{-1} ; mixed layers 53 and 70 m; Frew et al., 2006, 0.22 ± 0.03 and $0.55 \pm 0.06 \mu\text{mol m}^{-2} \text{d}^{-1}$, mixed
285 layers 80 and 120 m). Furthermore, the total upper water column Fe:C loss ratio is consistent with
286 previously reported Fe:C export ratios (given the significant ranges) in the SAZ from sediment
287 traps (Bowie et al., 2009: $50 \pm 38 - 248 \pm 125 \mu\text{mol mol}^{-1}$; Frew et al., 2006: $167 - 218 \mu\text{mol mol}^{-1}$).
288 It should be noted however that these Fe:C export ratios will include a lithogenic component and
289 as such are expected to be higher than our estimated uptake ratios.

290
291 Overall, estimated Fe:C uptake ratios and DFe loss rates seem to agree that the dominant loss
292 process for Fe in early summer (July - January) within the euphotic and total upper water column
293 is most likely driven by biological uptake, in comparison to late summer (January - February)
294 where the dominant processes are both biological consumption in the euphotic zone and
295 scavenging in the aphotic zone. The lack of change in DIN and depletion of DFe inventories during
296 late summer combined with continual growth, suggests that the system is supported by rapidly
297 recycled nutrients, in accordance with previous studies (Strzepek et al., 2005; Boyd et al., 2012;
298 2017; 2005; Tagliabue et al., 2014; Bowie et al., 2001). However, the observed emergence of a
299 distinct subsurface bloom below the mixed layer that persists throughout January (Supporting
300 Information Figure S1c) implies an insufficient DFe supply within the mixed layer to sustain
301 phytoplankton growth. These findings are corroborated by concurrent iron addition incubation
302 experiments from the mixed layer (Ryan-Keogh et al., 2018a), which show maximum increases in
303 photosynthetic efficiency and net chlorophyll growth rates following iron addition in January and
304 February, compared to December (no response). A transient MLD deepening event in February
305 that was linked to an increase in wind stress (Ryan-Keogh et al., 2018a), led to a subsequent
306 increase in phytoplankton biomass throughout the MLD (Supporting Information Figure S1c),
307 suggesting that storms may nonetheless play a role in entraining subsurface DFe and DIN in
308 support of surface water production utilising regenerated nitrogen (Nicholson et al., 2016, Ryan-
309 Keogh et al., 2018a). Unfortunately, monthly-scale sampling of DFe profiles is insufficient to
310 capture specific synoptic events that contribute to the seasonal progression of DFe supply and
311 removal e.g. i) the intrusion of subtropical waters linked to Agulhas eddies in the SAZ, which can

312 deliver Fe-rich, low macronutrient waters (Chever et al., 2010b), and ii) wind induced mixed layer
313 deepening events (e.g. in early-February). Future studies must therefore sample at a greater
314 frequency in line with the timescales of these synoptic events, in order to better capture the full
315 range of seasonal drivers of Fe-pool supply and demand.

316 317 **5. Summary**

318 This study examined the seasonal evolution of DFe relative to DIN within the upper water column,
319 exploring different mechanisms driving seasonal changes in DFe. This was achieved through
320 seasonal-scale observations of DFe profiles at a single station located in the SAZ of the south
321 Atlantic SO. Results show a progressive seasonal decrease in DFe inventories from July to
322 February in all depth horizons, while DIN decreases from July to January with no significant
323 change from January to February. During late summer (January to February), a temporal decrease
324 of DFe within both euphotic and aphotic reservoirs relative to DIN inventories suggests that the
325 processes that drive DFe loss are Fe specific. We propose that; i) in July, deep convective mixing
326 replenishes the mixed layer driving high Fe inventories. ii) This total upper water column reservoir
327 (both euphotic and aphotic) declines between July and January, due to biological Fe consumption
328 in support of phytoplankton growth (supported by Fe:C uptake ratios that fall within the reported
329 literature range). iii) During late summer (January to February), in addition to biological uptake in
330 the euphotic layer, the high Fe:C uptake ratio within the total upper water column and the observed
331 euphotic and aphotic zone DFe loss rates, suggests that aggregation of colloidal Fe and scavenging
332 onto settling particles are the dominant drivers of the observed Fe signal, with PP in the euphotic
333 layer likely supported by recycling and possible event-scale entrainment of nutrients.

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533

534 **Figure 1:** Map of (a) absolute dynamic topography (m) showing process station location and glider
535 position, with the position of sub-tropical front (STF) and sub-Antarctic front (SAF) as determined
536 by MADT gradients (Swart et al., 2010) from the CLS-AVISO product (Rio et al., 2011) and (b)
537 TS plot made from colocated (temporally and spatially) glider profiles (0 -1000 m) from each
538 occupancy indicating the presence of Antarctic intermediate water (AAIW) and sub-Antarctic
539 surface water (SASW).

540

541 **Figure 2:** Vertical profiles of (a) DFe (nM) with \pm standard deviation, (b) insert of upper water
542 column DFe concentrations, (c) vertical profiles of DIN (μ M) and (d) insert of upper water column
543 DIN concentrations.

544

545 **Figure 3:** Plots of the mean depth-integrated (a) DFe (μ mol m^{-2}) and (b) DIN (mmol m^{-2})
546 inventories with \pm standard deviations, between total, aphotic and euphotic reservoirs.

547

548 **Figure 4:** Plots of (a) the time series of PP_{wc} derived from glider chlorophyll concentrations from
549 the surface, mixed layer (MLD) and euphotic zone ($mol\ C\ m^{-2}\ d^{-1}$) and (b) estimates of Fe:C ratios
550 (μ mol mol^{-1}) for total and euphotic reservoirs over the season.

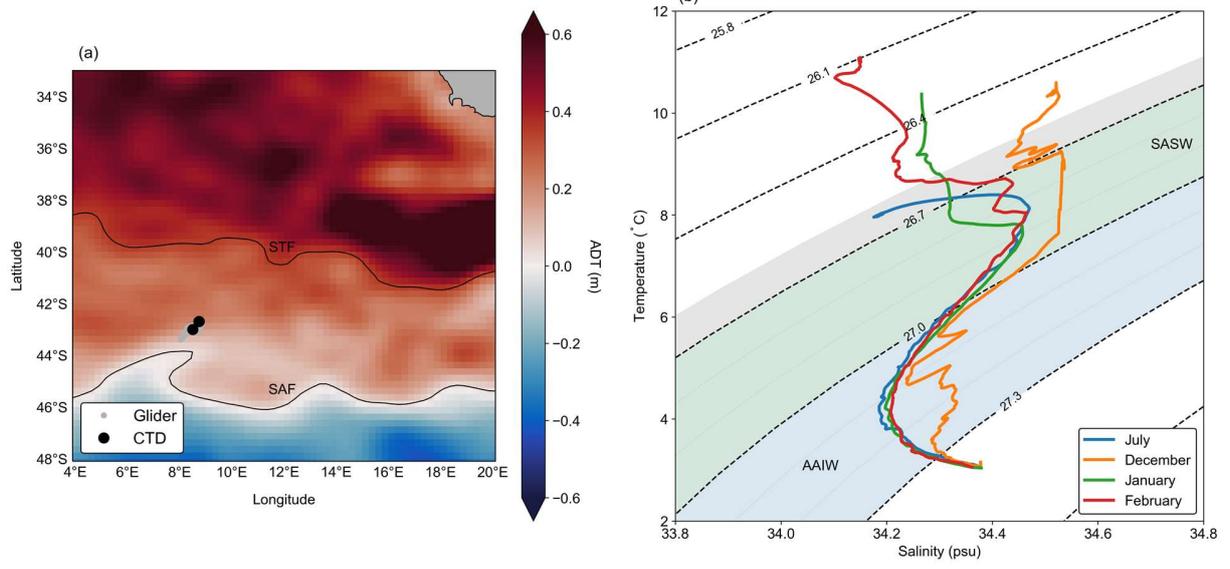


Figure 1

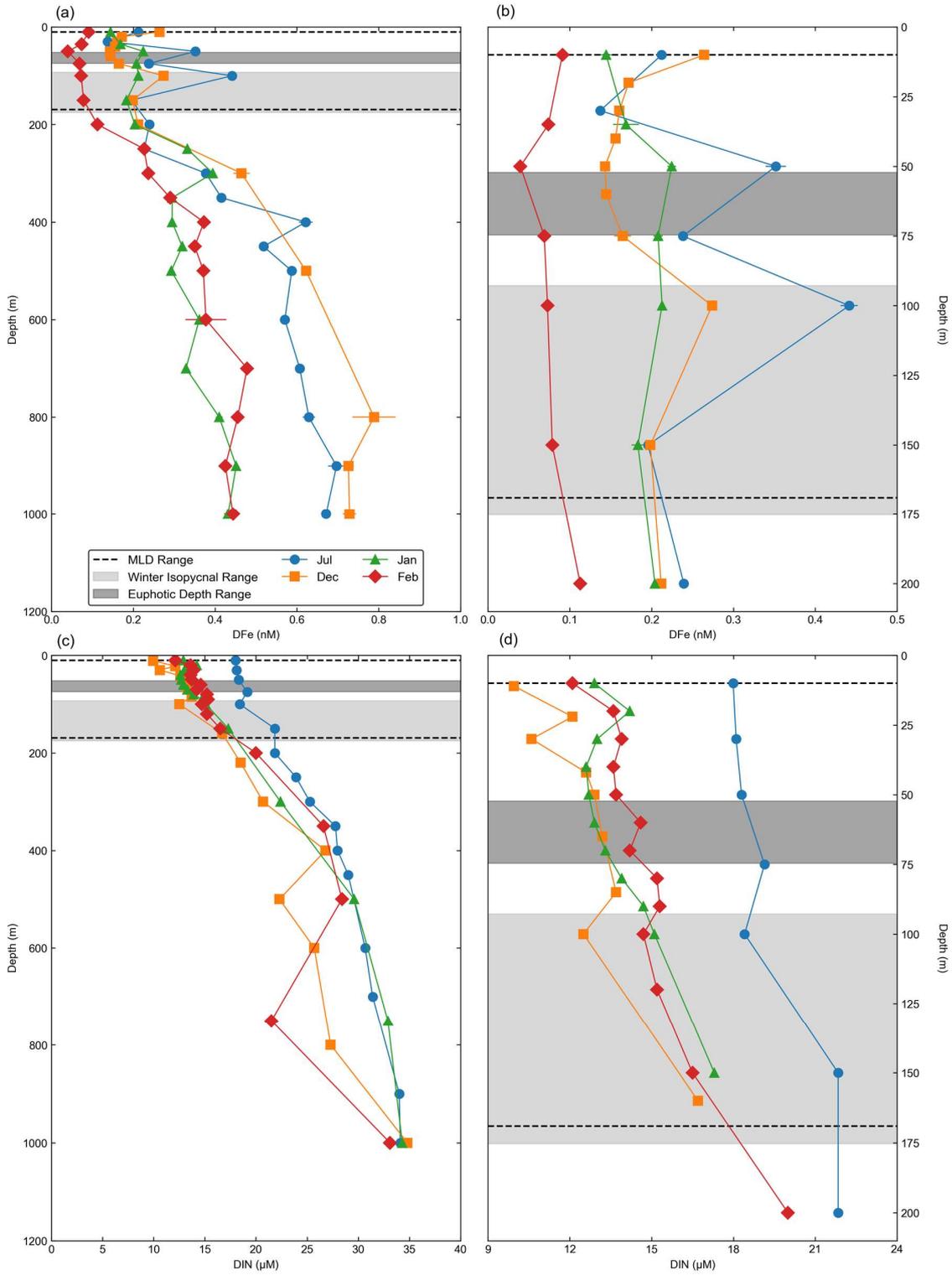


Figure 2

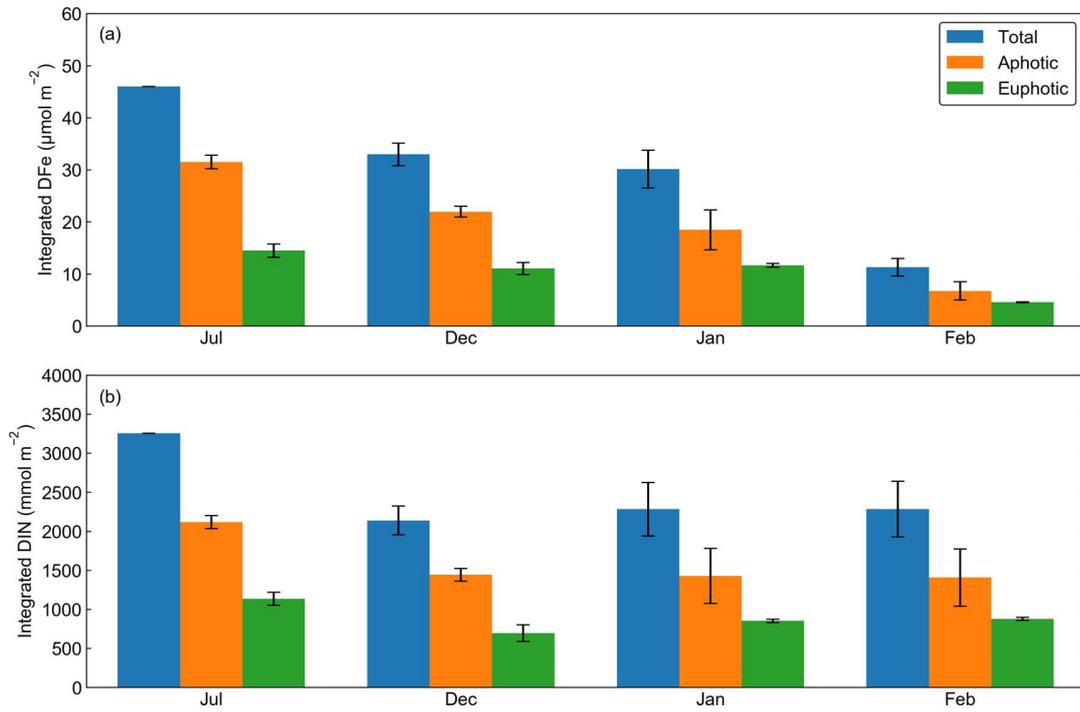


Figure 3

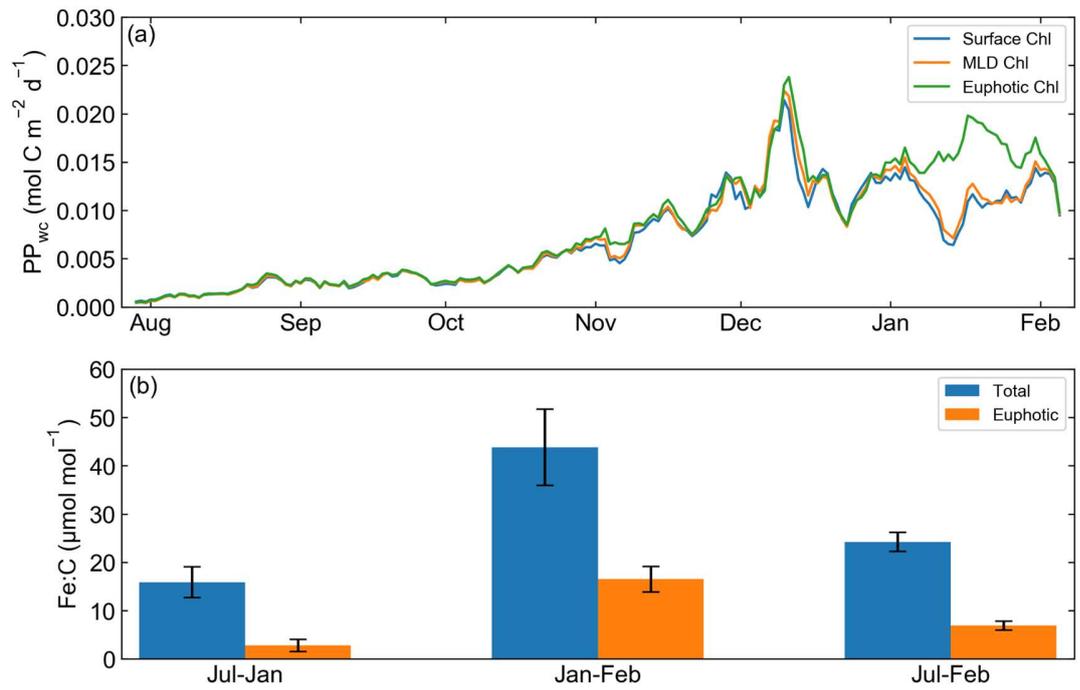


Figure 4