Manganese Limitation of Phytoplankton Physiology and Productivity in the Southern Ocean

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Abstract

Although iron and light are understood to regulate the Southern Ocean biological carbon pump, observations have also indicated a possible role for manganese. Low concentrations in Southern Ocean surface waters suggest manganese limitation is possible, but its spatial extent remains poorly constrained and direct manganese limitation of the marine carbon cycle has been neglected by ocean models. Here, using available observations, we develop a new global biogeochemical model and find that phytoplankton in over half of the Southern Ocean cannot attain maximal growth rates because of manganese deficiency. Manganese limitation is most extensive in austral spring and depends on phytoplankton traits related to the size of photosynthetic antennae and the inhibition of manganese uptake by high zinc in Antarctic waters. Importantly, manganese limitation expands under the increased iron supply of past glacial periods, reducing the response of the biological carbon pump. Overall, these model experiments describe a mosaic of controls on Southern Ocean productivity that emerge from the interplay of light, iron, manganese and zinc, shaping the evolution of Antarctic phytoplankton since the opening of the Drake Passage.

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12 Key Points:

- Mn scarcity in the Southern Ocean limits phytoplankton growth in a global
 biogeochemical model, especially during austral spring.
- The spatial extent of Mn limitation is sensitive to phytoplankton traits governing
 photophysiology and metal homeostasis.
- Greater dust deposition to the Southern Ocean expands the role of Mn limitation and
 restricts carbon export resulting from Fe fertilization.
- 19

20 Abstract

- 21 Although iron and light are understood to regulate the Southern Ocean biological carbon pump,
- 22 observations have also indicated a possible role for manganese. Low concentrations in Southern
- 23 Ocean surface waters suggest manganese limitation is possible, but its spatial extent remains
- 24 poorly constrained and direct manganese limitation of the marine carbon cycle has been
- 25 neglected by ocean models. Here, using available observations, we develop a new global
- 26 biogeochemical model and find that phytoplankton in over half of the Southern Ocean cannot
- attain maximal growth rates because of manganese deficiency. Manganese limitation is most
- extensive in austral spring and depends on phytoplankton traits related to the size of
- 29 photosynthetic antennae and the inhibition of manganese uptake by high zinc in Antarctic waters.
- 30 Importantly, manganese limitation expands under the increased iron supply of past glacial 31 periods, reducing the response of the biological carbon pump. Overall, these model experiments
- describe a mosaic of controls on Southern Ocean productivity that emerge from the interplay of
- 32 light, iron, manganese and zinc, shaping the evolution of Antarctic phytoplankton since the
- 34 opening of the Drake Passage.
- 35

36 Plain Language Summary

37 Because of the Southern Ocean's unique role in ocean circulation, Antarctic phytoplankton

profoundly influence the global carbon cycle. For instance, an increase in the supply of iron – the

39 main nutrient limiting Antarctic phytoplankton – is thought to have lowered CO₂ during past ice

40 ages by increasing phytoplankton photosynthesis. However, the potential for other essential

elements to limit Southern Ocean productivity is not well known. By accounting for

42 requirements of several nutrients in a global model, we have identified that manganese, an

- 43 essential cofactor in photosynthesis, can limit phytoplankton growth across the Southern Ocean.
- 44 The enduring role of manganese deficiency will likely influence the response of Southern Ocean
- 45 ecosystems to ongoing climate change.

47 **1 Introduction**

48 The persistent outgassing of CO₂ from the Southern Ocean to the atmosphere contributes

49 to the warm interglacial climate of the Holocene (Sarmiento & Toggweiler, 1984; Sigman et al.,

- 50 2010; Sigman & Boyle, 2000). South of the Polar Front, deep circumpolar water masses upwell
- 51 into the surface mixed layer, ventilating the deep ocean carbon reservoir and enriching surface
- 52 waters with high concentrations of the macronutrients nitrate, phosphate, and silicate (Martin,

53 1990; Sarmiento et al., 2004). Consumption of these macronutrients in support of phytoplankton

54 carbon fixation and the export of biomass to the deep ocean by the biological carbon pump can

⁴⁶

55	compensate for the leak of upwelled CO ₂ out of the ocean (Sigman et al., 2010), but only if
56	environmental conditions (light, temperature) permit growth and essential micronutrients, such
57	as iron (Fe), are in sufficient supply (Martin et al., 1990; Martínez-García et al., 2014).
58	Outside of the light-limited period around winter, Fe is considered to be the major factor
59	shaping phytoplankton growth in the Southern Ocean spring and summer (Boyd, 2002;
60	Tagliabue et al., 2014). Phytoplankton primarily need Fe for their photosynthetic apparatus,
61	especially photosystem I (PSI), which contains up to six-fold more Fe than photosystem II (PSII)
62	(Raven, 1990; Strzepek & Harrison, 2004). Accordingly, phytoplankton tend to adapt to Fe
63	limitation with elevated PSII:PSI ratios, which economizes Fe use (Strzepek & Harrison, 2004)
64	(although this response is surprisingly muted in Southern Ocean lineages (Strzepek et al., 2019)).
65	The primary production that underpins Southern Ocean ecosystems relies on deep winter mixing
66	to supply dissolved iron (dFe) to the euphotic zone, supplemented by additional sources from
67	dust, continental margins and the cryosphere (Tagliabue et al., 2014, 2017). In this context,
68	increases in iron supply from dust during glacial periods is postulated to alleviate phytoplankton
69	Fe limitation, enhancing both macronutrient utilisation and carbon export in the Southern Ocean
70	and reducing atmospheric CO ₂ (Jaccard et al., 2013; Martin, 1990; Martínez-García et al., 2014;
71	Sigman et al., 2010).

The use of Fe in the photosynthetic apparatus occurs alongside manganese (Mn), an essential component of the Mn₄O₅Ca oxygen-evolving complex of photosystem II (Raven, 1990). Phytoplankton Mn requirements are also driven by use of Mn as a cofactor in superoxide dismutase, arginase, and other metalloenzymes (Peers & Price, 2004; Twining & Baines, 2013), but uptake of Mn from seawater is complicated by the poor selectivity of phytoplankton metal transporters for Mn²⁺ in the presence of similar concentrations of Zn²⁺, Cu²⁺, and Cd²⁺ (Sunda &

Huntsman, 1996, 1998b, 2000). This is consistent with predictions from the Irving-Williams
Series, the periodic trend of increasing divalent metal-binding affinity of organic molecules
following the order $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ (Irving & Williams, 1953), which
shapes metal metabolism and physiology in all domains of life (Waldron & Robinson, 2009).
Below the euphotic zone, heterotrophic bacteria oxidize soluble Mn^{2+} to insoluble $Mn(III/IV)$
oxides, which accumulate in seafloor sediments (Johnson et al., 1996; Sunda & Huntsman,
1988), leading to low dissolved Mn (dMn, ~ 0.3 nM) at depth compared to concentrations of 1–5
nM found in the surface of oligotrophic gyres (Boyle et al., 2005; Hatta et al., 2015; Hulten et al.,
2017; Johnson et al., 1996; Landing & Bruland, 1987).
Mn-poor water masses in the deep ocean are primarily ventilated in the Southern Ocean.
Relative to other Fe-limited regions where Mn supply is greater, the first reports of dMn in the
Southern Ocean emphasized unusually low concentrations, proposing the potential for Mn co-
limitation alongside Fe (Martin et al., 1990). More recent surveys have confirmed that dMn in
both the Antarctic and Subantarctic zones can be < 0.05 nM, the lowest measured globally
(Browning et al., 2014; Latour et al., 2021; Middag et al., 2011, 2013). The Antarctic Zone south
of the Polar Front also features Zn^{2+} concentrations that are 100 to 1000 fold higher than
temperate and tropical regions (Baars & Croot, 2011), which should depress algal Mn uptake via
competition for membrane transporters. Indeed, recent experiments have indicated that Mn can
be the primary limiting nutrient to phytoplankton growth in the Drake Passage (Browning et al.,
2021) and the Ross Sea (Wu et al., 2019), supporting prior suggestions of Mn limitation in the
Southern Ocean (Browning et al., 2014; Buma et al., 1991; Martin et al., 1990). Despite this
emerging evidence, the scale of Mn limitation across the Southern Ocean is undefined. Global
models that have appraised Mn cycling have not considered growth limitation terms (Hulten et

101 al., 2017; Richon & Tagliabue, 2021) and simple, observation-based models that advocate for the possibility for Mn limitation in this region (Browning et al., 2021; Moore, 2016) have not 102 accounted for the interplay of ocean circulation and mixing, phytoplankton physiology, and 103 metal sources, sinks, and recycling pathways needed to simulate Southern Ocean 104 biogeochemistry in an integrated manner. Overall, this limits our understanding of how Mn 105 106 scarcity may impact phytoplankton growth and the strength of the biological carbon pump at large scales, particularly during fluctuations in Fe supply across seasons or during past or future 107 changes in climate. 108

109 Here, we incorporate phytoplankton Mn uptake and Mn requirements into a coupled global ocean physics-biogeochemistry model to assess the global impact of Mn limitation for the 110 first time. Our simulations explicitly represent a range of mechanistic processes, including 111 external inputs and internal cycling of Mn, alongside the biogeochemical cycles of carbon, 112 nitrogen, phosphorus, silicon, and iron. Our model results highlight a widespread impact of Mn 113 114 on phytoplankton growth that is most intense during the austral spring and underpinned by key phytoplankton traits governing light and resource acquisition. Moreover, additional simulations 115 using reconstructions of dust supply of both Fe and Mn during the Last Glacial Maximum period 116 117 demonstrate how the scale of Mn limitation is sufficient to impact the response of Southern Ocean productivity and the carbon cycle. Ultimately, relief of Fe limitation in the Southern 118 119 Ocean is compensated by an expansion of Mn limitation, an interplay that has likely driven the 120 evolution of polar phytoplankton over millions of years.

121 2 Materials and Methods

122 2.1 Biogeochemical cycles of Zn and Mn in the PISCES-BYONIC model

123

The PISCES-BYONIC model is based on PISCES-v2 (Aumont et al., 2015), with the

addition of global cycles of the micronutrients Mn, Zn, Cu and Co (Hulten et al., 2017; Richon & 124 Tagliabue, 2019, 2021; Tagliabue et al., 2018). The Fe cycle in PISCES-v2 has also been 125 modified to allow regulation reducing Fe uptake rate in nitrogen-limiting conditions, consistent 126 with recent measurements (Twining et al., 2020). This study adds equations representing 127 phytoplankton Mn uptake and Mn growth requirements to the PISCES-BYONIC model. The 128 129 modifications are described in detal below. Full details of the PISCES-v2 model can be found in Aumont et al. (Aumont et al., 2015) and equations governing the Mn and Zn biogeochemical 130 cycles are fully described in the Supplementary Information of Richon and Tagliabue (Richon & 131 132 Tagliabue, 2021). Briefly, the Mn model accounts for sources of Mn from atmospheric deposition, rivers, marine sediments, and hydrothermal vents. Mn in dust is assumed to be 25% 133 soluble and the sediment supply is enhanced at both low oxygen and at higher organic carbon 134 flux. In the model, Mn is removed from the ocean by bacterially-catalyzed precipitation of Mn 135 oxides, which sink to the seafloor. Rates of bacterial scavenging of dMn increase with increasing 136 temperature (Richon & Tagliabue, 2021; Tagliabue et al., 2018) but decrease when dMn falls 137 below a threshold concentration, which is important for replicating the residual dMn inventory in 138 the deep ocean (Hulten et al., 2017). High light and low oxygen also decrease the rate of Mn 139 140 scavenging and enable the dissolution of Mn oxides, most notably in the illuminated surface mixed layer and in low oxygen water masses in the tropics, respectively. Compared to Mn, the 141 Zn cycle in the model is less influenced by external sources (dust and riverine input) and more 142 143 by internal recycling mechanisms, including biological uptake and regeneration, as well as reversible scavenging onto particulate organic carbon (Weber et al., 2018). Bioavailable Zn is 144 145 calculated by equilibrium with a single ligand at a fixed concentration of 1 nM. A small fraction 146 of Zn uptake is also allocated to diatom frustules, and cycles in parallel to Si in the model

- 147 (Weber et al., 2018). Modelled Mn and Zn cycles in PISCES-BYONIC reproduce the major
- 148 features of their oceanic distributions (Richon & Tagliabue, 2021; see also Figs. S1, S2).

2.2 The minimum Mn requirement

Minimum phytoplankton requirements for Mn are defined by a manganese use efficiency (MnUE), whereby increasing Mn is needed to support increasing growth rates (Raven, 1990). The MnUE represents the rate that carbon biomass can be produced per catalytic Mn atom, having units of mol C day⁻¹ (mol Mn)⁻¹, and is described by:

154
$$MnUE_i = \frac{\mu_i}{Q_{Mn,Req}} \tag{1}$$

Where μ is the specific growth rate (day⁻¹) and Q_{Mn,Req} is the required quota, the amount needed to power photosynthesis and basal metabolism (units of mol Mn (mol C)⁻¹). The subscript *i* reflects separate calculations for diatom and nanophytoplankton functional types in the model. Q_{Mn,Req} is calculated as:

159
$$Q_{Mn,Req} = Q_{Mn,min} + 4 * \frac{Chl:C}{Chl:PSII}$$
(2)

Approximating growth of the cultured open ocean diatom *Thalassiosira oceanica* (Sunda, 1989; 160 Sunda & Huntsman, 1983, 1986), Q_{Mn,min} is set to 1 µmol Mn : mol C at a reference growth rate 161 of 1 day⁻¹, equal to an MnUE of 10⁶ mol C (mol Mn)⁻¹ day⁻¹; see Table 1. Conceptually this basal 162 163 requirement accounts for Mn metalloenzymes such as Mn superoxide dismutase, arginase, carbonic anhydrase, among others (Jensen et al., 2019; McCain et al., 2021; Peers & Price, 2004; 164 Twining & Baines, 2013). While it is likely that each of these Mn enzymes are uniquely 165 regulated based on intracellular or extracellular conditions, the scope and extent of this 166 regulation is poorly defined at present. We consider the constant non-photosynthetic Mn 167 requirement to be a relatively conservative approach that appears consistent with the observation 168 of increasing Mn requirements with increasing growth rate described by Sunda and Huntsman 169

- 170 (Sunda & Huntsman, 1998b), as well as more general theories of nutrient limitation (Droop,
- 171 1973; Raven, 1988).
- 172 Table 1. Model parameters added to the PISCES-BYONIC model for this study. The parameter
 - values are assigned following laboratory and field observations where possible. Parameters describing the
 Mn sources and sinks can be found in Richon and Tagliabue (2021)

till bouloes and	i binns can e		lion and Tagnadue (2021)	
Parameter	Value	Units	Description	Reference
Q _{Mn,min}	1.0	µmol mol ⁻¹	Mn requirement not associated	(Sunda, 1989; Sunda &
			with photosynthesis	Huntsman, 1986, 1996, 1998b)
Chl:PSII	1000	mol mol ⁻¹	Photosynthetic antennae size	Table S1
K _{Mn, nano}	5 x 10 ⁸	M-1	Binding constant for Mn' to	(Sunda & Huntsman, 2000)
K _{Mn} , diatom	1.67 x 10 ⁸		Mn transporter	
K _{Zn,a}	5 x 10 ⁸	M ⁻¹	Binding constant for Zn' to	(Sunda & Huntsman, 2000)
			Mn transporter	
KZn,b nano	1 x 10 ⁹	M ⁻¹	Binding constant for Zn' to the	(Sunda & Huntsman, 2000)
KZn,b diatom	0.33 x 10 ⁹		high affinity Zn transporter	
Q'Mn,max	6	µmol mol ⁻¹	Maximum Mn quota	SXRF Observations (Figure 2)
Q'Zn,max, nano	30	µmol mol ⁻¹	Maximum Zn quota	SXRF Observations (Figure 2)
Q'Zn,max, diatom	40			

The photosynthetic component of the Mn requirement is dictated by a dynamic 176 177 chlorophyll scheme already simulated in PISCES-v2 (Aumont et al., 2015), originally based on the photoacclimation model of Geider et al. (1997). The Mn quota associated with PSII is 178 calculated from the simulated Chl: C ratio by applying a fixed antennae size, represented as a 179 180 Chlorophyll: PSII ratio (Chl: PSII), and a stoichiometry of 4 Mn atoms per PSII (Raven, 1990). The standard model uses a Chl: PSII ratio of 1000 to simulate the global characteristics of 181 diatom and nanophytoplankton functional types. This value is in the upper end of the range of 182 both field and culture observations (Table S1), with the exception of recent characterizations of 183 Southern Ocean phytoplankton (Strzepek et al., 2019). It should be noted that phytoplankton Fe 184 limitation can lead to an uncoupling of the Chl antennae from the photosynthetic apparatus, 185 giving rise to large apparent Chl: PSII ratios that do not represent functional antennae-186 photosystem complexes (Behrenfeld & Milligan, 2013). This process is not included in the Chl 187 188 parameterisation scheme, and thus we chose the intermediate Chl: PSII ratio of 1000 to reflect

189	the functional antennae size in the model. To ensure that this scheme was not overestimating Mn
190	limitation for Southern Ocean phytoplankton, we calculated the Mn requirements inferred from
191	the photo-physiological data of Strzepek et al. (2019) (Figure 1). PSII Use Efficiencies from that
192	work (units: mol C (mol PSII) ⁻¹ day ⁻¹) were converted to Mn units via the Mn : PSII ratio (i.e. a
193	value of 4). Averaging across the 3 Southern Ocean phytoplankton characterized in that study,
194	grown at low irradiance under both low and high Fe availability, a relatively narrow range of
195	photosynthetic Mn requirement is predicted: $2.85 \pm 0.53 \ \mu mol \ Mn$: mol C at a reference growth
196	rate of 1 day ⁻¹ (note that, per Eq. 1, this value decreases as growth rate decreases). We compared
197	this to our model by applying the maximum Chl : C ratio of the diatom functional type (0.05 g
198	Chl (g C) ⁻¹ or 673 µmol Chl : mol C, assuming a molar mass of 891 amu for chlorophyll a
199	(Aumont et al., 2015)), the default antennae size of 1000, and the Mn:PSII ratio of 4. This
200	calculation results in a photosynthetic Mn requirement equal to 2.69 μ mol Mn : mol C (Fig. 1),
201	within the range of expected photosynthetic Mn requirements calculated from Southern Ocean
202	diatoms (Strzepek et al., 2019). Applying the larger Chl : PSII ratio of 2000, decreases this
203	requirement to 1.35 μ mol Mn : mol C, which appears to underestimate photosynthetic Mn
204	requirements for these isolates (Fig. 1).

$$\mu_{Mn,i} = MnUE_i * Q_{Mn,i} \tag{3}$$

In the model, the MnUE constrains phytoplankton growth rate, calculated as:

where Q_{Mn} is the realized Mn:C ratio, set by dMn and other parameters influencing Mn uptake (see next section). Mn limitation of phytoplankton growth emerges when the Mn-constrained growth rate falls below the background growth rate (i.e. $\mu_{Mn} < \mu$), the latter governed by light, temperature, iron, nitrogen, phosphorus and silica (for diatoms). The overall strength of Mnlimitation (dimensionless) is:

212
$$lim_{Mn,i} = \min\left(1, \frac{\mu_{Mn,i}}{\mu_i}\right) \tag{4}$$

213 while a state of Mn-deficiency is analogously calculated as:

214
$$def_{Mn,i} = \min\left(1, \frac{\mu_{Mn,i}}{\mu_{light,i}}\right)$$
(5)

where the light-limited growth rate (μ_{light}) reflects growth when other potentially limiting

216 nutrients, most notably Fe, are replete. The maximum required Mn quota associated with the

217 light-limited growth rate, Q_{MnReq,max}, can be calculated by substitution into Eq. 1.



218 219

220 Figure 1. Estimated photosynthetic Mn:C requirements of three Southern Ocean phytoplankton isolates, 221 the temperate diatom *T. oceanica*, and the diatom phytoplankton class in the PISCES-BYONIC model. 222 Estimates from culture experiments are based on the PSII Use Efficiency of Strzepek et al. (2019), which were conducted under low-light conditions – where the photosynthetic apparatus is expected to be 223 224 maximally upregulated – and under both high and low Fe availability (open and closed circles, respectively). The PSII Use Efficiency (units: mol C day⁻¹ (mol PSII)⁻¹) is converted to Mn:C by applying 225 1) a reference growth rate of 1 day⁻¹, which normalizes across species-specific maximum growth rates, 226 and 2) an Mn PSII⁻¹ stoichiometry of 4. Model values (horizontal lines) reflect maximally upregulated 227 Chl:C for the diatom class (0.05 g g⁻¹) converted to Mn:C units with variable Chl : PSII ratios. This 228 229 comparison suggests that the default Chl: PSII ratio of 1000 in the PISCES-BYONIC model is the best descriptor of these measurements, given the parametrization of Chl regulation, photosynthesis, and 230 growth rates in the model. Note that higher reported Chl : PSII in Strzepek et al. (2019) (~2000:1) leads to 231 a much higher Chl:C ratio than is simulated in the phytoplankton functional types represented in this 232 global biogeochemical model. 233

235 **2.2 Phytoplankton Mn uptake**

236 Manganese uptake in both phytoplankton classes follows standard Michaelis-Menten 237 kientics, modified to account for competetive inhibition due to Zn^{2+} .

238
$$\rho_{Mn,i} = V_{max,Mn} * \left(\frac{K_{Mn}[Mn']}{K_{Zn,a}[Zn'] + K_{Mn}[Mn'] + 1} \right)$$
(6)

where K_{Mn} represents the equilibrium binding affinity of the manganese transporter to Mn and K_{Zn,a} represents the affinity of Zn' to the same transporter. The maximum uptake rate, V_{max}, represents the number of transporter sites and a characteristic transport time. To reflect changes in the number of transporter sites, V_{max} is represented by the equation:

243
$$V_{max,Mn} = Q_{Mn_max,i} * \mu_{max,i} * R_{up,Mn} * R_{down,Mn} * R_{Zn}$$
(7)

where a maximum uptake rate, defined as the product of the maximum quota, Q_{Mn max,i}, and the 244 maximum growth rate is modulated by three physiological regulation terms: 1) R_{up}, transporter 245 upregulation in response to low Q_{Mn}, 2) R_{down}, transporter downregulation in response to high 246 Q_{Mn}, and 3) R_{Zn}, transporter downregulation in response to hyperaccumulation of internal Zn. 247 Each of these behaviors have been observed in the open ocean diatom T. oceanica (Sunda & 248 249 Huntsman, 1983, 1986, 2000), but corresponding experiments have not been performed for 250 Antarctic species thus far. In the standard model, R_{Zn} is set equal to 1, which indicates no downregulation of Mn uptake in response to high Q_{Zn} . It is important to note that this confers an 251 252 adaptive advantage to the modelled diatoms beyond that observed in T. oceanica and coastal species (Sunda & Huntsman, 1996, 1998a, 1998b, 2000). For simplicity, we have not accounted 253 for similar competitive inhibition by Cu²⁺ and Cd²⁺ because concentrations of these ions in the 254 Southern Ocean do not appear high enough to influence Mn uptake, in contrast to Zn^{2+} (Baars et 255 al., 2014; Baars & Croot, 2011; Heller & Croot, 2015). We expect that this omission may 256 slightly underestimate the impact of Mn limitation in the Antarctic zone. 257

The Mn maximum quota is adjusted from its prescribed value (Table 1) as a function of Mn requirements ($Q_{Mn,Req}$) and the fractional nitrogen limitation term (*Nlim;* range 0 – 1):

260
$$Q_{Mn_max,i} = Q_{Mn,Req} + \left(Q'_{Mn_max,i} - Q_{Mn,Req}\right) * Nlim$$
(8)

261 We note that this modification improves comparisons with Single Cell X-Ray Fluorescence

262 (SXRF) measurements of Mn quotas, which are low in oligotrophic regions despite high

dissolved Mn availability (Figures 2, S3). An equivalent change to $Q_{Fe_max,i}$ is also implemented,

which is also advocated by SXRF dataset (Twining et al., 2020).



265

Figure 2. Comparison of phytoplankton Mn, Zn and Fe quotas from three oceanic regions measured by
 SXRF. For SXRF measurements, horizontal lines represent the dataset median value, box dimensions
 represent 25th and 75th quartiles, and whiskers cover the 10th and 90th percentiles. Black symbols indicate
 5th and 95th percentiles. Data sources and number of cells analyzed are listed in Table S2.

270

271

The upregulation function, R_{up,Mn}, is defined, as for Fe in the original PISCES-v2 code:

272
$$R_{up} = 4 - 4.5 \left(\frac{\min(1, lim_{Mn})}{0.5 + \min(1, lim_{Mn})} \right)$$
(9)

and permits a maximum 4-fold upregulation when growth is strongly limited by Mn. The down-

274 regulation function, R_{down,Mn}, is parallels that for Fe in PISCES-v2:

275
$$R_{down} = \max\left(0, \frac{1 - f_{max,Mn}}{1.05 - f_{max,Mn}}\right)$$
(10)

where:

277
$$f_{max,Mn} = \frac{Q_{Mn,i}}{Q_{Mn_max,i}}$$
(11)

So that the uptake rate decreases as the ratio of Q_{Mn} to the maximum quota, Q_{Mn_max} , approaches a value of 1, avoiding build-up of cellular Mn above Q_{Mn_max} .

280 The Zn downregulation effect, R_{down,Zn}, is defined similarly to R_{down,Mn}, following the 281 equation:

282
$$R_{Zn} = \max\left(0.1, \frac{1 - f_{max,Zn}}{1.05 - f_{max,Zn}}\right)$$
(12)

where:

284
$$f_{max,Zn} = \frac{Q_{Zn,i}}{Q_{Zn_{max,i}}}$$
(13)

except that the minimum downregulation by R_{Zn} is set to 0.1 (instead of 0 for R_{down}), which avoids a complete shutdown of Mn uptake at high Zn^{2+} . Modelled Zn uptake is analogous to Mn, where uptake is proportional to Zn' according to Michalis Menten kinetics:

288
$$\rho_{Zn,i} = V_{max,Zn} \left(\frac{K_{Zn,b}[Zn']}{K_{Zn,b}[Zn']+1} \right)$$
(14)

289 and

290
$$V_{max,Zn} = Q_{Zn_max,i} * \mu_{max,i} * R_{up,Zn} * R_{down,Zn}$$
(15)

with
$$R_{up,Zn}$$
 and $R_{down,Zn}$ defined specifically for Zn in the same way as for Mn (Eq. 9, 10). In
addition, $Q_{Zn_max,i}$ is also decreased under N limitation as for Mn and Fe (Eq. 8).

293

294 **2.4 Model experiments**

The standard version of the PISCES-BYONIC model presented here includes Mn growth limitation and accounts for the transporter competition between Mn and Zn. The standard model

was integrated for 500 years using climatological offline physics fields to allow quasi 297 equilibrium of the biogeochemical tracers. We then conducted a set of parallel sensitivity tests, 298 all initialised from the same initial state as the full model. The sensitivity tests were designed to 299 test how different assumptions about the capabilities of Southern Ocean phytoplankton affected 300 the role of Mn in shaping biogeochemical cycles, and include: (1) a 'no Mn limitation' run, in 301 302 which phytoplankton growth in the full model was not affected by Mn, (2) a 'no Zn transporter interaction' run, where the transporter impact of Zn on Mn uptake was removed, (3) a 'Mn 303 downregulation by Zn hyperaccumulation' run, where down-regulation of Zn uptake due to Q_{Zn} 304 exceeding Q_{Zn max} also down-regulated Mn transport (i.e. Eq. 12 was implemented), (4) a 'very 305 large photosynthetic antennae' run, where photosynthetic Mn requirements were derived 306 assuming a Chl: PSII ratio of 2000 and (5) a 'moderate photosynthetic antennae' run, where Mn 307 costs were derived assuming a Chl: PSII ratio of 500 (see Table S1). To assess how accounting 308 for Mn limitation affected the response of the Southern Ocean Biological Carbon Pump, we 309 310 conducted two additional experiments where the standard model and the 'no Mn limitation' model were forced by increased dust input, characteristic of the Last Glacial Maximum (LGM) 311 perod, as described by Lambert et al. (2015). Accounting for LGM levels of dust input affected 312 313 the supply of both Fe and Mn.

314

2.5 Single cell X-ray Fluorescence (SXRF)

Carbon-normalized Mn, Fe, and Zn quotas of individual cells in Fig. 2 were compiled from previously published studies in Antarctic and Subantarctic waters and the North Atlantic Ocean (Twining, Baines, & Fisher, 2004; Twining, Baines, Fisher, et al., 2004). These data were supplemented with new data for Subantarctic cells collected from the Southern Ocean Time Series station (SOTS, 47°S, 142°E) in March 2018 during a cruise on the R/V Investigator

320	(cruise IN2018_v02; Sofen et al., In Revision). Cells were collected from 15–40 m between 7–18
321	March, 2018 (Table S2; Ellwood et al., 2020)). Fifty-nine cells were collected in total. North
322	Atlantic data were supplemented with cells collected from two stations in the North Atlantic in
323	summer 2017 during the ZIPLoC cruise (R/V James Cook, cruise JC150; Sofen et al., In
324	Revision). Cells were collected from 40 m depth. SXRF sample collection and analysis followed
325	previously published methods using stringent trace metal clean techniques (Twining et al., 2011).
326	Individual cells from plankton populations are known to exhibit significant intra-
327	population variability (Bucci et al., 2012). Outliers were identified following Twining et al.
328	(2019). Briefly, log-transformed C-normalized quotas were fit with an ANCOVA model (JMP,
329	SAS) that included log(biovolume), station, and cell type (diatom or nanoflagellate) as effects.
330	Individual quotas were removed from the dataset if the Jackknife distances of the Studentized
331	residuals of this model were greater than 3. Approximately 1% of cell quotas in the dataset were
332	removed through this process. Additionally, Zn or Fe quotas > 200 or $>300 \mu mol (mol C)^{-1}$,
333	respectively, were deemed to be impacted by abiotic material based on known physiological
334	ranges (Sunda & Huntsman, 1995a, 1995b) and were removed. This affected less than 5
335	measurements in the dataset.

336 **3 Results**

337 **3.1 Modelling minimum and realized manganese quotas**

To quantify the impact of Mn scarcity on the Southern Ocean biological carbon pump, we incorporated phytoplankton Mn limitation into the PISCES-BYONIC configuration of the global ocean biogeochemical model PISCES (Richon & Tagliabue, 2021). The PISCES-BYONIC model represents limitation of phytoplankton growth by five nutrients: nitrogen, phosphorus, silica (for diatoms), iron, and manganese, as well as light, and allows for variable

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343	cell chlorophyll and micronutrient quotas. The PISCES-BYONIC model reproduces global
344	patterns of dMn, dZn, and dFe from GEOTRACES observations (Figures 3a, S1 and S2), as well
345	as other key biogeochemical properties (Richon & Tagliabue, 2021; Tagliabue et al., 2016).
346	Minimum cellular requirements for Mn (normalised to cell carbon: Q_{MnReq}) are
347	represented in the model as the sum of the demand for oxygen-evolving complexes in PSII and a
348	basal requirement of Mn enzymes rooted in central metabolism, which then increase with
349	increasing growth rate as observed in both Fe fertilization experiments (Twining, Baines, &
350	Fisher, 2004) and culture studies (Sunda & Huntsman, 1998b). Modelled values of Q_{MnReq} are
351	lowest in the subtropical gyres, where growth rates are low, light is abundant and the
352	photosynthetic apparatus is downregulated. Meanwhile, the stronger seasonality of irradiance
353	and deeper mixed layers in the Southern Ocean, combined with episodes of fast growth during
354	Austral spring, lead to a markedly greater Mn demand that peaks in the Subantarctic zone
355	between 40–50°S (Figure 3b).
356	Mn uptake in the PISCES-BYONIC model is a function of bioavailable Mn^{2+} and Zn^{2+} ,
357	which compete for the same transporter following experimental constraints (Sunda & Huntsman,
358	1996, 1998b). The combination of low dMn and high dZn of waters upwelling into the Southern

Ocean leads to a minimum in Q_{Mn} between 60–70°S (Figure 3c). Close to the Antarctic continent and downstream of large islands (e.g. the Kerguelen Plateau in the Indian Sector), Q_{Mn} increases due to Mn inputs from margin sediments. However, Mn input to some coastal areas – notably the Ross Sea – appears insufficient to yield maximum Q_{Mn} , which is consistent with recent reports of

363 phytoplankton Mn-Fe co-limitation there (Wu et al., 2019).

a) Surface dMn (nM) b) $Q_{Mn,Req}$ (10⁻⁶ mol/mol) c) Q_{Mn} (10⁻⁶ mol/mol)



d) Mn limitation strength e) Fe limitation strength f) Mn deficiency (Q_{Mn}/Q_{MnReg,max})



ion, seasonal max(1 g) \triangle BCP due to Mn (%) h) \triangle NO₃ at surface (μ M)



tation in PISCES-BYONIC. Factors on in January, including (a) dissolved Mn ytoplankton chlorophyll and growth rate, growth rates dictate the Mn quota, Q_{Mn} . ere higher values indicate greater Mn t of Mn deficiency diagnosed from the nutrient replete, light-limited growth while d–f show seasonal minima. f) n decreases the biological carbon pump, e annual cycle), resulting in (h) an

377 **3.2 Southern Ocean footprints of Mn limitation and Mn deficiency**

Based on modelled Q_{Mn} and Q_{Mn,Req}, we calculated the proportion of maximum growth 378 rate allowed by Mn (lim_{Mn} ; Eq. 4) and subtracted this value from 1 to yield a unitless measure of 379 380 'Mn limitation' (Fig. 3d). Under this definition, higher values reflect more strongly Mn-limiting conditions. While large areas of the Southern Ocean are predicted to be 'Mn-limited' to some 381 extent, the model simulated a greater prevalence and intensity of Fe limitation in the same 382 regions (Fig. 3e), which is consistent with literature compilations of nutrient amendment 383 experiments in the Southern Ocean (Table S3). Although Fe limitation is much more prevalent in 384 our model, local pockets of Mn limitation reduce the strength of the biological carbon pump by 385 up to 30% (Fig. 3g) with unused Fe and macronutrients fuelling a small increase in carbon export 386 downstream. For context, this impact of Mn limitation on the biological carbon pump is similar 387 388 to that of hydrothermal Fe supply (Resing et al., 2015; Tagliabue & Resing, 2016). In PISCES-BYONIC, the effects of Mn limitation are focused primarily in the Subantarctic between 40-50 389 °S, especially in the Indian and Pacific sectors, with a smaller, patchier signal around 60 °S (Fig. 390 391 3g). Ultimately, the reduced efficiency of macronutrient utilisation due to Mn limitation causes an increase in residual annual mean surface nitrate concentration (Fig. 3h), which is redistributed 392 from the local sites of Mn limitation throughout the Southern Ocean by lateral mixing. 393

Beyond the small footprint for 'proximal' Mn limitation, we found that Q_{Mn} over most of the Southern Ocean did not strongly exceed Q_{MnReq} (Fig. 3b and c), indicating that Mn limitation might emerge rapidly with any increase in Fe supply. Indeed, the widespread Fe limitation typical of the Southern Ocean actually lowers Q_{MnReq} by enforcing slow growth rates. This indirect effect can be accounted for by defining a state of 'Mn deficiency,' which instead normalizes Q_{Mn} to the amount of Mn required to support growth rates in the absence of Fe limitation (i.e. $Q_{MnReq,max}$). Conceptually, this is similar to the additive responses observed in

bottle incubations where simultaneous addition of both Mn and Fe increase biomass more than 401 Fe alone (Browning et al., 2021; Wu et al., 2019). In the standard version of the model, over half 402 of the Southern Ocean experiences 'Mn deficiency' at some point during the seasonal cycle 403 (62% of waters south of 40 °S; Figure 3f). 404

405

3.3 Seasonal phasing of Mn limitation

The seasonal dynamics of ocean mixing across the Southern Ocean decouple the supply 406 of Mn and Fe, leading to seasonal evolution of nutrient limitation regimes. Winter mixing 407 supplies Fe from the ocean interior and is the dominant input of Fe across the Southern Ocean, 408 409 with the wintertime Fe stock then recycled by marine ecosystems throughout the spring and summer (Boyd et al., 2012; Strzepek et al., 2005; Tagliabue et al., 2014). In contrast to Fe, 410 entrainment by winter mixing does not elevate springtime mixed-layer Mn stocks notably, as 411 concentrations in the ocean interior are also low (Latour et al., 2021; Moore, 2016; Rigby et al., 412 2020). As a result, localized Mn limitation can emerge as the Southern Ocean stratifies, primarily 413 in November and December (Figure 4a, b), which hinders the progress of the austral spring 414 415 bloom. During this period, Mn is more limiting than Fe in our model for 49% of Southern Ocean surface waters south of 40°S. These waters are still characterized by low dFe concentrations, but 416 417 the winter Fe supply that persists into spring permits relatively high growth rates while suboptimal light levels also lead to elevated Chl, both of which increase Q_{MnReq}. By January and 418 February, the mixed layer dFe reservoir is depleted, resulting in Fe limitation exceeding Mn 419 420 limitation across 96% of the Southern Ocean south of 40°S (Figure 4c). The ecosystem then returns to light limitation when mixed layers deepen in autumn (Figure 4d). This seasonal 421 phasing between Mn and Fe limitation is not predicted from simpler models that do not account 422 for variable Mn requirements (Browning et al., 2021), but it is key to allowing the mixed-layer 423

Fe stock to be repeatedly recycled and persist later into summer (Boyd et al., 2012; Strzepek et al., 2005). The seasonal progression from Mn to Fe limitation in the model is also consistent with the prevalence of Fe limitation from prior Fe and Mn addition experiments, which have mostly been conducted in austral summer (see Table S3).

a) Sep-Oct





c) Jan-Feb

d) Mar-Apr

40 50 60 70

30



Figure 4. Seasonal phasing of Mn and Fe limitation. The difference between fractional Mn limitation and

- Fe limitation terms at the surface for (a) September–October, (b) November–December (c) January– February and (d) March–April. Positive values (in red) indicate greater Mn limitation than Fe limitation,
- February and (d) March–April. Positive values (in red) indicate greater Mn limitation than Fe limitation while negative values indicate greater Fe limitation (blue). Nitrogen-limited areas at low latitudes are
- 434 masked in white.
- 435

436 **3.4** Seasonal phasing of Mn limitation

Because the physiological characterization of important phytoplankton lineages is 437 incomplete (especially those from the Southern Ocean), we designed multiple sensitivity 438 439 experiments to examine how specific traits related to Mn uptake and use could affect the severity of Mn limitation. When we removed Zn inhibition of Mn uptake, there was little change in the 440 Subantarctic zone biological carbon pump anomaly caused by Mn limitation, but the 441 corresponding anomaly in the Antarctic Zone was eliminated because Mn uptake in these high 442 Zn waters could now meet Mn requirements (Figure 5, S4). Conversely, if the Zn-Mn 443 antagonism is exacerbated by enabling the downregulation of Mn transport at high Q_{Zn}, a trait 444 that has been observed in culture experiments (Sunda & Huntsman, 1996, 2000), then the impact 445 of Mn limitation in the Antarctic zone is expanded greatly (Fig. 5). This effect would be further 446 increased if other divalent metals that compete for Mn transporters (Cu^{2+} and Cd^{2+}) were also 447 found to reach significant levels in the Antarctic zone. While traits related to Zn-Mn interactions 448 are crucial to the emergence of Mn limitation in the Antarctic Zone, the broad signal of Mn 449 450 limitation throughout the Southern Ocean is regulated by photosynthetic traits. For instance, if the size of the photosynthetic antennae is increased to 2000 Chl: 1 PSII (Strzepek et al., 2019) or 451 reduced to 500 : 1 (Kolber & Falkowski, 1993; Lawrenz et al., 2013), then the overall impact of 452 Mn limitation is decreased or increased by nearly 50%, respectively (Fig. 5). 453





Figure 5. Influence of phytoplankton physiology on the severity of Mn limitation. The zonally integrated anomaly in the Biological Carbon Pump (Δ BCP) at 100 m depth (in grams carbon m⁻¹ year⁻¹) due to Mn limitation for the PISCES-BYONIC standard model is shown (black line), along with four sensitivity experiments: a model without Zn-Mn transporter competition (black dash), a model with Zn-Mn transporter competition intact and an added downregulation of Mn transport to prevent Zn hyperaccumulation at high Q_{Zn} (blue dash), and the standard model with the upper and lower bounds of the assumed Chl : PSII ratio (red and purple dashes, respectively).

465 **3.5** Response of Mn limitation to changing iron supply during the Last Glacial Maximum

The prevalence of Mn deficiency throughout much of the Southern Ocean implies that

there is the potential for Mn limitation to become more widespread when Fe supply increases.

- 468 This is analogous to the Last Glacial Maximum (LGM), when atmospheric dust fluxes to the
- 469 Southern Ocean were several-fold greater than found today (Lamy et al., 2014; Martin, 1990). In
- 470 an alternate version of our model without Mn limitation, the biological carbon pump is enhanced
- throughout the Southern Ocean when atmospheric dust supply is increased following paleo-
- 472 climate reconstructions (Lambert et al., 2015), as expected (Figure 6a). However, when Mn
- 473 limitation is considered (Fig. 6b), the increase in the biological carbon pump is stunted by >30%
- 474 across large regions in the Subantarctic Indian and Pacific sectors (Fig. 6c). Even though the
- 475 glacial dust scenario increases the supply of both Mn and Fe (indeed dust Mn is much more

soluble than Fe in our model; Baker et al., 2013), Mn limitation exceeds Fe limitation throughout 476 the Southern Ocean during spring, with Mn limitation in the Subantarctic Pacific and Indian 477 sectors now persisting through summer (Figure 7). Although these simulations do not consider 478 how parallel changes in ocean circulation may modulate growth conditions in the Southern 479 Ocean, our mechanistic modelling results agree with simpler diagnostic models (Browning et al., 480 481 2021) and provide new evidence that Mn was an important influence on the glacial carbon cycle across most of the Southern Ocean. Efforts to reconstruct glacial/interglacial changes in 482 sedimentary Mn sources, especially from the Antarctic continent, will be essential for refining 483 484 these conclusions.

Earth System Models also project enhanced Southern Ocean productivity by the end of 485 the 21st century due to an increasing Fe supply from the subtropics and the warming and 486 lengthening of the growth season due to sea ice melting (Misumi et al., 2014; Moore et al., 487 2018). Our simulations suggest that any alleviation of Fe limitation will lead to an expanded 488 impact of Mn deficiency that will add further uncertainty to future projections. This may be 489 particularly important if future warming selects for smaller photosynthetic antennae sizes (as 490 hypothesized in Strzepek et al. (2019)), as our modelling shows that this trait would increase 491 492 phytoplankton Mn requirements (Fig. 5).

a) \triangle BCP LGM, no Mn lim (gC m⁻² yr⁻¹)



- 494
- **Figure 6.** Expansion of Mn limitation with increasing dust supply. The change in the Biological Carbon
- 496 Pump (Δ BCP) in response to an increase in atmospheric dust supply of both Fe and Mn, based on
- 497 projections for the Last Glacial Maximum (LGM). Simulation were performed for (a) a model without
- 498 Mn limitation and (b) the standard PISCES-BYONIC model with Mn limitation feedbacks. The
- 499 difference (c) shows the impact of Mn on the Δ BCP responses to LGM dust, with blue shading indicating
- negative anomalies due to Mn limitation. Red areas in panel (c) are those where advection of residual
- 501 nutrients stimulate the BCP in downstream subtropical regions.



Figure 7. The difference between the fractional Mn limitation and Fe limitation term (normalized across
both phytoplankton functional types in the model) for the LGM dust experiment at the ocean surface for
(a) September–October, (b) November–December (c) January–February and (d) March–April. Color
shading is identical to Figure 4.

507

508 4.1 Discussion

We find consistent emergence of phytoplankton Mn limitation under a range of potential 509 physiological adaptations of polar phytoplankton. As a result, projections of past and future 510 changes to Southern Ocean productivity should account for the impact of Mn, alongside the 511 recognized roles of Fe and light. In regions of high Mn supply, the Southern Ocean biological 512 pump oscillates seasonally between light limitation in winter and Fe limitation during summer. 513 Elsewhere, the interaction between light, Mn and Fe will be an important component of the 514 seasonal cycle (Figure 8). Proximal Mn limitation and co-limitation manifests during periods of 515 516 enhanced Fe availability and sub-optimal light levels, particularly in the Subantarctic zone

during spring. The extent of the light-Mn-Fe co-limited regime over the year (Fig. 8) depends on 517 factors that regulate the demand for PSII (notably traits related to photosynthetic antennae size) 518 or any other process that increases Mn requirements, such as elevated growth rates in response to 519 iron supply or increased expression of Mn superoxide dismutase or other Mn metalloenzymes 520 under Fe limitation (McCain et al., 2021; Peers & Price, 2004). Although our model considers 521 522 Mn limitation to be independent of any co-occurring Fe deficiency (as in Liebig's Law of the Minimum), protein allocation models suggest that the combined effects of Mn and Fe deficiency 523 might depress growth rates further than singular Fe or Mn limitation (McCain et al., 2021; 524

525 Pausch et al., 2019; Peers & Price, 2004).





Manganese limitation

Iron limitation

Figure 8. A new perspective on the seasonal transitions between iron, manganese, and light limitation in
the Southern Ocean. Under conditions of high Mn supply, the light-Fe limitation seasonal regime is
dominant (blue arrow). As Mn supply decreases, a light-Mn-Fe limitation regime manifests (pink and red
arrows). The intensity of the Mn-limited component of the light-Mn-Fe limited regime is controlled by

531 photosynthetic physiology (chlorophyll antennae size, PSII:PSI ratio) as well as the supply of Fe and Zn.

533	In constructing the PISCES-BYONIC model, we have used the limited observational
534	dataset of phytoplankton cell quotas from the Southern Ocean to validate model predictions.
535	Although the model cannot account for the diversity of coexisting phytoplankton species
536	represented in cell-specific Synchrotron X-Ray Fluorescence (SXRF) measurements (Twining,
537	Baines, & Fisher, 2004), simulated cell quotas for Mn, Fe, and Zn follow the same large scale
538	trends found in SXRF datasets (Fig. 2). Modelled Q _{Fe} is several fold greater in the iron-rich
539	North Atlantic compared to the low dFe Southern Ocean (Figure S5), while observed and
540	modelled Q_{Zn} shows the opposite trend: Q_{Zn} peaks in the Antarctic, tracking gradients in dZn
541	(Figs. S2, S6). In contrast, SXRF measurements of Q_{Mn} are relatively similar between the
542	Southern Ocean and North Atlantic, generally falling between 2–5 µmol Mn (mol C) ⁻¹ (Fig. 2),
543	despite order-of-magnitude differences in dMn between the North Atlantic and the Southern
544	Ocean (Hatta et al., 2015; Latour et al., 2021; Middag et al., 2011). In our model, stabilization of
545	Q_{Mn} is achieved by down-regulating maximum Mn, Fe and Zn uptake rates when metal quotas
546	reach a prescribed maximum and, additionally, when phytoplankton are N-limited. This scheme
547	still allows modelled Q_{Mn} to reach lower values in some Southern Ocean regions than observed
548	by SXRF (Fig. S3), which may reflect the need for broader observational datasets of
549	phytoplankton cell quotas, especially in the Southern Ocean.

The principle uncertainty in our modelling originates from the lack of physiological data for phytoplankton species isolated from the Southern Ocean. Thus far, experiments with Antarctic phytoplankton have focused primarily on responses to Fe and light limitation, and do not include key information associated with Mn uptake and the regulation of Mn transporters (which are described in temperate species, notably *Thalassiosira oceanica* (Sunda & Huntsman, 1986, 2000)). For instance, it is not clear if polar phytoplankton can further optimize their Mn

556	uptake systems, or if improvement is prevented by fundamental constraints on the specificity of
557	Mn^{2+} versus Zn^{2+} binding described by the Irving-Williams series. The modelled footprint of Mn
558	limitation is sensitive to assumptions regarding transporter regulation and photosynthetic
559	antennae size (Fig. 5), but our standard model applies a Chl:PSII ratio that is a relatively good fit
560	with expected Mn requirements of Antarctic phytoplankton (Fig. 1) and also assumes a greater
561	ability to tolerate high Zn than is evident from culture experiments with T. oceanica. This
562	suggests that our projections of Mn limitation may be conservative. To accurately project the
563	influence of changing climate on the Southern Ocean biological carbon pump, more culture and
564	field studies focused on Antarctic phytoplankton are required to identify and constrain
565	physiological responses and trade-offs to Mn scarcity.

Finally, we note that the ultimate cause of Southern Ocean Mn deficiency – the upwelling 566 of deep ocean waters with high macronutrients and low Mn – has been in place since opening of 567 the Drake Passage and the establishment of the Antarctic circumpolar current during the Eocene 568 (Scher & Martin, 2006). As such, Southern Ocean phytoplankton have had millions of years to 569 adapt to the simultaneous scarcity of Mn, Fe, and light, which may be reflected in their 570 photosynthetic architecture. It is widely thought that selection for Fe-conservation traits alone 571 572 should lead to high PSII:PSI ratios in Southern Ocean phytoplankton, because Fe is mostly associated with PSI and alternate electron flows that avoid PSI are possible (Behrenfeld & 573 Milligan, 2013; Robert F Strzepek & Harrison, 2004). This strategy is borne out in temperate 574 575 open-ocean diatom lineages like T. oceanica, which show PSII : PSI exceeding 8:1, even when grown under very low irradiance (Strzepek et al., 2019; Strzepek & Harrison, 2004). In this 576 577 context, the comparatively lower PSII : PSI of ~1.7 (range 1.3 to 2.0) observed in Fe-limited 578 Southern Ocean phytoplankton is enigmatic (Strzepek et al., 2019) because the presence of genes

579	like plastoquinone	terminal oxidas	e should also allow	Antarctic phytoplankton t	o reach similarly
	1 1			1 2 1	

- high PSII : PSI ratios (Behrenfeld & Milligan, 2013; Moreno et al., 2018). All photosynthetic
- 581 Mn is found in PSII, and we estimate that increasing cellular PSII : PSI from 1.7 to 8 could triple
- photosynthetic Mn requirements relative to Fe (from 0.33 to 1.0 mol Mn : mol Fe; Fig. S7),
- drastically increasing the susceptibility to Mn limitation in the Mn-deplete Southern Ocean. We
- posit that the comparatively low PSII : PSI ratios in Southern Ocean phytoplankton may reflect
- an evolutionary trade-off to optimize photosynthesis in a Southern Ocean that has long been
- deficient in both Fe and Mn.

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594

595 **Open Research**

- Model output from this work will be deposited into Public Repositories (e.g. Zenodo) uponacceptance.
- 598

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AGU PUBLICATIONS

Global Biogeochemical Cycles

Supporting Information for

Manganese Limitation of Phytoplankton Physiology and Productivity in the Southern Ocean

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Contents of this file

Figures S1 to S7 Tables S1 to S3 Supplemental References



Dissolved Manganese, nM, 100-200m

Dissolved Manganese, nM, 0-100m



Dissolved Manganese, nM, 400-500m Dissolved Manganese, nM, 700-800m

Dissolved Manganese, nM, 900-1000mDissolved Manganese, nM, 2500-3000n



Fig. S1. Modelled dissolved manganese (dMn, annual average) and compiled observations from the Southern Ocean over various depth regions.



Fig. S2. Modelled dissolved zinc (dZn, annual average) and compiled observations from the Southern Ocean over various depth regions.



Fig. S3. Modelled Mn quotas across the global ocean in PISCES-BYONIC in in μ mol Mn (mol C)⁻¹. Areas where phytoplankton carbon biomass falls below 1 x 10⁻⁶ mol C L⁻¹ are masked in white.



Fig. S4. Zonally integrated rates of Mn uptake (μ mol m⁻¹ year⁻¹) for the standard PISCES-BYONIC model (black line), and sensitivity experiments with 1) no Zn-Mn transporter competition (black dash), and 2) a feedback forcing downregulation of Mn transporters at elevated Q_{Zn} (blue dash). Also shown are zonal averages of dissolved Zn (in nM, divided by 10 for scale, red dash) and phytoplankton Zn quota normalized to the maximum Zn quota (range 0 – 1, red line). Compare with Figure 5 in the Main Text.



Fig. S5. Modelled Fe quotas across the global ocean in PISCES-BYONIC in μ mol Fe (mol C)⁻¹. Areas where phytoplankton carbon biomass falls below 1 x 10⁻⁶ mol C L⁻¹ are masked in white.



Fig. S6. Modelled Zn quotas across the global ocean in PISCES-BYONIC in μ mol Zn (mol C)⁻¹. Areas where phytoplankton carbon biomass falls below 1 x 10⁻⁶ mol C L⁻¹ are masked in white.



PSII:PSI ratio

Fig. S7. Comparison of PSII : PSI ratios and Chl : PSII ratios among Southern Ocean phytoplankton and the temperate diatoms *T. oceanica* and *T. weissflogii* using low iron (open circles) and high iron (filled circles) culture experiments from Strzepek et al. (2019). Dotted lines show predicted relative Mn : Fe requirements for photosynthesis (i.e. a ratio of 0.1 indicated 10-times more Fe is required than Mn). Required Mn:Fe ratios were calculated assuming 1) PSII contains 2 Fe atoms and 4 Mn atoms, 2) PSI contains 12 Fe and cytochrome b6 contains 5 Fe, and 3) that PSI and cytochrome b6 are in a 1:1 ratio. We note that *T. oceanica* is predicted to require as much Mn as Fe due to high PSII : PSI ratios, which is consistent with experimental data presented by Sunda (1989).

Temperate Phytoplankton		
Thalassiosira weissflogii	130 - 260	Dubinsky et al., 1986
	560 - 590	Suggett et al., 2004
	320 - 480	Strzepek & Harrison, 2004
	461 - 534	Strzepek et al., 2019
	1,000	Silsbe et al., 2015
Thalasiosira pseudonana	420 – 930 1,650	Sunda & Huntsman, 1998 Silsbe et al., 2015
Thalassiosira oceanica	260 - 270 220 - 270	Strzepek & Harrison, 2004 Strzepek et al., 2019
Skeletonema costatum	590 – 610 1.151	Falkowski et al., 1981 Silsbe et al., 2015
Ditvlum brightwellii	1.110	Silsbe et al., 2015
Phaeodactylum tricornutum	420 - 570	Friedman & Alberte, 1986
Chaetocerus muelleri	520 - 590 1 042	Suggett et al., 2004 Silshe et al., 2015
Dunalialla tartiolocta	500 620	Falkowski et al. 1081
	540 - 740	Suggett et al., 2004
Emiliana huxleyi	540 - 650	Suggett et al., 2004
	480 – 720 775	Suggett et al., 2007 Silsbe et al., 2015
Isochrysis galbana	51-219	Dubinsky et al., 1986
Phaeocystis globosa	961	Silsbe et al., 2015
Aureococcus anophageffrens	720 - 950	Suggett et al., 2004
Prorocentrum minimum	260 - 365	Dubinsky et al., 1986
	430 - 530	Suggett et al., 2004
	725	Silsbe et al., 2015
Tetraselmis striata	790	Silsbe et al., 2015
Pycnococcus provasolii	621 - 930	Suggett et al., 2004
Rhodomonas salina	470 - 510	Suggett et al., 2004
Storeatula major	440 - 520	Suggett et al., 2004
Prochlorococcus strain SS120	270	Bibby et al., 2001, 2003
Synechococcus WH7803	240 - 290	Suggett et al., 2004
Antarctic Phytoplankton		
Phaeocystis antarctica	1280 - 1850	Strzepek et al., 2019
	630 - 1960	Trimborn et al., 2019
Proboscia inermis	1440 - 2070	Strzepek et al., 2019
Eucampia antarctica	1710 - 3540	Strzepek et al., 2019
Chaetoceros debilis	120 - 2540	Trimborn et al., 2019
Field studies		
Subtropical and Tropical Atlantic	330 - 420	Suggett et al., 2006
Celtic Sea	530 - 720	Moore et al., 2006
Subpolar North Atlantic)	380 - 1700	Macey et al., 2014
	400 - 833	Moore et al., 2005
Subarctic Pacific	280 - 450 (coastal) 520 - 580 (open ocean)	Schuback & Tortell, 2019
Southern Ocean	450 ± 350 (winter) 1580 ± 1400 (summer)	Ryan-Keogh et al., 2018
Biogeochemical Model		
Global	1000(500 - 2000)	This study

Table S1. Estimated Chlorophyll a:PSII ratios from culture and field studies. Organism / Region Chl a : PSII (mol mol⁻¹) Reference

Region	Cruise	Station	Lat	Lon	Depth	Date	#	Reference
			(°N)	(°E)	(m)		cells	
Antarctic	SOFeX	19	-66	-172	20	24 Jan	17	Twining, Baines,
						2002		& Fisher, 2004;
								Twining, Baines,
								Fisher, et al., 2004
		27	-66	-172	20	2 Feb	17	Twining, Baines,
						2002		& Fisher, 2004;
								Twining, Baines,
<u> </u>	COF N	_		1.50	20	10.1		Fisher, et al., 2004
Subantarctic	SOFeX	1	-56	-1/2	20	12 Jan	6	I wining, Baines,
						2002		& Fisher, 2004;
								Twining, Baines,
		11	56	172	20	20 Ion	0	Twining Daines
		11	-30	-1/2	20	20 Jan 2002	9	8 Fisher 2004:
						2002		Twining Baines
								Fisher et al 2004
	SOTS	TM02	-47	142	15-30	7 Mar	25	*
	~ ~ ~ ~					2018		
		TM04	-47	142	15-40	9 Mar	18	*
						2018		
		TM05	-47	142	15-30	18 Mar	16	*
						2018		
N. Atlantic	GA02	2011-10	32	-64	25	19 Nov	30	Twining et al.,
						2011		2015
		2011-12	30	-57	25	23 Nov	13	Twining et al.,
						2011		2015
		2011-16	26	-45	25	30 Nov	24	Twining et al.,
						2011		2015
		2011-20	22	-36	25	3 Dec	9	Twining et al.,
		2	22	5 4	40	2011	22	2015
	ZIPLOC	2	22	-54	40	11 July	22	ጥ
		7	22	21	40	2017	15	*
		1	22	-31	40	5 Aug 2017	13	
						2017		

Table S2. Summary of phytoplankton metal quota samples included in Figure 2.

* Sofen et al. Metal contents of autotrophic flagellates from contrasting open-ocean ecosystems. *Limnology* and Oceanography Letters. In Review.

Study / Reference	Region	Lat (°N)	Lon (°E)	Month	Limiting Nutrient
		-54.7	-58.0	Nov	Fe
	Drake passage	-55.4	-57.7	Nov	Fe
	(Northern)	-55.6	-58.0	Nov	Fe
Duoumine et al		-55.8	-57.8	Nov	Fe
Browning et al.,	Dualta Dagaa aa	-56.6	-57.4	Nov	Mn
2021	(Control)	-56.8	-57.2	Nov	Mn/Fe
	(Central)	-58.1	-56.4	Nov	Mn
	Droko Bossogo	-58.7	-56.1	Nov	Fe
	(Southorn)	-59.6	-55.5	Nov	Fe
	(Southern)	-61.0	-54.6	Nov	Replete
We at al. 2010	Ross Sea	-77.62	165.4	Dec	Replete
wu et al., 2019	(McMurdo Sound)	-77.62	165.4	Jan	Mn/Fe
		-76.3	-179.6	Nov	Replete
Sedwick et al.,	Ross Sea	-76.3	-177.5	Dec	Replete
2000		-75	-172	Dec	Fe
		-76.3	-117.4	Jan	Fe
Sedwick &	Bass Saa	-76.3	-170.4	Dec	Fe
DiTullio, 1997	Ross Sea	-76.3	-170.4	Jan	Fe
Saharak at al	Atlantia Saatar Dalar Front	-47	-6	Oct/Nov	Fe
1007	Atlantic Sector, Folar Floht	-50	-6	Oct/Nov	Fe
1997	Atlantic Sector, ACC	-53	-6	Oct/Nov	Fe
	Weddell Sea	-59	-6.2	Oct/Nov	Fe
	Weddell/ACC confluence	-59	-49	Dec	Mn/Fe
Buma et al., 1991	Weddell Sea	-62	-47	Dec	Fe
	Scotia Sea	-57	-49	Dec	Fe
Martin at al 1000	Page Saa	-75	-173	Jan/Feb	Fe
Iviaitiii et al., 1990	NUSS Sea	-72	167	Jan/Feb	Fe

Table S3. Summary of published Southern Ocean Mn addition bio-assays.

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