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4 **Seasonal cycling of zinc and cobalt in the Southeast Atlantic along the**
5 **GEOTRACES GA10 section.**

6

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20

21 **Abstract**

22 We report the distributions and stoichiometry of dissolved zinc (dZn) and cobalt (dCo) in sub-
23 tropical and sub-Antarctic waters of the Southeast Atlantic Ocean during austral spring 2010
24 and summer 2011/12. In sub-tropical surface waters, mixed-layer dZn and dCo concentrations
25 during early spring were 1.60 ± 2.58 nM and 30 ± 11 pM, respectively, compared with summer

values of 0.14 ± 0.08 nM and 24 ± 6 pM. The elevated spring dZn concentrations resulted from an apparent offshore transport of elevated dZn at depths between 20 – 55 m, derived from from the Agulhas Bank. In contrast, open-ocean sub-Antarctic surface waters displayed largely consistent inter-seasonal mixed-layer dZn and dCo concentrations of 0.10 ± 0.07 nM and 11 ± 5 pM, respectively. Trace metal stoichiometry, calculated from concentration inventories, suggest a greater overall removal for dZn relative to dCo in the upper water column of the Southeast Atlantic with an inter-seasonally decreasing dZn/dCo inventory ratios of 19 to 5 mol mol⁻¹ and 13 to 7 mol mol⁻¹ for sub-tropical surface water and sub-Antarctic surface water, respectively. In this paper, we investigate how the seasonal influences of external input and phytoplankton succession may relate to the distribution of dZn and dCo, and variation in dZn/dCo stoichiometry, across these two distinct ecological regimes in the Southeast Atlantic.

37

38 1. Introduction

39 The trace metal micronutrients zinc (Zn) and cobalt (Co) play an important role in the
40 productivity of the oceans as key requirements in marine phytoplankton metabolism (Morel,
41 2008; Twining and Baines, 2013). Zinc is required for the acquisition of inorganic carbon and
42 organic phosphorus via the carbonic anhydrase and alkaline phosphatase metalloenzymes,
43 respectively (Morel et al., 1994; Shaked et al., 2006; Cox and Saito, 2013). The requirement
44 for Co stems from its obligation in the biosynthesis of vitamin B₁₂ (Raux et al., 2000; Rodionov
45 et al., 2003) and, like Zn, its potential roles as a metal cofactor in carbonic anhydrase and
46 alkaline phosphatase (Morel et al., 1994; Jakuba et al., 2008; Saito et al., 2017). Significantly,
47 both dissolved Zn (dZn) and Co (dCo) are often scarce in surface seawater with mean
48 concentrations that are often similar to, or relatively depleted, compared with typical cellular
49 requirements of phytoplankton (Moore et al., 2013; Moore, 2016). Hence, dZn and dCo
50 availability have the potential to regulate phytoplankton metabolism and growth rates in some

51 ocean regions (Sunda and Huntsman, 1992; Saito et al., 2002; Franck et al., 2003; Shaked et
52 al., 2006; Bertrand et al., 2007; Jakuba et al., 2012; Mahaffey et al., 2014; Chappell et al., 2016;
53 Browning et al., 2017).

54 The role for Zn and Co in carbonic anhydrase establishes an interaction between their ocean
55 cycles, whereby biochemical substitutions between the enzyme-bound metals enables a
56 stoichiometric plasticity in their cellular requirements that can negate the effect of limited
57 availability. For example, a number of eukaryotic algae can substitute Zn for Co, as well as
58 cadmium (Cd), in carbonic anhydrase when seawater dZn concentrations are low (Price and
59 Morel, 1990; Sunda and Huntsman, 1995; Lane and Morel, 2000; Xu et al., 2007; Saito and
60 Goepfert, 2008; Kellogg et al., 2020). In contrast, the prokaryotic picocyanobacteria
61 *Synechococcus* and *Prochlorococcus* appear to have an absolute Co requirement (Sunda and
62 Huntsman, 1995; Saito et al., 2002; Hawco and Saito, 2018). The availability and stoichiometry
63 of dZn and dCo may therefore also exert a key control on phytoplankton community structure
64 in some ocean regions (Leblanc et al., 2005; Saito et al., 2010; Chappell et al., 2016).

65 With the arrival of GEOTRACES research cruises, a number of studies have provided
66 comprehensive data on the basin-scale distributions of Zn and Co in the Atlantic Ocean (e.g.
67 Bown et al., 2011; Noble et al., 2012, 2017; Wyatt et al., 2014; Roshan et al., 2015; Middag et
68 al., 2018). Such efforts have transformed our understanding of the biogeochemical processes
69 associated with Zn and Co cycling (Saito et al., 2017; Vance et al., 2017; Weber et al., 2018;
70 Tagliabue et al., 2018; Roshan et al., 2018) yet there are still geographically important regions
71 of the Atlantic that remain largely understudied, including the Southeast Atlantic.

72 The Sub-Tropical Front (STF) of the Southeast Atlantic represents the convergence of warm,
73 predominately macronutrient-limited Sub-Tropical Surface Water (STS) and cold, iron-
74 limited but macronutrient enriched sub-Antarctic Surface Water (SASW), creating one of the
75 most dynamic nutrient regimes in the oceans (Ito et al., 2005; Browning et al., 2014; Moore,

76 2016). Here, the relative supply and availability of macronutrients and iron (Fe) exert an
77 important control in maintaining the elevated phytoplankton stock and productivity that is
78 typical of this frontal region, particularly during austral spring and summer (Moore and Abbott,
79 2000; Ito et al., 2005; Browning et al., 2014). Dissolved Zn is also depleted in SASW that flows
80 northwards to converge with STSW at the STF (Wyatt et al., 2014). However, the potential
81 role for Zn in the mediation of phytoplankton distribution and community structure in this
82 region is currently unclear.

83 Using data from two UK-GEOTRACES cruises (transect GA10) this study examines the
84 seasonal availability and ecological stoichiometry of dZn and dCo, by analysis of their
85 relationships with phosphate, in upper ocean waters of the Southeast Atlantic. These data,
86 together with measurements of phytoplankton pigment biomass and community structure, offer
87 an improved knowledge of the seasonal influences of external input and phytoplankton
88 succession on the distribution and cycling of Zn and Co in these dynamic waters.

89

90 2. Methods

91 2.1. Sampling methods

92 Seawater samples were collected during two UK-GEOTRACES cruises in the South Atlantic
93 Ocean (GA10, Fig. 1). The first cruise (D357) took place during austral spring 2010 (18th
94 October to 22nd November 2010), sampling the Southeast Atlantic on-board the *RSS*
95 *Discovery*. During D357, two transects were completed between Cape Town and the zero
96 meridian that represent early austral spring (D357-1) and late austral spring (D357-2),
97 respectively. The second cruise (JC068) took place during austral summer 2011/2012 (24th
98 December 2011 to 27th January 2012), along the same transect of the first cruise and continuing
99 along 40°S between Cape Town and Montevideo, Uruguay, on-board the *RSS James Cook*. For
100 JC068, we present here only the repeat transect data between Cape Town and 13°W that

101 represents the Southeast Atlantic aspect of this transect. The stations occupied during the three
102 transects were not identical, but rather represent a coverage of the Southern Ocean and sub-
103 tropical waters present. Where stations were reoccupied during one or more transects, they
104 have the same station number.

105 All sampling bottles were cleaned according to the procedures detailed in the GEOTRACES
106 sample handling protocols (Cutter et al., 2010). Seawater and particulate samples below 15 m
107 depth were collected using a titanium-frame CTD with 24 trace metal clean 10 L Teflon-coated
108 OTE (Ocean Test Equipment) Niskin bottles deployed on a plasma rope. Sub-samples for
109 dissolved trace metal analysis were filtered through 0.8/0.2 μm cartridge filters (AcroPakTM
110 500, Pall) into 125 mL low density polyethylene bottles inside a class 1000 clean air container.
111 Each sub-sample was acidified to pH 1.7 (0.024 M) by addition of 12 M hydrochloric acid
112 (HCl, UpA, Romil) under a class 100 laminar flow hood. Vertical sampling for dissolved trace
113 metals was augmented by surface samples collected at each station using a towed ‘fish’
114 positioned at approximately 3-5 m depth. Fish samples were filtered in-line and acidified as
115 described for samples collected from the titanium sampling system. Particulate samples were
116 collected onto acid clean 25 mm, 0.45 μm , polyethersulfone membrane disc filters (Supor[®],
117 Pall) and stored frozen (-20°C) until shore-based analysis.

118

119 **2.2. Trace metal analysis**

120 Dissolved Co was determined in the ISO accredited clean room facility (ISO 9001) at the
121 University of Plymouth (UK) using flow injection with chemiluminescence detection,
122 modified from the method of Cannizzaro et al. (1999) as described by Shelley et al. (2010).
123 Briefly, dCo was determined in UV-irradiated samples using the reaction between pyrogallol
124 (1,2,3-trihydrobenzene) and hydrogen peroxide formed in the presence of Co. Standards (20 –
125 120 pM Co) were prepared in 0.2 μm filtered low-dCo seawater ($16.5 \pm 5.2 \text{ pM}$, $n = 15$) by

126 serial dilution of a 1000 ppm Co ICP-MS standard (Romil, UK). The accuracy of the analytical
127 method was validated by quantification of dCo in SAFe (S and D2) and GEOTRACES (GD)
128 reference seawater (Table 1). There was no detectable analytical dCo blank and the limit of
129 detection (3σ of the lowest concentration standard) was 1.98 ± 0.87 pM ($n = 15$).
130 Dissolved Zn was determined using flow injection coupled with fluorescence detection,
131 modified from the method of Nowicki et al. (1994) and described previously for this
132 GEOTRACES section by Wyatt et al. (2014). The accuracy of the analytical method was
133 validated by quantification of dZn in SAFe (S and D2) reference seawater (Table 1). The blank
134 for dZn FIA was 0.14 ± 0.13 nM and the limit of detection (3σ of the lowest concentration
135 standard) was 0.01 ± 0.01 nM ($n = 15$).
136 Measurement uncertainties were estimated after the Nordtest approach (Worsfold et al., 2019)
137 where a combined uncertainty (u_c) is computed from day-to-day within-lab reproducibility and
138 uncertainties associated with the determination of reference materials (Table 1). This approach
139 creates higher uncertainties than those previously published for dZn and dCo analyses but
140 provides a more realistic estimation of analytical uncertainty. During this study, the u_c for dZn
141 and dCo analysis was 22 and 19 %, respectively, similar to the 13 – 25 % reported by Rapp et
142 al. (2017) for the determination of trace metals, including dZn and dCo, by on-line pre-
143 concentration and high-resolution sector field ICP-MS detection. The elevated u_c within our
144 data results from the greater uncertainty surrounding the very low dZn and dCo concentration
145 SAFe S reference sample whereas the dZn and dCo u_c using only the Safe D2 are <5 %.
146 Hereafter, when presenting low dZn and dCo concentrations for comparison with
147 phytoplankton biological requirements (Section 3.5), we apply a fixed u_c of 20 % to our data.
148 Total particulate trace metals (i.e. pZn, pCo, pTi) were determined using inductively coupled
149 plasma-mass spectrometry (Thermo Fisher XSeries-2) following a sequential acid digestion
150 modified from Ohnemus et al. (2014). Potential interferences (e.g. $^{40}\text{Ar}_{16}\text{O}$ on ^{56}Fe) were

151 minimized through the use of a collision/reaction cell utilizing 7 % H in He and evaluation of
152 efficiency and accuracy assessed using Certified Reference Material (CRM). Full details of the
153 method and CRM results can be found in Milne et al. (2017).

154

155 **2.3. Nutrients, phytoplankton, temperature and salinity**

156 The dissolved macronutrients phosphate (PO_4^{3-}), silicic acid (Si(OH)_4 but referred to as Si
157 hereafter) and nitrate (determined as nitrate + nitrite, NO_3^-) were determined in all samples for
158 which trace metals were determined, in addition to samples collected from a stainless steel
159 rosette. Macronutrients were determined using an AA III segmented-flow AutoAnalyzer (Bran
160 & Luebbe) following colorimetric procedures (Woodward and Rees, 2001). Salinity,
161 temperature and depth were measured using a CTD system (Seabird 911+) whilst dissolved O_2
162 was determined using a Seabird SBE 43 O_2 sensor. Salinity was calibrated on-board using
163 discrete samples taken from the OTE bottles and an Autosal 8400B salinometer (Guildline)
164 whilst dissolved O_2 was calibrated using a photometric automated Winkler titration system
165 (Carritt and Carpenter, 1966). Mixed-layer depths (MLD) were calculated using the threshold
166 method of de Boyer Montégut et al. (2014), where MLD is identified from a linear interpolation
167 between near-surface density and the depth at which density changes by a threshold value
168 (0.125 kg m^{-3}).

169 Measurements of phytoplankton pigment biomass and community structure were made on
170 discrete samples collected using a 24 position stainless-steel CTD rosette equipped with 20 L
171 OTE Niskin bottles. For chlorophyll-*a* analysis, samples were filtered ($0.7 \mu\text{m}$ Whatman GF/F)
172 and then the filters extracted overnight in 90 % acetone (Holm-Hansen et al., 1965). The
173 chlorophyll-*a* extract was measured on a pre-calibrated (spinach chlorophyll-*a* standard,
174 Sigma) Turner Designs Trilogy fluorometer. High performance liquid chromatography
175 (HPLC) samples (0.5 – 2 L) for accessory pigment analyses were filtered ($0.7 \mu\text{m}$ Whatman

176 GF/F), flash frozen in liquid nitrogen and stored at -80 °C prior to analysis using a Thermo
177 HPLC system. The matrix factorization program CHEMTAX was used to estimate the
178 contribution of taxonomic groups to total chlorophyll-*a* (Mackey et al., 1996). Concentrations
179 of nanophytoplankton, *Synechococcus*, *Prochlorococcus* and photosynthetic picoeukaryotes
180 were analysed by analytical flow cytometry (AFC) using a FACSort flow cytometer (Becton
181 Dickenson, Oxford, UK) according to the methods described in Davey et al. (2008) and Zubkov
182 et al. (2003).

183

184 **3. Results and Discussion**

185 **3.1. Hydrographic setting and macronutrient distributions**

186 The prominent waters masses along the D357 and JC068 transects (Fig. 2) were identified by
187 their characteristic thermohaline and macronutrient properties (Sarmiento et al., 2004; Ansorge
188 et al., 2005; Browning et al., 2014). Wyatt et al. (2014) provide a more detailed description of
189 the JC068 hydrography along the entire GA10 section. Whilst we aim to compare the nearshore
190 versus offshore distributions of micro- and macronutrients, note that sub-Antarctic mode water
191 was not sampled for trace metals during the D357-2 late spring transect, and therefore only the
192 early spring and summer values are discussed for SASW hereafter.

193

194 ***Surface mixed-layer***

195 During all three transects the STF was identified by a sharp potential temperature (θ) gradient
196 in the upper 200 m with the θ 15°C isotherm corresponding well to changes in macronutrient
197 concentrations between STSW and SASW. North of the STF, mixed-layer macronutrient
198 concentrations (Table 2) decreased in STSW between the three occupations of the transect. The
199 largest relative depletion observed was for NO_3^- with a ~2.7-fold reduction in mean inventory
200 concentration from 870 to 326 $\mu\text{mol m}^{-3}$ between early spring and summer, whilst PO_4^{3-} and

201 Si concentrations were reduced 1.5- and 1.4-fold, respectively. The largest absolute depletion
202 was observed for Si with a reduction of $848 \mu\text{mol m}^{-3}$ between early spring and summer.
203 Conversely, summer SASW mixed-layer mean concentrations of NO_3^- , PO_4^{3-} and Si were
204 relatively 1.6, 1.4 and 2.1-fold lower than early spring, respectively, whilst the largest absolute
205 depletion of $1912 \mu\text{mol m}^{-3}$ was observed for NO_3^- . SASW mixed-layer concentrations of NO_3^-
206 and PO_4^{3-} were at least 2.1-fold higher than for STSW during the study, whilst the Si
207 concentration was at least 1.5-fold lower, highlighting the relative deficiencies in major
208 nutrients between high and low latitude derived surface waters (Sarmiento et al., 2004; Moore,
209 2016).

210

211 ***Sub-surface waters***

212 The Southern Ocean derived Sub-Antarctic Mode Water (SAMW) and underlying Antarctic
213 Intermediate Water (AAIW) were identified using their characteristic core potential density
214 ($\sigma\theta 26.8 \text{ kg m}^{-3}$) (Sarmiento et al., 2004; Palter et al., 2010) and thermohaline ($S < 34.4$, θ
215 $> 2.8^\circ\text{C}$) properties (Fig. 2). Wyatt et al. (2014) have identified these water masses along this
216 section between 200 and 500 m. During all three transects, low sub-surface (50 – 500 m)
217 macronutrient concentrations were observed between 13 and 16°E , associated with a salinity
218 maxima. The feature conforms to the mean locality and depth range of Agulhas water
219 (Duncombe Rae, 1991), clearly highlighting the penetration of Indian Ocean water into
220 northward flowing SAMW.

221

222 **3.2. Zn and Co distributions of the Southeast Atlantic Ocean**

223 ***Surface mixed-layer***

224 Figure 3 shows the dZn and dCo distributions for the upper 500 m of the Southeast Atlantic for
225 the D357 and JCO68 transects. For full-depth dZn distributions along JC068 refer to Wyatt et

226 al. (2014). In the surface mixed-layer, dZn and dCo concentrations ranged from 0.01 to 4.57
227 nM and 1 to 50 pM, respectively. The large range in dZn concentrations resulted from an
228 apparent offshore transport of elevated dZn within STSW between 20 – 50 m during early
229 spring (1.48 – 4.57 nM; Stns. 1 – 2) that was reduced by late spring (0.48 – 1.76 nM; Stns. 0.5
230 – 1.5) and was absent during summer (0.01 – 0.13 nM; Stns. 1 – 2). Similarly, but to a lesser
231 extent, elevated dCo concentrations were observed in STSW between 10 and 50 m during early
232 and late spring (15 – 50 pM), compared with summer (18 – 33 pM). Our findings are consistent
233 with previous observations of elevated dissolved and particulate trace metals over the same
234 depth range in waters close to South Africa, including Co, Fe, Mn, and Pb (Chever et al., 2010;
235 Bown et al., 2011; Boye et al., 2012; Paul et al., 2015). We postulate that these trace metal
236 enrichments can arise from either atmospheric inputs, and/or from the lateral advection of
237 metal-enriched waters from the Agulhas Current (AC) and/or South African continental shelf,
238 and discuss this further in Sect. 3.3. In SASW, mixed-layer dZn and dCo concentrations ranged
239 from 0.01 to 0.25 nM and 3 to 18 pM, respectively, during the study, significantly lower than
240 STSW values, with the lowest concentrations observed during the summer transect (Table 2).

241

242 ***Sub-surface waters***

243 During the early spring D357-1 transect, elevated dZn and dCo concentrations were observed
244 between the surface mixed-layer and 500 m (1.48–3.85 nM and 39–62 pM, respectively) at the
245 station closest the South African continent (Stn. 1). Here, the highest dZn concentrations were
246 associated with the dZn-enriched waters (20–55 m) described above for the surface mixed-
247 layer. During the late spring D357-2 transect, the near-shore (Stns. 0.5–1) dZn concentrations
248 were lower (0.31–1.76 nM) whilst dCo remained similar to early spring values (27–57 pM).
249 During summer, near-shore (Stn. 1) sub-surface dZn concentrations were markedly lower
250 (0.03–0.50 nM) than spring values whilst dCo concentrations (17–52 pM) were only

251 marginally lower. In offshore waters, sub-surface dZn concentrations ranged from 0.01 to 1.01
252 nM across all three transects with extremely low values in the upper 400 m (0.22 ± 0.21 nM)
253 and the highest values between 400 and 500 m. The absence of a significant return path for
254 dZn with SAMW to waters above 400 m at this latitude (Wyatt et al., 2014; Vance et al., 2017)
255 is likely an important control on dZn distributions across all three transects. In contrast, dCo
256 concentrations were depleted in the upper 200 m (1–35 pM) and elevated in SAMW (23–56
257 pM) suggesting that these Southern Ocean derived waters also play an important role in upper
258 water column dCo distributions of the South Atlantic.

259 To assess whether seasonal changes in subsurface supply could influence dissolved Zn and Co
260 concentrations in the upper water column of the Southeast Atlantic, we examined the metal
261 versus PO_4^{3-} distributions of underlying SAMW and AAIW. Throughout this paper metal: PO_4^{3-}
262 will be used to indicate an uptake remineralisation ratio derived from a regression slope, whilst
263 metal/ PO_4^{3-} will denote a concentration ratio. Figure 4 and supplementary table 1 show how
264 the dZn: PO_4^{3-} regression slope for SAMW and AAIW varied little between the three transects.
265 These slopes are a function of the pre-formed micro- and macronutrient concentrations and the
266 uptake/remineralisation ratio of the sources waters, as well as mixing during advection between
267 the Southern Ocean and South Atlantic (Vance et al., 2017; Middag et al., 2018). The dZn: PO_4^{3-}
268 slopes steepen with the introduction of AAIW with higher dZn/ PO_4^{3-} concentration ratios, yet
269 it is the relatively shallow slopes of overlying SAMW that imply a low, and relatively
270 consistent, subsurface supply of dZn to STSW and SASW of the South Atlantic (Wyatt et al.,
271 2014). The shallower waters overlying SAMW clearly show elevated dZn concentration,
272 specifically during the spring transects, compared with what could be delivered if subsurface
273 supply was the dominant source governing dZn availability in surface waters (Fig. 4). It is
274 therefore unlikely that a change in subsurface supply from underlying SAMW is responsible
275 for the change in dZn inventories of STSW and SASW between the three transects.

276 Similarly, the dCo:PO₄³⁻ regression slope varied little between the three transects (Fig. 4 and
277 Supp. Table 1). In dCo:PO₄³⁻ space, a single slope can be fit to SAMW and AAIW with no net
278 scavenging effect on dCo distribution over the upper 1000 m. Like dZn, the waters overlying
279 SAMW displayed spring dCo concentrations elevated above that potentially delivered via
280 SAMW supply. During summer however, SAMW may provide a subsurface source of dCo
281 (Fig. 4c) to overlying waters highlighting how Southern Ocean derived waters may play
282 important, yet different, roles in upper water column metal distributions of the Southeast
283 Atlantic.

284

285 **3.3. Shelf derived sources of Zn and Co**

286 Potential sources of trace metals to surface waters of the Southeast Atlantic include
287 atmospheric inputs from South Africa and Patagonia (Chance et al., 2015; Menzel Barraqueta
288 et al., 2019) as well as interactions with shelf and slope waters of the Agulhas Bank (Bown et
289 al., 2011; Boye et al., 2012; Paul et al., 2015). During the D357 spring transects, elevated
290 mixed-layer dZn and dCo concentrations (up to 4.57 nM and 50 pM, respectively; Sect. 3.2)
291 were observed at stations closest the Agulhas Bank shelf and slope (Stns. 0.5, 1, 1.5 and 2).
292 Here, we compare these metal elevations with respect to the aforementioned sources. Firstly,
293 we encountered only brief, light rain during the study, thus minimal wet deposition of
294 atmospheric aerosol. By combining the median atmospheric dry deposition flux for soluble Zn
295 and Co for the Southeast Atlantic (Zn 6.0 and Co 0.05 nmol m⁻² d⁻¹; Chance et al., 2015) with
296 the mean mixed-layer depth (34 m) for STSW during D357, dust dissolution is estimated to
297 add approximately 5.5 and 0.05 nmol m⁻³ dZn and dCo, respectively, over a one month period.
298 These inputs are low compared with the mixed-layer metal inventories, representing <1 % of
299 dZn and dCo concentration in STSW during the D357 transects (Table 2), and would not be
300 sufficient to generate distinct mixed-layer maxima. It is likely, therefore, that the dZn and dCo

301 elevations originated from the advection of metal-enriched waters from the western Agulhas
302 Bank, a region identified as a distinct source of both dissolved and particulate trace metals to
303 the Southeast Atlantic (Chever et al., 2010; Bown et al., 2011; Boye et al., 2012; Paul et al.,
304 2015), and/or from the leakage of Indian Ocean water into the Southeast Atlantic via the AC.
305 The detachment of Agulhas rings and filaments from the AC during its retroflection back
306 towards the Indian Ocean constitutes a source of Pb to the surface Southeast Atlantic along the
307 D357 transects (Paul et al., 2015). Whilst we observed elevated mixed-layer dZn and dCo at
308 ~15°E during both D357 transects, the absence of metal enrichment across the depth of the AC
309 salinity maxima (Figs. 2 and 3) suggests that the signal must be entrained from elsewhere.
310 Furthermore, dZn concentrations from the AC along the east coast of South Africa do not
311 exceed 0.5 nM in the upper 200 m (Gosnell et al., 2012). It is therefore likely that the dZn and
312 dCo enrichment was derived from the Agulhas Bank. The AC has been shown to meander over,
313 and interact with, the Agulhas Bank, forming eddies and filaments on the shoreward edge of
314 the AC proper, that tend to move northwards along the western shelf edge and into the
315 Southeast Atlantic (Lutjeharms and Cooper, 1996; Lutjeharms, 2007), potentially delivering
316 shelf-derived sedimentary material. We found no evidence of a fluvial signature in our data,
317 and no significant fluvial source for trace elements to our study region has been reported in the
318 literature. We focus here on the more likely scenario of sedimentary inputs as the driver of
319 mixed-layer dZn and dCo elevations at the shelf and slope stations during D357. Despite no
320 available particulate trace metal data for the D357-1 early spring transect for direct comparison
321 with the highest dZn and dCo elevations, we observed elevated mixed-layer particulate Zn
322 (pZn; 0.08–1.40 nM) and Co (pCo; 8–49 pM) at stations closest South Africa during the D357-
323 2 late spring transect (Stns. 0.5, 1 and 1.5, Fig. S1), coincident with elevated dZn (0.05–1.82
324 nM) and dCo (1–43 pM). Furthermore, for the upper 500 m at stations 0.5 and 1, we found
325 strong positive correlations between particulate aluminium and titanium (pAl:pTi, slope 41.7

326 mol mol⁻¹, Pearson's r 0.99, n = 15), as well as particulate Fe and titanium (pFe:pTi, slope 10.2
327 mol mol⁻¹, Pearson's r 0.99, n = 15), indicative of a strong lithogenic source. Whilst there are
328 presently no South African sedimentary data against which we can compare our water column
329 values, our pAl:pTi and pFe:pTi slope ratios are in excess of upper crustal mole ratios (34.1
330 and 7.3 mol mol⁻¹, respectively; McLennan, 2001). These 500 m ratios are also steeper than the
331 aggregate slopes for the full depth Atlantic Ocean away from hydrothermal sources (32.1 and
332 7.4 mol mol⁻¹, Pearson's r >0.97, n = 593, Schlitzer, 2018). Given the refractory nature of
333 lithogenic pTi across diverse oceanic environments (Ohnemus and Lam, 2015), this may
334 suggest the resuspension and dissolution of Agulhas Bank sediments enriched in dAl and dFe,
335 followed by westward offshore transport, a common feature of the Bank's physical circulation
336 during spring and summer (Largier et al., 1992). Such processes may in turn provide an
337 additional source of dZn and dCo to STSW of the Southeast Atlantic. For example, Little et al.
338 (2016) proposed that oxygen-deficient, organic-rich, continental margin sediments may
339 constitute a significant global sink within the marine Zn cycle. These sediments could
340 additionally provide a local source of dZn following remineralisation. Recent model outputs
341 have likewise highlighted oxygen-deficient, boundary sediments as a dominant external source
342 of Co to the oceans (Tagliabue et al., 2018). Given that oxygen depleted (<45 µM) bottom
343 waters are prevalent across the western Agulhas Bank (Chapman and Shannon, 1987;
344 Chapman, 1988), considered to arise from high organic matter input to sediments and its
345 bacterial decomposition, a sedimentary source of dZn and dCo appears likely.

346

347 **3.4. Trace metal stoichiometry of the upper Southeast Atlantic**

348 In addition to seasonal variations in the lateral advection of continentally derived trace metals,
349 the lower dZn and dCo concentrations in STSW during summer, compared with spring, likely
350 reflect differences in biological utilisation. Here, we examine the micro- and macronutrient

concentration inventories to assess the trace metal stoichiometry of the Southeast Atlantic over seasonal timescales. The data were grouped into STSW and SASW regimes, with STSW defined by $\theta \geq 15^{\circ}\text{C}$. This isotherm was located at a mean depth of 144 ± 96 m across the study, compared with a mean mixed-layer depth of 39 ± 10 m, and thus the inventories for SASW were determined over this depth for comparison with STSW (Table 2). Early and late spring STSW samples in the depth range 20 - 55 m that clearly exhibited continentally derived elevated dZn and dCo were removed from the analysis in order to compare stoichiometry with respect to biological processes. For SASW, micronutrient sampling did not occur during late spring and therefore only early spring and summer values are compared.

Distinct temporal trends in the stoichiometric relationship with PO_4^{3-} were evident for both dZn and dCo (Fig. 4). Within STSW, the dZn/ PO_4^{3-} inventory ratio ranged from 699 to $1876 \mu\text{mol mol}^{-1}$ (Table 2) with the highest value observed during early spring and the lowest during summer. Combined with summer dZn concentrations 4-fold lower than early spring, this suggests strong biological uptake of dZn alongside PO_4^{3-} between seasons. In contrast, lower dZn/ PO_4^{3-} ratios of 372 and $188 \mu\text{mol mol}^{-1}$ were observed in SASW during early spring and summer, respectively. Here, the absolute change in dZn concentration between spring and summer was lower than for STSW, but was greater for PO_4^{3-} , likely reflecting the increased availability of PO_4^{3-} in these Southern Ocean derived waters (Table 2) and an open-ocean phytoplankton community that have lower trace metal requirements than their counterparts north of the STF. Such dZn/ PO_4^{3-} ratios sit at the lower end of cellular Zn/P reported for the diatom and haptophyte-type phytoplankton typical of this region ($\sim 100 - 1100 \mu\text{mol mol}^{-1}$; Twining and Baines, 2013 and refs. therein), highlighting the importance of micronutrient processes with respect to Zn availability.

In contrast to dZn, the spatiotemporal variation observed for STSW dCo/ PO_4^{3-} was small with ratios ranging from 82 to $129 \mu\text{mol mol}^{-1}$ (Table 2), likely reflecting external inputs to the

376 oceans and biological Co requirements that are typically 4-fold less than for Zn (Ho et al.,
377 2003; Roshan et al., 2016; Hawco et al., 2018). The STSW dCo/PO₄³⁻ ratio decreased between
378 early and late spring transects, potentially in part due to the westward expansion of STSW
379 during late spring (Fig. 2) and subsequent mixing with SASW depleted in dCo relative to PO₄³⁻
380 (Fig. 3). This dilution is likely also true of dZn and Si, yet their STSW concentration inventories
381 may be sufficiently high as to mask this effect. Unfortunately, an insufficient quantity of late
382 spring SASW data are available with which to affirm this postulation. The highest dCo/PO₄³⁻
383 ratio was observed during summer due to the preferential biological removal of PO₄³⁻ relative
384 to dCo.

385 In SASW, dCo/PO₄³⁻ was consistently low with ratios of 23 and 26 µmol mol⁻¹ for early spring
386 and summer, respectively. Much higher inventory ratios of ~580 µmol mol⁻¹ can be calculated
387 over similar depths for open-ocean North Atlantic waters (GA03 Stns. 11-20, Schlitzer et al.,
388 2018), likely reflecting an elevated atmospheric Co input and/or an extremely low surface PO₄³⁻
389 inventory (Wu et al., 2000; Martiny et al., 2019).

390 Our results provide evidence for the greater availability and preferential removal of dZn
391 relative to dCo in the upper water column the Southeast Atlantic based on STSW dZn/dCo
392 inventory ratios of 19, 17 and 5 mol mol⁻¹ for the three transects and SASW ratios of 13 and 7
393 mol mol⁻¹ for early spring and summer, respectively (Table 2). With relatively consistent inter-
394 seasonal dCo inventories for STSW and SASW, indicating a more balanced ecophysiological
395 regime with regard to dCo organisation, the change in dZn/dCo inventory stoichiometries
396 principally reflects changes in dZn concentration. We postulate that the inter-seasonal
397 variations in dZn and dCo availability and stoichiometry of the Southeast Atlantic reflect
398 changes in the relative nutritional requirement of resident phytoplankton and/or biochemical
399 substitution of Zn and Co to meet nutritional demand.

400

401 **3.5. Phytoplankton controls on trace metal ecological stoichiometry**

402 Here we discuss the principle phenomena that together likely explain our observations of
403 seasonally decreasing dZn/dCo inventory stoichiometries in STSW and SASW of the
404 Southeast Atlantic: i.e. the preferential removal of dZn, relative to dCo, leading to low dZn
405 availability, and differences in phytoplankton assemblages with different cellular metal
406 requirements.

407 Satellite images show elevated surface chlorophyll concentrations across the Southeast Atlantic
408 STF, compared with waters further north and south, with peak concentrations observed during
409 summer in January 2012 (Fig. 1). Profiles of total chlorophyll-*a* concentration (Fig. S2) also
410 show maximum summer values in the upper water column of STSW (1.02 mg m^{-3}) and SASW
411 (0.49 mg m^{-3}) compared with spring values (<0.61 and $<0.36 \text{ mg m}^{-3}$, respectively). This is
412 consistent with the hypothesis that increasing irradiance, coupled with shallower mixed-layer
413 depths (de Boyer Montégut et al., 2004), result in enhanced growth conditions across the STF
414 between September and February (Browning et al., 2014). Diagnostic pigment analyses (Fig.
415 5a) indicated that eukaryotic nanophytoplankton, specifically *Phaeocystis*-type haptophytes,
416 dominated the early spring STSW chlorophyll-*a* content (73 %) but with a reduced contribution
417 during summer (20 %). Maximum growth rates for cultured *Phaeocystis antarctica* have been
418 achieved under elevated Zn concentrations (Saito and Goepfert, 2008), and thus, the dominance
419 of this haptophyte would likely contribute to the removal of dZn between spring and summer.
420 Furthermore, an increased summer diatom contribution (13 % chlorophyll-*a* compared with
421 near zero during spring transects) would have further reduced the dZn inventory, with diatoms
422 having at least 4-fold higher cellular Zn/P ratios than co-occurring cell types (Twining and
423 Baines, 2013).

424 The fact that both *Phaeocystis* and diatomaceous nanophytoplankton maintain a contribution
425 to the summer STSW chlorophyll-*a* complement, when dZn availability is low, is intriguing.

426 Both *P. antarctica* and the large, coastal diatoms *Thalassiosira pseudonana* and *Thalassiosira*
427 *weissflogii* have been shown to be growth limited in culture by free Zn²⁺ concentrations ≤ 10
428 pM (Sunda and Huntsman, 1992; Saito and Goepfert, 2008). A simple estimate of summer
429 STSW free Zn²⁺ availability, based on North Atlantic organic complexation data (>96 %;
430 Ellwood and Van den Berg, 2000), indicated free Zn²⁺ averaged $6.3 \pm 5.3 \mu\text{M}$, suggesting the
431 potential for growth limitation of these phytoplankton. In addition, when comparing the
432 Southeast Atlantic dZn stoichiometry with the cellular requirements of phytoplankton grown
433 under growth rate limiting conditions (Fig. 6), we found summer STSW dZn/PO₄³⁻ to be in
434 deficit of the requirements of coastal *T. pseudonana* but not those of the smaller, open-ocean
435 diatom *T. oceanica*. The variation in cellular Zn/P between small and large phytoplankton is
436 related to the higher surface-area-to-volume ratio of smaller cells, and the limitation of
437 diffusive uptake rates at low Zn²⁺ concentrations (Sunda and Huntsman, 1995). This would
438 suggest that the lower dZn availability in summer STSW should influence phytoplankton
439 species composition by selecting for smaller organisms with lower cellular Zn requirements,
440 and confirmed by a ratio of picophytoplankton to nanophytoplankton at least 4-fold higher
441 during summer compared with spring values. The comparison further implies that the presence
442 of *Phaeocystis* and diatoms in summer STSW may be linked with their metabolic Zn-Co-Cd
443 substitution capability, potentially allowing them to overcome some portion of their Zn
444 deficiency. Largely connected to carbonic anhydrase enzymes, several species of eukaryotic
445 phytoplankton are capable of biochemical substitution of Zn, Co or Cd to maintain optimal
446 growth rates under low trace metal conditions (Price and Morel, 1990; Sunda and Huntsman,
447 1995; Lee and Morel, 1995; Lane and Morel, 2000; Xu et al., 2007; Saito and Goepfert, 2008;
448 Kellogg et al., 2020). For example, metabolic substitution of Co in place of Zn has been
449 observed to support the growth of *P. antarctica*, *T. pseudonana* and *T. weissflogii* in media
450 with Zn²⁺ < 3 pM (Sunda and Huntsman, 1995; Saito and Goepfert, 2008; Kellogg et al., 2020).

451 Thus, the lower mixed-layer dCo inventory of summer STSW, relative to early spring, may be
452 in part related to enhanced dCo uptake through biochemical substitution alongside the growth
453 of phytoplankton with distinct Co requirements.

454 In contrast to *Phaeocystis*, *E. huxleyi*-type haptophytes were near-absent in spring STSW (<5
455 % chlorophyll-*a*; Fig. 5a) and increased in contribution during summer (18 %). *Emiliania*
456 *huxleyi* appear to have a biochemical preference for Co over Zn (Xu et al., 2007), which could
457 potentially be a contributing factor to the increased fraction of this haptophyte in summer
458 STSW. Based on Co organic complexation data for Southeast Atlantic STSW (>99 %; Bown
459 et al., 2012), however, even the maximum dCo concentration of 56 pM (estimated free Co²⁺
460 $0.56 \pm 0.11\mu\text{c}$ pM) observed for STSW during this entire study would limit the growth of
461 cultured *E. huxleyi* in the absence of Zn or Cd (Sunda and Huntsman, 1995; Xu et al., 2007).

462 This is supported by inter-seasonal dCo/PO₄³⁻ stoichiometries in deficit of the cellular
463 requirements of cultured *E. huxleyi* (Fig. 6). Despite this, Xu et al. (2007) showed that *E.*
464 *huxleyi* can maintain significant growth at only 0.3 pM Co²⁺ in the presence of Zn, with the
465 limitation by, and substitution of these metals reported to occur over a range of free ion
466 concentrations (0.2–5 pM) that is relevant to summer conditions of the Southeast Atlantic. This
467 assessment implies an additional need for Zn in phytoplankton nutrition due to low dCo
468 availability throughout the Southeast Atlantic, which may accelerate the decrease in dZn/dCo
469 inventory ratio between seasons.

470 The elevated summer STSW chlorophyll-*a* concentrations were accompanied by increased cell
471 concentrations of the *Synechococcus* and *Prochlorococcus* (up to 100 and 400 cells μL^{-1} ,
472 respectively) relative to early spring abundance (Fig. 5b). This pattern suggests an inter-
473 seasonal community shift towards smaller picocyanobacterial cells that is coincident with
474 decreased dZn availability. *Synechococcus* and *Prochlorococcus* are thought to have little or
475 no Zn requirement and relatively low Co requirements (growth limited by ≤ 0.2 pM Co²⁺; Sunda

476 and Huntsman, 1995; Saito et al., 2002). This, alongside their small cell size, hence greater
477 capacity for acquiring fixed nitrogen under conditions where this nutrient is depleted, may
478 allow these prokaryotes to flourish following depletion and export of Zn associated with
479 *Phaeocystis* and diatom blooms. This supposition is supported by a persistently high abundance
480 of *Synechococcus* and *Prochlorococcus* (>1000 cells μL^{-1}), relative to eukaryotic
481 nanophytoplankton, in the dZn depleted surface waters of the Costa Rica Dome (Saito et al.,
482 2005; Ahlgren et al., 2014; Chappell et al., 2016). Here, surface dCo concentrations were
483 maintained above that of surrounding waters by the biological production of Co-binding
484 ligands (Saito et al., 2005). The increased abundance of these prokaryotic autotrophs in summer
485 STSW of the Southeast Atlantic may have also contributed to the inter-seasonal decrease in
486 dCo inventory.

487 In contrast to STSW, cells counts of eukaryotic phytoplankton and prokaryotic cyanobacteria
488 in SASW varied little between early spring and summer (Fig. 5b), indicative of a more balanced
489 ecophysiological regime. The fractional contribution of *Phaeocystis* (Fig. 5a), the dominant
490 contributor to the SASW chlorophyll-*a* complement, was similar between transects at 54 and
491 44 %, respectively, whilst the contribution of *E. huxleyi* increased from 19 to 33 % between
492 spring and summer, respectively. Whilst it is proposed that the low Fe supply rate to these
493 waters provides a dominant control on phytoplankton biomass and composition (Browning et
494 al., 2014), low dZn and dCo availability may also be important drivers of such change. The
495 Summer SASW dZn inventory ($0.08 \pm 0.07 u_c$ nM) and stoichiometry with PO_4^{3-} (Fig. 6)
496 indicate growth limiting conditions for *Phaeocystis* and *E. huxleyi* in the absence of
497 cambialistic metabolism (Sunda and Huntsman., 1995; Saito and Goepfert, 2008; Xu et al.,
498 2007). The presence of these phytoplankton therefore indicates Zn biochemical substitution
499 occur in oceanic waters of the Southeast Atlantic. A lower Co half-saturation growth constant
500 for cultured *P. antarctica* ($K_m = \sim 0.2$ pM Co^{2+}), compared with *E. huxleyi* ($K_m = \sim 3.6$ pM

501 Co²⁺), further suggests that *Phaeocystis* species may more effectively occupy low dZn and dCo
502 environments (Saito and Goepfert, 2008), such as SASW of the South Atlantic.
503 Conversely, the absence of a significant diatom contribution to summer SASW chlorophyll-*a*
504 (Fig. 5a), relative to early spring, is surprising as the summer dZn/PO₄³⁻ inventory ratio is in
505 excess of the cellular Zn/P requirements of typical oceanic diatoms such as *T. oceanica* (Fig.
506 6). Furthermore, whilst the dCo/PO₄³⁻ ratio of summer SASW is in deficit of the cellular Co/P
507 below which growth limitation of *T. oceanica* may occur, this species has been shown to grow
508 effectively at Co²⁺ <0.1 pM in culture in the presence of Zn (Sunda and Huntsman, 1995). The
509 low diatom fractional contribution to summer SASW may be instead related to low Fe
510 availability (Browning et al., 2014) and stress-induced Si exhaustion. In support of this, we
511 calculate summer SASW mixed-layer Si concentrations ($0.9 \pm 0.3 \mu\text{M}$) to be 50 % of early
512 spring values ($1.8 \pm 0.2 \mu\text{M}$) with a dissolved NO₃⁻/Si stoichiometry of 3.8 mol mol⁻¹ close to
513 the 4 mol mol⁻¹ shown to limit diatom growth in culture (Gilpin et al., 2004), and in contrast to
514 the 2.9 mol mol⁻¹ calculated for early spring.

515

516 **3.6. Conclusion**

517 We report the distributions of dZn and dCo in the upper water column of sub-tropical and sub-
518 Antarctic waters of the Southeast Atlantic during austral spring and summer periods. We
519 identify an apparent continental source of dZn and dCo to sub-tropical waters at depths between
520 20 – 55 m, derived from sedimentary inputs from the Agulhas Bank. In contrast, open-ocean
521 sub-Antarctic surface waters displayed largely consistent inter-seasonal mixed-layer dZn and
522 dCo concentrations indicating a more balanced ecophysiological regime with regard to their
523 organisation. The vertical distributions of dZn and dCo in the upper water column were similar
524 to that of PO₄³⁻ indicating biological drawdown in surface waters and mixing with underlying
525 Southern ocean-derived waters travelling equatorward significantly influences their

526 distribution. Absolute trace metal concentrations alongside concentration inventory ratios
527 suggest the preferential utilization of dZn, relative to dCo, in the Southeast Atlantic with
528 dZn/dCo decreasing from 19 to 5 mol mol⁻¹ between early spring and summer in STSW and
529 from 13 to 7 mol mol⁻¹ in SASW. This pattern is consistent with our understanding of the
530 cellular requirement of phytoplankton (Twining and Baines, 2013). The inter-seasonal removal
531 of dZn results in summer concentrations that are potentially growth limiting for certain
532 phytoplankton species estimated to be present in these waters by diagnostic pigment analyses.
533 We therefore suggest cambialistic metabolic substitution between Zn and Co, and potentially
534 Cd, is an important factor regulating the growth, distribution and diversity of phytoplankton in
535 the Southeast Atlantic.

536

537 *Data availability.* The trace metal and macronutrient data sets used for analyses in this study
538 are available at <https://www.bodc.ac.uk/geotraces/data/idp2017/> (GEOTRACES GA10) and
539 phytoplankton data at <https://www.bodc.ac.uk/>.

540

541 *Competing interests.* The authors declare that they have no conflict of interest.

542

543 *Author contribution.* MCL and EPA acquired the funding. NJW, MCL, AM, TJB, EMSW, and
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547

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832

833

834

835 Table 1. Analytical validation results for open ocean surface seawater (SAFe S), 1000 m
836 seawater (SAFe D2) and 2000 m seawater (GEOTRACES GD). All concentrations are in nM
837 (± 1 std. dev.). Consensus value conversion = 1.025 kg/L. ND indicates sample not determined.

838

	SAFe S	SAFe D2	GEOTRACES GD
Zn (FIA)	0.060 (0.020) $n = 7$	7.723 (0.091) $n = 12$	ND
Zn consensus value	0.071 (0.010)	7.616 (0.256)	1.753 (0.123)
Co (FIA)	0.004 (0.001) $n = 3$	0.049 (0.001) $n = 2$	0.073 (0.004) $n = 5$
Co consensus value	0.005 (0.001)	0.047 (0.003)	0.067 (0.001)

839

840

841 Table 2. Southeast Atlantic dissolved micro- and macronutrient mean concentration inventories
842 for the upper water column during early spring (D357-1), late spring (D357-2) and summer
843 (JC068) transects. STSW and SASW waters were defined using the $\theta 15^{\circ}\text{C}$ isotherm (Section
844 3.4) and are compared with total inventories calculated for the shallower mixed layer (in
845 parenthesis) that include continental inputs of dissolved Zn and Co. Zn/PO₄³⁻, Co/PO₄³⁻ and
846 Zn/Co represent the concentration inventory ratios for STSW and SASW, respectively. STSW
847 = Sub-Tropical Surface Water, SASW = Sub-Antarctic Surface Water.

848

Oceanographic Regime	Transect	Zn (nmol m ⁻³)	Co (nmol m ⁻³)	NO ³⁻	PO ₄ ³⁻ ($\mu\text{mol m}^{-3}$)	Si(OH) ₄	Zn/PO ₄ ³⁻ ($\mu\text{mol mol}^{-1}$)	Co/PO ₄ ³⁻ ($\mu\text{mol mol}^{-1}$)	Zn/Co (mol mol ⁻¹)
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STSW	Early spring	624 (1597)	32 (30)	2694 (870)	333 (203)	3735 (2790)	1876	97	19
	Late spring	384 (592)	23 (17)	1846 (763)	276 (191)	2781 (2326)	1387	82	17
	Summer	158 (139)	29 (24)	1557 (326)	226 (139)	2711 (1942)	699	129	5
SASW	Early spring	182 (112)	14 (13)	6035 (5300)	615 (566)	1875 (1847)	296	22	13
	Summer	83 (94)	12 (10)	4143 (3388)	439 (400)	1027 (886)	188	26	7

849

850

851

852 Figure 1. The Southeast Atlantic stations sampled for dissolved Zn and Co along the GA10
 853 section during UK-GEOTRACES cruises D357 (red circles) and JC068 (black circles),
 854 overlain a VIIRS monthly composite image of chlorophyll-*a* concentrations for January 2012
 855 (<https://oceancolor.gsfc.nasa.gov/>). Two transects were completed during D357 between Cape
 856 Town and the zero meridian that represent early austral spring 2010 (D357-1; Stns. 1, 2, 3, 4,
 857 5 & 6) and late austral spring 2010 (D357-2; Stns. 0.5, 1, 1.5, 2.5, 3.5, 4.5), respectively. JC068
 858 took place during austral summer 2011/12 and we present here only the repeat transect data
 859 between Cape Town and 13°W (Stns. 1, 2, 3, 7, 8, 9, 11). STSW = Sub-Tropical Surface Water,
 860 SASW = Sub-Antarctic Surface Water, AC = Agulhas Current, AR = Agulhas retroflection.

861

862 Figure 2. Upper 500 m potential temperature (θ) and dissolved PO_4^{3-} distributions for the
 863 Southeast Atlantic along early spring (a,b; D357-1), late spring (c,d; D357-2) and summer (e,f;
 864 JC068) transects. The dominant Southern Ocean (SASW & SAMW) and South Atlantic
 865 (STSW) water masses that influence the distribution of nutrients are shown. The θ 15°C
 866 isotherm (solid contour) represents a practical definition of the STF location, whilst SAMW is
 867 identified by the median potential density ($\sigma\theta$) isopycnal 26.8 kg m^{-3} (dashed contour, see Sect.
 868 4.1.). STSW = Sub-Tropical Surface Water, SAMW = Sub-Antarctic Mode Water, AAIW =
 869 Antarctic Intermediate Water.

870

871 Figure 3. Upper 500 m dissolved Zn and Co distributions for the Southeast Atlantic along early
 872 spring (a,b; D357-1), late spring (c,d; D357-2) and summer (e,f; JC068) transects. The STF is
 873 delineated by θ 15°C (solid contour), whilst the influence of SAMW is evident by the median
 874 potential density ($\sigma\theta$) isopycnal 26.8 kg m^{-3} (dashed contour, see Section 4.1.). STSW = Sub-
 875 Tropical Surface Water, SAMW = Sub-Antarctic Mode Water, AAIW = Antarctic Intermediate
 876 Water. Note the changing y-axis scales for dZn distribution.

877

878 Figure 4. The dissolved Zn and Co versus PO_4^{3-} distribution for the Southeast Atlantic during
 879 early spring (a,b; D357-1), late spring (c,d; D357-2) and summer (e,f; JC068) transects. The

880 green and red lines indicate the dZn:PO₄³⁻ regression slopes for SAMW and AAIW,
881 respectively. The yellow line indicates the dCo:PO₄³⁻ regression slope for SAMW and AAIW
882 combined. The equations for regression lines are detailed in Supplementary table 1. SAMW =
883 Sub-Antarctic Mode Water, AAIW = Antarctic Intermediate Water. The full depth dZn:PO₄³⁻
884 relationship along JC068 can be found in Wyatt et al. (2014).

885

886 Figure 5. Seasonal differences in (a) pigment-derived taxonomic contributions to total
887 chlorophyll-*a* (percentage), and (b) AFC counts of *Synechococcus*, *Prochlorococcus*,
888 nanophytoplankton (approx. >2μm) and photosynthetic picoeukaryotes (approx. <2μm) in the
889 Southeast Atlantic.

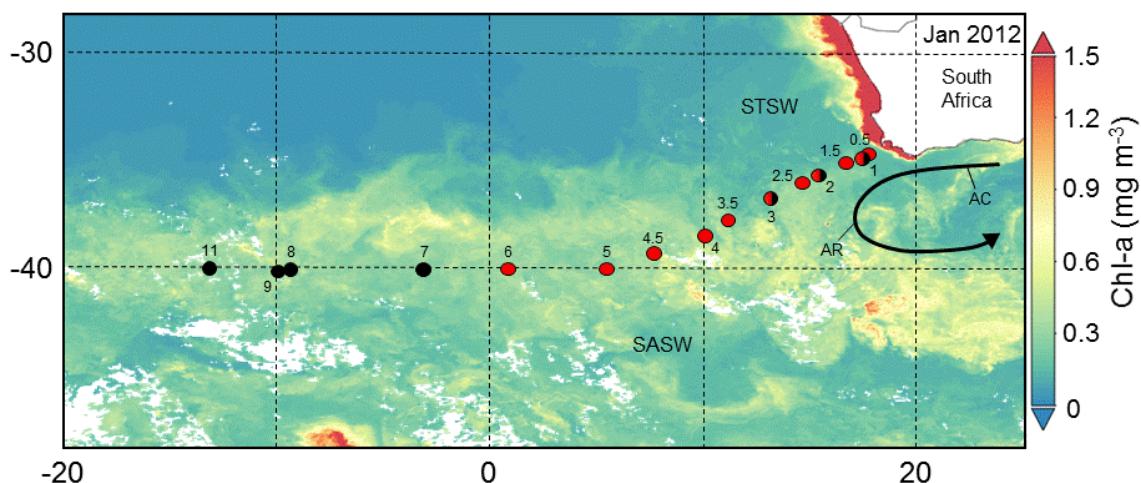
890

891 Figure 6. Metal/PO₄³⁻ inventory ratios for the upper water column of the Southeast Atlantic
892 (horizontal bars) compared with laboratory estimates of cellular ratios in eukaryotic
893 phytoplankton below which growth limitation occurs (solid vertical lines represent Zn:P with
894 no added Co to media whilst dashed lines represent Co:P with no added Zn; phytoplankton
895 data from Sunda and Hunstman, 1995). Error bars on inventory ratios represent 20 % combined
896 uncertainty for dZn and dCo analyses (see Section 2.2). This figure is adapted from that in Saito
897 et al. (2010) and implies that inter-seasonal differences in metal/PO₄³⁻ stoichiometry could
898 impact phytoplankton community composition in the Southeast Atlantic.

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902

903 Figure 1.

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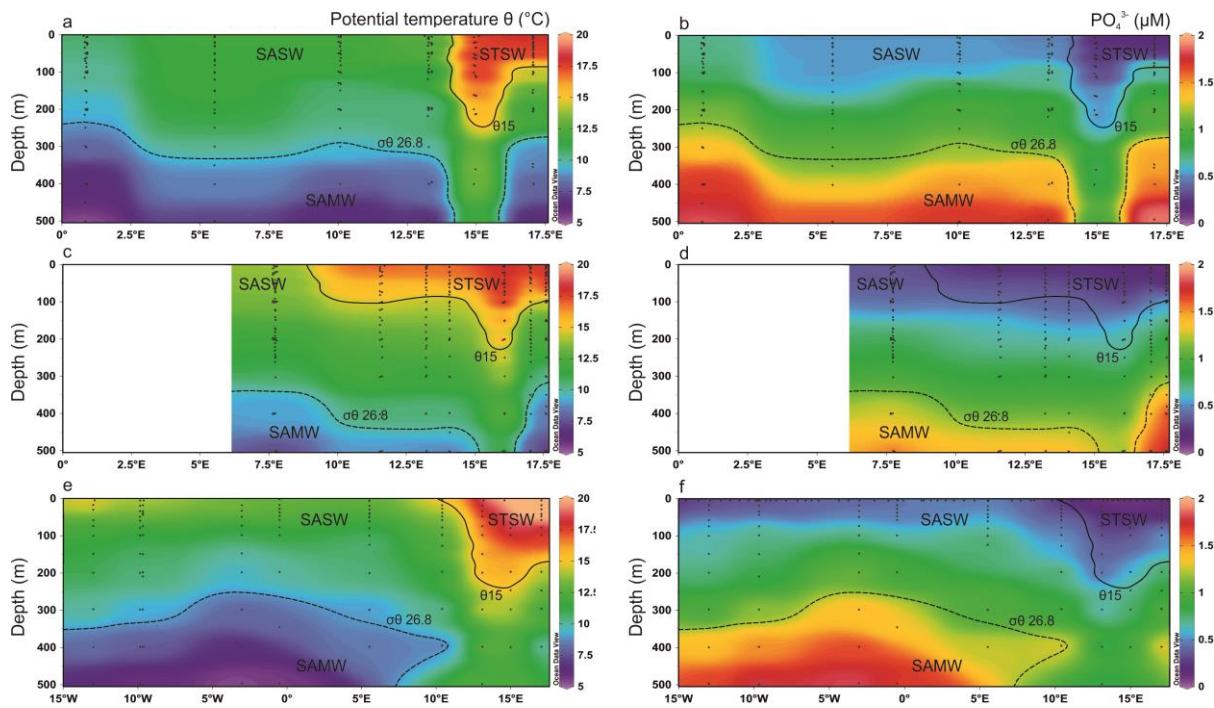
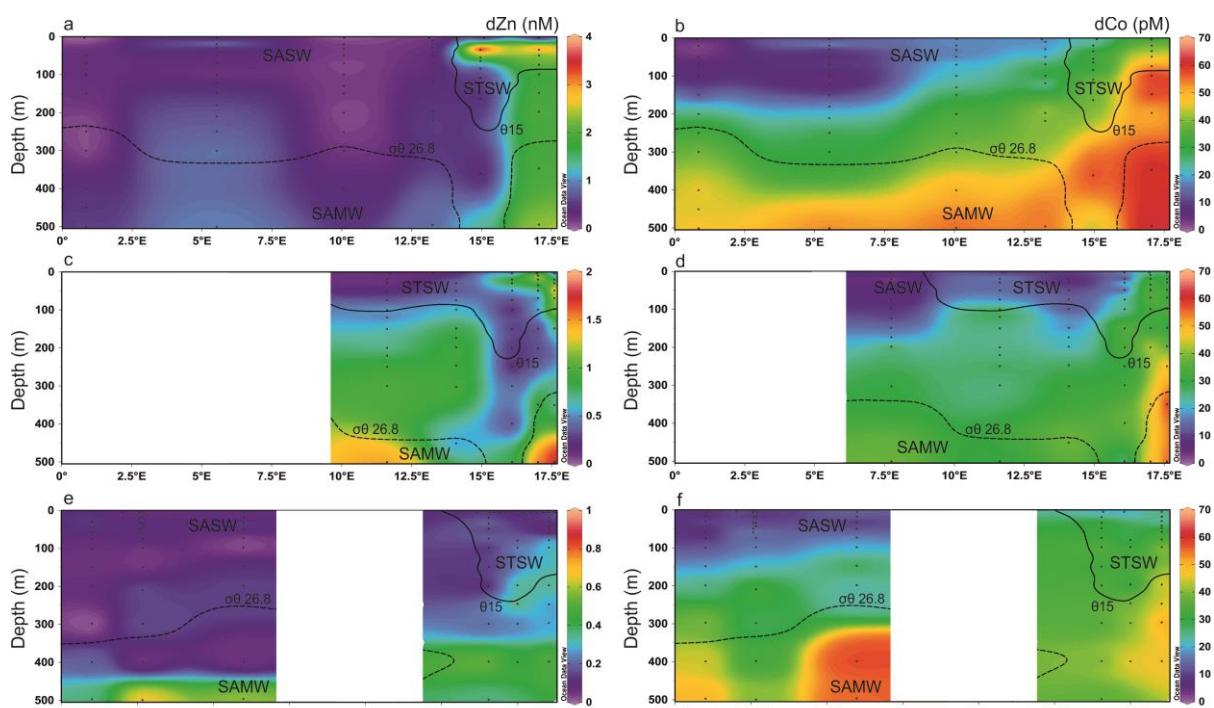
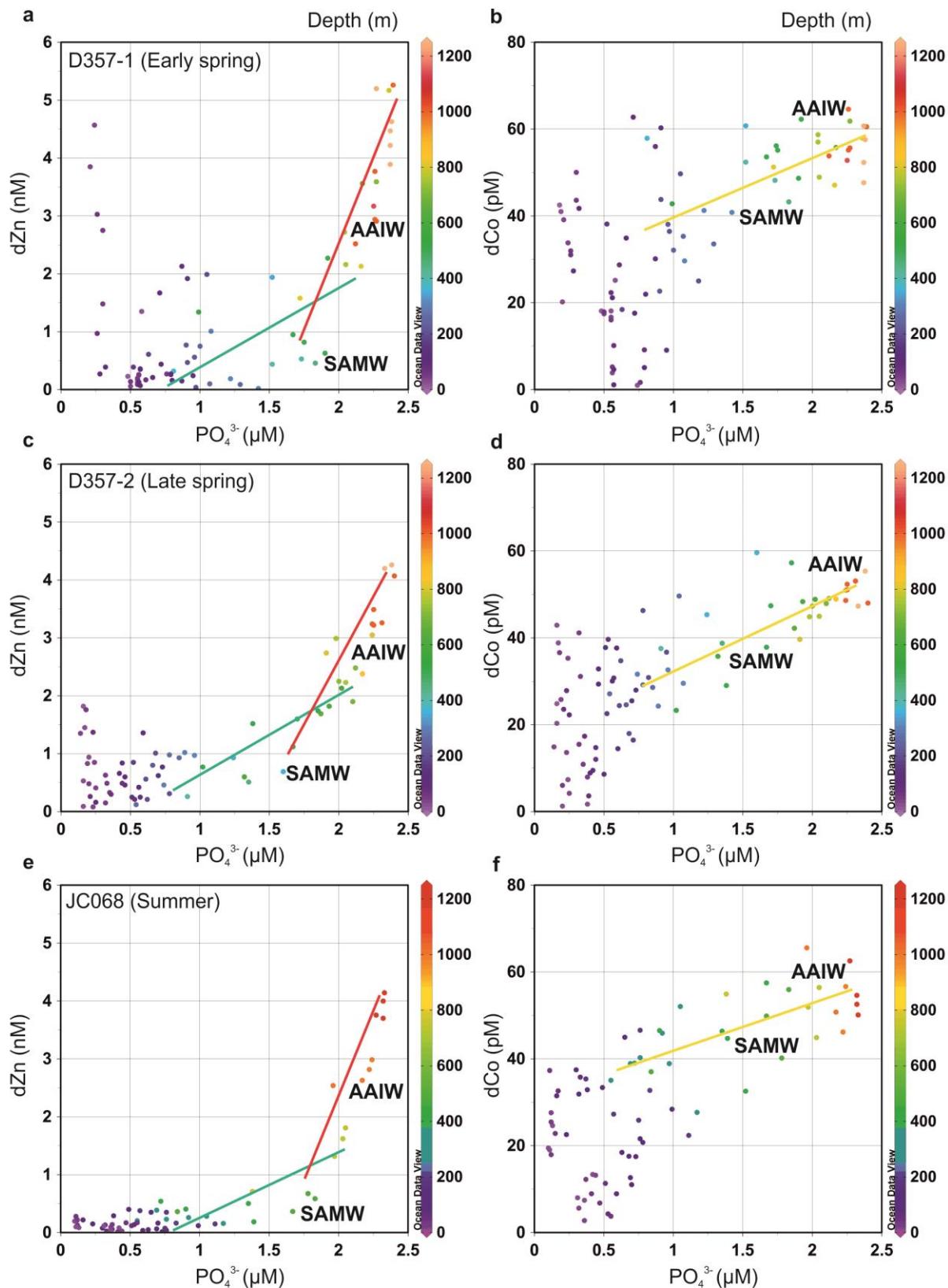


Figure 2.



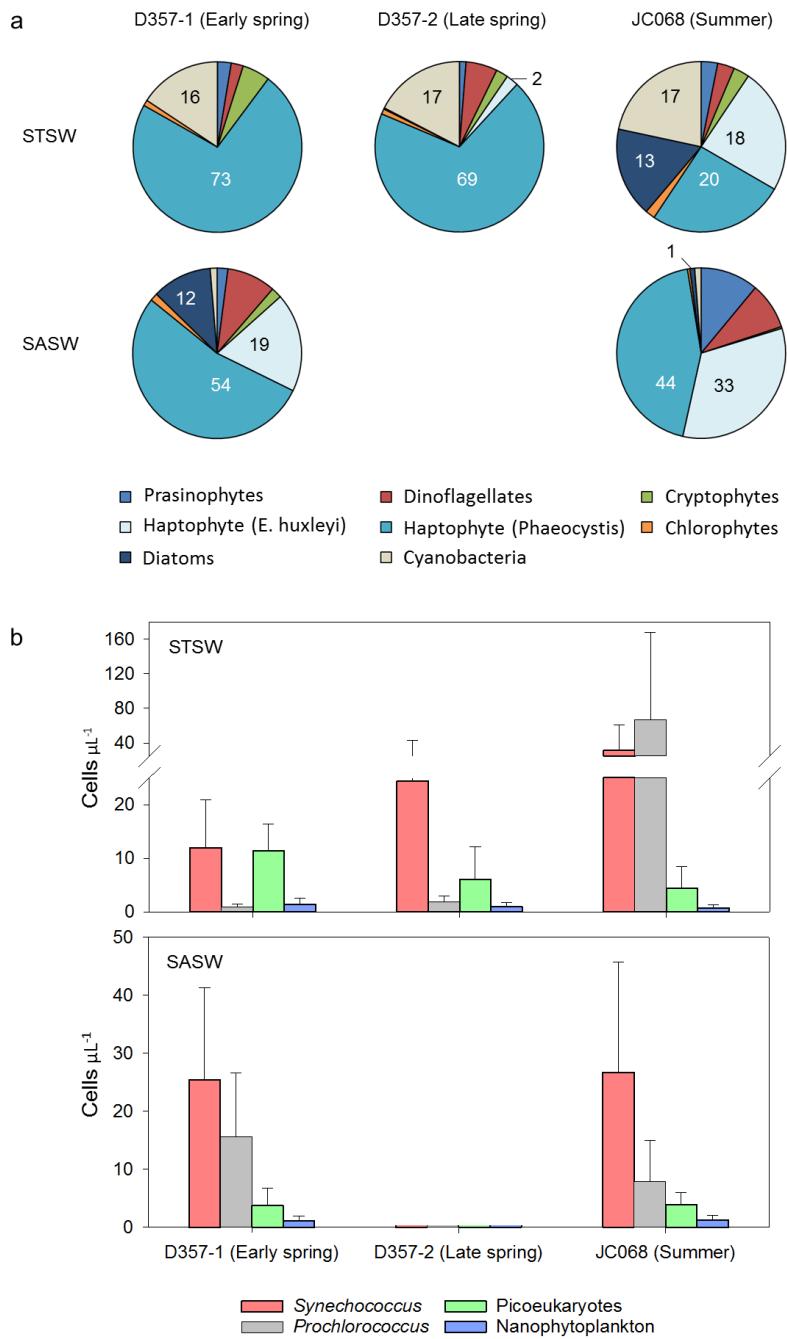


912

913 Figure 4.

914

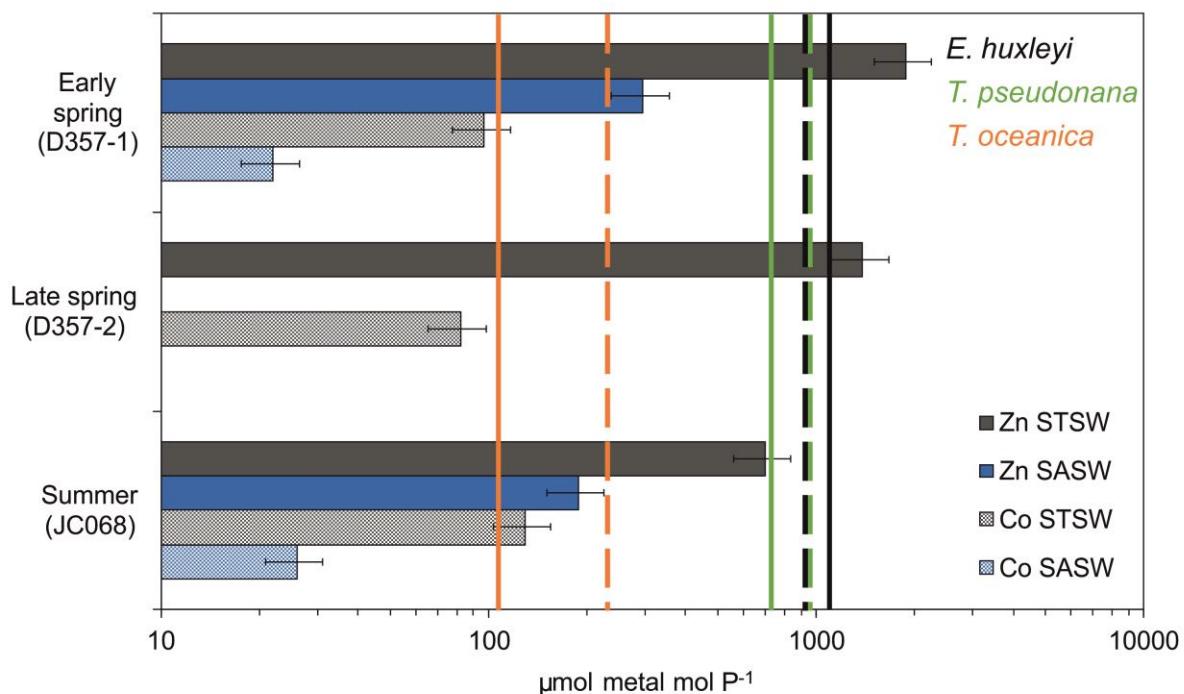
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