Response to reviewers

Lines numbers referred to in our responses represent those of the amended, resubmitted manuscript.

Reviewer 1:

General comments:

My main problem with the stoichiometry section is the use of regression slopes that are not presented as such, nor is it reported on how many data points the regression is based or whether the correlations are significant. The influence of mixing or the varying influence of other sources (as detailed by the authors in section 3.3) on the correlation is not considered. Including of data to a certain depth (rather that a water mass or density gradient) is very likely to lead to artefacts, especially given that the sampling resolution (number of stations and depths) as well as oceanographic conditions changed between occupations. Please see the detailed comments below, but I would recommend the authors base this discussion on upper water column inventories and changes therein rather than slopes of regressions.

We agree with reviewer 1 that the use of regression slopes to determine metal/PO4 and Zn:Co ratios is subject to artefacts arising from water mass mixing and that these artefacts are not thoughtfully discussed. The important influence of mixing on regression slopes has been documented in a number of recent publications for the Atlantic Ocean (e.g. Middag et al., 2019; Middag et al., 2020; Middag et al., 2018). We acknowledge therefore that we cannot assume a slope is only the result of uptake and remineralisation without considering mixing or other processes.

Following the suggestion of reviewer 1, we have changed the way we approach these ratios and now use concentration inventories for STSW and SASW to calculate these ratios for the different transects. We have therefore amended section 3.4 (lines 344-397) accordingly. Changing to inventory ratios did not largely affect the results and we still observed decreasing Zn/Co ratios with seasonal progression. Section 3.5 (lines 399-510) on ‘phytoplankton impacts on trace metal stoichiometry’ is therefore also not largely affected.

We now use the potential temperature of 15 C to identify STSW during all three transects and use this isotherm to inform the presence and depth of STSW at each station. We have stated exactly how the two waters masses have been defined on lines 349-352.

Importantly, we now calculate the inventories of Zn, Co and PO4 over the same depth at each station, which we feel eliminates discrepancies associated with the use of different depths, as was previously the case (i.e. 500 m for Zn/ P slopes and 360 m for Co/P slopes).

Finally, using the slopes of regression for Zn/P and Co/P, we have now included in the metals distributions section 3.2 (lines 255-279) a more thoughtful assessment of the varying influences, particularly sub-surface supply, that may affect our metal distributions, thus concentration inventories.

Specific comments:

Station numbers that are not whole integers I find confusing, what is the rationale for that?

Whilst we agree that integers can be confusing, we believe there is sufficient reason keeping the station numbers as they are. First, the reason why we have integers is that there was a medical evacuation during the cruise, and the choice was made to occupy interval stations in-between our principle stations. Thus we ended up with stations 0.5, 1.5 etc. in addition to 1, 2, 3. Second, previous publications from the same D357 and JC068 cruise have used these integer numbers and we believe it would therefore be confusing to any reader familiar with these publications. Finally, the data have been submitted to the BODC repository in the format presented here. It if we were to alter the station numbers in this manuscript it would be confusing to any reader wishing to extract the data for further investigation. We have decided to keep our station numbers identical to that submitted to BODC.

21-23 slightly awkward sentence, please rephrase for clarity.

Agreed. We have rephrased lines 21-23 to read: 'In sub-tropical surface waters, mixed-layer dZn and dCo concentrations 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'.

51 not clear, how can a concentration be similar or depleted relative to biological requirements, wouldn't that depend on the amount of phytoplankton?

Yes indeed, the biological trace metal requirements of phytoplankton would reflect the phytoplankton structure and biomass. To make it clear that we are comparing the cellular requirement of typical phytoplankton we have replaced the term 'biological requirements' with 'cellular requirements' on line 45. This term is also that used in the referenced Moore et al. (2013) and Moore (2016).

64 what is 'near-absolute' ?

We agree that the use of the term 'near-absolute Co requirement' is not clear. Initially this term was chosen to reflect the possible role for Zn in organic P acquisition in Synechococcus but again this is not clear. As there is currently no published evidence for Co substitution for Zn in Synechococcus and Prochlorococcus, we have changed to this to the term 'absolute Co requirement' on line 58.

Intro could refer to the body of recent GEOTRACES work on Zn in the Atlantic (e.g. Middag et al., 2019; Roshan et al., 2018; Roshan and Wu, 2015; Vance et al., 2017; Weber et al., 2018), especially with respect to the use of regressions and uptake stoichiometry (Middag et al., 2019). Additionally, given the intensive study of the Atlantic basin in the GEOTRACES programme and other expeditions, findings on the biochemistry (notably sources) of other TEI's could be relevant for Zn and Co as well.

A valid point is made by Reviewer 1 that we could make better use of the current body of literature on Zn in the Atlantic. This is also true of Co and other trace elements and isotopes. Incorporating such a literature review may extend the introduction significantly. We have therefore briefly referenced the great body of work GEOTRACES has produced on Zn and Co in the Atlantic prior to introducing the data sparse Southeast Atlantic as our study region (lines 62-68).

101 plasma rope; assume this is a brand name?

'Plasma rope' refers to the wire construction of the James Cook trace metal-clean winch system used during this study.

174 'was not largely sampled' unclear, please rephrase.

Agreed. We have rephrased this sentence on lines 186-189 to 'sub-Antarctic mode water was not sampled for trace metals during the D357-2 late spring transect.'

181 suggest 'between the three occupations of the transect'.

Agreed and amended in the text on line 195.

220-221 not clear if atmospheric deposition plays a significant role, flux is called modest, but not clear if it contributes to the elevated metal concentrations described. Reading on I realise this is revisited, leading to confusion here and repetition later so I suggest to not discuss the source in this results section and leave the whole discussion to section 3.3.

We agree that having this initial discussion on the influence of dust is not required here. We now leave all discussion on atmospheric vs. continental sources to section 3.3. The text in section 3.2 (lines 232-235) now reads: “We postulate that these trace metal enrichments can arise from either atmospheric inputs, and/or from the lateral advection of metal-enriched waters from the Agulhas Current (AC) and/or South African continental shelf, and discuss this further in Sect. 3.3.”

231 some explicit explanation in the text seems required to explain that not all stations were sampled in all seasons, took me a while to figure out why sometimes station 1 was the near shore station and sometimes stations 0.5 and 1 are the nearshore region.

We agree that this is somewhat confusing, as stations were not always occupied during each cruise. In addition to the Figure 1 caption, that explicitly details the stations that were occupied during each of the three transects, we have included an explanation in the Sampling Methods (section 2.1) that the stations occupied during the three seasons were not identical, and rather represent a coverage of the Southern Ocean and Sub-Tropical waters present (lines 98-101). We feel that this, in conjunction with detailed station identification in the text (e.g. the station closest the South African continent (Stn. 1.) during early spring) should make it clear to the reader which season, station and water mass we are referring to at any given time.

237 range from

The text on lines 248-249 has been changed to “In SASW, sub-surface dZn concentrations ranged from 0.01 to 1.01 nM.”

292 unclear why sediment resuspension would lead to a relative increase of pFe and pAl with respect to pTi? What would the pAl/pTi and pFe/pTi in sediments be and how does that relate to known values? Please clarify and consider discussing similarities/differences between the data and interpretations for this region and for the data from the GA02 section for Al and Fe where sources such as sediment resuspension were also discussed.

Shelfs seas are areas of high biological production with subsequent deposition of organic matter into sediments (Little et al, 2016 doi.org/10.1130/G37493.1). This can result in an enrichment in bio-relevant metals relative to refractory crustal-type elements, such as titanium, in shelf surface sediments. Reductive dissolution and resuspension of such sediments, a common feature of the Agulhas Bank region, may result in water column ratios of particulate Al, Fe, Zn and/or above that of the typical upper continental crust composition as well as elevated dissolved metal concentrations.

Whilst there are no South African sedimentary data against which we can compare our water column data, our pAl/pTi and pFe/pTi slope ratios (42 & 10 mol/mol, respectively) are in excess of upper continental crust ratios (34 & 7 mol/mol, respectively). These water column ratios are also greater than the aggregate slopes for the Atlantic Ocean (32 & 7 mol/mol; GEOTRACES IDP2017), suggesting an additional input of particulate bio-relevant metals over refractory Ti.

The authors of this manuscript feel it unnecessary to discuss the similarities/differences in particulate Al and Fe between this study and others, as the use of Fe and Al in the present study is solely to identify a sedimentary source and potential for sedimentary Zn and Co enrichment. However, we have clarified this section to better discuss how the high organic matter input to sediments in the region, and its bacterial decomposition, may enrich resuspended sediments in bioactive metals such as Zn, Co and Fe. The text has been amended (lines 322-343) accordingly.

295 please clarify if this is about dissolved or particulate metals (throughout this discussion).

We agree that it is not clear what species of metal we are referring to here. We have explicitly made clear both here (line 355) and elsewhere in the document when we are referring to dissolved, particulate or total metal concentrations.

311 (Middag et al., 2019; Middag et al., 2020; Middag et al., 2018) have demonstrated the influence of mixing is important, if not the most important factor, driving the slopes of metal-nutrient relationships. One cannot assume the slope is only the result of uptake and remineralisation without considering mixing or other processes as also illustrated by Saito et al., 2017 (their fig 4 g and 10 c).

We fully acknowledge that slopes of regression for the upper water column are largely driven by water mass mixing, as well as scavenging and abiotic inputs, as have been recently shown for Zn in the Atlantic Ocean (e.g. Saito et al 2017; Middag et al 2018; 2019). As mentioned in response to 'general comments' we have now moved to a concentration inventory approach to calculate the nutrient stoichiometry of surface water masses of the Southeast Atlantic (section 3.4). We still utilise metal:PO4 slopes in section 3.2, but now use these to discuss Zn and Co distribution throughout the upper water column and how inter-seasonal variations in sub-surface supply may impact such distributions.

316 were some stations/depths excluded or was the excess calculated and subtracted from the observations for the regressions? Not clear.

The term 'excess' is a little misleading here as we have not calculated an excess using established methods such as Zn*. We do not feel such a calculation would be appropriate for such shallow waters. We therefore simply removed individual samples from coastal stations (STSW) that were clearly elevated in trace metals compared with background values. These enriched samples can be clearly seen in Figure 4. We have rearranged the text in section 3.4 (lines 353-356) to better clarify that we removed individual sample data that exhibited 'elevated' trace metal concentrations derived from the continental margin.

320 why is the full water column shown in fig 4, whereas the rest of the paper and the regressions are about the upper water column? The full water column distribution for Zn looks similar to results from the GA02 section, where it was demonstrated that mixing between water masses was the most important factor and the slope of the regression was not representative for the ecological stoichiometry. Moreover, the slope of regression is taken to a depth of 500 m in the case of Zn. Are the authors suggesting uptake of Zn and PO4 over the upper 500 m? A change in the slope is most likely (at least partly) representing a change in the concentration estimate for one of the endmembers (SASW or STSW mixing with SAMW), which seems very likely given that the STF is not at the same location between occupations and the number of stations north and south of the front changes too. It is hard to judge due to the scale of fig 4a and without knowing which data points are included in which regression, but I'm not convinced that the change in slope is representative of changes in stoichiometric uptake. For early spring, it would seem the regression is influenced by some elevated deep values towards the continent that are likely related to small changes in circulation as depletion of Zn in the deep part of the water column seems unlikely (it was also argued by the author themselves this change in concentration is likely related to changes in sources). At the very least, the influence of mixing should be explored and plots should be shown for each regression

with the number of data points and p values for the regression. Importantly, a sensitivity analysis should be done for changing the depth to which the data is included in the regression, i.e. what is the effect of excluding the highest values (or including even higher values even deeper) or excluding the station closest to shore. I suspect the slope of regression is more influenced by slight changes in the sampling of the water masses present (due to changes in the stations and actual depths sampled as well as oceanographic variation (SAMW seems to have shoaled in the summer comparted to early spring), as stated in the ms, the water column was depleted till 400 m and concentrations only increase below that depth and those deep values drive the steepness of the slope) in combination with influence of the suspected sediment sources, rather than being influenced by variations in biological uptake over the season.

We thank the author for bringing this to our attention and have now fully revised our manuscript to address these concerns. We agree that the regression slopes are heavily influenced by changes in the water masses present rather than uptake and remineralisation

In section 3.2 (lines 256-280), we now use the relationships between metals and phosphate over the upper 1200 m (Figure 4) to highlight how variation in the sub-surface supply may influence Zn and Co distribution between the three occupations of our transect. Figure 4 has been thoroughly revised accordingly.

326 If the biological uptake ratio deviates from the dissolved ratio at whatever depth is taken as the 'endpoint' of the regression (i.e. the highest concentrations included in the regression), or if the regression has a non-zero intercept, it will lead to a change in slope. Especially for regressions that are not actually linear or have a non-zero intercept, such as the Zn-PO4 relationship, the use of regression slopes lead to interpretation errors (see also Middag et al., 2018).

We agree that the use of regression slopes can lead to interpretation errors depending on the depth the regression is performed over and the highest concentrations in the regression.

Please see our response to previous comments that explain that we now use concentration inventories to calculate ecological stoichiometry.

329 largely the same comments as for Zn, I am not convinced by this approach.

Please see our response to previous comments that explain that we now use concentration inventories to calculate ecological stoichiometry.

338-342 Based on concentration depletions I would agree, but not based on regression slopes. Also the statement that this preferential uptake is in contrast to the STSW needs a bit of context (here and elsewhere) as the preferential uptake is relative to a reference situation; the actual decrease in P of ~0.1 uM in STSW is still an order of magnitude larger than the Zn decrease of ~1.4 nM or the Co decrease of several pM.

Thank you for advising us here. We are now using concentration inventories for set water masses to calculate metal/PO4 stoichiometries rather than slopes of regression. When discussing changes in Zn/P versus Co/P, we have now provided context by explicitly explaining the biological requirements of Zn, relative to Co (lines 373-375). We now never refer to the preferential removal of a metal relative to PO4.

343 the greater Zn requirement relative to Co is well established.

We agree that the greater Zn requirement relative to Co is well established and fully cite the relevant literature throughout the discussion, specifically in section 3.5. However, highlighting the greater removal of Zn between spring and summer links nicely to changes in community structure detailed in section 3.5.

We have restructured the text on lines 388-389 to read ‘Our results provide evidence for the greater availability and preferential removal of dZn relative to dCo in the upper water column the Southeast Atlantic’.

348-351 changes in concentration yes, but I do not believe the ratio’s as derived are valid. And is this a novel finding? I thought changes in relative requirements of (micro-)nutrients as the season and community composition progresses was well established given that we know different species have different requirements? (apologies, working from home due to the Covid-19 situation and do not have my usual access to the literature to check).

As detailed in previous responses, we now utilise concentration inventories for set water masses to derive ecological stoichiometry for Zn and Co with little change to our interpretation.

Whilst seasonal changes in community composition are known to be influenced by, and also influence nutrient availability, only one study has explored such interactions in the Southeast Atlantic at the transition between subtropical and southern ocean derived waters. Browning et al (2014; doi:10.5194/bgd-10-11969-2013) have shown Fe and macronutrient regimes largely control phytoplankton ecophysiology in the Southeast Atlantic, yet this will be the first time Zn and Co data will be connected with biological community data in this region.

354 ‘principle, interlinked’ does not seem right.

Agreed, we have removed the term ‘interlinked’ and the sentence on lines 400-401 now reads: “Here we discuss the principle phenomena that together likely explain our observations of seasonally decreasing Zn:Co stoichiometries in STSW of the Southeast Atlantic.”

358-360 not sure I follow; the depletion leads to lower demand (I would think supply) and I do not follow the role of the microbial loop remineralisation; if everything was remineralised in the surface waters, the Zn:Co should stay constant or am I missing something?

We agree that this sentence on microbial loop remineralisation is confusing. We have now removed this phrase entirely from the document. More importantly, we have significantly revised section 3.5 (lines 404-510) and now feel this section flows much better. Principally, we now introduce the chlorophyll distributions, and fractional contribution to chlorophyll by different phytoplankton groups, at the start of this section. This allows us to then explore phytoplankton distribution relative to Zn and Co availability in both STSW and SASW during each of the transects.

362 I see how the uptake rate of an individual element can increase, but what does an increased uptake rate of a ratio imply?

This sentence has been removed from the revised manuscript. Section 3.5 now explores Zn and Co availability in surface waters of the SE Atlantic and compares this with the cellular requirements of phytoplankton estimated to be present.

390 preferential with respect to what? As far as I know, most (if not all) phytoplankton have a larger Zn requirement than Co, so the faster (absolute) depletion of Zn compared to Co should occur regardless of which phytoplankton species is dominant.]

Agreed. Yes, the preferential removal of Zn relative to Co would occur regardless of which phytoplankton is dominant. We have removed the term ‘preferential’ from line 416.

411 is this confirmed by the flow cytometry data?

Thank you for bringing this oversight to our attention. Yes, the switch to smaller cells in STSW during summer is confirmed by FC data and we have now included this in the text. Lines 434-438 now reads: ‘This would suggest that the lower dZn availability in summer STSW should influence phytoplankton species composition by selecting for smaller organisms with lower cellular Zn requirements, and confirmed by a ratio of picophytoplankton to nanophytoplankton at least 4-fold higher during summer compared with spring values’.

423 why are there no reference Co:P vertical lines in fig 6 like for Zn:P to see how the observations match up with lab studies (e.g. from the here cited Xu et al study).

We agree that it would be more insightful to include the Co:P lines in Fig 6 and have now included these as per Zn:P. We have also converted Fig. 6 horizontal bars to now represent concentration inventories for STSW and SASW, rather than slopes of regression.

434 again confused about the microbial loop remineralisation, please clarify how changes in uptake ratios are related to remineralisation in the microbial loop.

Agreed that our use of the term ‘microbial loop’ is somewhat vague. We have restructured lines 463-466 to state: ‘This assessment implies an additional need for Zn in phytoplankton nutrition due to low dCo availability throughout the Southeast Atlantic, which may accelerate the decrease in dZn/dCo inventory ratios between seasons’.

435 not yet detailed if the thus far mentioned species belong to nano whereas Synechococcus and Prochlorococcus belong to the pico’s, this should be mentioned for those readers that not often deal with this.

In discussion section 3.5, make it clear that we are referring to eukaryotic nanophytoplankton where we first discuss Phaeocystis and diatoms (lines 411-412), and prokaryotic picocyanobacteria when we first refer to syns and pros (e.g. line 58, lines 468-471).

464 in line 461 it was stated the concentrations were similar to (and sometimes below) the requirements, so how is it evidence for substitution? I would think this is an indication it could occur.

Agreed. We have not shown direct evidence that substitution is occurring, rather we have presented the factors that indicate substitution is potentially important for this region at certain times of the year. We have revised the text to state this more clearly on lines 495-496.

467 Do the authors mean there is little change in the Zn:P and this is above the requirements for T. I oceanica? Please clarify.

Yes, we are stating that the dissolved Zn/PO4 inventory ratio is lower than the cellular Zn/P requirement of T oceanica and have made this specifically clear on lines 500-502.

482-483 positive slope are indeed indicative of uptake, but not necessarily shallow remineralisation. A positive slope would also be observed with surface uptake and deep remineralisation if nutrients in the subsurface are replenished via advection, e.g. with SAMW.

We agree with reviewer 1’s suggestion that positive slopes of regression are not indicative of shallow remineralisation. We have revised this section on lines 519-522 to read: ‘The vertical distributions of dZn and dCo in the upper water column were similar to that of PO43- indicating biological drawdown in surface waters and mixing with underlying Southern ocean-derived waters travelling equatorward significantly influences their distribution.'

485 this is not new, it is well known the absolute requirement of phytoplankton is higher for Zn than for Co (e.g. Twining and Baines, 2013).

Agreed. We have restructured this paragraph (lines 522-526) and to state that our results reflect what we know about preferential removal of Zn relative to Co using the literature. It is the removal of Zn between seasons, and the potentially growth limiting concentrations towards the end of the growing period, that are important in the context of our study.

Table 1, how was the conversion done from consensus values in nmol/kg to nM? I get a different value if I use a density of 1.025 kg/L.

An oversight on our part. We originally used the deep-water ratio of 1.0275 kg/L but have now corrected these consensus values using 1.025 kg/L. We have included this unit conversion in the Table 1 caption.

Table 2, Zn:Co is not explained, was this derived from the Zn-P and Co-P relationship slope or a regression of Zn vs Co? p values for the regressions should be reported/mentioned too.

We agree with reviewer 1 that we need to better explain how we calculate Zn/Co. Originally, this was calculated as the Zn/P:Co/P ratio based on slopes of regression as outlined on line 344 of the original text. We have now changed this text to state how we calculated Zn/Co using our new concentration inventories (Lines 350-357, line 388-390) approach for set water masses. Zn/Co is also now clearly defined in the Table 2 legend.

Reviewer 2

General comments:

The key interpretations presented by Wyatt and coauthors seem primarily to be based on 2 assumed conditions: (1) that this study was Lagrangian in nature (i.e. that individual water parcels were sampled at three separate time points, meaning that changes in measured parameters over the seasons are caused only by biological uptake in that parcel and not by changing from one parcel to another), and (2) that metal and macronutrient distributions in this region are driven by vertical control through in-situ biological uptake and remineralisation, with no component influenced by water mass circulation and mixing. I do not think either of these conditions is supported by hydrographic data and the current understanding of global distributions of nutrient-type metals and macronutrients in the marine environment. Because these form the basis for the interpretations and discussion (sections 3.4-3.6), I think that properly addressing them may result in significant changes to the structure and key findings of the study.

We thank reviewer 2 for their comments and agree with their general assessment. Originally, we assumed a semi-lagrangian approach whereby we assumed STSW and SASW moved horizontally (using potential temperature 15 C as a boundary) but not vertically with depth. We previously fixed our regression analyses to 500 for Zn and 360 m for Co and assumed uptake and remineralisation were the driving influences behind the positive relationships. This was not the best approach and we thank reviewer 2 for bringing this to our attention. In reality, the depth of STSW varies on a station-by-station basis, as well as being more laterally pronounced during the late spring transect. We now use the 15 C potential temperature to identify STSW at each station, for each season, allowing us to assess the ecological stoichiometry of the water masses more consistently. This can be found clearly explained in the revised manuscript (lines 350-353) and also in the legends of figures 2 and 3.

We now use a concentration inventory based approach, rather than slopes of regression, to calculate ecological stoichiometry and both Zn and Co are now assessed over the same identical water parcel.

We still use slopes of regression in section 3.2 (lines 256-280) to consider how sub-surface supply may influence our trace metals distributions. We hope our interpretation on the distribution and of Zn and Co is now better aligned with the available hydrographic data.

Specific comments:

1) Sampling for this study took place across two cruises in Austral spring 2010 and one cruise in Austral summer 2011-2012. These seasonal data are used to infer biological uptake throughout the growing season, and many sections present calculation of absolute amounts or relative amounts of nutrients removed. And this calculated removal is compared to address preferential removal of certain nutrients over others. However, the authors also note seasonal variability within the timeframe of a couple weeks at the more coastal sites, where a local source was observed in one of the two Austral spring 2010 cruises. Additionally, it is clear that water mass characteristics changed both in terms of depth distributions at one location (e.g. the depth range of STSW) and spatial distributions in surface waters across the sampling campaigns, in addition to potentially variable trace metal signatures of source waters. I realize that it may be difficult to constrain this, and most studies don't offer data to address seasonal variability. But I would like the authors to address to what extent seasonal variability can be impacted by different source water characteristics across the different sampling seasons and years rather than assuming differences are entirely biological.

Whilst it is indeed difficult to constrain, we feel we have made a significant attempt to identify to what extent the seasonal variability in different source waters influenced our data. For example, section 3.3 identifies and discusses how a seasonal influence was observed from waters originating from the Agulhas bank, that appears to carry an enriched metal signature above that we would expect from the Agulhas Current. However, we acknowledge that STSW varies considerably between early and late spring with respect to its horizontal distribution and we have now addressed this more robustly in the text. By defining STSW as waters with potential temperature ≥15 C, and only assessing metal distributions and stoichiometry over this temperature range rather than fixed depths, we are better able to assess how seasonal changes in depth and spatial distribution may influence metal concentrations. Finally, using the slopes of metal/PO4, we have now considered the influences that deeper water masses deeper may have and the trace metal signatures they may bring.

2) The abstract and conclusions identify that depth distributions of metals and macronutrients are considered to be driven by local uptake in surface waters and shallow remineralisation in subsurface waters (e.g. Lines 30-31; 482-483). This interpretive framework is used to derive the metal-macronutrient regressions in Table 2, which are differentiated by surface water regimes, but are determined based on depth ranges (Zn: < 500 m, Co < 360 m) well beyond the extent of these surface waters. These depth ranges include subsurface water masses of different origin. The regressions, in turn, are used for the discussion of sections 3.4-3.6, (as well as figure 6). It is clear from a growing

body of work that metal-macronutrient distributions throughout the world ocean are controlled to a significant extent by water mass circulation (e.g. Vance et al., 2017, doi: 10.1038/ngeo2890; de Souza et al., 2018, doi: 10.1016/j.epsl.2018.03.050; Middag et al., 2018, doi: 10.1016/j.epsl.2018.03.046; Weber et al., 2018, doi: 10.1126/science.aap8532; Middag et al., 2019, doi: 10.1029/2018GB006034). This is especially true in a region where water masses of different origins mix, such as the location of this study. Additionally, it is clear that metals and macronutrients may have different remineralisation length scales (e.g. Ohnemus et al, 2019, doi: 10.1029/2018GB006145) and, for Zn and Co specifically, may be impacted by mid-depth scavenging (John and Conway, 2014, doi: 10.1016/j.epsl.2014.02.053; Hawco et al., 2018, doi: 10.1016/j.marchem.2017.09.001; Roshan et al., 2018, doi: 10.1029/2018GB006045; Weber et al., 2018; Ohnemus et al., 2019). Therefore, while the mixed layer metal and macronutrient distributions may be impacted primarily by biological uptake and removal, subsurface distributions will be impacted by advected preformed concentrations, remineralisation of biogenic material along the flow path (possibly at variable metal:macronutrient ratios), decoupling of metal and macronutrient remineralisation as well as potential scavenging of metals from the water column.

I recommend that the authors revisit their interpretations to incorporate these aspects of global metal and nutrient distributions. For example, the decreasing PO4 concentrations in deeper samples from spring to summer in figure 2 suggests that factors other than biological uptake and remineralisation are acting here.

We would like to acknowledge that both reviewer 1 and 2 make clear that the use of regression slopes to determine metal/PO4 and Zn/Co ratios is subject to artefacts arising from water mass mixing and that these artefacts are not thoughtfully discussed in the initial submission. The important influence of mixing on regression slopes has been documented in a number of recent publications for the Atlantic Ocean (e.g. Middag et al., 2019; Middag et al., 2020; Middag et al., 2018). We acknowledge therefore that we cannot assume a slope is only the result of uptake and remineralisation without considering mixing or other processes.

Following the suggestion of reviewer 1, we have changed the way we approach these ratios and now use concentration inventories for STSW and SASW to calculate these ratios for the different transects. We now use the potential temperature of 15 C to identify STSW during all three transects and use this isotherm to inform the presence and depth of STSW at each station.

For SASW, we calculate the concentration inventories over the upper 144 m. This is the mean depth of the 15 C isotherm for STSW (lines 350-353) and allows a consistent comparison between the two water masses. Importantly, we now calculate the inventories of Zn, Co and PO4 over the same depth at each station, which we feel eliminates discrepancies associated with the use of different depths, as was previously the case (i.e. 500 m for Zn/ P slopes and 360 m for Co/P slopes).

Finally, using the slopes of regression for Zn/P and Co/P, we have now included in the metals distributions section 3.2 a more thoughtful assessment of the subsurface influences that may affect our metal distributions with respect to global distributions.

Analytical precision and uncertainty – I ask the authors to incorporate analytical precision and uncertainty in derived relationships more robustly into their discussion. These are key instances where I found this lacking:

The reproducibility of triplicate analyses is mentioned in section 2.2 as 1-5%. However, this does not seem to be incorporated into figures, and available data of replicates suggest that the uncertainty may in fact be much larger, especially at low concentrations. Two zinc analytes are reported for

replicate seawater analyses (SAFe S and D2). Among these, SAFe S has 1SD precision of 33%. For Co, 4 replicated seawater analytes are presented (low Co surface water, SAFe S, D2 and GD). The 1SD precision of the lower Co values among these is ~25-30%. Since many of the Zn and Co data presented here are very low concentrations, it seems that these higher uncertainties at low concentrations may be important. These data, likely from multiple analytical sessions, also give a better representation of external reproducibility than individual replicates measured in succession, and may be the more meaningful constraint for comparisons.

We agree with reviewer 2 that we need to more robustly asses the uncertainty surrounding our data and incorporate this assessment into our discussion.

Previously, our 1-5 % estimate of reproducibility was based on triplicate analysis of individual samples and did not include day-to-day variability across multiple analytical sessions. Subsequently, we have performed a 'Nord Test' (Worsfold et al., 2019; doi: 10.3389/fmars.2018.00515) to calculate a combined uncertainty (Uc). We feel this this Uc yields a more realistic estimate of uncertainty, particularly when assessing low concentration trace metal data. We have thoroughly described this Uc in section 2.2 (lines 133-150) and have made it clear that we apply a fixed Uc of 20% when presenting low concentration data in section 3.5, and make it very clear when doing so. There is no real need to apply this UC when discussing inventory ratios as the uncertainty surrounding higher concentration data is low. We have also factored this Uc into Figure 6.

We would like to point out that when the Nord Test approach was applied to other low level concentration FIA analyses, the uncertainty was equally as high i.e. 10-20 % reported for dFe by FIA (Worsfold, 2019; doi: 10.3389/fmars.2018.00515).

Table 2 lists regression slopes for metals and PO4. The correlation coefficients ´ for these are at times quite low, suggesting that there may be significant uncertainty for the slope. Please include the uncertainty on the slopes, and incorporate these into the calculated Zn:Co ratios and the discussion of metal-macronutrient and metal-metal trends.

We have now adopted a concentration inventory approach to calculate Zn:Co rates, as it was rightly pointed out that a great deal of uncertainty in the slope-based approach may come from the influence of water mass mixing advection deeper in the water column. With that being said, we agree with reviewer 2 that it is important to assess the uncertainty in the calculation of these ratios. We have therefore factored a combined uncertainty (Uc) into the calculation of Zn/Co ratios. This will allow the reader a more meaningful way in which to assess the differences in ratio between seasons and also inshore vs offshore waters. Whilst this uncertainty is not shown in table 2, to avoid confusion with a number of other values (e.g. Zn/P, Co/P, STSW vs mixed layer etc), we have displayed this Uc on figure 6 and stated such in the figure legend.

Derivation of metal-PO4 trends (section 3.5, table 2, figure 3) – As addressed above, a key parameter which forms the bulk of the discussion and interpretations is the regression slope for metals and macronutrients derived from the different regions and cruises. Given its importance to this manuscript, the derivation of these values should be shown somewhere. Figure 3 shows metal-macronutrient cross plots differentiated by cruise, but not differentiated by water masses and depth ranges over which the data are considered. At present, it is difficult to assess the validity of the calculated values and interpretations based on the presentation of the data.

By now using a concentration inventory approach we hope that it will become easier for the reader to assess the validity of our calculated Zn/Co ratios for the different water masses. This will be aided by Figures 2 and 3, that clearly delineate the water masses for each season, and Table 2 that present the concentration data used in the calculation of Zn/Co ratios.

I ask the authors to illustrate how the values presented in Table 2 were determined, including more precisely identifying which data were excluded due to local metal sources and omitting the data from depth ranges not considered (Zn > 500 m, Co > 360 m). As addressed in #2 above, these should also include more clarity regarding what water mass criteria are considered relevant.

In place of slopes of regression, we are now utilising concentration inventories to determine the Zn/Co ratios used in the discussion sections 3.4 and 3.5. Because we are now using the 15 C isotherm to identify STSW depth at each station, the depth range for both Zn and Co is now identical at each station rather than two different depths used for the slope based approach. How and why we determined these inventories has been clearly outlined at the start of section 3.4 (lines 350-357) and also in Table 2 legend. We hope this will better clarify that we removed individual sample data that exhibited ‘elevated’ trace metal concentrations derived from the continental margin.

In general, it would be good to include more concentration ranges when discussion relative changes in metal and nutrient concentrations (e.g. Lines 181-187).

Agreed. We have made better use of the absolute concentrations when discussing both changes in nutrients (specifically lines 195-206) and trace metals (section 3.2) throughout the text.

Some of the data reported here are from the same cruise as published data (Wyatt et al., 2014, doi: 10.1002/2013gb004637), but I did not see any mention of this. Are some of these data previously published?

Some of these data from the JC068 summer transect have been previously published in the paper Wyatt et al (2014; doi: 10.1002/2013gb004637) as identified by reviewer 2. Whilst we often refer to this published paper, we have not made clear which aspects of our data set have been published in this paper and we apologise for this oversight. We have now made it explicitly clear in hydrography section 3.1 (lines 185 and 212) that Wyatt et al (2014) provide a more detailed description of the JC068 hydrography along the entire GA10 section. We have also made it clear in Zn and Co section 3.2 (lines 222) that full depth Zn data from JC068 can be found in Wyatt et al (2014). In Figure 4 we have made it clear that the JC068 Zn:P relationship for the full water column can be in Wyatt et al (2014).

Lines 296-303: Use of “lithogenic”. Lithogenic refers to something derived from the terrestrial earth that is then transported to the ocean, but in this section it is also used to refer to biogenic material in sediments and/or authigenic minerals. Please clarify this.

We agree that we have misused the term ‘lithogenic’. Throughout the entire text, we now use ‘lithogenic’ to refer solely to terrestrially derived, refractory material with no biogenic or authigenic modification (i.e. mineral dust or upper continental crust material). Specifically, in section 3.3 (lines 325 and 330) we now make it clear that we postulate the Agulhas Bank sediments to be enriched in trace metals as a result of biogenic material decay.

Lines 468-470: Si concentrations. These numbers are very close to each other, especially considering the uncertainty.

Agreed. Even though we have slightly revised these values (lines 507-510), the spring (1.8 ± 0.2 µM) and summer (0.9 ± 0.3 µM) Si concentrations are indeed very close to each other but are typical of low Si, Southern Ocean-derived waters. We do not think the absolute concentrations should be the primary focus even though summer values are lower than spring. Instead concentrations should be assessed alongside the dissolved NO3:Si stoichiometry that may indicate Fe and Si stress. The change in NO3/Si between spring (2.9:1) and summer (3.8:1) is more pronounced than just the Si concentration change and we have restructured this paragraph to better convey this notion to the reader. Please note that the spring NO3/Si ratio has changed from 0.4 to 2.9 between our first and revised manuscript due to a miscalculation.

Figure 3: I think it is confusing to present the Zn data as three different z axis ranges. Could two be used instead of three? Also, the 26.8 isopycnal and T = 15 contours are different than in Figure 2.

Whilst we have endeavoured to display the Zn concentration for the three transects on the same scale (Figure 3), we have found it near-impossible to do this whilst clearly, and correctly, displaying the coastal influence that changes between early spring and summer. We have however, made the change in Zn scale evident by clearly stating this in the Figure 3 legend. We have also fully revised this figure so that all isopycnals and isotherms are identical between plots 2 and 3.

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

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Abstract

Commented [WN1]: The concentration and stoichiometric values have been amended here to reflect we now use concentration inventories to estimate Zn/Co stoichiometry. The text has been amended to reflect these changes.

We report the distributions and stoichiometry of dissolved zinc (dZn) and cobalt (dCo) in sub-tropical and sub-Antarctic waters of the Southeast Atlantic Ocean during austral spring 2010 and summer 2011/12. In sub-tropical surface waters, mixed-layer dZn and dCo concentrations 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 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.

1. Introduction

Commented [NW2]: Our introduction has been revised to include relevant geotraces literature.

The trace metal micronutrients zinc (Zn) and cobalt (Co) play an important role in the productivity of the oceans as key requirements in marine phytoplankton metabolism (Morel, 2008; Twining and Baines, 2013). Zinc is required for the acquisition of inorganic carbon and organic phosphorus via the carbonic anhydrase and alkaline phosphatase metalloenzymes, respectively (Morel et al., 1994; Shaked et al., 2006; Cox and Saito, 2013). The requirement for Co stems from its obligation in the biosynthesis of vitamin B_{12} (Raux et al., 2000; Rodionov et al., 2003) and, like Zn, its potential roles as a metal cofactor in carbonic anhydrase and alkaline phosphatase (Morel et al., 1994; Jakuba et al., 2008; Saito et al., 2017). Significantly, both dissolved Zn (dZn) and Co (dCo) are often scarce in surface seawater with mean concentrations that are often similar to, or relatively depleted, compared with typical cellular requirements of phytoplankton (Moore et al., 2013; Moore, 2016). Hence, dZn and dCo availability have the potential to regulate phytoplankton metabolism and growth rates in some ocean regions (Sunda and Huntsman, 1992; Saito et al., 2002; Franck et al., 2003; Shaked et al., 2006; Bertrand et al., 2007; Jakuba et al., 2012; Mahaffey et al., 2014; Chappell et al., 2016; Browning et al., 2017).

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

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

The Sub-Tropical Front (STF) of the Southeast Atlantic represents the convergence of warm, predominately macronutrient-limited Sub-Tropical Surface Water (STSW) and cold, iron-limited but macronutrient enriched sub-Antarctic Surface Water (SASW), creating one of the most dynamic nutrient regimes in the oceans (Ito et al., 2005; Browning et al., 2014; Moore, 2016). Here, the relative supply and availability of macronutrients and iron (Fe) exert an important control in maintaining the elevated phytoplankton stock and productivity that is typical of this frontal region, particularly during austral spring and summer (Moore and Abbott, 2000; Ito et al., 2005; Browning et al., 2014). Dissolved Zn is also depleted in SASW that flows northwards to converge with STSW at the STF (Wyatt et al., 2014). However, the potential role for Zn in the mediation of phytoplankton distribution and community structure in this region is currently unclear.

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

2. Methods

2.1. Sampling methods

Seawater samples were collected during two UK-GEOTRACES cruises in the South Atlantic Ocean (GA10, Fig. 1). The first cruise (D357) took place during austral spring 2010 (18th October to 22nd November 2010), sampling the Southeast Atlantic on-board the *RSS Discovery*. During D357, two transects were completed between Cape Town and the zero meridian that represent early austral spring (D357-1) and late austral spring (D357-2), respectively. The second cruise (JC068) took place during austral summer 2011/2012 (24th December 2011 to 27th January 2012), along the same transect of the first cruise and continuing along 40ºS between Cape Town and Montevideo, Uruguay, on-board the *RSS James Cook*. For JC068, we present here only the repeat transect data between Cape Town and 13°W that represents the Southeast Atlantic aspect of this transect. The stations occupied during the three transects were not identical, but rather represent a coverage of the Southern Ocean and sub-tropical waters present. Where stations were reoccupied during one or more transects, they have the same station number.

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

2.2. Trace metal analysis

Dissolved Co was determined in the ISO accredited clean room facility (ISO 9001) at the University of Plymouth (UK) using flow injection with chemiluminescence detection, modified from the method of Cannizzaro et al. (1999) as described by Shelley et al. (2010). Briefly, dCo was determined in UV-irradiated samples using the reaction between pyrogallol (1,2,3-trihydrobenzene) and hydrogen peroxide formed in the presence of Co. Standards (20 – 120 pM Co) were prepared in 0.2 µm filtered low-dCo seawater (16.5 ± 5.2 pM, n = 15) by serial dilution of a 1000 ppm Co ICP-MS standard (Romil, UK). The accuracy of the analytical method was validated by quantification of dCo in SAFe (S and D2) and GEOTRACES (GD) reference seawater (Table 1). There was no detectable analytical dCo blank and the limit of detection (3σ of the lowest standard addition) was 1.98 ± 0.87 pM.

Dissolved Zn was determined using flow injection coupled with fluorescence detection, modified from the method of Nowicki et al. (1994) and described previously for this GEOTRACES section by Wyatt et al. (2014). The accuracy of the analytical method was validated by quantification of dZn in SAFe (S and D2) reference seawater (Table 1). The blank for dZn FIA was 0.14 ± 0.13 nM and the limit of detection (3σ of the lowest standard addition) was 0.01 ± 0.01 nM.

Measurement uncertainties were estimated after the Nordtest approach (Worsfold et al., 2019) where a combined uncertainty (u_c) is computed from day-to-day within-lab reproducibility and uncertainties associated with the determination of reference materials (Table 1). This approach creates higher uncertainties than those previously published for dZn and dCo analyses but provides a more realistic estimation of analytical uncertainty. During this study, the u_c for dZn and dCo analysis was 22 and 19 %, respectively, similar to the 13 – 25 % reported by Rapp et al. (2017) for the determination of trace metals, including dZn and dCo, by on-line pre-concentration and high-resolution sector field ICP-MS detection. The elevated u_c within our data results from the greater uncertainty surrounding the very low dZn and dCo concentration SAFe S reference sample whereas the dZn and dCo u_c using only the Safe D2 are <5 %. Hereafter, when presenting low dZn and dCo concentrations for comparison with phytoplankton biological requirements (Section 3.5), we apply a fixed u_c of 20 % to our data.

Commented [NW3]: We have included an estimate of uncertainty that is more appropriate than the use of the standard deviation of triplicate peaks. We apply this uncertainty to low concentration metal data in sections 3.5.

Total particulate trace metals (i.e. pZn, pCo, pTi) were determined using inductively coupled plasma-mass spectrometry (Thermo Fisher XSeries-2) following a sequential acid digestion modified from Ohnemus et al. (2014). Potential interferences (e.g. $_{40}$Ar$_{16}$O on $_{56}$Fe) were minimized through the use of a collision/reaction cell utilizing 7 % H in He and evaluation of efficiency and accuracy assessed using Certified Reference Material (CRM). Full details of the method and CRM results can be found in Milne et al. (2017).

2.3. Nutrients, phytoplankton, temperature and salinity

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

Measurements of phytoplankton pigment biomass and community structure were made on discrete samples collected using a 24 position stainless-steel CTD rosette equipped with 20 L OTE Niskin bottles. For chlorophyll-*a* analysis, samples were filtered (0.7 µm Whatman GF/F) and then the filters extracted overnight in 90 % acetone (Holm-Hansen et al., 1965). The chlorophyll-*a* extract was measured on a pre-calibrated (spinach chlorophyll-*a* standard, Sigma) Turner Designs Trilogy fluorometer. High performance liquid chromatography (HPLC) samples (0.5 – 2 L) for accessory pigment analyses were filtered (0.7 µm Whatman GF/F), flash frozen in liquid nitrogen and stored at -80 °C prior to analysis using a Thermo

HPLC system. The matrix factorization program CHEMTAX was used to estimate the contribution of taxonomic groups to total chlorophyll-*a* (Mackey et al., 1996). Concentrations of nanophytoplankton, *Synechococcus*, *Prochlorococcus* and photosynthetic picoeukaryotes were analysed by analytical flow cytometry (AFC) using a FACSort flow cytometer (Becton Dickenson, Oxford, UK) according to the methods described in Davey et al. (2008) and Zubkov et al. (2003).

3. Results and Discussion

3.1. Hydrographic setting and macronutrient distributions

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

Surface mixed-layer

Commented [WN4]: Whilst the changes are minimal, the concentration changes for the mixed layer have changed

During all three transects the STF was identified by a sharp potential temperature (θ) gradient in the upper 200 m with the θ 15°C isotherm corresponding well to changes in macronutrient concentrations between STSW and SASW. North of the STF, mixed-layer macronutrient concentrations (Table 2) decreased in STSW between the three occupations of the transect. The largest relative depletion observed was for NO_3^- with a ~2.7-fold reduction in mean inventory concentration from 870 to 326 µmol m^{-3} between early spring and summer, whilst PO_4^{3-} and Si concentrations were reduced 1.5- and 1.4-fold, respectively. The largest absolute depletion was observed for Si with a reduction of 848 µmol m^{-3} between early spring and summer. Conversely, summer SASW mixed-layer mean concentrations of NO_3^-, PO_4^{3-} and Si were relatively 1.6, 1.4 and 2.1-fold lower than early spring, respectively, whilst the largest absolute depletion of 1912 µmol m^{-3} was observed for NO_3^-. SASW mixed-layer concentrations of NO_3^- and PO_4^{3-} were at least 2.1-fold higher than for STSW during the study, whilst the Si concentration was at least 1.5-fold lower, highlighting the relative deficiencies in major nutrients between high and low latitude derived surface waters (Sarmiento et al., 2004; Moore, 2016).

Sub-surface waters

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

3.2. Zn and Co distributions of the Southeast Atlantic Ocean

Surface mixed-layer

Commented [NW5]: Whilst changes are minimal, some mixed layer trace metal data have changed.

Figure 3 shows the dZn and dCo distributions for the upper 500 m of the Southeast Atlantic for the D357 and JCO68 transects. For full-depth dZn distributions along JC068 refer to Wyatt et al. (2014). In the surface mixed-layer, dZn and dCo concentrations ranged from 0.01 to 4.57

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

Sub-surface waters

During the early spring D357-1 transect, elevated dZn and dCo concentrations were observed between the surface mixed-layer and 500 m (1.48–3.85 nM and 39–62 pM, respectively) at the station closest the South African continent (Stn. 1). Here, the highest dZn concentrations were associated with the dZn-enriched waters (20–55 m) described above for the surface mixed-layer. During the late spring D357-2 transect, the near-shore (Stns. 0.5–1) dZn concentrations were lower (0.31–1.76 nM) whilst dCo remained similar to early spring values (27–57 pM). During summer, near-shore (Stn. 1) sub-surface dZn concentrations were markedly lower (0.03–0.50 nM) than spring values whilst dCo concentrations (17–52 pM) were only marginally lower. In offshore waters, sub-surface dZn concentrations ranged from 0.01 to 1.01

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

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

Commented [NW6]: We have thoroughly revised this section to investigate how changes in sub-surface supply may influence Zn and Co distributions of the SE Atlantic between seasons. To do this, we utilize metal:PO4 regression slopes.

Similarly, the dCo:PO_4^{3-} regression slope varied little between the three transects (Fig. 4 and Supp. Table 1). In dCo:PO_4^{3-} space, a single slope can be fit to SAMW and AAIW with no net scavenging effect on dCo distribution over the upper 1000 m. Like dZn, the waters overlying SAMW displayed spring dCo concentrations elevated above that potentially delivered via SAMW supply. During summer however, SAMW may provide a subsurface source of dCo (Fig. 4c) to overlying waters highlighting how Southern Ocean derived waters may play important, yet different, roles in upper water column metal distributions of the Southeast Atlantic.

3.3. Shelf derived sources of Zn and Co

Potential sources of trace metals to surface waters of the Southeast Atlantic include atmospheric inputs from South Africa and Patagonia (Chance et al., 2015; Menzel Barraqueta et al., 2019) as well as interactions with shelf and slope waters of the Agulhas Bank (Bown et al., 2011; Boye et al., 2012; Paul et al., 2015). During the D357 spring transects, elevated mixed-layer dZn and dCo concentrations (up to 4.57 nM and 50 pM, respectively; Sect. 3.2) were observed at stations closest the Agulhas Bank shelf and slope (Stns. 0.5, 1, 1.5 and 2). Here, we compare these metal elevations with respect to the aforementioned sources. Firstly, we encountered only brief, light rain during the study, thus minimal wet deposition of atmospheric aerosol. By combining the median atmospheric dry deposition flux for soluble Zn and Co for the Southeast Atlantic (Zn 6.0 and Co 0.05 nmol m^{-2} d^{-1}; Chance et al., 2015) with the mean mixed-layer depth (34 m) for STSW during D357, dust dissolution is estimated to add approximately 5.5 and 0.05 nmol m^{-3} dZn and dCo, respectively, over a one month period. These inputs are low compared with the mixed-layer metal inventories, representing <1 % of dZn and dCo concentration in STSW during the D357 transects (Table 2), and would not be sufficient to generate distinct mixed-layer maxima. It is likely, therefore, that the dZn and dCo elevations originated from the advection of metal-enriched waters from the western Agulhas Bank, a region identified as a distinct source of both dissolved and particulate trace metals to the Southeast Atlantic (Chever et al., 2010; Bown et al., 2011; Boye et al., 2012; Paul et al., 2015), and/or from the leakage of Indian Ocean water into the Southeast Atlantic via the AC. The detachment of Agulhas rings and filaments from the AC during its retroflection back towards the Indian Ocean constitutes a source of Pb to the surface Southeast Atlantic along the D357 transects (Paul et al., 2015). Whilst we observed elevated mixed-layer dZn and dCo at ~15ºE during both D357 transects, the absence of metal enrichment across the depth of the AC salinity maxima (Figs. 2 and 3) suggests that the signal must be entrained from elsewhere. Furthermore, dZn concentrations from the AC along the east coast of South Africa do not exceed 0.5 nM in the upper 200 m (Gosnell et al., 2012). It is therefore likely that the dZn and dCo enrichment was derived from the Agulhas Bank. The AC has been shown to meander over, and interact with, the Agulhas Bank, forming eddies and filaments on the shoreward edge of the AC proper, that tend to move northwards along the western shelf edge and into the Southeast Atlantic (Lutjeharms and Cooper, 1996; Lutjeharms, 2007), potentially delivering shelf-derived sedimentary material. We found no evidence of a fluvial signature in our data, and no significant fluvial source for trace elements to our study region has been reported in the literature. Whilst we cannot exclude an uncharacterized fluvial input, we focus here on the more likely scenario of sedimentary inputs as the driver of mixed-layer dZn and dCo elevations at the shelf and slope stations during D357. Despite no available particulate trace metal data for the D357-1 early spring transect for direct comparison with the highest dZn and dCo elevations, we observed elevated mixed-layer particulate Zn (pZn; 0.08–1.40 nM) and Co (pCo; 8–49 pM) at stations closest South Africa during the D357-2 late spring transect (Stns. 0.5, 1 and 1.5, Fig. S1), coincident with elevated dZn (0.05–1.82 nM) and dCo (1–43 pM). Furthermore, for the upper 500 m at stations 0.5 and 1, we found strong positive correlations between particulate aluminium and titanium (pAl:pTi, slope 41.7 mol mol^{-1}, Pearson's *r* 0.99, *n* = 15), as well as particulate Fe and titanium (pFe:pTi, slope 10.2 mol mol^{-1}, Pearson's *r* 0.99, *n* = 15), indicative of a strong lithogenic source. Whilst there are presently no South African sedimentary data against which we can compare our water column values, our pAl:pTi and pFe:pTi slope ratios are in excess of upper crustal mole ratios (34.1 and 7.3 mol mol^{-1}, respectively; Mclennan, 2001). These 500 m ratios are also steeper than the aggregate slopes for the full depth Atlantic Ocean away from hydrothermal sources (32.1 and 7.4 mol mol^{-1}, Pearson's *r* >0.97, *n* = 593, Schlitzer, 2018). Given the refractory nature of lithogenic pTi across diverse oceanic environments (Ohnemus and Lam, 2015), this may suggest the resuspension and dissolution of Agulhas Bank sediments enriched in dAl and dFe, followed by westward offshore transport, a common feature of the Bank's physical circulation during spring and summer (Largier et al., 1992). Such processes may in turn provide an additional source of dZn and dCo to STSW of the Southeast Atlantic. For example, Little et al. (2016) proposed that oxygen-deficient, organic-rich, continental margin sediments may constitute a significant global sink within the marine Zn cycle. These sediments could additionally provide a local source of dZn following remineralisation. Recent model outputs have likewise highlighted oxygen-deficient, boundary sediments as a dominant external source of Co to the oceans (Tagliabue et al., 2018). Given that oxygen depleted (<45 µM) bottom waters are prevalent across the western Agulhas Bank (Chapman and Shannon, 1987; Chapman, 1988), considered to arise from high organic matter input to sediments and its bacterial decomposition, a sedimentary source of dZn and dCo appears likely.

3.4. Trace metal stoichiometry of the upper Southeast Atlantic

Commented [WN7]: Our interpretation in this section has changed to reflect that we are now using concentration inventories, instead of slopes of regression, to calculate trace metal stoichiometry. The way we define STSW and SASW using potential temperature 15 C is now clearly defined here.

In addition to seasonal variations in the lateral advection of continentally derived trace metals, the lower dZn and dCo concentrations in STSW during summer, compared with spring, likely 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, where STSW equals $\theta \geq 15$°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, thus the inventories for SASW were determined over this depth accordingly (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.

Commented [NW8]: Here we clearly state how STSW and SASW are defined when calculating inventory ratios.

Commented [NW9]: Here we state that we have removed spring STSW values that displayed a clear enrichment in Zn and/or Co concentration compared with background values.

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 µmol 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 µmol 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 (~100 – 1100 µmol 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 µmol mol^{-1} (Table 2), likely reflecting external inputs to the oceans and biological Co requirements that are typically 4-fold less than for Zn (Ho et al., 2003; Roshan et al., 2016; Hawco et al., 2018). The STSW dCo/PO_4^{3-} ratio decreased between early and late spring transects, potentially in part due to the westward expansion of STSW during late spring (Fig. 2) and subsequent mixing with SASW depleted in dCo relative to PO_4^{3-} (Fig. 3). This dilution is likely also true of dZn and Si, yet their STSW concentration inventories may be sufficiently high as to mask this effect. Unfortunately, an insufficient quantity of late spring SASW data are available with which to affirm this postulation. The highest dCo/PO_4^{3-} ratio was observed during summer due to the preferential biological removal of PO_4^{3-} relative to dCo.

In SASW, dCo/PO_4^{3-} was consistently low with ratios of 23 and 26 µmol mol^{-1} for early spring and summer, respectively. Much higher inventory ratios of ~580 µmol mol^{-1} can be calculated over similar depths for open-ocean North Atlantic waters (GA03 Stns. 11-20, Schlitzer et al., 2018), likely reflecting an elevated atmospheric Co input and/or an extremely low surface PO_4^{3-} inventory (Wu et al., 2000; Martiny et al., 2019).

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

3.5. Phytoplankton controls on trace metal ecological stoichiometry

Commented [WN10]: Here we have amended our interpretation to reflect that we now use concentration inventories, rather than slopes of regression, to calculate trace metal stoichiometry. This section has be restructured slightly to better reflect out interpretations.

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

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

The fact that both *Phaeocystis* and diatomaceous nanophytoplankton maintain a contribution to the summer STSW chlorophyll-*a* complement, when dZn availability is low, is intriguing. Both *P. antarctica* and the large, coastal diatoms *Thalassiosira pseudonana* and *Thalassiosira weissflogii* have been shown to be growth limited in culture by free Zn^{2+} concentrations ≤10 pM (Sunda and Huntsman, 1992; Saito and Goepfert, 2008). A simple estimate of summer STSW free Zn^{2+} availability, based on North Atlantic organic complexation data (>96 %; Ellwood and Van den Berg, 2000), indicated free Zn^{2+} averaged $6.3 \pm 5.3u_c$ pM, suggesting the potential for growth limitation of these phytoplankton. In addition, when comparing the Southeast Atlantic dZn stoichiometry with the cellular requirements of phytoplankton grown under growth rate limiting conditions (Fig. 6), we found summer STSW dZn/PO_4^{3-} to be in deficit of the requirements of coastal *T. pseudonana* but not those of the smaller, open-ocean diatom *T. oceanica*. The variation in cellular Zn/P between small and large phytoplankton is related to the higher surface-area-to-volume ratio of smaller cells, and the limitation of diffusive uptake rates at low Zn^{2+} concentrations (Sunda and Huntsman, 1995). This would suggest that the lower dZn availability in summer STSW should influence phytoplankton species composition by selecting for smaller organisms with lower cellular Zn requirements, and confirmed by a ratio of picophytoplankton to nanophytoplankton at least 4-fold higher during summer compared with spring values. The comparison further implies that the presence of *Phaeocystis* and diatoms in summer STSW may be linked with their metabolic Zn-Co-Cd substitution capability, potentially allowing them to overcome some portion of their Zn deficiency. Largely connected to carbonic anhydrase enzymes, several species of eukaryotic phytoplankton are capable of biochemical substitution of Zn, Co or Cd to maintain optimal growth rates under low trace metal conditions (Price and Morel, 1990; Sunda and Huntsman, 1995; Lee and Morel, 1995; Lane and Morel, 2000; Xu et al., 2007; Saito and Goepfert, 2008; Kellogg et al., 2020). For example, metabolic substitution of Co in place of Zn has been observed to support the growth of *P. antarctica*, *T. pseudonana* and *T. weissflogii* in media with Zn^{2+} <3 pM (Sunda and Huntsman, 1995; Saito and Goepfert, 2008; Kellogg et al., 2020). Thus, the lower mixed-layer dCo inventory of summer STSW, relative to early spring, may be in part related to enhanced dCo uptake through biochemical substitution alongside the growth of phytoplankton with distinct Co requirements.

In contrast to *Phaeocystis*, *E. huxleyi*-type haptophytes were near-absent in spring STSW (<5 % chlorophyll-*a*; Fig. 5a) and increased in contribution during summer (18 %). *Emiliania huxleyi* appear to have a biochemical preference for Co over Zn (Xu et al., 2007), which could potentially be a contributing factor to the increased fraction of this haptophyte in summer STSW. Based on Co organic complexation data for Southeast Atlantic STSW (>99 %; Bown et al., 2012), however, even the maximum dCo concentration of 56 pM (estimated free Co^{2+} $0.56 \pm 0.11u_c$ pM) observed for STSW during this entire study would limit the growth of cultured *E. huxleyi* in the absence of Zn or Cd (Sunda and Huntsman, 1995; Xu et al., 2007). This is supported by inter-seasonal dCo/PO_4^{3-} stoichiometries in deficit of the cellular requirements of cultured *E. huxleyi* (Fig. 6). Despite this, Xu et al. (2007) showed that *E. huxleyi* can maintain significant growth at only 0.3 pM Co^{2+} in the presence of Zn, with the limitation by, and substitution of these metals reported to occur over a range of free ion concentrations (0.2–5 pM) that is relevant to summer conditions of the Southeast Atlantic. This assessment implies an additional need for Zn in phytoplankton nutrition due to low dCo availability throughout the Southeast Atlantic, which may accelerate the decrease in dZn/dCo inventory ratios between seasons.

The elevated summer STSW chlorophyll-*a* concentrations were accompanied by increased cell concentrations of the *Synechococcus* and *Prochlorococcus* (up to 100 and 400 cells μL^{-1}, respectively) relative to early spring abundance (Fig. 5b). This pattern suggests an inter-seasonal community shift towards smaller picocyanobacterial cells that is coincident with decreased dZn availability. *Synechococcus* and *Prochlorococcus* are thought to have little or no Zn requirement and relatively low Co requirements (growth limited by ≤0.2 pM Co^{2+}; Sunda and Huntsman, 1995; Saito et al., 2002). This, alongside their small cell size, hence greater capacity for acquiring fixed nitrogen under conditions where this nutrient is depleted, may allow these prokaryotes to flourish following depletion and export of Zn associated with *Phaeocystis* and diatom blooms. This supposition is supported by a persistently high abundance of *Synechococcus* and *Prochlorococcus* (>1000 cells μL^{-1}), relative to eukaryotic nanophytoplankton, in the dZn depleted surface waters of the Costa Rica Dome (Saito et al., 2005; Ahlgren et al., 2014; Chappell et al., 2016). Here, surface dCo concentrations were maintained above that of surrounding waters by the biological production of Co-binding ligands (Saito et al., 2005). The increased abundance of these prokaryotic autotrophs in summer STSW of the Southeast Atlantic may have also contributed to the inter-seasonal decrease in dCo inventory.

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

Conversely, the absence of a significant diatom contribution to summer SASW chlorophyll-*a* (Fig. 5a), relative to early spring, as the dZn/PO_4^{3-} inventory ratio is in excess of the cellular Zn/P requirements of typical oceanic diatoms (Fig. 6). In addition, whilst the dCo/PO_4^{3-} ratio of summer SASW is in deficit of the cellular Co/P below which growth limitation of *T. oceanica* may occur, this species has been shown to grow effectively at Co^{2+} <0.1 pM in culture (Sunda and Huntsman, 1995). The low diatom fractional contribution to summer SASW may be instead related to low Fe availability (Browning et al., 2014) and stress-induced Si exhaustion. In support of this, we calculate summer SASW mixed-layer Si concentrations (0.9 ± 0.3 μM) to be 50 % of early spring values (1.8 ± 0.2 μM) and a dissolved NO_3^-/Si stoichiometry of 3.8 mol mol^{-1} close to the 4 mol mol^{-1} shown to limit diatom growth in culture (Gilpin et al., 2004), and in contrast to the 2.9 mol mol^{-1} calculated for early spring.

3.6. Conclusion

Commented [NW11]: We have modified the conclusions slightly to reflect out new concentration inventory approach.

We report the distributions of dZn and dCo in the upper water column of sub-tropical and sub-Antarctic waters of the Southeast Atlantic during austral spring and summer periods. We identify an apparent continental source of dZn and dCo to sub-tropical waters at depths between 20 – 55 m, derived from sedimentary inputs from the Agulhas Bank. In contrast, open-ocean sub-Antarctic surface waters displayed largely consistent inter-seasonal mixed-layer dZn and dCo concentrations indicating a more balanced ecophysiological regime with regard to their organisation. The vertical distributions of dZn and dCo in the upper water column were similar to that of PO_4^{3-} indicating biological drawdown in surface waters and mixing with underlying

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

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

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

Author contribution. MCL and EPA acquired the funding. NJW, MCL, AM, TJB, EMSW, and HAB collected samples at sea. NJW conducted the Zn and Co measurements, EMSW the macronutrient measurements and TJB the phytoplankton measurements. NJW prepared the manuscript with significant contributions from all co-authors.

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

	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)

Table 2. Southeast Atlantic dissolved micro- and macronutrient mean concentration inventories for the upper water column during early spring (D357-1), late spring (D357-2) and summer

(JC068) transects. STSW and SASW waters were defined using the θ 15°C isotherm (Section 3.4) and are compared with total inventories calculated for the shallower mixed layer (in parenthesis) that include continental inputs of dissolved Zn and Co. Zn/Co represents the concentration inventory ratio for STSW and SASW, respectively. STSW = Sub-Tropical Surface Water, SASW = Sub-Antarctic Surface Water.

Oceanographic	Transect	Zn	Co	NO^{3-}	PO$_4^{3-}$	Si(OH)$_4$	Zn/PO$_4^{3-}$	Co/PO$_4^{3-}$	Zn/Co
Regime		(nmol m^{-3})		(μmol m^{-3})			(μmol mol^{-1})		(mol mol^{-1})
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

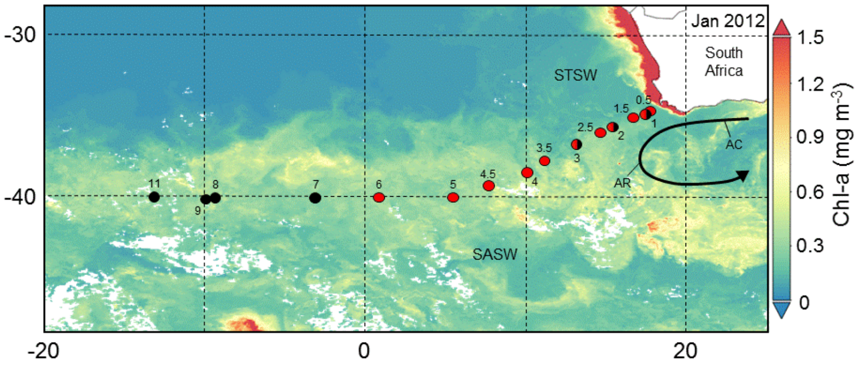

Figure 1. The Southeast Atlantic stations sampled for dissolved Zn and Co along the GA10 section during UK-GEOTRACES cruises D357 (red circles) and JC068 (black circles), overlain a VIIRS monthly composite image of chlorophyll-*a* concentrations for January 2012 (https://oceancolor.gsfc.nasa.gov/). Two transects were completed during D357 between Cape Town and the zero meridian that represent early austral spring 2010 (D357-1; Stns. 1, 2, 3, 4, 5 & 6) and late austral spring 2010 (D357-2; Stns. 0.5, 1, 1.5, 2.5, 3.5, 4.5), respectively. JC068 took place during austral summer 2011/12 and we present here only the repeat transect data

between Cape Town and 13°W (Stns. 1, 2, 3, 7, 8, 9, 11). STSW = Sub-Tropical Surface Water, SASW = Sub-Antarctic Surface Water, AC = Agulhas Current, AR = Agulhas retroflection.

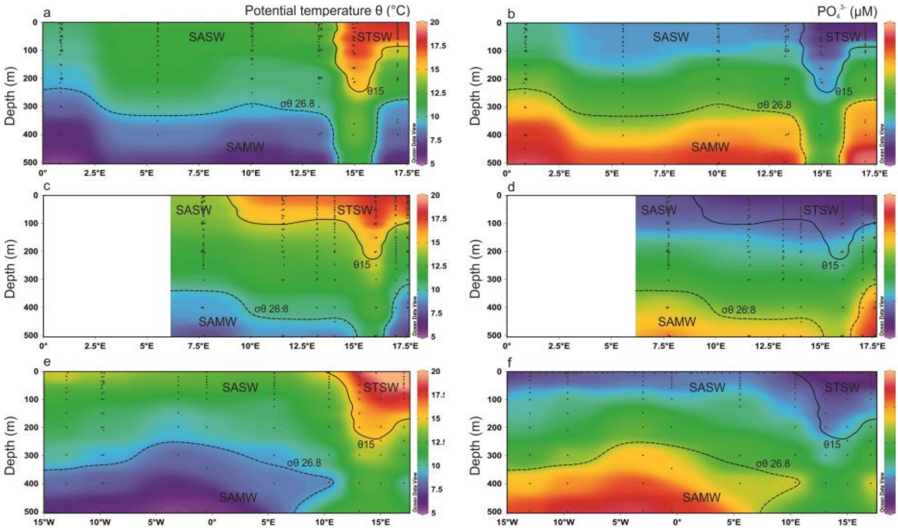

Figure 2. Upper 500 m potential temperature (θ) and dissolved PO_4^{3-} distributions for the Southeast Atlantic along early spring (a,b; D357-1), late spring (c,d; D357-2) and summer (e,f; JC068) transects. The dominant Southern Ocean (SASW & SAMW) and South Atlantic (STSW) water masses that influence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

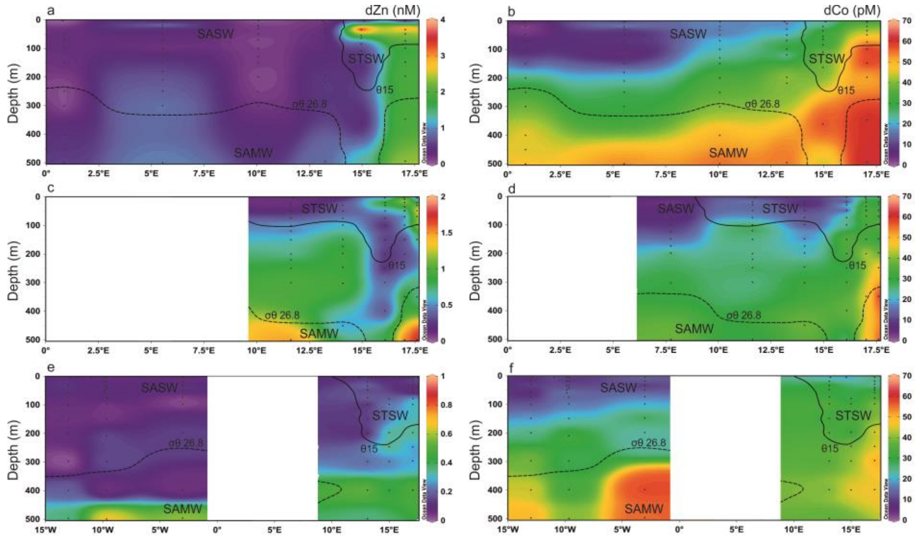

Figure 3. Upper 500 m dissolved Zn and Co distributions for the Southeast Atlantic along early spring (a,b; D357-1), late spring (c,d; D357-2) and summer (e,f; JC068) transects. The STF is delineated by θ 15°C (solid contour), whilst the influence of SAMW is evident by the median potential density (σθ)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

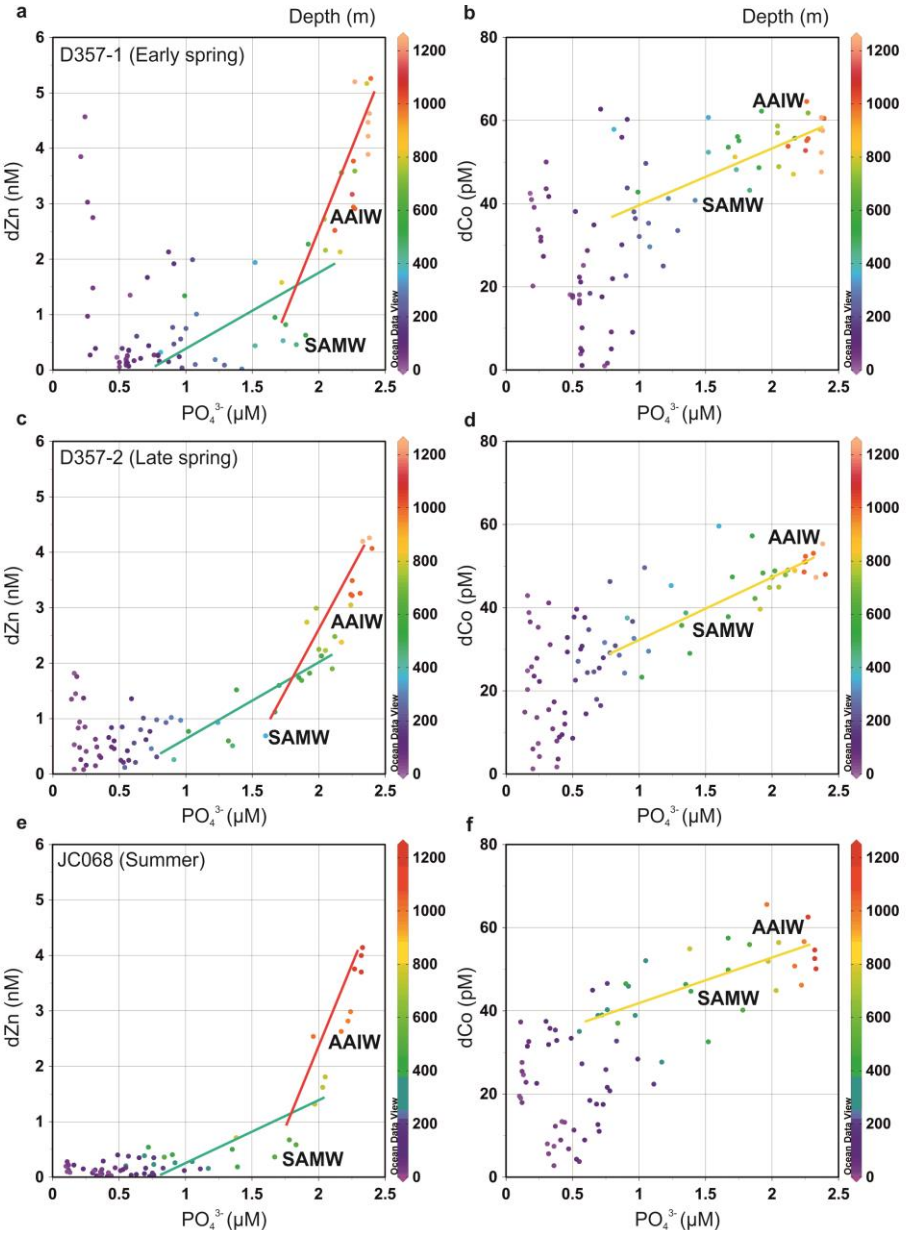

Figure 4. The dissolved Zn and Co versus PO_4^{3-} distribution for the Southeast Atlantic during early spring (a,b; D357-1), late spring (c,d; D357-2) and summer (e,f; JCO68) transects. The green and red lines indicate the dZn:PO_4^{3-} regression slopes for SAMW and AAIW, respectively. The yellow line indicates the dCo:PO_4^{3-} regression slope for SAMW and AAIW combined. The equations for regression lines are detailed in Supplementary table 1. SAMW =

Sub-Antarctic Mode Water, AAIW = Antarctic Intermediate Water. The full depth dZn:PO$_4^{3-}$ relationship along JC068 can be found in Wyatt et al. (2014).

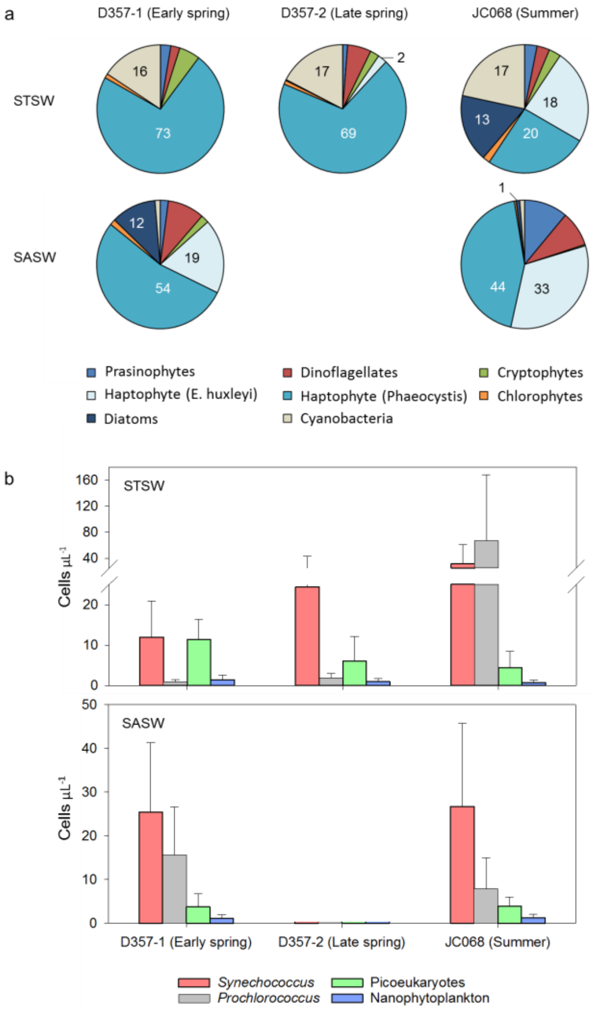

Figure 5. Seasonal differences in (a) pigment-derived taxonomic contributions to total chlorophyll-*a* (percentage), and (b) AFC counts of *Synechococcus*, *Prochlorococcus*, nanophytoplankton (approx. >2µm) and photosynthetic picoeukaryotes (approx. <2µm) in the Southeast Atlantic.

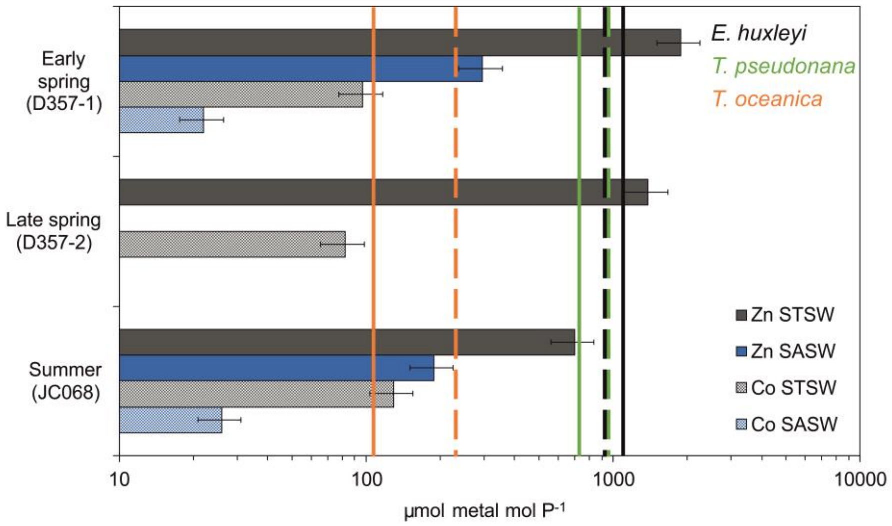

Figure 6. Metal/PO_4^{3-} inventory ratios for the upper water column of the Southeast Atlantic (horizontal bars) compared with laboratory estimates of cellular ratios in eukaryotic phytoplankton below which growth limitation occurs (solid vertical lines represent Zn:P with no added Co to media whilst dashed lines represent Co:P with no added Zn; phytoplankton data from Sunda and Hunstman, 1995). Error bars on inventory ratios represent 20 % combined uncertainty for dZn and dCo analyses (see Section 2.2). This figure is adapted from that in Saito et al. (2010) and implies that inter-seasonal differences in metal/PO_4^{3-} stoichiometry could impact phytoplankton community composition in the Southeast Atlantic.