

Interactive comment on “Seasonal cycling of zinc and cobalt in the Southeast Atlantic along the GEOTRACES GA10 section” by Neil J. Wyatt et al.

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Authors response to interactive comments on “Seasonal cycling of zinc and cobalt in the Southeast Atlantic along the GEOTRACES GA10 section” by Neil J. Wyatt et al.

The authors of this manuscript would like to thank the reviewers for their well-considered review and advice on preparing our manuscript for publication in Biogeosciences. We believe the reviewers present extremely valid comments, particularly on the ‘interpretation of data’, that has led us to reconsider how we approach certain aspects of the data. Specifically, we acknowledge and agree with the suggestion that the use of slopes of regression to infer biological uptake and remineralisation is flawed by the varying influences of other sources on the correlation, most notably water mass

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mixing of deeper waters that have the potential to alter slopes of regression. Secondly, we acknowledge that the important influences of water mass mixing and/or various other influences on our trace metal distributions had not been fully explored. To address these concerns the slopes of regression between metals and PO₄ are now used to investigate the influence of water mass mixing, and other biogeochemical factors, on our upper water column metal distributions as part of section 3.2. Importantly, concentration inventories for the set water masses STSW and SASW are now utilized to calculate surface water ecological stoichiometry. Using water masses instead of slopes of regression has not largely changed our interpretation and we still observe decreasing the same pattern of Zn:Co stoichiometry between early, late and summer transects in STSW. At the same time, this new approach has allowed us to separate out the water masses more effectively. We feel our trace metal ecological stoichiometry section 3.4 is now better aligned to the spatial and depth changes we observe in STSW and SASW between the three transects.

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 than 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

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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 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 85 m. This is the mean depth of the 15 C isotherm for STSW (85 ± 11 m) 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 varying influences that may affect our metal distributions, thus inventories.

Specific comments:

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

We agree that the use of integers for station labels is confusing and we suggest a change to sequential station numbers based on distance from Cape Town i.e. Station 1 is nearest Cape Town whilst Station 9 is furthest.

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

Agreed. We have rephrased to read: "In sub-tropical surface waters, mixed layer dZn

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and dCo concentrations during early spring were 3.16 ± 1.35 nM and 39 ± 9 pM, respectively, compared with summer values of 0.18 ± 0.08 nM and 26 ± 7 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'. 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'. We have also made this same change to line 373-374 on the original manuscript.

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

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produced on TEI's and particularly Zn and Co in the Atlantic prior to introducing the data sparse Southeast Atlantic as our study region (original manuscript line line 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 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.

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 now warranted. We now leave all discussion on atmospheric vs continental sources to section 3.3. The text in section 3.2 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 dur-

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ing each cruise. In addition to the existing 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. 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 has been changed to "In offshore waters, 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.

Shelf 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 ra-

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tios 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.

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 when referring to dissolved, particulate or total metal concentrations throughout the text.

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).

Agreed. 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. We still utilise metal/PO₄ slopes in section 3.2, but now use these to discuss the nutrient distribution throughout the upper water column and more thoroughly discuss the aforementioned processes on these

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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 and therefore simply removed individual depths from coastal stations that were clearly elevated in trace metals relative to the linear metal/P slope. These samples are displayed in Figure 4. We have rearranged the text in section 3.4 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 end-members (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

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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 compared 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. We now use the relationships between metals and phosphate over the upper 500 m to highlight the interaction between mixing and other varying processes on the distribution of Zn and Co in distribution section 3.2, rather than in the trace metal ecological stoichiometry section 3.4. We have revised Figure 4 to display only the upper water column, rather than full depth, as the full depth Zn/P relationship has been presented previously in Wyatt et al (2014). This has allowed us to discuss the water mass and scavenging influences that are relevant to the upper water column more effectively. Our ecological stoichiometry section 3.4 is now based on concentration inventories for the water masses STSW and SASW with the data used in these calculations clearly defined in section 3.4.

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

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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 $\sim 0.1 \mu\text{M}$ in STSW is still an order of magnitude larger than the Zn decrease of $\sim 1.4 \text{ nM}$ or the Co decrease of several pM.

Thank you for advising us here. As we are now using concentration inventories for set water masses to calculate metal:PO₄ stoichiometries, we feel the depletion of trace metals relative to PO₄ is still valid. However, we acknowledge that the absolute change is still larger for PO₄ than for trace metals, due to a biological PO₄ requirement that is ~ 1000 fold higher (Twining and Baines, 2013), and have made this explicitly clear both here and elsewhere in the text where we compare absolute nutrient concentration changes.

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

We agree that the greater Zn requirement relative to Co is well established. 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 this

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paragraph to acknowledge the preceding work on Zn vs Co requirements and have referenced accordingly (Price and Morel, 1990; Sunda and Huntsman, 1995; Xu et al., 2007; Saito and Goepfert, 2008).

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. The ecological stoichiometry calculated from concentrations displays a STSW Zn:Co ratio that decreases between spring and summer from 54 to 7 mol:mol, compared with 29 to 11 mol:mol using the regression based approach. We therefore believe that both the concentration depletion and ecological stoichiometry reflect changes in the nutritional requirement of resident phytoplankton and discuss this further in section 3.5. Whilst seasonal changes in community composition is known to change in response to, 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 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."

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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 significantly revised this and the following paragraphs to clearly explain that Zn is depleted in surface waters between seasons, increasing the demand for Co through enzymatic substitution and changes in phytoplankton assemblage. Remineralisation in deeper waters may also influence our concentration inventories and also the Zn:Co inventory ratio, depending on the length scale of remineralisation of Zn and Co. This is now assessed through the use of concentration inventories rather than slopes of regression.

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

The wording of this sentence may not be clear. We are not stating there is an increased uptake rate of a ratio, but rather the ratio of Zn:Co uptake is positively correlated with Zn availability. That is, as Zn is depleted below growth limiting concentrations, the Zn uptake rate decreases relative to the Co uptake rate, effectively lowering the Zn:Co uptake ratio. We have tried to better clarify this sentence in the text.

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 replaced the term 'preferential' with 'significant' to reflect the increased Zn requirement of diatoms compared with other phytoplankton.

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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 these data in the text. For example, the ratio of picophytoplankton to nanophytoplankton was at least 4-fold higher during summer compared with spring.

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 this sentence to state that an additional requirement for dZn, due to low dCo availability, may reduce Zn/Co inventory ratios, rather than a change in Zn:P slope through microbial loop remineralisation.

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.

We have altered the text in the methods section 2.3 to identify the taxonomic groups belonging to nanophytoplankton, picocyanobacteria and picoeukaryotes. Further, where relevant, the text in discussion section 3.5 now distinguishes between nano- and picosized phytoplankton.

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

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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.

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.

We agree this sentence needs some clarity. Here, we are stating that the ecological Zn:P stoichiometry in SASW of the Southeast Atlantic is greater than the cellular requirement for *T. oceanica* growth in culture (Fig 6). Therefore, the low diatom contribution in these waters appears unrelated to Zn, or P given these are Southern Ocean derived waters, and rather may be related to low Fe and Si. Fe stress has been shown in SASW for this study by Browning et al (2014; doi:10.5194/bg-11-463-2014).

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. In section 3.2 we now utilise these positive slopes to discuss the influences on the distribution of trace metals in the upper water column and have restructured the conclusions to reflect this.

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 and that below to state that our results reflect what we know about preferential removal of Zn relative to Co using the literature, and that it is the removal between seasons that result in potentially growth limiting concentrations towards the end of the growing period that are important in the context

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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 approach for set water masses. These calculations are also documented in the Table 2 legend.

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