

## ***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 PO<sub>4</sub> 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 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.

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AC: 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. 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 to describe the distribution of Zn and Co through the upper water column but now we consider additional influences on these slopes, such as mixing and other processes that are specific to trace metals. 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

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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.

AC: 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 appear 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. Furthermore, by defining STSW as waters with potential temperature  $\geq 15$  C, we are better able to assess how seasonal changes in depth and spatial distribution may influence metal concentrations. Finally, using the slopes of metal/PO<sub>4</sub>, 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.,

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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 PO<sub>4</sub> concentrations in deeper samples from spring to summer in figure 2 suggests that factors other than biological uptake and remineralisation are acting here.

AC: We would like to acknowledge that both reviewer 1 and 2 make clear that the use of regression slopes to determine metal/PO<sub>4</sub> 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

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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 ( $85 \pm 11$  m) and allows a consistent comparison between the two water masses. Importantly, we now calculate the inventories of Zn, Co and PO<sub>4</sub> 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 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.

AC: We agree with reviewer 2 that we need to more robustly assess 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 in-

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dividual 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) whereby we combined the day-to-day instrumental performance with the uncertainty surrounding the CRM samples. We feel this this 'combined relative uncertainty (CRU)' yields a more realistic estimate of analytical precision and will incorporate this approach into our methods section 2.2. Adopting this approach, we estimate a preliminary CRU of 8-20 % for dZn analyses during this study. The higher end of the dZn CRU is largely driven by the greater variability associated with the low concentration SAFe S measurements, as reviewer 2 rightly states. We would like to point out at this stage 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). By using CRU, we now have a more meaningful constraint with which to assess our very low concentration Zn and Co data. We will factor the maximum CRU into all values we present to provide the reader with a more accurate assessment of potential trace metal concentrations. We will also incorporate uncertainty estimates into figures 4 and 6 and acknowledge accordingly in figure legends.

Table 2 lists regression slopes for metals and PO<sub>4</sub>. The correlation coefficients 'r' 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.

AC: We have now adopted a concentration inventory approach to calculate Zn:Co rates, on the advice of reviewer 1, 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 any uncertainty, based on analytical accuracy and preci-

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sion (combined relative uncertainty) 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.

Derivation of metal-PO<sub>4</sub> 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.

AC: 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 along with any uncertainty in these 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.

AC: 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. The depth range for both Zn and Co is now identical 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 and also in Table 2. This rearrangement of the text will better clarify that we removed individual sample data that exhibited 'elevated'

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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).

AC: Agreed. We have made better use of the absolute concentrations when discussing both changes in nutrients and trace metals 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?

AC: Zn 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 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 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.

AC: 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). In section 3.3 (Shelf Sources) we now make it clear that we postulate the Agulhas Bank sediments to be enriched in trace metals as a result of biogenic material

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decay.

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

AC: Agreed. The spring ( $1.8 \pm 0.2 \mu\text{M}$ ) and summer ( $0.8 \pm 0.4 \mu\text{M}$ ) 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, however, and instead concentrations should be assessed alongside the dissolved  $\text{NO}_3\text{:Si}$  stoichiometry that may indicate Fe and Si stress. The change in  $\text{NO}_3\text{:Si}$  between spring (0.4:1) 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.

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.

AC: Due to the changes in Zn concentration between seasons, we have found it difficult to settle on a single concentration scale to most appropriately present our data. This has led to different z axis in Figure 3 as reviewer 2 points out. We have now settled on two different concentration scales on the advice of reviewer 2. Reviewer 2 also rightly points out that the 26.8 isopycnal and  $T = 15$  contours are different in figures 2 and 3. This is an oversight on our part due to the use of two bottle files with different resolution for the hydrographic data, from which these contours are derived. We have now combined all data into a single file that will allow us to create plots with identical density and temperature properties.

Figure 6: The vertical lines are showing potential points where growth limitation is induced. In this case, would it be better for the bars to represent surface nutrient availability ratios rather than slopes of the regressions?

AC: Yes indeed. Throughout this manuscript, we have now converted our slopes of re-

gression analyses to concentration inventories that will better reflect nutrient availability in the upper water column. Figure 6 has been modified accordingly.

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