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

Anonymous Referee #2

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Dr Wyatt and co-authors present a high-quality Zn and Co dataset from the southeast Atlantic Ocean from repeat cruises along the same transect. Furthermore, the authors incorporate a great additional suite of biogeochemical data to aid interpretations. This study exemplifies key directions that should shape the future directions of the GEOTRACES community as it transitions from single time point, single metal, basin-scale snapshots to more targeted process studies including multiple biogeochemically connected metals, biological community data and seasonal variability. I thank the authors from bringing this great study together, and congratulate them on the quality of the work. I believe this study aligns well with the aims/scope of biogeosciences, and will be of clear interest to the community. However, I have significant concerns with the interpretational framework as well as aspects of the presentation at present. I feel that these must be addressed further before the manuscript can be considered for publication.

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.

These more major general framework suggestions, as well as general and line-specific comments, are detailed below. Given the extent of these more general comments, I am limiting detailed line-specific comments at this stage.

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.

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.

If the authors feel their interpretations were correct as is, I ask them to add a new section to clearly discuss why the above global-scale controls on metal and macronutrient distributions do not apply to their dataset.

Additional suggestions

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:

âĂć The reproducibility of triplicate analyses is mentioned in section – 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. âĂć 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.

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.

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.

Minor and line-specific comments

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).

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?

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.

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

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.

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?

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