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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 #1

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This manuscript presents an interesting data set on Zn and Co for an important frontal region of the ocean. In this region, biochemical processes have the potential to impart a signature on the water masses that form here, and thus influence regions elsewhere. The data seem of high quality, the manuscript is generally well written and the biogeochemical cycling of the bio-essential metals Zn and Co is important and of current interest in the field. However, it seems there might be some potential caveats in the interpretations.

The section on sources (3.3) was easy to follow and I only have some minor comments (see below). However, I have a problem with the data presentation and the interpretation relating to the stoichiometry section (3.4). Given that the following section (3.5) is based on the stoichiometry section, I'm not entirely sure about this last section, but

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I think the overall discussion is valid based on changes in the upper water column inventories. However, some clarification is needed on the role of 'microbial loop remineralisation' (see specific comments), and the novelty of some of the findings seems slightly overstated.

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.

Overall, this is a valuable data set that should be published, but in my opinion, the data presentation and interpretation needs to be reconsidered.

Specific comments:

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

21-23 slightly awkward sentence, please rephrase for clarity

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

64 what is 'near-absolute' ?

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 sto-

ichiometry (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.

101 plasma rope; assume this is a brand name?

174 'was not largely sampled' unclear, please rephrase

181 suggest 'between the three occupations of the transect'

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

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.

237 range from

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.

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

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

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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)

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

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 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

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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.

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)

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

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 uM in STSW is still an order of magnitude larger than the Zn decrease of $\sim$1.4 nM or the Co decrease of several pM.

343 the greater Zn requirement relative to Co is well established

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).

354 ‘principle, interlinked’ does not seem right

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?

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

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.

411 is this confirmed by the flow cytometry data?

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).

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

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.

437 fig 5b I suppose?

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.

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

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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.

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)

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

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.

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