Biogeosciences Discuss.,
doi:10.5194/bg-2016-511-AC1, 2017

Biogeosciences
Discussions
Open Access

Interactive comment on "The Acceleration of Dissolved Cobalt's Ecological Stoichiometry due to Biological Uptake, Remineralization, and Scavenging in the Atlantic Ocean" *by* Mak A. Saito et al.

Mak A. Saito et al.

msaito@whoi.edu

Received and published: 22 May 2017

We thank the reviewer(s) for their comments on the manuscript. We provide point-by-point responses here, although we were not able to obtain a digital (non-pdf) version of the review so reviewer comments are paraphrased or quoted. In general, we feel that we can incorporate the reviewer's suggestions or in some cases there was a misunderstanding about the data or interpretation they are interested in being elsewhere in the paper. I think the major scientific point of this paper is that dissolved Co : phosphate ratios are extraordinarily diverse, far more so than for any other macro or micronutrient

by a large margin. This paper attempts to capture the full extent of this stoichiometric diversity particularly in its effect on the dissolved phase, with novel connections to the particulate and biochemical phases. To do so required employing some new approaches using simple statistical methods, and using the power and confidence associated with a large number of statistical analyses rather than stringent methods on single or few analyses of a large dataset as done previously.

The reviewers ask about the methods used: "all this approach based on multifactorial calculations of the processes is indeed little convincing without the detail and the methodology of the used calculations". There are two issues here. First, regarding the methods, there is no multifactorial analysis, simply a Matlab script that repeats a simple two-way linear regression many times on groupings of 5 depths many times across the sections in order to achieve the high-resolution stoichiometry targeted in this study. This method is simple and is fully documented in the methods. We will add suggested additional information about the length of the vectors. The vector addition is also documented in the paper already in the discussion, and is used primarily as an example scenario (e.g. what vectors could be added to result in the observed negative vector).

Second, regarding the question about the linear regression approach - we understand the reviewer's concern about statistical choices. Specifically, the reviewer suggests increasing the threshold from r= |0.7| to |0.88| and the number of data points per regression from 5 to 8. In response, we point out that this exact broader scale analysis with more data and higher r2 values was conducted and presented in this manuscript as described in Section 3.2 as "aggregate" datasets (and the regressions figures themselves are shown in Noble et al., 2017 BG in press Figure 11, r2 vary from 0.67 to 0.92). After presenting these large scale and more significant features, we argue that there is large amount of upper euphotic zone data that was excluded in order to acquire these high r2 regressions, yet likely represents real increased stoichiometric features. This "profile-based" analysis approach was applied to measure these shallow phenomena. The high resolution approach requires smaller depth intervals in order to capture the resolution because they are increasing (and accelerating) towards the surface. For many years we have observed a significant increase in slope in the upper photic zone which we have believed to be a real biochemical effect. With sectional datasets now available, we are able to combine dissolved, particulate, and biochemical protein datasets in this manuscript to study this phenomenon. For the dissolved samples to be expanded to 8 depth would result in a loss of depth resolution in which these features would be obscured (this effectively imposes an assumption of a constant stoichiometry rather than an increasing one). We can present all of the r value data that is above our threshold so the reader can evaluate the quality of the regressions themselves (this used to be part of Fig 3 but we removed it to make the figure panels larger). To change to 8 points and arbitrarily higher r values thresholds is ignoring the motivation for this study to tease a subtle but apparently widespread signal from the euphotic zone, which is also supported by particulate and protein data here and which is found across two ocean sections.

The reviewer also comments on how: “Only the middle point is used in vector analysis”. This is a misunderstanding. For each 5-depth point regression the resulting slopes are plotted centered around the data, which is the midpoint within the 5-points. We could easily switch the choice of depth to be any of the 5-depth points within the regression, but centering at its midpoint seemed most logical.

The reviewers’ second main concern is regarding the lack of consideration of a mixing vector in the vector analysis. The reviewers incorrectly state that we “argue that only remineralization and scavenging govern the deep distribution of cobalt in the North Atlantic”. On the contrary we state that “These scavenging signals co-occur with distinct water masses identified by OMPA analysis, implying that these scavenging processes are being integrated on decadal-to-century timescales of deepwater circulation processes within the ocean interior.” While it is true that water mass mixing could alter the ratio of Co and P, mixing itself is not a process that removes or add Co or P from the dissolved phase (except in estuaries). Moreover, the ratios of the dCo and PO4

provided in the review produce an almost identical ratio of 32 and 31-35 (40, 70-80pM dCo; 1.25 and 2.25 PO4), so mixing these NADW and AABW water masses would not create a significant vector in Co:P space by their example. We could add a mixing vector to the plot as we did in our original vector diagram for upwelling (Noble et al., 2008). Our point here is that in these localized fine scale regression analyses vertical processes of uptake remineralization and scavenging, whose signals are clearly integrated through horizontal advection, can explain the large variation and change in sign of the Co:P slopes. For a revision we can add in a mixing vector and/or further elaborate and clarify on the role of mixing in vector analyses.

The reviewer suggests using the water mass analysis in this study of end member distributions: ”since the complete analysis of water-masses is available, as performed by Jenkins et al., 2015), the combination of end-members weighted by the proportion of each water-mass will help to determine if a located depth is a source (remineralization) or a sink (scavenging) for dCo in the deep sea.” We point out that this water analysis has already been included and is shown in Figure 2 for the North and South Atlantic Zonal sections including the following text that relates to the reviewer’s suggestion. “These scavenging signals co-occur with distinct water masses identified by OMPA analysis, implying that these scavenging processes are being integrated on decadal-to-century timescales of deepwater circulation processes within the ocean interior (Noble et al., submitted). Specifically, negative slopes water masses were found to be in the Denmark Straits Overflow Water/Antarctic Bottom Water/Iceland Scotland Overflow Water (DSOW/AABW/ISOW) and Classical Labrador Seawater (CLSW; Fig. 2) water masses both of which have long deepwater transit times (Jenkins et al., 2015).” We argue that the negative vectors we observe are the influence of slow scavenging processes accumulating on isopyncals during advection, and hence that the influence of scavenging and mixing are combined in the negative vectors we observe. The reviewers imply that mixing of Co is a conservative process (without any scavenging), but we respectively disagree with this argument from Dulaquais et al., 2014, and argue that the data shown here, and in a more substantive manuscript on Co scavenging (Hawco et al, Marine Chemistry in revision) provide evidence of mesopelagic scavenging. In particular, in the latter manuscript a comparison of dCo with C14 ages in DIC showed basin scale scavenging processes between the Atlantic and Pacific basins. Much of the reviewer's interest in scavenging is more pertinent to the Hawco et al. manuscript, while the present manuscript focuses on the dynamic variation in dCo:P relationships in the vertical dimension, which must include some discussion on the unusual negative slopes in the mesopelagic and deep ocean and how the shift from remineralization to scavenging can result in the transition in positive to negative slopes as shown in Figure 10. The reviewer states that we are inconsistent with Moffett and Ho's Co and Mn microbial oxidation dataset which did not find measurable Mn oxidation at BATS. This is incorrect, Moffett and Ho found phytoplankton uptake dominates within the euphotic zone at 60m, which is consistent with our uptake/remineralization vector based on positive slopes at this depth. Moffett and Ho did not present uptake rates in the mesopelagic in that manuscript.

The reviewer suggests an alternate means for particulate Co-Mn correlations, "The strong Co–âĂŘMn correlation can be interpreted in another way than that actually proposed: it is indeed possible that the biogenic Co fraction is remineralized while the authigenic fraction (scavenged fraction) is not (i.e.; the one way trip of Co presented by authors)". We appreciate the reviewers considering and describing this scenario in detail. This interpretation is actually the phenomenon we are presenting and arguing for in every aspect they discuss (an increasing importance of scavenged/authigenic particulate for pCo and pMn with depth resulting in the pCo:pMn relationship and the increased pCo:pP relationship). We are glad to hear they agree! We point out that it is this authigenic pCo formation process that in turn creates the negative dCo:dPO4 slopes in the dissolved phase we have been debating above. We have found that the connections between dissolved and particulate phases are fascinating yet can also be confusing and take time to fully consider given the mirroring/opposite effects the phases can have on each other and out community's limited experience in direct comparisons of dissolved and particulate data.

The reviewer states that the vector approach does not take into account differential remineralization. This is an interesting point, but I think it is not true. The profile-based regression analysis does not include any a priori assumption about stoichiometry or remineralization efficiency. It is simply a measurement of dCo and dP change in response to each other in the vertical dimension. There were no Co* values reported in Hawco 2016 or Noble 2012, but it is here. I understand the hypothesis: an alternate explanation for vertical structure is the preferential remineralization of P over Co creating the Co deficiency, as an alternative to scavenging. This is a useful alternate perspective that we will add to the discussion. Reflecting on it now, there are several datasets that argue against differential remineralization being the major driver in dCo distributions: 1) the scavenged like profile is inconsistent with this (implying removal rather than slowed accumulation), 2) the correlation of pCo and pMn in the mesopelagic is consistent with biotic Mn oxidation rather than with slow Co remineralization (which would not create a correlation with Mn), and 3) the negative slopes of dCo:P are consistent with Co loss rather than slowed accumulation (which would be a positive slope still). To clarify the prior and current observation of increased dCo in the OMZ plumes were not interpreted as a result of slowed / differential remineralization but reduced Mn and Co scavenging.

The reviewer suggests incorporating data from Dulaquais et al into the study. There is already a lot of data within this study and there were some intercalibration challenges at the western portion of the North Atlantic. As a result, we think this approach investigating the large diversity of Co:P relationships is useful as a beginning, and we encourage those authors to examine their datasets with these methods in the future.

The reviewer comments on our choice of a Co* ratio from the pCo:pP North Atlantic ratio, and argues that it should instead use the lower Twining from phytoplankton species. This is a good comment and one we also wrestled with. We point out that Redfield et al's original studies used oceanic particulate carbon, nitrogen and phosphate ratios as well, and they have been interpreted as being reflective of the aggregate community, so there is precedent for working from the aggregate particulate phase. The cell specific numbers from Twining et al. are taxon-specific and span 140-3000 depending on the group (their Table 5). We were transparent about the challenge of selecting a single Co:P in the manuscript, yet we feel the cohesive structure in the visualization of Co* is compelling, even if its interpretation is not fully understood as of yet. We could change our value to the suggested value, and will consider this in the revision. We point out that though that the choice of any the Co:P value will not affect the trends observed in this visualization, since any change in Co:P will be applied linearly to all Co* values.

Specific comment section:

Regarding the statement about growing human use of cobalt: we can remove these statements. They are expanded and referenced briefly in the accompanying BG manuscript. Although statements of context and relevance seem reasonable, for example papers studying mercury biogeochemistry include a sentence or two stating its environmental relevance. Since most people are unaware that lithium ion batteries are in most cases lithium cobalt batteries, raising awareness of their connection to ocean biogeochemistry seems a worthy goal in raising public awareness.

The documentation for the method for dCo is presented in the accompanying in press manuscript Noble et al., BG. This is a data analysis paper, rather than a data presentation paper. We can duplicate it here perhaps in abbreviated form though.

We have requested detection limit data for the phosphate measurements, and will add them to the methods as requested. For many of the shallowest samples in GA03 the nutrient team did not provide values (presumably below DL values) and hence there is no correlation given.

We will comment on agreement of Co:P with Dulaquais et al., thank you for pointing this out.

The reviewer asks for clarification about the bioavailability of labile cobalt and complexed cobalt. They state: “according to the method labile cobalt is also complexed and is not equivalent to inorganic cobalt”. We disagree with this somewhat – the labile cobalt may be inorganic or weakly bound cobalt. The reviewer states that we have previously stated that complexed cobalt is bioavailable and asked us to clarify this. We have argued and presented data to show that some phytoplankton, namely the cyanobacteria, can access strongly complexed cobalt. This seems reasonable since they have an absolute requirement for Co (albeit a very small requirement) and they live in the euphotic zone where there is typically no detectable labile cobalt. Cultures studies of eukaryotic phytoplankton have been consistent with their use of only inorganic cobalt thus far.

The reviewer suggests using the a P-limited C:P ratio for our conversion of Sunda and Huntsman’s Co:P and Zn:P dataset (1995). We point out that that study was not P-limited so that is not appropriate here. This would be appropriate for our environmental datasets, but fortunately we are using Co:P data rather than Co:C data so no conversion is needed.

Fig 12 low r2 values: we are not arguing these are significant, but showing the trends obviously have a negative rather than positive slope. Would could remove the r2 values, but wanted to be fully transparent since we are showing the negative slope lines. We can either remove the lines or state that we do not imply they are significant other than having a negative sign.

Fig 6: Slopes reported on bottom values. That is a good point, we will double check the script as to why it is being reported.

The reviewers state: “p 16 lines 1-7: It will be demonstrated only when the advection vector will be implemented. If the advection vector is the same direction, scavenging, remineralization and advection will have to be quantified to estimate the length of the vectors.” As discussed above, our interpretation of the scavenging vector is that it is a gradual accumulation of scavenging of Co upon the water mass during circulation, and hence advection is included. We can further clarify this in the text.

The reviewer comments on how Co is being considered largely from a biogenic and scavenged phase. We can include a lithogenic correction in a subsequent version for the particulate phase.

Other small comments are repeats of from above or will be corrected/attended to.

We appreciate the reviewer's efforts in this extensive review.

Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-511, 2016.