

Review of "The acceleration of dissolved cobalt's ecological stoichiometry due to biological uptake, remineralization and scavenging in the Atlantic Ocean" (Saito et al.) by Gabriel Dulaquais and Marie Boye

The manuscript provides a new and large dataset of quality of the scarcest micronutrient cobalt. This study brings some new approaches of the interpretation of the cobalt biogeochemical cycle with the connection of rare data of metaproteomic metalloenzyme distribution. This manuscript is generally well written and clearly organized, but it is really long and it could be shortened in several places.

The publication of the manuscript will be obviously of great interest for the scientific community. However, it needs major revisions and clarifications on several points (see below), new calculations and perhaps additional data.

All this approach based on multifactorial calculations of the processes is indeed little convincing without the detail and the methodology of the used calculations. Furthermore, important processes are missing in these attempts of qualitative budget of the cycle of Co and its ratio with phosphate in the Atlantic Ocean. The terms of physical dynamics (as the advection of the bodies of water) are not indeed taken into account, and the external sources (as the atmospheric deposition) poorly considered. It is problematic since it has been previously shown that those later terms could be important and significant in the Co budget, especially the circulation and water-masses mixing in the intermediate and deep oceans that can help to close the budget at a basin scale (see papers of Dulaquais et al. in the Atlantic and the Mediterranean Sea). Furthermore, particulate Co is mainly considered as being biogenic in this work (apart when referring to precipitates with manganese oxides), whereas there are evidences of lithogenic origin of pCo in open ocean, notably in areas receiving Saharan dust inputs such as the ITCZ in the North Atlantic, and from resuspension of margin sediments and advection of such Co-enriched waters.

We thus recommend considering those missing terms and to detail the digital methodology used before being able to publish this paper.

General comments

The vector analysis is a very new and interesting approach. Nevertheless, we are concerned at first by the robustness of the approach, since the authors consider a vector significant for $|r| > 0.7$, which means $r^2 > 0.49$. Also by taking into account that the authors use 5 points for the vector regression, the authors should use a value for r^2 of 0.77, at least, to consider that the regression is significant. Thus, we recommend to use $|r| > 0.88$ for the interpretation of the vector analysis, or to include 8 points in their regressions. This new criteria for the value of r might change the issues of this work and the interpretation of the data.

In addition, only the middle point is apparently used for the vector analysis, whereas some data before the last depth are considered (e.g.; circled in Figures 5&6), which is not in adequacy with the methodology described in the method part.

Our second major concern in this vector approach is that the authors completely hide the mixing vector. The dilution and mixing processes between the different water masses are indeed not treated in the paper, whereas they could be important in the cycle of Co. Since the authors argue that only scavenging and remineralization govern the deep distribution of cobalt in the deep Atlantic, which fully contrasts with study by Dulaquais et al. (2014a), the authors must include then the mixing vector to confirm their conclusions. An example of the importance of mixing process in the dCo deep distribution is given by its concentrations in NADW and AABW that are, respectively, of ~ 40 pM and ~70-80 pM for dCo, and of 1.25 and 2.25 for soluble reactive phosphates. Thus, mixing of these 2 water-masses gives by a South East vector that appears to be similar to the vector observed by authors. Consideration of these dynamic processes could in turn reinforce their conclusions, or on the contrary completely change them. Another example is the AABW. By following the reasoning of the authors, dCo should decrease in this water-mass from south to north. However instead, dCo increases along its northern pathway in the Atlantic as observed by Dulaquais et al. (2014). This northward increase is also visible in the authors's data set when combining their CoFemug and NAZT cruises datasets.

One possibility to remedy with dynamic processes would be to add advection vector between the different dCo end-members measured in the different water-masses. Authors can also use their datasets from NAZT and CoFeMug cruises, and combine them with the one's of Dulaquais et al. (2014a) in this way. Since the complete analysis of water-masses is available (as performed by Jenkins et al., 2015), the combination of the different 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. Finally, when advection will be included in the vector analyzes and if it is significant, section 3.3 will have to be revisited.

We are also concerned about how authors determined the length of the vectors in their analyzed because the direction of a vector does not translate the intensity of it, thus scavenging might be of strong influence for the direction of the vector but its length is maybe small and poorly influences the distribution. In connection with this, the vector direction strongly depends of the magnitude of each component, thus estimation of Mn oxides and remineralization component will change by adding a third mixing vector.

In their vector approach, the authors do not take into account also the possibility of a differential remineralization between Co and P (in section 3.1, p 7, lines 1-11). Differential remineralization between macro- and micro-nutrients is now admitted and such differential remineralization seems to occur in these waters, as evidenced by the negative Co* values obtained in the Eastern Atlantic OMZ. In OMZs, oxidative scavenging of dCo is indeed considerably limited (Hawco et al., 2016; Noble et al., 2012), thus if Co* is negative in this remineralization zone, it probably indicates that Co is less remineralized than P.

Dulaquais et al. studies in the Atlantic (2014a, 2014b) are poorly cited for their observations and measurements of dCo along the pathway of the different water masses, and they are even occulted for the dCo/P correlations they recorded in the Sargasso Sea and the Equatorial Atlantic, which are nevertheless close to those reported in this study. These works should be included across the different parts of the manuscript when it is pertinent (remineralization, Co-P correlation, possible transport of Co across the different water masses).

In addition, Co* plot seems to be in accordance with Dulaquais et al. studies: Co* is positive in the surface layer that could be interpreted by a higher biological remobilization of Co than P in the upper layer (Dulaquais et al., 2014b), and its negative value in the remineralization zone of the OMZ can be interpreted by a lower remineralization of Co than P (Dulaquais et al., 2014a).

We are concerned about uncertainties on the phosphate measurements in the North Atlantic subtropical gyre (in section 3.2.3), wherein these phosphate concentrations are the lowest recorded in the surface ocean. Uncertainties on the slopes and correlations recorded should be noticed in regards with phosphate analyses.

The idea of a one-way back from dissolved to particulate fraction in the mesopelagic zone (section 3.2.7, p 15, lines 7-15) can be more robust by using particulate labile Co data in the deep sea, which might be available from Twining et al. (2015). If not available, this consideration should be weighted because it is in contradiction with Moffett and Ho (1996) study "In the Sargasso Sea [...] cobalt uptake was nonoxidative, biologically mediated, and enhanced by low to moderate levels of light. It is probably due primarily to uptake by phytoplankton". Moreover, Wu et al. (2014) estimated that the oxydation of Mn is restricted in the deep Atlantic along the GA03 section, thus co-oxydation of Co should also be restricted.

The correlation between pCo and pMn is indicative of a covariance between the two elements in the particulate fraction (section 3.3, p 17-18), but it does not indicate that the vertical particulate flux (and thus scavenging) of cobalt increases with depth. Sediment traps or ²³⁴Th data are indeed needed to constrain this flux. Alternatively, this flux can be modeled at a first glance using Martin's curves and Co/C data set probably available from this cruise.

The strong Co-Mn 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). In these conditions, even if scavenging is slow and restricted, particulate Co partitioning will shift from the biogenic (organic) to the authigenic (mineral) fraction and a strong correlation between Mn and Co will appear. This possibility can be further assessed using the data presented in this study: for instance the particulate Co:P correlation gives a slope of 159 μM:M in the upper 400 m and shifts to a constant 900 μM:M in the deep ocean. If cobalt is only scavenged when phosphate is remineralized, the Co:P slope should gradually shift to a negative value, given a high pCo (scavenging) when pP is low (remineralization). Because it is not observed, it is possible then that the biogenic pCo fraction is decreasing with depth while authigenic is increasing with depth. Then, the particulate Co:P ratio can be parameterized as following:

$$\text{Mean Co:P} = x * (\text{Co:P})_{\text{biogenic}} + y * (\text{Co:P})_{\text{authigenic}} \text{ with } x \text{ and } y [0;1] \text{ and } x + y = 1, \text{ and } (\text{Co:P})_{\text{biogenic}} \ll (\text{Co:P})_{\text{authigenic}}$$

In these conditions, the Co:P slope will gradually increase with depth to a maximum when all the biogenic P is remineralized, as it is observed by authors (Figure 11c). Adding a z color scale for depth on pCo:pP data (in Figure 13) may also help to discern such shift. Moreover, if Co is less efficiently remineralized than P, this Co:P will also be enhanced.

The occurrence of scavenging is highly probable in the deep sea (and it is not the debate here) but because its timescale is slow (Noble et al., 2012), estimating its magnitude is crucial to compare it with other fluxes (advection) and to determine which terms govern the distribution of dCo in the deep Atlantic. Scavenging can occur at a low rate and thus can less impact the distribution than mixing processes. To firmly demonstrate that scavenging is only driving the deep distribution of dCo, additional data of particles fluxes are needed. These estimations of fluxes will serve to quantify the scavenging flux and rate, and then, to compare with the rate of mixing at each layer. Then, if the scavenging rate overwhelms mixing it will be demonstrated, otherwise an alternative vision has to be included in the discussion.

The Q used for cobalt star does not seem pertinent regarding the value recorded by Twining et al. (2015) of 150 $\mu\text{M}:\text{M}$. The Q used by authors must be the one recorded in phytoplankton especially if caveats exist on the soluble reactive phosphate measurements at extremely low concentrations. Negative Co^* observed in the OMZ should be discussed. If a major source of dCo occurs in this area, Co^* should be positive and not negative.

Conclusion would probably have to be modified after inclusion of new calculations and mixing estimations. The lithium ion batteries comment, which is never discussed in the paper, should be removed.

Specific comments

Abstract: The lithium ion battery comment in the abstract is not discussed elsewhere in the text, it has to be removed then.

P 4: The method part for determination of dCo is poorly documented in the manuscript. Even if the method is detailed in the accompanying manuscript, the limit of the detection of the method, the reference water measurements and the relative standard errors are specifically needed because of the use of the vector analysis.

P 5: Since surface phosphate concentrations are extremely low in the subtropical Atlantic and because phosphate data are crucial for the analyses of the acceleration of the dCo/P ratio and the vector analysis, the limit of detection and quantification of soluble reactive phosphate (SRP) should explicitly be indicated in the method part, as well as the lowest concentration of SRP measured in this study for the interpretation of the data. Considering the extremely low SRP measured, caveats on the dCo/P correlation at low phosphate concentrations must be mentioned.

P 7: The high dCo:P value observed in the north Atlantic subtropical gyre (67 $\mu\text{M}:\text{M}$) is in excellent agreement with Dulaquais et al. (2014b) of 64 $\mu\text{M}:\text{M}$, and it should be noted.

P 8, lines 1-4 ("Labile cobalt is likely highly bioavailable relative to complexed cobalt"): According to the method, labile cobalt is also complexed and is not equivalent to inorganic Co. It is the fraction that can exchange with the added ligand at the potential of deposition. This fraction is dependent of several factors and cannot be defined as the bioavailable fraction without evidences. Furthermore, in previous studies of the authors, complexed cobalt is described as the bioavailable fraction for cyanobacteria that produce strong organic ligands (Saito et al., 2003; Saito et al., 2005). These two opposite views should be better explained here.

Section 3.2.6: Authors used a C/P ratio of 106:1, which is 2-3 times lower than the ratio given by Bertilson et al. (2003) in depleted cultures, and 1.5 times lower than the one's recorded by Twining et al. (2015) in picoplankton (of 153.1 ± 26). We recommend using the values recorded in phytoplankton cell during the cruises.

P 15, line 20: Moffett and Ho have observed the prevalence of biological uptake in Sargasso seawater, and that microbial oxidation was predominant in estuarine seawater.

P 16, lines 1-7: It will be demonstrated only when the advection vector will be implemented. If the advection vector is in the same direction, scavenging, remineralization and advection will have to be quantified to estimate the length of the vectors.

P16 (equation 1): Error in the denominator (should be dz). Advection must be included.

Caption of Figures 3 and 4: may have troubles in labeling the sub-figures.

Table 1: Dulaquais et al. (2014b) also recorded Co/P correlation in the Atlantic and it has to be integrated.

Figure 2: The total dissolved Co axes should be on the same scales. What about the SACW? Why the Ross Sea is included in the figures?

Figure 3: Error in the caption (should be (b), (f); instead of (b), (e)). Only show vectors when $r > 0.88$

Figure 4: is not easy readable. Inserts must be bigger and include mixing vector in Figure 4a. Error in the caption (should be "blue", instead of "black", when referring to positive slopes). In Figure 4a&d, depth can be added as a z parameter. The sum of the positive and negative vector weighted to the intensity of the dCo/P correlation might be useful to see whether positive or negative slopes exceed vector. Figure 4 b&e are not really used for the discussion.

Figure 5: Some bottom depths and depth just above them are circled and it is not in accordance with the 5 points regression method used.

Figure 6: Uncertainties on the vector should be added, and only vector with $r^2 > 0.77$ should be presented.

Figure 7: dCo data are needed here.

Figure 10: Mixing vector must be included.

Figure 12e-j-k: Are correlations with a r^2 of 0.39, 0.43, 0.12; and calculated on 3-6 points really significant?

Figure 13: can add color scale as z axis.

Figure 14: Isoclines are needed and focus on the upper 1000 meters also.