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Discussions

Interactive comment on "A seasonal study of dissolved cobalt in the Ross Sea, Antarctica: micronutrient behavior, absence of scavenging, and relationships with Zn, Cd, and P" *by* M. A. Saito et al.

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The page numbering in the file received for review differed from the online version of the manuscript. In the following review the line numbering referred to is the same as that found online at www.biogeosciences-discuss.net/7/6387/2010/doi:10.5194/bgd-7-6387-2010.

Overview:

This manuscript presents data on dissolved cobalt speciation in the Ross Sea, Antarctica. The dataset is high quality and provides a unique insight into Co biogeochemistry in the Southern Ocean. The paper outlines the various hypotheses and findings clearly and the conclusions reached are logical and well supported. Some sections could be reduced or modified however as outlined below in order to highlight aspects of this work. This is an excellent and welcome addition to both Cobalt biogeochemistry in seawater and Antarctic research.

General Comments:

Metal Quotas:

There are a number of other papers that are relevant to the subject of elemental stoichiometry that should be included in the discussion if at all possible. These include works examining the differences between taxa (Finkel et al., 2007; Ho et al., 2003; Quigg et al., 2003) and the influence of light (Finkel et al., 2006) and cell size (Finkel et al., 2010). In the present manuscript both the influences of light and temperature may play a role, in addition to iron limitation (Twining et al., 2004), in reducing the growth rate of organisms and thus increasing the metal quota for non-limiting metals. It would be useful then for the present manuscript to examine these processes also for how they may influence the Co:P ratio found in different oceanic regions.

Zn speciation in the Antarctic:

Recent work by my own group in the Atlantic sector of the Southern Ocean (Baars and Croot, 2010; Croot et al., 2010) has shown that throughout the water column, total dissolved Zn concentrations were high and strongly correlated to silicate. Speciation data indicated that Zn ligands were almost always saturated leading to high concentrations of labile Zn as the authors also report in the Ross Sea. It appears that in waters south of the Polar Front there is no need for organisms to substitute Co for Zn as Zn is easily bioavailable. Indeed we found that the disappearance ratio Zn:P in surface waters increased as you approached the continent and this has also recently been reported in direct analysis of particulate material from the Southern Ocean (Diaz et al., 2010;

Sherrell et al., 2010).

Lack of simultaneous Zn and Cd data:

The paper relies on datasets for Cd and Zn from the Ross Sea which were obtained during a different cruise (Fitzwater et al., 2000). It obviously would have been more ideal to have comparable Zn and Cd measurements from the same bottles as the Co data but this is not always possible. It would be useful therefore to include other data from the Ross Sea in addition to the Fitzwater et al. work, as there is a significant amount of work published on this (Capodaglio et al., 1991; Capodaglio et al., 1998; Corami et al., 2005; Frache et al., 2001) There is also relevant information on high metal quotas for cadmium in higher organisms in the Ross Sea (Bargagli et al., 1996).

The manuscript also compares metal and nutrient data from the Ross Sea to the North Pacific, it would be more appropriate to include data from the adjacent Southern Ocean for Co and Phosphate (Ellwood, 2008) and from other parts of the coastal Antarctic and Southern Ocean (Ellwood et al., 2005; Martin et al., 1990; Sañudo-Wilhelmy et al., 2002; Westerlund and Öhman, 1991).

There is also the question of how to interpret datasets for total dissolved Co that did not incorporate a UV irradiation step. This is important as the dithiocarbamate extraction method may not have extracted Co(III) complexes. It was thought that the dithiocarbamates reduced Co(III) to Co(II) but this to my knowledge has not been tested on open ocean samples. So how do we compare between data sets? It is important as it obviously has a bearing on the calculation of metal quotas and the determination of residence times for Co (see specific comments below). Some discussion of this issue would help clarify this issue for the future.

Particulate Co data:

Information on particulate Co would have been useful in the context of comparing the Co:P ratio in the phytoplankton with the disappearance ratios calculated using the water

column data. Do the authors know if there are any particulate Co data from the Ross Sea or adjacent regions?

Scavenging:

It would be a useful exercise here to define scavenging in a more robust manner, to clearly separate different processes such as; biological uptake in the photic zone, biologically mediated scavenging in intermediate waters and abiotic particle related scavenging throughout the water column. One work missing from the present manuscript on the role of Co(II) oxidation by bacteria is the work of Lee and Fisher (1993) who provide some data on the temperature impact on Co(II) oxidation which indicates that Co oxidation may be more temperature sensitive than Mn oxidation which of course could be significant for the Ross Sea.

B12 lability:

The issue of whether the Co in B12 is labile or not to this voltammetric technique is of interest here and some statement about this would help in the interpretation of the data. The reason for requesting this is that the published values for the conditional stability constants for vitamin B12 (log K = 16.4) and coenzyme B12 (log K = 15.5) in seawater (Ellwood and Berg, 2001) would indicate that these species could be partly labile to the method employed in the present work. However in examining the original work (Ellwood and Berg, 2001) it is clear that the values were calculated from titrations that had no curvature, indicating the ligands were fully saturated as you would expect when the ligands were added as fully complexed species in the first place, and in this situation no meaningful value of log K can be calculated. A further additional reason for doubting these values is that under the conditions used in their study all of the Co in the B12 complexes would have been in the inert Co(III) state (Scheffold et al., 1987). The problem exists now that these same values were recently included in a major review paper on marine ligands and siderophores (Vraspir and Butler, 2009) thus spreading these contentious data further.

The non-lability of B12 and related complexes is most likely a large part of why it is necessary to UV irradiate samples prior to determining the total concentration. This then raises another issue with regard to how do we now compare old datasets for Co that did not include this step. Should the better comparison be between the present day labile Co measurements and the earlier dithiocarbamate extraction method. Though it was thought that the dithiocarbamates may reduce Co(III) to Co(II) during extraction this was not ever properly evaluated to my knowledge. Overall for the present manuscript the comparison with other datasets is problematic for the nutrient drawdown ratios as the dissolved Co from the earlier data is most likely underestimated.

Other labile Co species:

A recent paper (Yang and van den Berg, 2009) indicates that humic and fulvic material may be the potential ligands for the labile Co species, this possibility should be included in the discussion section of the current work.

Shorten section 3.4:

This section could be significantly shortened as presently it goes to great lengths to cover a number of options, however there is data available that makes much of the discussion here in the end redundant. While the original text provides a lot of useful information for readers unfamiliar with this topic, in the final version of the paper it would be best suited that this section was shorter and more direct in order to improve the readability.

Specific Comments: (sp –spelling, gr-grammar)

P6388 Line 5. Report the number of samples this was based on.

P6391 Line 27. As discussed above another work of relevance here is that of Lee and Fisher (1993) who found that Co oxidation was more strongly influenced by temperature than Mn oxidation. Also it was recently shown that for one marine bacteria it does not oxidize Co(II) in the absence of Mn(II) (Murray et al., 2007).

P6395 Line 2. As this is a catalytic method the temperature at which the analysis was performed is important to know. The authors should list here what temperature this work was performed at and how well the temperature was controlled.

P6395 Line 3. The equilibration time used to determine the labile Cobalt should be reported in this section also. Also if there were any temperature changes this should be reported also.

P6395 Line 20. The 0.4 μm filtration could possibly still include archaea. While I do not think this is a problem in this work it raises a question about what role they may play in Co biogeochemistry. Though they are currently not known to oxidize Mn(II) (Tebo et al., 2005), nor presumably Co(II), they do apparently play a role in nitrogen dynamics in the Southern Ocean (Kalanetra et al., 2009). Is there any data available on their abundance in the Ross Sea?

P6395 Line 20. What evidence is there that an equilibration time of 24 hours is sufficient? I could envisage that the added Co(II) may be complexed by any free ligands relatively quickly but it is unlikely that the radioactive isotope would be in equilibrium with the Co(III) contained in complexes such as B12 as the dissociation of those complexes would be expected to be very slow. Thus it is most likely that equilibrium is established with the labile Co(II) pool but not with the total Co pool. Thus uptake rates may be better normalized to the labile pool rather than the total Co pool.

P6396 Line 13. The uptake rate here is based on a linear calculation but later it is assumed to be first order (P6415 Line 18). Do the authors have any further time points for the uptake of Co to support either mechanism? Also how different are the results if only the labile Co concentration is used (see related comment above)?

P6402 Line 7. See the general comment above regarding B12 and labile Co.

P6405 Line 9. See the general comment above regarding growth rate dilution.

P6407 Line 28. Given that there is labile Zn throughout the water column south of the

Polar Front in the Antarctic (Baars and Croot, 2010; Baars et al., 2010), and the authors report the same phenomena (P6411 line 12), thus it is unlikely that any cells in the Ross Sea are diffusion limited for Zn. Thus this and the next section could be significantly reduced in size as there is probably little impact of the free Zn concentration in the Ross Sea on cell size.

P6409 Line 16. (sp) Rayleigh

P6411 Line 12. See the general comment on this above.

P6411 Line 20. (sp) Rayleigh

P6412 Line 20 (sp?) trifecta (this is the common English spelling), I could not find a dictionary definition for trifeca.

P6415 Line 16. As noted above the added radiotracer was most likely not in equilibrium with the inert Co pool and thus this will lead to a very short residence time for the total Co pool. The authors should also make the calculation using the labile Co concentration, as this would provide a realistic estimate for how fast the labile Co pool is turning over.

P6416 Line 11. Given that the Zn is not limiting it is unlikely that diatoms in coastal Antarctic waters would need to use Co to replace Zn for enzymatic functions. Thus this section could be significantly shortened.

Table 1. There are other relevant data for the Antarctic and surrounding seas that should be included here as the datasets exist and are available (Ellwood, 2008; Ellwood et al., 2005; Martin et al., 1990; Sañudo-Wilhelmy et al., 2002; Westerlund and Öhman, 1991).

Table 1. The table should include some information on whether the total Co data was obtained after UV irradiation or not.

Table 2. There are other more recent datasets that would improve this table also (see

general comment above).

Figures 8 and 9. As noted above it would be more useful to also include results from seas adjacent to the Ross Sea.

Figure 11. This figure is interesting but might be improved by resolving the abundance of each of the algal groups through CHEMTAX (Mackey et al., 1996) and plotting these results against the Co uptake. A similar approach has been used in the Skaggerak for comparing dissolved Co with species composition (Croot et al., 2002).

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