Biogeosciences
Discussions

Interactive comment on "Coastal Sources, Sinks and Strong Organic Complexation of Dissolved Cobalt within the US North Atlantic GEOTRACES Transect GA03" *by* Abigail E. Noble et al.

Anonymous Referee #1

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Noble et al. present cobalt measurements from two GEOTRACES transects across the North Atlantic (USGT10, Oct 2010, and USGT11 Nov-Dec 2011). Full depth sections are shown for Labile Co (LCo), total dissolved Co (DCo), and particulate Co (pCo). The study provides important methodology, a comprehensive dataset and a detailed analysis of Co sources, sinks, and cycling. The results provide significant new insight into the complex oceanic cycle of this important micro-nutrient.

The data is of high quality as evident through oceanographic consistency, intercalibration stations, and ensured by frequent blank checks and control samples. This is particularly important for the challenging electrochemical measurements for LCo and DCo at low pM concentrations. The authors also reveal an important and very interest-

ing storage issue for Co measurements that needs to be taken into account in future studies and which may lead to new insight into Co cycling. Storage artifacts were prevented by preserving samples in heat sealed bags with O2 absorbant or immediate shipboard analysis. Missing from the methods section appears to be a detailed descripiton of pCo determination.

Where appropriate, the results from the North Atlantic are compared to an earlier study in the South Atlantic, allowing new insights resulting from differential oxygen concentrations and dust input in both regions. The manuscript is very good in separating influences of the OMZ, sedimentary processes, dust, riverine/coastal sources, hydrothermal inputs, etc. often using additional parameters (Fe, Mn, O2, aerosols, etc.) measured during the same cruise or using literature data to constrain Co cycling. Seasonality and dynamic effects are also discussed.

Overall, Noble et al., present a very careful study with a comprehensive dataset and a detailed data analysis which justifies the rather long ms. Some of the figures could be moved to the SI and the captions could be shortened. Below is a list of specific comments with suggestions for minor revisions or cosmetic changes.

Specific comments ——————— The frequently used terminology 'labile Co' and 'strong Co binding ligands' mixes kinetic (labile) and thermodynamic aspects (strong ligands). For example, in P1L16, the authors conclude that strong Co binding ligands where not in excess of total Co below the euphotic zone because labile Co was measured. Based on this and other studies, as also mentioned in the introduction, it is likely that labile Co is Co(II) and inert Co is Co(III). There is a possible conversion from labile, weakly bound Co(II) to inert, strongly bound Co(III) by oxidation. Some of the ligands that may bind Co(II) weakly may be strong ligands for Co(III) and thus it cannot be excluded that Co was remineralized as Co(II) and may, with time, be converted to inert/strongly complexed Co(III) without an apparent excess of strong Co ligands. I would suggest to add a short review of these aspects and a clarification of terminology to the speciation section in the introduction (P4L7).

P6L8 Add methodology for pCo (particulate suspended Co) determination

P9L3 A detection limit of 1.8 pM for DCo is mentioned (3x standard deviation of blank) which is significantly lower than detection limits reported in earlier studies using similar methodology. Is the peak for 1.8pM actually measurable or inferred from the intercept of standard additions? A figure showing exemplary chromatograms for the blank analysis in a new Supplemental Information document might be helpful.

P10L2 'The results demonstrate that...' -> I found this sentence complicated. Do you mean that results for GEOTRACES standards are in agreement with consensus values?

P10L16 'These results are in good agreement wiht those from the GEOTRACES inter-calibration...' -> Are the results within the standard deviation of GEOTRACES consensus values? Provide a reference where these values can be found again here.

P13L28 It is stated that the storage issue for dissolved Co is more severe in the North Atlantic than in other regions. This is very interesting and the authors suggest that it may be related to dust and colloidal loading. In general, it seems almost clear that the 'loss' of Co is because Co(II) is being oxidized to an inert Co(III) form. This can be particularly pronounced in regions with high labile Co(II) and high ligand concentrations or high colloidal concentrations that can bind Co(III). Perhaps you could mention this redox aspect again in the discussion of the storage effect.

P15L29 Studies are referenced showing that the OMZs in the South Atlantic and in the North Atlantic show elevated Mn and Fe. Are the elevated concentrations in the OMZs of the two regions comparable? Does Co seem to be slower to be scavenged when reaching higher O2 than Fe and Mn, similar to your discussion of the hydrothermal Co:Mn ratios (this could be added to your conclusion of a low O2 threshold for Co plume formation, P16L17)?

P18L6 '..the relationship with salinity was similar for labile Co...' -> maybe add the

fraction of labile Co from freshwater input

Sections 3.4.1 and 3.4.2 particularly (but also others): The sections might benefit from adding a few actual concentration ranges to the qualitative description (e.g., P16L9, 'Despite higher mesopelagic oxygen concentrations in the North Atlantic, the dissolved Co concentrations were also higher here...'; P16L14, '... have now been found to harbour high concentrations of Co'; P17L5 '...contain very elevated concentrations of Co...'). Maybe also add some concentration ranges for Fe and Mn from the literature?

P17L17 'Oxygen concentrations are also much higher in ULSW than within the Mauritianian Upwelling plume...demonstrating that low O2 in not necessarily critical to sustaining subsurface Co plumes' -> Does the higher O2 in ULSW compared to the Mauritanian OMZ go along with lower DCo concentrations? In Fig 10 you show a linear plot of LCo and DCo vs. O2 but this plot does not seem to include the stations along the western part of the transect. Does Fig. 10 include the ULSW stations you mention in this paragraph? If not, this should be mentioned in the caption.

Section 3.4.4 is a very long section, maybe subdivide to make reading easier?

P19L16 Were the shipboard aerosol samples at BATS and BATS region collected during the same cruise?

P21L26 and P22L24: You mention that Co from dust might make up a larger contribution if dissolution is slow and happens gradually from sinking particles. However, I found it very interesting that the linear DCo vs. O2 relationships in the North Atlantic and South Atlantic were comparable (Fig 10D). Does that not imply that the Co concentrations are mainly controlled by sedimentary reductive dissolution processes and water column scavenging so that the influence of dissolution of Co after atmospheric deposition is indeed negligible?

P24L8 The authors state that DCo:DMn and DFe:DMn are cosistent with diluted hydrothermal fluids. As the contribution of the hydrothermal vent to dissolved DFe and

DMn pools is much larger than for the DCo pool, do you need to subtract the surrounding 'background' DCo concentration for a comparision (also in Fig. 8)?

P24L23 A trend is observed in which Co:Mn from hydrothermal sources increases with dilution but Fe:Mn follows the opposite trend and this is disucssed in context of oxidative removal rates. However, given a much higher relative dissolved 'background' Co concentration compared to the hydrothermal input, this trend should be expected. The background Co concentration may need to be subtracted for these calculations.

P25L9 Have Al concentrations also been measured during this cruise? How strong was the MOW signal at the sampled stations?

Section 3.5 is rather complex and long to describe a variable influence of nepheloid layers. Could this section be shortened?

P26L1 Results for USGT11-06 and 11-10 are described. What about USGT11-08 where the highest suspended particle mass was measured? Maybe mention results for all three stations at the beginning of the paragraph before going into further discussion.

P27L15 'This dramatic difference where some bottom water samples along the western margin show slight enrichment while some bottom samples along the eastern margin show strong depletion...' -> I did not see this dramatic difference in Fig. 9. All profiles seem to show more or less a decrease in LCo and DCo and an increase in pCo except for station 10-09.

P28L16 The authors conclude that a similar DCo:O2 relationship in the North and South Atlantic could be related to the oxygen needs of Mn oxidation and co-oxidation. This point may deserve further explanation and a reference. By and large, I came to the understanding that DCo:O2 is governed by your previous descriptions of reductive sedimentary dissolution and scavenging after re-oxidation (biotic and abiotic).

P28L33 'implications for the ecological balance' -> Maybe you could shortly mention why this should have implications for the ecological balance or give a reference for Co

limitation here.

Section 3.7: Somewhere in this section, I was hoping for an overview of particular labile and inert Co sources or sinks, i.e. dust, sedimentary processes, uptake, etc. and maybe a discussion in context of Co oxidation states. I suggest to add this overview if it can be incorportated without adding too much text to the already long mansucript.

P30L11 'To our knowledge, this is the first report of linear relationships between labile Co and P' -> A similar linear relationship in the eastern North Atlantic has been reported previously by Baars et al, 2015.

P30L16 Maybe add references here. As mentioned above, this may not only be a question of complexation but also of oxidation of Co(II) to Co(III).

P30L16 A lower slope of LCo:P below the photic zone is reported than in the upper photic zone. I did not see this contrast in Fig. 11.

P31L3 Why are four stations chosen? Are the results with these stations representative for the whole dataset?

P31L22 What is this reference for?

P31L28 'This offset between the labile and total cobaltclines suggests that biological processes act quickly enough to complex labile Co...' -> However could this difference be simply explained by preferential uptake of labile Co acting to remove labile Co, leaving the inert, strongly complexed Co pool (see also caption in Fig. 12)?

P32L6 '...rates of uptake, complexation, diffusion,... ' -> maybe add redox reactions to this list

Figures: captions - These are rather long to summarize the main points in the text. Can these be shortened? There are too many figures. In particular there are a number of figures showing reduntant Co vs. P plots. Could Figs. 13 and 14 be moved to a SI section? Fig.6 also shows Co vs. P, maybe remove these and give a reference to Fig.

10 and 11. If further figures might need to be removed, maybe show Figs. 2+3 in the SI as well. I suggest to add deg W or deg N to the station numbers in all figures and text for orientation.

Fig. 1: The bathymetry contrast is not very good Fig. 7: Which depths are chosen for the surface data? Fig. 14: Give a reference for SF6 data

Technical corrections ——————————— P10L22 '(Duluquais Refs)' -> Correct reference P10L13 'due it having' -> 'due to it having' P15L17 'GEOTRACES complaint' -> 'GEOTRACES compliant' P19L6 '... have displayed...' -> '... were...' P37L28 'AOU' -> has not been defined (apparent oxygen utilization) and is not mentioned in the main text P37L29 'NAZT' -> I suggest to write out the abbreviation as it is only used one more time in the ms.