

Reviewer 2 Comments and Author Response

Rebecca J. Chmiel and coauthors present an original, high-quality investigation of why the dissolved cobalt inventory of specific coastal Antarctic seas has decreased between 2005/6 and 2017/18. They achieve this by comprehensively exploring cobalt speciation, stoichiometry, and uptake rates alongside that of zinc and cadmium, trace metals with inter-related ocean biogeochemical cycles. With climate induced changes in the cycling of trace metals related to that of carbon, this decadal-scale study is both timely and thoughtful. I thank the authors for bringing this thought-provoking work together and congratulate them on the quality of the paper. Overall, I believe this study aligns well with the aims/scope of BG and will be of clear interest to the marine biogeochemical community.

My specific comments are relatively minor but reflect aspects of the paper I thought could be improved/clarified.

Specific Comments

Whilst this is an intriguing investigation of the coastal Antarctic Co cycle, the important big picture insight I took from this paper was that climate driven changes in the Antarctic coastal Fe cycle may be responsible for dramatic regional shifts in micronutrient biogeochemistry and limitation patterns. This point could be emphasized more in the introduction, without the need for drastic changes to the text. At present there is one sentence at the end, broadly describing shifts in Zn/B12 limitation as a result of a warming climate, but with no mention of the influence of Fe supply.

[Authors' Response] In this study, we have been careful to clarify that we only observed changes to the dCo cycle, including changes in vitamin B12 uptake, and dCo concentrations relative to other trace nutrients. While we believe that these changes may be linked to perturbations in the dFe cycle, this finding is speculative and has not been confirmed.

However, we have modified the final sentence of the introduction to clarify our hypothesis that the observed perturbations may be due to a changing dFe cycle. The sentence now reads: "The results presented by this study reveal a substantial perturbation of the Co cycle, a shift towards vitamin B₁₂ and/or Zn limitation, and possible, but unconfirmed, perturbations to the dissolved iron (dFe) cycle in coastal Antarctic waters impacted by high rates of glacial ice melt and a warming climate."

Was dZn measured during CORSACS? If Zn limitation is in part driving the dCo inventory differential between CORSACS and CICLOPS, it would be interesting to read whether there has been a change in dZn concentration over this same time period?

[Authors' Response] The discovery of Zn limitation in Terra Nova Bay and the change in dZn concentration over time are highly interesting phenomena discovered during the CICLOPS Expedition that deserves its own paper. This journal article is Kellogg et al.,

(In Review), as well as Kellogg et al., (2022) – chapter 6 of Dr. Riss Kellogg’s thesis (<https://dspace.mit.edu/handle/1721.1/144738>).

Could you say something about the broad pattern of sampling during CICLOPS at the start of the methods section? Where samples taken sequentially from Amundsen Bay to Ross Sea to Terra Nova Bay? On line 364 it is stated that surface dissolved metal concentrations decreased in this order, perhaps due to seasonal drawdown but I am unsure of the sampling timeline between the locations.

[Authors’ Response] Samples were not taken sequentially from the Amundsen Sea to the Ross Sea to Terra Nova Bay. Instead, the CICLOPS expedition transited from the Amundsen Sea to the Ross Sea between Station 4 and Station 22, then moved between the Ross Sea and Terra Nova Bay intermittently until the end of February. The sampling timeline between locations should be clear from the sequential numbering of stations. Thus, while some time-dependent, seasonal can be inferred, we do not claim this is the sole explanation for the regional differences observed, with the exception of the Amundsen Sea, which was only sampled early in the season.

To clarify the expedition track, we have added a sentence to Section 2.1: “The expedition track first mapped a transect from the Amundsen Sea, through the Ross Sea, and ending in Terra Nova Bay (Stations 4–22) over 10 days from December 31, 2017 to January 9, 2018, and then sampled at stations between Terra Nova Bay and the western Ross Sea for the remainder of the expedition. “

Sections 2.2 and 2.3: Can you please clarify which samples were analyzed at sea versus the land-based laboratory? It is a little difficult to decipher at present. Importantly, were any seawater samples (and/or GSC / internal standard) analyzed both at sea and on land for intercalibration purposes?

[Authors’ Response] We have added a sentence to clarify: “Total dCo concentrations for stations 57 and 60 were analyzed in the laboratory, while all other total dCo and labile dCo concentrations were analyzed at sea.”

An internal standard was run before each sample batch, both in the laboratory and at sea. No GEOTRACES intercalibration standards, including GSC2, were run at sea.

Line 244: Shipboard incubator? Was this on deck with flow-through water and natural day/night cycle or temperature controlled with constant screened lighting? Please expand slightly.

[Authors’ Response] This sentence has been modified to read: “All incubation bottles were then sealed and placed in a flow-through shipboard incubator on the deck that exposed the incubations to a natural day/night cycle and surface-temperature seawater for 24 hours. The incubator was shielded by black mesh screening to allow 20% ambient light penetration.”

Lines 359-365: This section briefly describes the pattern of decreasing surface trace metal concentrations between sampling locations and the possible mechanisms for this. Has any statistical test been performed to resolve this decreasing trend or is this assumption based on trace metal mean concentration values?

[Authors' Response] The noted trend of decreasing surface dissolved metal concentrations are based on average concentrations and standard deviations. We believe this is clear in the text and no changes have been made.

Figure 7 clearly shows dCo:PO₄ slopes are being calculated below the mixed layer. Are underlying waters consistent between the geographic sampling locations, and/or could seasonal changes in subsurface water impact slope-based stoichiometry?

[Authors' Response] Due to the coastal location and thus highly dynamic hydrography of the samples locations, the underlying waters of each location are likely to vary by geographic region. Also, due to the vertical nature of the dissolved metal vs. dPO₄³⁻ regressions in the deep ocean, only 3 of 9 slopes displayed an R² value above 0.50 (Table 3), indicating very weak linearity between dissolved metals and dissolved phosphate, and so the deep slopes are difficult to use for regional comparison.

That said, the deep Amundsen Sea and deep Terra Nova Bay regions display dCo : dPO₄³⁻ slopes that are more linear (R² > 0.70), and their slopes are quite similar (Amundsen Sea: 0.59 ± 0.06 mmol : mol, R² = 0.72; Terra Nova Bay: 0.64 ± 0.03 mmol : mol, R² = 0.80), indicating apparent consistency in deep cobalt stoichiometry between the underlying waters of the Amundsen Sea and Terra Nova Bay.

The metal uptake values presented in this paper are especially interesting. However, throughout the text I found inconsistent expressions of the metal uptake term (ρ) that made me stop and question my understanding of the text and figures. For example, the use of ρ Co and non-italicized ρ Co for cobalt uptake rates, whilst pCo is also used to define particulate Co. The same is true for Zn and Cd. In this instance, I suggest the italicized variant for element specific uptake rates for the text, figures, and tables. Further, the use of ρ M, non-italicized ρ M, and ρ TM for trace metal uptake rates. With pM also used extensively in the paper as a unit of concentration, I would suggest the italicized ρ M for defining trace metal uptake rates.

[Authors' Response] Thank you for your attention on this matter – the ρ M (metal uptake) vs p (particulate) vs. pM (picomolar) terminology is unfortunately confusing. Any use of non-italicized ρ Co was in error and has been corrected throughout the text, figures and tables to ρ Co. The one use of ρ TM instead of ρ M used in the text was an inconsistency that has been corrected.

Lines 521-524: Whilst there appears to be a clear concentration difference between CORSACS and CICLOPS mean Co profiles (Figures 8 and 9), there also appears to be considerable variability within the CICLOPS profiles. Do you have a feel for how sampling site variability within and between the cruises may have impacted the deep water dCo and labile dCo inventories shown in figure 9?

[Authors' Response] The standard deviations of the deep dCo and deep labile dCo inventories are given in Table 4 and shown as the error bars in Figure 9c. As you noted, the variability (standard deviation) of deep mean dCo concentrations were higher during the CICLOPS expedition (8 pM) compared to the CORSACS-1 (4 pM) or CORSACS-2 (6 pM) expeditions. The deep labile dCo inventories show no such differences in variability, as both show a standard deviation of 7 pM. This is an interesting point to compare, and the following sentence has been added to Sect. 4.3:

“Note that the CICLOPS expedition mean deep dCo inventory displayed a higher standard deviation (8 pM) compared to the CORSACS-1 (4 pM) and CORSACS-2 (6 pM) expeditions, indicating a higher variability of deep dCo concentration within the sites and depths sampled; no difference in standard deviation was observed within the deep labile dCo inventories of the CICLOPS and CORSACS-2 expeditions (both 7 pM).”

Lines 1015-1018: As your box model nicely shows, increased uptake, mixing and burial of DOM are all part of enhanced dCo removal from the water column, yet burial is excluded here.

[Authors' Response] We have added a sentence to the conclusion to describe the role of DOM and Co burial in the summary of the proposed mechanism. This passage now reads: “The decrease in dCo throughout the water column compared to prior observations is indicative of a multi-year mechanism, whereby the removal of dCo from the surface mixed layer via uptake over the summer has been propagated into the deep ocean via winter mixing, resulting in a decrease in dCo concentration throughout the water column. This mechanism is reliant upon increased Co uptake into organic matter and an increase in the burial rate of Co as organic matter.”

Technical corrections

Line 42: DOM does not necessarily need to be defined here as no further use in the abstract, but rather at first mention in the main text.

[Authors' Response] The definition of the acronym POM (note: I believe this comment was intended to address POM not DOM) has been removed.

Line 128: Please provide the location of the Saito Laboratory.

[Authors' Response] This change has been made, and the passage now reads: “...supplied by the Saito laboratory (Woods Hole Oceanographic Institution; Woods Hole, MA, USA).”

Line 131: Is this a clean-air van?

[Authors' Response] Yes, the passage has been update to read: “...After deployment, the X-Niskin bottles were transported to a trace metal clean-air van and pressurized with high-purity (99.999 %) N₂ gas.”

Line 132: Please use the term ‘macronutrients’ as used elsewhere in this paper.

[Authors’ Response] This passage has been updated to read: “Seawater samples for macronutrients, dCo and trace metal analysis...”

Line 234: I think the reader will be interested in what resin you used for preconcentration.

[Authors’ Response] Since the full ICP-MS methods for these specific samples are described elsewhere, details such as preconcentration resin type have been omitted.

Line 235: What is the elution matrix, 1 M nitric acid?

[Authors’ Response] See above.

Line 242: What container/volume was the seawater used for the uptake experiments collected into from the TM rosette?

[Authors’ Response] Similar to above, since the full incubation experiment methods and results for this specific data are described in detail elsewhere, methodological details have been omitted from this paper.

Line 252: Please clarify that pigment samples were collected from the trace metal CTD, as per macronutrients?

[Authors’ Response] The pigment samples were not collected from the trace metal rosette, but from a standard rosette CTD deployed separately, but often within an hour or two of the trace metal rosette. This has been clarified in the text and the passage now reads: “Phytoplankton pigment samples were collected from a non-trace metal rosette deployed separately from the trace metal rosette, and were filtered and analyzed for select pigments...”

Line 299: No need to repeat (≥ 100 m depth) here as explained in the paragraph prior. Can just use ‘deep’

[Authors’ Response] The “(≥ 100 m depth)” in this sentence has been removed.

Line 303: Move the depths (770 m and 780 m) to line 302; i.e., elevated near-seafloor signal at Station 41 (770 m and 780 m)’...

[Authors’ Response] This change has been made. The sentence now reads: “The high standard deviation of deep dCo in Terra Nova Bay is partially driven by the elevated near-seafloor signal at Station 41 (770 m and 780 m); when the two deepest points at Station 41 are omitted, the average deep dCo in Terra Nova Bay was 36 ± 10 pM.”

Line 329: dFe has not yet been defined in the text.

[Authors' Response] dFe is now defined earlier, at the end of the introduction.

Line 359: I think the Zn concentration should be in units of nM rather than pM.

[Authors' Response] This is correct, the dZn concentration has been changed to nM, not pM.

Line 366-367: I would perhaps remove the term surface seawater, or replace with upper ocean, as the surface is generally defined as 10 m within this paper and <100 m as deep water.

[Authors' Response] The term "surface" has been removed and the passage now reads: "...uptake rates of Co, Zn and Cd within seawater collected from 0–200 m were determined..."

Line 379: Remove the word 'spikes'.

[Authors' Response] The word "spikes" has been removed.

Line 408: Depths at which an uptake rate **is** below detection.....

[Authors' Response] The word "is" has been added here.

Line 414: dCo and labile dCo **vertical** profiles.....

[Authors' Response] The word "vertical" has been added here.

Lines 507-519: Would this paragraph on the nepheloid layer be better placed within its own subsection rather than with stoichiometry?

[Authors' Response] The reasoning for adding the nepheloid layer discussion into the stoichiometry discussion was that it decoupled dCo and dPO₄ ratios and thus impacted Co stoichiometry. However, I like this suggestion of a separate nepheloid layer subsection, and I believe it will help to orient readers within this long discussion section.

The paragraph describing the nepheloid layer is now section "4.2 Elevated dCo concentrations within a benthic nepheloid layer".

Line 577: I think it may read better as; 'In contrast, the 2006 CORSACS-2 expedition reported the presence of labile dCo at five stations with concentrations of 17 ± 7 pM at 6 m depth and 14 ± 9 pM at 16 m depth, with reported labile : total dCo ratios of 0.37 ± 0.13 and 0.28 ± 0.17 , respectively.'

[Authors' Response] This sentence has been updated as suggested.

Line 677: Perhaps consider moving the final paragraph on depth thresholds up to line 671. It appears to me the reader would be better served understanding how the inflection points were chosen prior to the differences between metal:PO4 slopes.

[Authors' Response] As suggested, the sentences describing the depth threshold have been moved up, and the sentences describing the results of the depth-based analysis have been made into their own paragraph following the description of the analysis.

Line 825: Do you mean 1% lability, as per line 767?

[Authors' Response] Yes, thank you for catching this typo. The line now reads: "...the maximum diffusion limit estimation assumed a speciation of 1% labile metals."

Line 937: 3550 pmol **dCo** m⁻² y⁻¹

[Authors' Response] This change has been made and the line now reads: "A F_{Neph} was calculated to be 3550 pmol dCo m⁻² d⁻¹ to the deep ocean..."

Line 1064: Do you mean panels d-f?

[Authors' Response] Yes, this has been changed from "In panels d-e..." to "In panels d-f".

Table 1: The surface and deep sections of this table have different labelling for n<DL column.

[Authors' Response] This inconsistency has been fixed.

Figure 1: The stars and circles are small and quite difficult to differentiate on paper and even more so on screen. Could these be enlarged or made clearer?

[Authors' Response] The star symbols in Figure 1 have been enlarged.

Figure 6a: This figure would benefit from X and Y-axis lines.

[Authors' Response] We decided not to add x and y-axis lines to this figure, as it would not follow the style of the other stoichiometry figures in this paper. However, we did correct typos in the x-axes; in subplot (a) we changed "Dissolved dPO₄⁻³" to "Dissolved Phosphate" and in subplots (b-e) we changed "dPO₄⁻³" to "dPO₄³⁻". A similar x-axis error was updated in Figure 7.

Figure 11, Line 940: Please define the Co cycle as black arrows, as the pCo cycle has black text. Same with the pCo cycle (orange arrows).

[Authors' Response] This correction has been made.

Table 6: Is the burial flux here calculated as dCo or pCo? Line 960 suggests pCo yet this term falls under the dCo loss parameters.

[Authors' Response] The burial flux is calculated as particulate Co. We have changed the third table heading from "dCo loss parameters" to "Co loss parameters".