

Author Response to Anonymous Referee #1

Referee comment on "Major processes of the dissolved cobalt cycle in the North and equatorial Pacific Ocean" by Rebecca Chmiel et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-305-RC1>, 2021

This is a review of the paper titled “Major processes of the dissolved cobalt cycle in the North and equatorial Pacific Ocean” by Rebecca Chmiel et al. for consideration in Biogeosciences Discussions. The authors show high quality dissolved and labile cobalt data from a recent GEOTRACES expedition (GP15) to the North and South Pacific Oceans. Co shows evidence of biological uptake and remineralization in the surface ocean and scavenging with depth, accordant with its typical global distribution. While hydrothermal sources were observed and discussed, persistent oxygen minimum zones sampled in this study were determined to be a larger input of dissolved Co to intermediate waters. The distribution of labile vs organically-complexed Co, as determined by UV radiation, is discussed throughout, highlighting in particular the importance of ligands in protecting dCo in Pacific deep waters. Comparison to particulate samples, collected by pumping, and Fe and Mn are also discussed at select stations.

I found this manuscript to be an enjoyable and easy read. While these processes are being explored across multiple elements for other GEOTRACES parameters, this manuscript provides a nice foundation for oxidative release, scavenging, and mixing of deep waters along this transect. The organization supported the findings and the logic of conclusions throughout. I thought the addition of other dissolved metals (Fe and Mn) and particle species (pCo, POC, etc) to be complimentary rather than extraneous in telling the story. The figures were likewise appropriate and well-designed.

I recommend acceptance to Biogeosciences following minor revisions as outlined below. General comments to this manuscript: While there was thorough discussion of possible processes it felt a little long and I was having trouble following the deep water/POC export and modeling sections as a result. I wonder if there is a way to streamline? It seems that you discuss deep water Co trends through the lens of Co:PO₄, labile Co, and then again in a separate section. I also thought that the mention in the conclusions about deepwater Fe-Mn nodules as a source of Co could be expanded slightly. Do you expect this inventory to increase with increased deoxygenation, for example? How efficient are Fe-Mn nodules in scavenging Co? Just thinking this would be of interest to a broader community and inform ongoing deepwater mining studies.

- Thank you for your review and comments. It is good to hear that despite the manuscript's length, it was an enjoyable read. We have organized the paper by relevant processes and not by oceanographic location, and so restructuring the deep water discussion to one section of the manuscript would unfortunately not aid reader comprehension.

Although the question of how deep dCo will change with deoxygenation is an interesting one, it is not one we are able to answer with the simple estimation performed in section 4.5. Any further analysis of the effects of deoxygenation on Pacific Co would likely require a dedicated modeling study, which we believe to be a very compelling idea for future work.

We have also slightly expanded the paragraph on seafloor mining in the conclusion to include a clearer description of the Fe-Mn crusts and Mn nodules, and their importance to the geoscience community. Neither actively scavenge dCo – instead, dCo is scavenged to pCo via Mn-oxide

formation in the water column, and the sinking oxides slowly build the nodule along the seafloor via accretion. This paragraph now reads:

“This study improves our understanding of dCo dynamics in the Pacific water column, but it should be mentioned that many are interested in Pacific Co biogeochemical cycling as it relates to Co scavenging and mineralization along the seafloor and the emerging deep sea mining industry. When dCo is scavenged and removed from the water column in the form of pCo incorporated into Mn-Oxide particles, it sinks and forms vast regions of ferro-manganese oxide crusts embedded with metal-rich nodules that accrete slowly along the seafloor (Aplin and Cronan, 1985). These nodules are formed from Mn oxide deposition over millennia and are rich in Co, Ni, Cd, Zn and rare earth elements (REEs) (Cameron et al., 1981; Hein et al., 2013). Such deposits are of interest to many because of the potential for deep-sea mining in the region, especially in the Clarion-Clipperton Zone of the central North Pacific basin. Here, international mining operations to extract Fe-Mn nodules along the seafloor could be within the decade. The value of Co ore, which is currently only mined terrestrially, has been increasing in demand over the past two decades due to the metal’s use in personal electronic devices and sustainable energy solutions like electric vehicle batteries, and many believe that mining the vast, concentrated deposits of Co on the Pacific seafloor could alleviate this demand (Hein et al., 2013). However, deep-sea mining and the potential heavy-metal rich sediment plumes it could create may have serious ramifications to the relatively fragile and unexplored benthic ecosystem in the region (Drazen et al., 2020; Fuchida et al., 2017; Sharma, 2011). Although the technology and facilities required to mine the deep sea have proven to be both complicated and expensive (Cameron et al., 1981), the potential new source of Co ore could, in theory, help support widespread adoption of electric vehicle fleets (Hein et al., 2013).”

Line comments:

Line 121: “The Chelex resin was prepared as described...”

- This sentence now reads “The Chelex resin was prepared as described...”

Line 135: Can you clarify if the labile dCo analyses were done on the exact same sample as the total dCo? Or an aliquot? If I understand correctly, the total dCo was done using an aliquot, does that mean that the rest of the sample is only able to be used for repeat labile analyses in the future?

- Both labile and total dCo samples were aliquoted from the same 60 mL sample bottle, and this has been clarified in the text, which now reads “... 11 mL of sample seawater was aliquoted from the sample bottle into 15 mL acid-washed polypropylene vials...”

Lines 495-496: I wonder if this was true in the Arctic as well, since you just compared the Alaskan source to Arctic processes?

- It was! The Arctic Ocean also shows a negative correlation between dCo and salinity within the Transpolar Drift. This comparison has been added.

Line 501: What are typical river endmember concentrations of Co in this area?

- There's little published data of dCo from rivers in this region. A GEOTRACES–affiliated fieldwork team from the Charette and Fitzsimmons labs collected riverine and estuarine samples from the Alaskan coast near station 1 that are currently unpublished, showing ICP “labile” dCo data around 4-18 nmol/kg. However, as was discussed in the labile methods section, this is not directly comparable to electrochemical dCo data. For this reason, we have not included observed endmember values for Alaskan riverine dCo, but we are confident our endmember estimate of ~13 nM dCo is a very reasonable estimate.

Line 505: By “open” do you mean open ocean or yet unknown?

- Open ocean - this has been clarified and now reads “... is mixing with an open ocean endmember that contains...”

Line 536: ODF stands for “Oceanographic Data Facility”, I believe this is wrong in your acknowledgements as well. I would mention it is hosted at Scripps Institution of Oceanography.

- This correction has been made. The connection to Scripps was already mentioned in the macronutrients methods section (Sect. 2.1) and in the acknowledgements.

Line 541: Can you clarify which samples are coming from the ODF rosette? The FIA Fe and Mn samples?

- This was explained in the methods section 2.6, but additional clarification has been added in the discussion section to make the distinction clear to readers. The section now reads “...the dFe:xs³He and dMn:xs³He ratios from the ODF cast, measured via FIA,...” and “...the GTC profile dFe and dMn values, measured via ICP-MS,...”

Line 578+595-596: It is odd to mention the flux from hydrothermal vents twice with different units. Can you combine these sentences?

- The second mention of the global Co hydrothermal flux has been removed.

Line 591: local scavenging of the labile or ligand-bound Co?

- Labile Co – this has been clarified and now reads “...likely due to local scavenging of labile dCo before it is transported...”

Line 749: “expeditions”

- This spelling correction has been made.

Lines 843-845: Will this model now be updated to reflect these new Co data?

- The discussion of model data as it compares to the observed data has been updated to reflect more on the future of the model and how this comparison will be used to improve upon future iterations of the model. The final paragraph of this section now reads:

“Recognizing inconsistencies between expected model dCo distributions and observed transect dCo distributions is an effective way to test and improve upon the biogeochemical model’s parameters. The parameterization of ligand-bound cobalt in the deep Pacific, for example, could

be improved by decreasing the assumed concentration of inert, organically bound dCo in deep water masses. It should be noted that the biogeochemical model was optimized for the global ocean Co cycle, and not specifically for the Pacific Ocean, which likely contextualizes much of the offset between the observed and model transects, particularly for inconsistencies within the O₂ and PO₄ distributions. The model also did not incorporate a hydrothermal vent source to the Pacific, which we concur is an appropriate omission on a basin scale. Future iterations of the Co biogeochemical model will consider the successes and inconsistencies presented here and continue to improve upon our conceptualization and parameterization of the marine cobalt cycle.”