Review #3

Review of ‘Elevated sources of cobalt in the Arctic Ocean’ by Bundy et al.

The authors present novel data from an understudied region. The data appears of high quality, is definitely very interesting and as such should be published. Generally the paper is well written, but the methods and results section seem quite long. I like that the methods are detailed, but given that most methods have been described before I wonder if all details are required here and if the methods section could be condensed. The results section already contains quite some discussion. This should either be moved to the discussion, or perhaps a combined results/discussion section is more suitable for this paper (i.e. where the actual results section only briefly describes the basin wide distribution). The number of figures is also quite large and I encourage the authors to reconsider if they need them all as the sheer volume of data presented is a bit overwhelming.

Thank you for the comments. We have shortened the methods section where possible, and have moved some sentences from the results section to the discussion, particularly from the modeling results section (section 3.5). We realize the volume of data and the numbers of figures is quite large, however for completeness we have kept all of the figures and tables.

Generally, the discussion is interesting, but I thought it was strange that work already published from this cruise (e.g. Jensen et al., 2019) or the German/Dutch GEOTRACES cruises (both 2015 and 2007 GEOTRACES IPY) is barely (or not at all) discussed. There is already quite some work that provides very nice context for the current study, e.g. the work on Fe and Fe binding ligands in the TPD from the GN04 transect, the Jensen Zn study or the Mn and Fe work from the GIPY 11 cruise (data in IDP). The same can be said for the comparison with the Atlantic where the comparison is made with data quite far south along the zonal GA03 rather than the also available meridional GA02 data that seems more relevant for the discussion of advection into the Atlantic.

As discussed in the specific comments below, we have added many of these references throughout the discussion section. We have kept our current comparison to GA03, but we have mentioned that a similar signal was observed in GA02 in LSW.

In the section on correlations, mixing as a driving factor in such correlations is ignored (see also specific comments) and this is something that in my opinion should be addressed. The comparison with the data from 2009 is definitely interesting, but way overstated. Most importantly, 2 data points in time are not proof of a trend. Moreover, there could be seasonal variation (as it appears the stations were not occupied at the same time/season) and the stations locations are actually quite far apart. Notably the width (area) of the adjacent/closest shelf is very different and stations were positioned differently with respect to fluvial input and the Bering Strait. In this study it is argued that the shelf is the most important source of Co. Thus higher concentrations in the vicinity of the large shelf area of the Chukchi Sea and Bering Strait compared to the narrow Canada basin shelf are maybe not that surprising and this needs to be explored in context of the local hydrography and currents. I also noted (based on Fig 9) that the role that bacteria play differs between the regions for the 2009 and 2015 data.

We discussed some of these suggestions below in the specific comments. We believe that the stratification in the Arctic basin which impedes mixing between the Pacific waters and Atlantic waters as shown in this work (and others), would suggest that the impact of mixing of water masses on the Co:P stoichiometry observed is minimal. The water masses in this region have very little exchange (Figure 2) and thus the primary drivers of changes in the deep Co:P ratios are likely due to internal cycling.

We have also noted this extensively below, but we did not intend to suggest that our dCo from 2009 and 2015 is definitive evidence that Co is increasing over time in the Arctic, as we discussed many caveats in the manuscript. However, we do feel it is an important observation to document in our work.

The conclusions were not completely appropriate for the current ms. The data/ms did not show at all that the Co distribution has implications for Arctic ecosystems and it is unclear how the observation of a unique Co distribution affects future changes in micro nutrients. As stated above, I do not believe that Co was shown in this work to be increasing over time. The idea that (changing) conditions in the Arctic affect the North Atlantic Ocean downstream is not new and this should be acknowledged.

We have reworked section 4.3 and 4.4 of the discussion to make it clearer that we were not trying to say that our data shows that dCo has unequivocally been increasing over time in the Arctic. We have pointed out that our data suggests that dCo is increasing, however we recognize that the data is limited. However, since others have noted the same trend in other tracers, we do not believe our conclusions our unjustified. We have cited several papers that have also noted increases in shelf-derived tracers in the Arctic over time and their affects to the downstream North Atlantic (Charette et al., 2020; Kipp et al., 2018; van der Loeff et al., 2018).

Specific comments 40-43 limitation by cobalamin does not necessarily imply Co limitation as cobalamin production can be low regardless of the Co levels. So most of the cited studies do not demonstrate Co limitation.

We clarified this sentence to read, "Due to its low concentrations, strong organic complexation, and its presence in cobalamin, dCo or cobalamin have been found to be limiting or co-limiting nutrients for phytoplankton growth in several regions (Bertrand et al., 2007, 2015; Browning et al., 2017; Martin et al., 1989; Moore et al., 2013; Saito et al., 2005). Growth limitation can be due to either a lack of dCo, or cobalamin (Bertrand et al., 2012; Bertrand et al., 2007; Browning et al., 2017), as cobalamin is only synthesized by cyanobacteria and some archaea (Doxey et al., 2015)."

76-80 it is stated there are regionally specific features, but the examples are not really specific regional features. Perhaps rephrase?

This sentence was removed.

92 awkward sentence, please rephrase

This has been rephrased as "This study examined dCo, LCo, and pCo in two different transects in the Canadian sector of the Arctic Ocean."

94 what is meant with 'interpreting the role of external sources and internal cycling to the distribution'?

We meant that we used the model to evaluate our hypotheses about the key factors in controlling dCo distributions in the Arctic. We changed this sentence to, "We then used a Co biogeochemical model (Tagliabue et al., 2018) in order to evaluate hypotheses about the role of external sources and internal cycling to the observed Co distributions, the potential of the Arctic to be a net source of Co to the North Atlantic, and to identify Co sources and sinks that may be sensitive to future changes in this rapidly changing ocean basin."

109 was sampled

We left this sentence as is.

131 can you compare filtered and unfiltered samples? Perhaps state this will be addressed later in the ms

This was addressed later in the manuscript.

295 this detection limit is at least an order of magnitude too high for open ocean Mn, notably in the deep. Is it a typo?

This is not a typo, and refers to the detection limit of shipboard flow injection analyses of dMn and not ICP-MS analyses.

324 Fe was already defined

Thank you, this has been fixed.

389 given that the data from the Canadian geotraces cruise was unfiltered, I do not think it is appropriate to call is dissolved (dCo)

This section is about the GN01 data, which are all filtered.

408 how is the % sea ice melt determined?

This is determined from $\delta^{18}O$ data (Newton et al., 2013). This reference has been added.

427what is the % Pacific water based on?

Same as above.

427 here and elsewhere, the number of significant figures for Co concentrations does not seem to match the reported precision.

All data presented have the correct number of significant figures.

470 awkward sentence, please rephrase

This has been rephrased.

471 what does 'that' refer too?

This has been rephrased to, "Similar to dCo, there was no observable enhancement of LCo in PHW, with LCo distributions closely following that of dCo and other shelf-enhanced trace metals such as dFe and dMn."

508 confused, 'capture the major processes contributing to modeled sources and sinks' not sure what is meant here.

This has been amended to, "In order to explore the major processes contributing to the modeled dCo sources and sinks, the proportion of the dCo signal in two distinct depth horizons was further investigated using a set of sensitivity experiments."

516-517 Jensen et al 2019 argued that low oxygen in the sediments plays an important role for Zn and evidence for denitrification in the sediments was presented. This should also affect Co despite the fact that oxygen is not low in the water column. If denitrification occurs in the sediments, isn't it likely that also reductive dissolution of sedimentary Mn-oxides occurs? (however this discussion seems out of place in the results section)

Yes, it is possible that there may be denitrification occurring in the sediments which could impact the dMn and dCo distributions. This is accounted for indirectly in the model by the sediment Co source being a function of the particulate organic carbon (POC) flux, which is a primary driver of anoxic sediments and thus denitrification.

516-534 this section is not as clearly written as the rest of the ms (specifically the last sentence was impossible to follow for me). Perhaps this can be remedied?

We have re-worded several sentences in this section.

540-554 There is a problem with this section as for the Arctic (but also elsewhere, e.g. Aguilar-Islas A. and Bruland K. W. (2006)) it has been demonstrated that Mn in the surface of the open ocean basin is mainly derived from fluvial input, not sediments (Middag et al., 2011 (doi:10.1016/j.gca.2011.02.011). The latter study was not the exact same region, but fluvial input will be a strong source of Mn in this region too, and this needs to be discussed. However, Zn (Jensen et al., 2019) has been shown to have an important sedimentary source and might be a better proxy?

Middag et al. (2011) and Charette et al. (2020) both suggest that dMn in the Arctic has both a fluvial and sedimentary source. In the Arctic, it is difficult to disentangle the shelf and riverine processes, as the riverine inputs interact with the shelf before being transported to the open basins (Kipp et al. 2018). The same is true for the dCo, which we mention in section 4.1. We have amended this section to highlight that although we believe the shelf signal to be the primary dCo source, we note that the fluvial inputs are very important in the open basin due to the TPD.

571 discussion of the recent TPD paper here seems appropriate as well as some recent Fe work

Yes, these references have now been updated since the recent publication of Charette et al. (2020), Colombo et al., (2020) and Tonnard et al. (2020).

572/573 'track shelf inputs due to interactions between the sediment-water exchange processes' quite vague, not sure what this means/implies

We have clarified this sentence to indicate that radium is a tracer for shelf inputs.

582-584 What about deposition of riverine Co in the shelf sediments and subsequent remobilization?

Yes, this could be another process on the shelf that is contributes to elevated dCo and is mentioned later on in this section.

590 also argued for Fe (https://doi.org/10.1016/j.marchem.2017.10.005; https://doi.org/10.1029/2018JC014576)

We have added these references.

597 see mentioned refs for humic-like substances and Fe in the TPD, seems very relevant here.

Yes, these have been added.

662 what is meant with depth here? I assume the slopes are determined per station and the depth is the station depth or am I wrong? Please clarify

We have reworded this to be "versus depth."

654-670 there is a growing body of work demonstrating mixing and water mass circulation is a primary factor in driving the slopes of metal-nutrient relationships that is ignored here while the mixing of Pacific and Atlantic origin water could have a strong effect (e.g. Vance et al., 2017, doi: 10.1038/ngeo2890; de Souza et al., 2018, doi:10.1016/j.epsl.2018.03.050; Middag et al., 2018, doi: 10.1016/j.epsl.2018.03.046;Weber et al., 2018, doi: 10.1126/science.aap8532; Middag et al., 2019, doi:10.1029/2018GB006034; Middag et al., 2020 doi: 10.3389/fmars.2020.00105).

This is very important to consider in other ocean basins, but there is very little mixing in the Arctic between water masses due to the strong stratification, so we do not think this is significant *here. This is also likely not as important for dCo, which has a much shorter residence time (~ 200 years) compared to some of the longer residence time elements mentioned in these references.*

676 continues?

This has been changed.

702 after a 40% correction, the 2015 data is 400% higher than the 2009 data. This seems to be in contrast to line 688 where it is stated that without correction the 2015 data is 3.5 times higher.

This has been corrected.

703-704 could there be a factor of seasonality (did the sampling occur in same time of year relative to start of ice melt and river discharge)? And 2 data points in time hardly makes a trend! The difference is interesting for sure, but currently the significance is really overstated, as there is no way of telling what the Co concentrations were in other years. What about the enormous difference in the size of the nearby shelf regions between the 2 expeditions?

Yes, both samplings were done in the same month of the year (October). We have discussed many of these points extensively in this section, and have been transparent about the caveats. Many others have also observed increases in fluvial and shelf tracers over time in the Arctic however (Doxaran et al., 2015; Drake et al., 2018; Kipp et al., 2018; van der Loeff et al., 2018; Tank et al., 2016; Toohey et al., 2016), so we do believe that our data could be pointing to an increase in dCo over time as well. We have thoroughly explained these caveats in this section.

"The increase in dCo over time in the Arctic is interesting, and has been documented for other tracers in the Arctic. Kipp et al. (2018) and van der Loeff et al. (2018) noted that ^{228}Ra has increased over time in the central Arctic. They suggest that increases in shelf and/or river inputs from thawing permafrost are the source of this elevated ^{228}Ra (Kipp et al., 2018; van der Loeff et al., 2018). The increase in metal inventories over time on Arctic shelves is consistent with this observation. The majority of the variance (~70%) in dCo in the upper 100 m on the U.S. GEOTRACES transect could be explained by a shelf source, and the remainder was likely associated with river inputs (Fig. 11). If these sources are similar to the sources of dCo in 2009, then an increase in either a shelf or river flux could be responsible for the dramatic increase in dCo over time. While there is not enough data to state whether the river dCo flux has in fact changed over time in the Arctic and the observed changes could be due to seasonal or interannual variability, several other studies have documented an increase in river discharge due to increases in permafrost melt over time (Doxaran et al., 2015; Drake et al., 2018; Kipp et al., 2018; van der Loeff et al., 2018; Tank et al., 2016; Toohey et al., 2016). The increase in river discharge has the potential to considerably increase trace metal inventories in the future Arctic Ocean, perhaps particularly for those metals that are strongly organically complexed, thus protecting against scavenging in the estuarine mixing zone (Bundy et al., 2015). These increases in metals over time will have implications for metal stoichiometries and phytoplankton growth in a changing Arctic Ocean."

719-720 an increase in fluvial discharge as well as timing of ice melt could also affect primary productivity on the shelf and thus sedimentary oxygen conditions and Co supply from the sediments (similar to Zn; Jensen et al 2019). And what about increased SGD, could that play a role?

We do not think that SGD could be playing a role here because there are no marine terminating glaciers in this region to our knowledge. Primary production certainly could play a role, and these have been mentioned in this section.

725 I have some issues with this section. First, it is very odd to compare only to the zonal Noble et al. study when in this discussion the comparison to the meridional Dulaquais study would make much more sense as that also has observations much closer to the Arctic (and also states: 'the LSW was characterized by relatively high DCo concentrations'). This data is available from the IDP. Moreover, LSW is not the only water mass of Arctic origin, also the deeper components of NADW are of Arctic origin (Denmark Strait Overflow Water and Iceland-Scotland Overflow Water). So if LSW is elevated in Co due to its Arctic origin, why is LSW elevated relative to ISOW and DSOW that are also of Arctic origin? This needs to be addressed.

We have added the Dulaquais et al. (2014) reference in this section. We have discussed in this section that the LSW signature is likely a combined signal of Arctic inputs and additional dCo inputs picked up on the shelf in the Labrador Sea, and that is part of the reason why we do not think there is a similarly visible signal in ISOW and DSOW. Additionally, the high dCo is confined to the upper water column in the Arctic and thus is less likely to contribute to these deep water masses. LSW is also fresher and has lower silicate compared to ISOW and DSOW (Jenkins et al. 2015), additionally suggesting an influence from surface waters.

749 not sure what the T-S plot shows/adds or how it supports the hypothesis; basically it shows that dCo is lower in LSW than in the source waters, but you do not need a T-S plot to show this.

We have kept this figure because we think it is the best way to show the two datasets concurrently.

773 where does the Zn data come from? According to the caption it is from this study, but this is the first mention of it. Again the comparison to the GA03 section rather than the more relevant GA02 section is very odd in my opinion as all data is accessible in the IDP and provides data (and insight from the associated publications) much closer to the Arctic. I really urge the authors to make use of the data (and insights) available from the international GEOTRACES efforts.

The Zn data from the Arctic is from Jensen et al. (2019) and S. John (unpublished). The remaining data is from the GEOTRACES IDP 2017. Both Noble et al. (2016) and Dulaquais et al. (2014) observed similar signatures of high dCo in LSW, so we feel like either dataset is appropriate for this comparison. We have now discussed this more thoroughly in this section.

779 quite similar. What is this statement based on given that the medians are more than a factor of 2 apart? I see there is considerable overlap, but not sure if 'quite similar' is the observation all readers would make based on the presented graph. Some explanation seems required.

We have changed this to be "similar."

781 Bit of a jump from Co to total metal concentrations. For metals with different biogeochemistry this might be different and an increase in fluvial supply in the Arctic (of e.g. scavenged Al) might have no consequence for transport to the Atlantic.

We of course acknowledge that there will not be increases in all other trace metals, though it is plausible for those that show similar correlations with shelf and fluvial inputs (Charette et al. 2020).

783-785 do not follow this sentence; the total inventory of Zn is small compared to Zn? And why is the Jensen et al., 2019 only briefly mentioned here? As indicated above, the comparison to the cycling of Zn would have been relevant elsewhere in this ms too.

Here, we were stating that the total inventory of dCo in the ocean is much smaller than dZn, so small changes to dCo sources may have a disproportionate impact compared to increases in dZn fluxes. We have added some discussion of the Zn distributions throughout the manuscript, while being mindful of length.

791-792 This ms has not demonstrated there is any influence of the Co distribution (or the changing Co concentrations) on the Arctic ecosystem, just that Co concentrations could be changing. Moreover, given that Co concentrations are high, I fail to see how a further increase in Co is affecting the ecosystem. And how does the unique Co distribution affect future changes in micro nutrients?

This sentence was meant to highlight the distinct distributions of dCo in this basin compared to other open ocean regions (Figure 3). We also discussed how because the primary sources of dCo in this basin were found to be from a combination of shelf sediments and rivers, and that these sources have been shown to be increasing over time for many other tracers, that it is possible for dCo to continue to change over time as well.

799 as stated before, this cannot be stated like this based on 2 data points in time!

We have clarified throughout the manuscript that we are merely provide intriguing evidence that dCo is increasing over time in the Arctic. We have also added the following sentence in section 4.3, "We recognize these two Arctic dCo datasets are limited in temporal coverage and have methodological differences; however, we felt a responsibility to transparently present these observations of dCo increases in the Arctic Ocean to raise community awareness of this potential environmental change."

805 similar interpretations were also invoked based on e.g. the micronutrient distributions along the GA02 section (e.g. Cd, Zn, Ni, Fe and Fe binding ligands, Co). I do not mind this is not a completely novel finding, but it is appropriate to acknowledge this idea was postulated before and in fact could strengthen the case for this study on Co.

These other datasets have been mentioned in the preceding section.

Not all figures have units on the axis (color bar fig 8, y axis fig 11) The cited references in the text are not all in reference list

Both have been amended.

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