

Review of 'Seasonal dispersal of fjord meltwaters as an important source of iron to coastal Antarctic phytoplankton' by Forsch et al.

This manuscript aims to constrain the input and dispersal of Fe and Mn rich fjord water in an Antarctic Fjord. This is an interesting and important objective given that these metals are important drivers of primary productivity in the Southern Ocean, including coastal areas. Whereas it is known glacial melt must supply these metals, much is unknown about the underlying processes or the effective fluxes into Fe and or Mn limited waters that are generally located further away from direct sources. To tackle this difficult question, a whole suite of methods is used, including water column profiles, sediment and ice sampling as well as modeling work. This is a very comprehensive study and I really liked to conceptual model (Figure 10) that brings together all the different aspects, however, this clarity and synthesis is somewhat lacking in the text. Despite being generally well written from a language point of view, the text is often not clear (see specific comments) and the text sections are not always well connected. For example, the section on ligands (4.5) provides some discussion on (changes in) ligand concentrations and binding strengths, but ends with a very general section on the potential role of ligands in keeping Fe in solution but no real novel insights from the current data (or comparison to recent insights from an Arctic glacier Fe-speciation study, see specific comments). More importantly, the role of ligands or the balance between solubilization and scavenging is not at all considered in the modelling approach in the next section. In fact, I struggled to see what we learn about Fe in the modelling approach using conservative tracers, given that the elusive balance between solubilization and rapid scavenging / precipitation reactions is one of the most important reasons for our limited understanding of the Fe biogeochemical cycling. In the appendix, a 10% dissolution of TDFe is considered conservative, but no consideration is given to how much of this actually remains in solution and hence is subject to long range transport to Fe-poor regions. I realize it is no easy feat to constrain this, but I think it should be discussed and the modelling section could be shortened considerably.

Overall, I think this manuscript will provide a valuable addition to the literature. Nevertheless, it would benefit from shortening and conveying the novel insights from the data more clearly as well as tying the different sections in the discussion better together (so that it is more one story rather than different aspects that only in the conceptual model really come together). I also noted that while Mn is often mentioned in the manuscript, it does not appear at all in the conclusions whereas I'm confident there are some interesting new insights into the biogeochemical cycle from Mn based on this dataset.

R: We thank Reviewer #2 for their constructive comments and criticisms. We have made improvements to the discussion of ligands by a comparison to recent literature in the Arctic. Our conservative tracer approach has been informative in terms of parsing out the potential importance of different sources of iron around Antarctica (e.g. Dinniman et al. 2020, St-Laurent et al., 2017). A more complex model which includes iron chemistry is beyond the scope of this work, which is a first look at the potential importance of fjord-based glacial melt as a source of iron to coastal Antarctica. We have also improved our discussion of manganese and place this work in the context of recent literature indicating the role of both Fe and Mn in limiting primary production in the Southern Ocean. We have improved the length of the article by shortening and moving much of the modeling discussion to the supplemental. Additionally, the conclusion is shortened. We address each comment by line using boldface formatted text.

Specific comments:

In the introduction I missed Mn considering that Mn is known to be (co-)limiting, even in coastal waters such as the Ross Sea (<https://doi.org/10.1038/s41467-019-11426-z>)

R: We will make changes to include Mn in our discussion and conclusion. This will be reflected now in the title, discussion of trace element dispersal/implications for downstream primary production, and conclusions.

120-130 bit late now, but surprised by the choice for stainless steel rather than titanium as used in TM ice core drilling and notably the razor could have easily been replaced by a ceramic knife

R: Sampling of glacial ice was opportunistic, and precautions were taken to reduce the chance of contamination. We agree that ceramic is a better choice and will be strongly considered for future work.

292 the work by Bown et al 2017 (<https://doi.org/10.1016/j.dsr2.2016.07.004>) seems relevant here

R: Relevant citation added.

327 not sure I would describe an R^2 of 0.48 as highly correlated. And given the equation $LpFe = TDFe - dFe$, does a correlation between dFe and $LpFe$ indeed imply exchange? I would assume the correlation is inherent to the definition.

R: We changed this sentence to “correlated.” The correlation does not necessarily imply exchange, therefore we have removed this statement.

389 'particulate Fe are associated with more crystalline and thus less labile Fe oxides'; less labile than the 'comparable fraction is refractory and is not liberated by any of the solution treatments (31%).' mentioned in the previous sentence?

R: The crystalline Fe oxides mentioned in 388 are more labile than the refractory silicates. These oxides are less labile than the poorly crystalline oxides mentioned in 384. For clarity, the sentence is revised to, "Other fractions of particulate Fe are associated with more crystalline Fe oxides (goethite, hematite) and the minerals magnetite and pyrite."

475 'Since glacial meltwater is restricted to the surface, it constitutes a significant input of Fe to the surface throughout the growth season'; seems the statement on significance should come after the discussion in the following lines.

R: This statement will be moved to the end of the paragraph.

504 what is the statement on light limitation based on?

R: This is based on our conceptual phenology of the bloom (Pan et al. 2020). We believe for most of the year, phytoplankton growth is light-limited due to low availability of light (steep topography surrounding the fjord blocks sunlight or sea ice cover occurs late-Fall until early Spring). We have added the Pan et al. reference to this sentence.

517-520 how were crustal vs authigenic material and the reported fraction identified?

R: These were determined using the following equation, for which average crustal values were taken from estimates of the average composition of the upper continental crust.

$$\% \text{ crustal} = ([\text{TpAl}] * \text{Me:Al}_{\text{crustal}}) / [\text{TpMe}]$$

The remaining fraction, after accounting for % biological (0% for all samples), is assumed to be authigenic. This will be clarified in the subsequent version of the manuscript.

524 'indicating a large oxide fraction is associated with this particulate matter' this statement is not explained (or referenced)

R: An oxide fraction in plume particulate matter is inferred by comparing TDAI:TDTi (64 mol:mol) and TpAl:TpTi (39 mol:mol). Both ratios are elevated above average upper crust ratios, and the observation that total dissolvable fraction is

more enriched in Al than total particulates indicates Al is associated with oxide fractions (Kryc et al. 2003), since Al is a heavily scavenged element by oxyhydroxides at oceanic pH levels and these will solubilize with a dilute HCl leach. We will include a brief explanation in support of this claim.

534-535 875 nM is higher than TDFe measured (346.95 ± 160.40 nM); why does this suggest settling loss through flocculation is likely occurring? TDFe is also made up of particles that could be emitted from the glacier. I agree there is loss and settling of Fe, but the argument based on TDFe eludes me.

R: We assume that most of the LpFe is produced during rapid oxidation of the reduced pool of dFe (as Fe(II)aq). Therefore, LpFe+dFe would represent the endmember concentration of Fe(II)aq within zero salinity anoxic subglacial meltwater.

537 – 539 also, the extrapolation approach here excludes any precipitation and is likely an underestimation of the endmember concentration.

R: We account for precipitation through the conversion of dFe to LpFe, since LpFe represents a recently precipitated/adsorbed fraction of dFe. See above comment.

541- 543 'However, subglacial... shelf (Schodlok et al., 2016).' What is the relevance of this sentence, not clear

R: Advective transport under ice shelves could further reduce the flux of dissolved iron once upwelled into the euphotic zone 10s-100s km away from the point source of meltwater discharge (Krisch et al. 2021). The text was changed to clearly state the relevance.

543 what export efficiency, previous sentence was on the width of the shelf?

R: The point here was that boundary scavenging, if not accurately represented, could lead to a large overestimate of the contribution of subglacial meltwaters to the euphotic zone, which is hundreds of km from the point of discharge. We will revise this sentence for clarity.

558-587 what is the point of this section? The calculated sediment efflux of Fe is much higher than the global average which is somehow related to bioturbation, but how is not made clear. It is stated bioturbation would decrease the efflux, so how does it explain the higher than average efflux? Reference is made to Marsay, but it is not clear to me what the relation is between the current and those observations. This section should be clarified and can probably be shorter/ more succinct

R: The point of this section is to arrive at a plausible scenario to explain two things: high estimated efflux values based on diffusive flux, and the enrichment of oxides at the sediment-water interface.

D_{Fe} maxima down-core could support high concentrations of dFe in surficial porewaters. We believe that the high rates of bioturbation and abundance of organic matter following bloom sedimentation could sustain dissimilatory processes deeper in the cores, which results in down-core local maxima in dFe. Diffusion coefficients based on bioturbation are smaller than those based on molecular diffusion, therefore we do not know if bioturbation enhances the dFe flux from the sediments. However, we do think that bioturbation enhances redox cycling within the sediments through the mixing process. The enrichment of labile Fe oxides in the top few centimeters demonstrates rapid oxidation of reduced Fe, and potential formation of colloidal Fe and labile particulate Fe.

Additionally, we point out that the global average from Dale et al. (referenced line 568) is for continental margins, so one would expect fluxes in the fjord to be considerably different since they are coastal.

Efflux estimates in Marsay et al. (2014) might more accurately show the effect of these processes on the efflux from reducing sediments to the water column following significant oxidation and reversible scavenging, since we argue diffusive flux estimates are upper limits (line 585). Therefore, large uncertainties remain as to the net flux of dFe from sediments following rapid oxidation at the sediment-water interface. The diffusion coefficients of colloidal Fe have not been determined, but would be substantially lower (by orders of magnitude) compared to Fe(II).

We agree with the reviewer that this section can be considerably improved and condensed.

561 'The result is deviation from results based on diffusion alone' Rephrase

R: Since diffusion coefficients based on bioturbation are smaller than those based on molecular diffusion, we have removed this sentence as we do not have evidence to support the claim that epibenthic fauna affect the sedimentary efflux of metals. However, as noted in the previous response, redox cycling is enhanced through bioturbation. We will reference Burdige and Christensen (submitted to *Gochem. Cosmochim. Acta*).

564 greater deposition than what?

Compared to data from the adjacent continental shelf. Sentence will be revised.

577 what flux estimates, those of Pb?

R: We are referring to dFe flux estimates. This will be explicitly stated.

582 DIR is never used

R: Removed.

621 how does a scaling of dFe to LpFe correspond to an increase in eL between seasons. Please clarify

R: Excess ligands, defined in line 616, also scale with LpFe. However, we can change our choice of word (“correspond”) since there is no clear reason for why an excess of ligands would scale with increased dFe and LpFe.

625 how does this compare to Arctic glacier work? Could ligands be outcompeted by particle scavenging? (Ardiningsih et al., 2020
<https://doi.org/10.1016/j.marchem.2020.103815>)

R: It is possible that particle surface sites are responsible for the large excess of ligands in the fjord, especially in the Fall. However, our samples are filtered of particles >0.4 μm , thus we would not observe this. In the Fall, a greater $L_{\text{c}}:d\text{Fe}$ ratio compared to late-Spring, combined with a lower average conditional stability constant of the ligand pool results in a lower complexation capacity and inferred ability to compete with particle binding sites. However, we might then expect for the fraction of dFe and LpFe to reflect a greater enrichment of particles, which is not observed.

A sentence to this effect (with citation) will be added to the revised manuscript.

636-637 so the excess (strong?) ligands originate from Bransfield Strait? Not clear

R: It is possible that the ligands originate from outside the fjord, or there is a source common to these coastal regions. We will add text as to the possible sources of the ligands considering recent literature. For example, exopolymeric substances (EPS) are a well-defined pool of strong ligands present at high concentrations in sea ice (Lannuzel et al. 2015). Following sea ice melt, these ligands, presumably in far excess of dFe in sea ice, could be released into the surface waters. A short discussion on the [potential] sources of ligands will be included in the subsequent version.

642-643 Not necessarily, only if ligand induced dissolution occurs which is not demonstrated here

R: The sentence is made more speculative.

650-660 some general global implications regarding ligands are mentioned, but what is the insight generated from the current data?

R: We will keep the first couple of sentences here, and then focus our discussion to this study. We believe the most important finding is the seasonal change in quality and quantity of ligands. In the bloom initiation, overall ligand strengths are higher than in the Fall. However, concentrations of ligands increase following the bloom. Concurrently, dFe concentrations increase and do not saturate the ligands to the same extent as in late-Spring. This is due to a lower complexation capacity of the ligand pool resulting from a considerably weaker ligand pool. Therefore, the dFe pool in the Fall is more subject to boundary scavenging (as free Fe).

663 what is the relation between icebergs, vertical shear and katabatic winds?
Mentioning of icebergs seems out of place here

R: For clarity, mention of icebergs is removed. The line of thought is that icebergs would provide additional shear and thus, mixing with katabatic winds and “stir” the upper water column.

665 what is meant with ‘export the surface layer efficiently’

R: ‘Efficiently’ is removed.

679 export of surface water?

R: Yes, surface water. Resolved.

682-697 what is the point of this exercise were Fe is assumed to behave conservatively (i.e. like $\delta^{18}\text{O}$ used to estimate the meltwater fraction) whereas we know it does not, especially not in a productive region. The final statement (it is expected that the input of glacial meltwater throughout the melt season would supply some dFe to the surface) could have been made without this section.

R: The high concentrations of organic ligands found within the fjord offer a possible means of stabilizing a significant fraction of dFe. The modeling study provided insight on the distribution of dFe throughout the fjord region and thus

local variations in dFe availability for primary producers. However, we will leave the final statement and take this opportunity to reduce the text length since a comparison to the Gerlache Strait is not needed when the results are too variable.

698-723 this whole section does not contribute a single insight into the biogeochemical cycle of Fe (or new insights into the actual dispersion of melt water), so what does it contribute to the ms?

R: We included this section to highlight the limitations of using the dye experiments to model the dispersion of surface glacial meltwater. This text will be condensed and moved to the supplementary as we think it is important to consider. The main text will mention that the limitation of using the dye experiments are discussed in supplementary under a heading to that effect.

700 the $\delta^{18}\text{O}$ approach should differentiate between meteoric and sea ice melt so the MWf should not be influenced by sea ice melt.

R: The modeled meltwater flux is different than the flux inferred by isotopic mass balance. The issue with the mass balance estimate is that export of meltwater implies non-steady state conditions and will result in an underestimate of meteoric input to the fjord. Pictures from the glacial cameras displayed large amounts of icebergs lingering in the fjord over long periods, which is a likely source of meteoric meltwater that cannot be modelled and was attempted to be parameterized with the modelled meltwater flux. The modeled flux “best recreates observed salinity and temperature profiles in Andvord Bay...over 4 months (Hahn-Woernle et al. 2020).” (line 703)

724-729 this section I found very confusing; dFe observations were made prior to a wind event; the model predicts upwelling if there is wind and the model results of upwelling are supported by the observations prior to upwelling? Also, how am I to see the elevated dFe in late spring at station S3 in fig3? No stations are labelled and the color scale is more or less homogenous (all blue).

R: Station S3 has been added to fig. 3. Multiple re-occupations of S3 during the late Spring cruise (LMG15010) showed elevated surface dFe concentrations following the Dec. 10 wind event. We refer to the supplemental for dFe concentrations to demonstrate an increase in concentration in the surface during the late Spring cruise: $[\text{dFe}]_{\text{avg}}$ (prior to Dec. 10) = 3.19 nM; $[\text{dFe}]_{\text{avg}}$ (after Dec. 10) = 4.14 nM (compared to average surface value within the fjord = 2.47 nM;

line 289). We use dFe observations prior to upwelling with the model-derived vertical velocities to derive the upwelling Fe flux.

The color scale will be modified to highlight the variability in [dFe] in the late Spring.

746 Only if Fe remains in solution and is not taken up by phytoplankton along the way, do we know anything about this?

R: The length-scale for dFe in productive surface waters is typically very short (e-fold length-scale ~25 km.). Thus, with some distance from the continental shelf, much of the dFe may be removed if not stabilized as nanoparticles or organic ligands. Annett et al. (2017), show for the '600 line' on the PAL LTER sampling grid, concentrations of dFe decrease from ~0.9 nM to 0.1 nM within 30 km of the coast. The authors suggest organic ligands are responsible for stabilizing a consistent 0.1 nM dFe over the entire continental shelf. However, we believe that since sampling occurred during peak bloom conditions, that biological removal is the primary control of concentrations in this location.

From our study, we note that Station B (Fig. 1) located on the continental shelf has a surface dFe concentration of ~1.2 nM in the Fall. This instead could represent the late-productive season concentration remaining in surface waters following replenishment from coastal sources. This could be confirmed by measuring the organic ligands from these shelf waters.

756 this point was just made in line 734

R: We make the distinction between vertical mixing (diapycnal) and localized upwelling (displacement of subsurface waters). Both processes are consequences of the katabatic winds investigated in the dye experiments.

768 what geochemical data?

R: This statement has been revised. At present, the Mn:Fe geochemical data does not allow us to distinguish sedimentary versus subglacial sources since distinct oxidation kinetics of Fe and Mn will alter these endmember ratios towards higher values.

774-775 confusing sentence; export of subsurface dye leads to a low surface concentration due to proximity to the surface?

R: Upper ocean physics is controlled by the katabatic winds, which exports the surface layer across the fjord mouth. Thus, subsurface water entrained into the surface are also subject to export resulting in low concentrations within the fjord. We will re-phrase.

775 'The upper ocean is more subject to changes in the upper ocean dynamics' that seems like an open door to me...

R: Changed to "subject to changes in wind stress."

783 not sure it was shown, more argued / suggested

R: Changed to "argued."

786-787 how does the comparison of dFe and the meltwater fraction in fig 3 'support to the modeled dynamics' ?

R: Elevated concentrations of dFe and meltwater are found within the inner fjord and at Sill 3. Both of these locations are identified as places where upwelling of subsurface water masses, potentially containing subglacial plume water, occurs. This explanation is added to the text.

807 why would intensifying coastal currents lessen the likelihood for pulsed export of meltwater-derived Fe?

R: Coastal currents develop fronts that prevent lateral exchange. The strength of these fronts is dependent on the densities of coastal currents relative to the meltwater-influenced water masses.

826 where is Barilari Bay and why is it relevant?

R: Barilari Bay is a fjord containing tidewater glaciers influenced by warm (above-freezing) ocean temperatures, yet is similarly productive to Andvord Bay. The location of Barilari Bay is now briefly described in the text.

828-829 how can a single wind event along the WAP export 36 km³ of meltwater if the total Antarctic meltwater discharge is only 32.5 – 97.5 km³ yr⁻¹?

R: The focus of the Pattyn et al. (2010) is on modeling basal melt production due to geothermal heating. This estimate does not consider basal melting of ice shelves in contact with warm ocean water and is therefore an inaccurate (low)

estimate for total meltwater. Since Pattyn et al. is unrealistic, we will compare more recent, improved estimations of meltwater flux.

833 also larger than the total annual meltwater discharge. Something is incorrect or very unclear

R: See previous comment.

843 why would a phytoplankton bloom lead to decreased ligand concentrations, not clear and contradictive to section 4.5

R: Since increased turbidity is expected to decrease the magnitude of local phytoplankton blooms, the source of ligands decreases. The sentence is re-phrased: "To a first approximation, decreases in the magnitude of local phytoplankton blooms and associated ligand sources is expected to reduce efficacy of solubilization of particulate Fe and natural fertilization downstream resulting from this leaky fjord."

Citations not included in main text, referred to in comment responses:

Kryc, K. A., Murray, R. W. and Murray, D. W.: Al-to-oxide and Ti-to-organic linkages in biogenic sediment: relationships to paleo-export production and bulk Al/Ti, *Earth Planet. Sci. Lett.*, 211(1), 125–141, doi:[https://doi.org/10.1016/S0012-821X\(03\)00136-5](https://doi.org/10.1016/S0012-821X(03)00136-5), 2003.

Dinniman, M. S., St-Laurent, P., Arrigo, K. R., Hofmann, E. E. and van Dijken, G. L.: Analysis of Iron Sources in Antarctic Continental Shelf Waters, *J. Geophys. Res. Ocean.*, 125(5), e2019JC015736, doi:<https://doi.org/10.1029/2019JC015736>, 2020.

Krisch, S., Hopwood, M. J., Schaffer, J., Al-Hashem, A., Höfer, J., Rutgers van der Loeff, M. M., Conway, T. M., Summers, B. A., Lodeiro, P., Ardiningsih, I., Steffens, T. and Achterberg, E. P.: The 79°N Glacier cavity modulates subglacial iron export to the NE Greenland Shelf, *Nat. Commun.*, 12(1), 3030, doi:10.1038/s41467-021-23093-0, 2021.

Burdige, D., and Christensen, J.: Iron biogeochemistry in sediments on the western continental shelf of the Antarctic Peninsula. (submitted to *Geochim. Cosmochim. Acta*).

Lannuzel, D., Grotti, M., Abemoschi, M. L. and van der Merwe, P.: Organic ligands control the concentrations of dissolved iron in Antarctic sea ice, *Mar. Chem.*, 174, 120–130, doi:<https://doi.org/10.1016/j.marchem.2015.05.005>, 2015.