

Interactive comment on “Potentially Bioavailable Iron Delivery by Iceberg-hosted Sediments and Atmospheric Dust to the Polar Oceans” by Rob Raiswell et al.

Anonymous Referee #2

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This is a very well and logically written paper which deals with an aspect of the iron cycle which is poorly constrained, namely the flux of iron coming from particulate sources to the polar oceans. I find the paper a comprehensive and informative synthesis of the current knowledge in this area, with useful new data informing the different iron fluxes. A key strength of this paper is that it also establishes the uncertainties on these fluxes and the areas where future research is needed. The end result is pleasingly robust, clearly laying out uncertainties and making good use of statistical tests for determining reproducibility. As such I recommend publication of the manuscript, subject to the authors addressing the following major point and considering the minor changes.

We thank the referee both for the encouraging and supportive comments, as well for the constructive suggestion to consider anthropogenic sources. We accept that our focus on mineral dust alone is likely to underestimate the supply of potentially bioavailable Fe and we will add relevant material as follows to estimate potential combustion sources. Line numbers refer to those identified by the referee, whose responses are given in italics to differentiate them from our responses.

Major point:

I just have one major comment - The paper assumes all dust to be low in solubility based on their samples. However, there are two issues with this –

Firstly, although dust solubility is open to interpretation, a number of studies have shown that anthropogenic dust sources may be important, and even more important in some areas of the globe - e.g. iron from combustion, biomass burning etc... e.g. Sedwick et al., 2007 (10.1029/2007GC001586), Luo et al., 2008 (10.1029/2007GB002964) Ito et al., 2013 (10.1029/2012GB00437), Ito 2015 (10.1021/acs.estlett.5b00007) to name just a few. . . This delivery of anthropogenic aerosols is likely to be highly variable and

as such may not be captured by a small number of samples or from natural sources – that seems especially likely if there is no high Fe solubility in your aerosol samples as would be expected for anthropogenic Fe (e.g. Sedwick et al., 2007; up to 19%; 10.1029/2007GC001586). If this is the case, then dust sources in your paper may be seriously underestimated– indeed a recent study attributed sporadic high deposition of soluble Fe to Antarctica from biomass burning and it could be the dominant particulate dust Fe source to the Southern Ocean (Winton et al., 2016; 10.1002/2015GB005265.; Ito et al 2015). By only assuming low Fe solubilities, the paper seems to miss this possible Fe source.

Secondly, but by using dust samples from other areas of the globe, it may be that you are poorly representing Antarctic dust, especially combustion Fe sources. I would say that the integrated composition of dust delivered to the Southern Ocean is probably not very similar to the dusts sampled in this manuscript. So while I realize that it is difficult to draw any strong conclusions about the effect of anthropogenic sources of dust to the polar oceans based on your dataset, I think it needs discussion in the paper in the context of uncertainties on the dust flux being calculated.

We will review the suggested literature with respect to anthropogenic sources. We will make the point that our ascorbic acid extractable iron data (FeA) probably represents mineral dust that has undergone little atmospheric processing. This FeA data produces a flux of 0.14 to 0.64 $\mu\text{mol}/\text{m}^2/\text{yr}$ to the SO (assuming an area of $19 \times 10^6 \text{ km}^2$). Estimates have also been made of soluble Fe fluxes of 0.3 to 2.0 $\mu\text{mol}/\text{m}^2/\text{yr}$ to East Antarctic snow (Edwards and Sedwick, 2007; using 0.01 M HCl) and 0.64 to 2.5 $\mu\text{mol}/\text{m}^2/\text{yr}$ to the Baseline Sector of the SO (> 45°S) receiving dusts sampled at the Cape Grim station (Winton et al., 2015; using ~ 4M acetic acid with hydroxylamine hydrochloride). Both sites are believed to have sampled clean air with little anthropogenic addition and their low flux estimates match our FeA flux data. Winton et al. (2016) found a flux of total dissolved Fe (2.5 $\mu\text{mol}/\text{m}^2/\text{yr}$) at Roosevelt Island, using a 1M HCl leach. Fe was considered to be delivered by local and remote dust sources augmented by combustion sources. Comparisons are difficult due to the different methodologies used to determine solubility but our ascorbic acid leach is at a relatively high pH, compared to the other leaches, and has tended to produce lower Fe data compared to estimates from clean and contaminated samples. We suggest that our FeA data provide a reasonable benchmark to compare to mineral dust and iceberg fluxes delivered to the SO, bearing in mind the uncertainties in the solubility methodologies, the analytical data and the flux estimates.

Estimates of combustion iron sources are very dependent on the model assumptions, especially for solubility. Luo et al. (2008) show maps of the global variations in the ratio of soluble Fe from combustion to total soluble Fe. This ratio ranges from 10-40% % in the SO (>60°S) and 20 to 60% in the AO (>60°N). Ito (ETSL v.2, 70-75) also suggests that the soluble Fe from dust contributes around 50% of the total soluble Fe flux to both the SO and the AO. We will add this material to the text and annotate the table to indicate that our FeA flux represents mineral dust little influenced by combustion sources, and may thus underestimate supply to

the SO and the AO by up to 50%.

There are also a small number of minor comments that require the authors attention:

L17 I think 'dusts' could be 'dust' here and in other places. Dust is usually used as a plural. But at authors discretion

Line 17. We will change dusts to dust.

L23 What about other forms of iron in dust? Think it would be good to make this clearer here. Nanoparticulate Fe is unlikely to be the only bioavailable form.

Line 23. We shall add as follows to line 18. '.....nanoparticulate ferrihydrite. Ferrihydrite is the most soluble and potentially bioavailable iron (oxyhydr)oxide mineral and can be extracted by ascorbic acid in contrast to other forms of iron (lepidocrocite, goethite, hematite) that are less soluble. However these may be solubilised by further processing in seawater, e.g by grazing' (see our line 210).

L39 There are recent Fe-isotope informed calculations for multiple sources also –eg. Conway and John 2014 (doi:10.1038/nature13482). I think this would be a valuable citation here, especially as an emerging approach to constraining different sources of dissolved Fe, including dust and particulate bound Fe.

Line 39. Good idea. We will add these citations and explain that isotopes have potential to constrain the different sources discussed here.

L42 I think you can remove the ' prior to iceberg-hosted'

Line 42. 'the' will be removed, as suggested.

L74 The Tagliabue reference should be 2016?

Line 74. 2015 will be amended to 2016.

L79 of' Antarctica would read better.

Line 79. 'of' will replace 'in' as suggested.

Lines 147-150. Some more detail of collection would be good here. How was the window cleaned etc? There is not detail of how the med samples were collected. It's important to demonstrate that these samples were obtained cleanly.

Line 147-150. The collection of bulk samples such as these after dust storms from clean surfaces are unlikely to be significantly affected by contamination, and such samples have been utilised in other studies (see for example Shi et al., 2009, Env. Sci Tech., 43, p. 6592 and Herut et al, Limnol. Oceanog., 47, p.871.

L158 Needs a space before 10

Line 158. Space can be added.

L162 What is 2-line and 6-line ferrihydrate? Might be worth clarification for the reader.

Line 162. We shall add as follows. Ferrihydrite only exists as a fine grained and highly defective nanomaterial. The chemical formula is indeterminate but approximates to $\text{Fe}_4\text{HO}_8 \cdot 4\text{H}_2\text{O}$. The diffraction pattern contains two scattering bands (2-line ferrihydrite) in its most disordered state, and a maximum of six strong lines (6-line ferrihydrite) which result from differences in the size of the constitutive crystallites (Hiemstra, 2013). The two-line form is also called hydrous ferric oxide (HFO).

L184 This section misses references and coverage of other techniques which post date the Jickells and Spokes work (it is quite an old study now...) for leaching dust – such as ultrapure water leaches or seawater or acidic leaches, as carried out by American groups such as Sedwick et al. or Buck/Landing et al. or the Conway et al study you cite - and as such rather underrepresents the dust solubility literature.

Line 184. We will expand this section to compare the relative merits of ultra-pure water leaches (Sedwick et al., 2007; Winton et al., 2015), seawater leaches (Conway et al., 2015) and the hydroxylamine hydrochloride leach (Berger et al, 2008; Winton et al., 2015).

L325 This is a long sentence, please add a comma after sources
Line 325. Comma can be added after 'sources', as suggested.

L344 Conway et al also appear to show some seawater-leached data for the Dome C samples.

Line 344. The seawater leach data ($0.15 \pm 0.13 \text{ mg/m}^2/\text{yr}$) were not significantly different from the pH 5.3 meltwater leach data ($0.09 \pm 0.17 \text{ mg/m}^2/\text{yr}$) which does not appear to be important in this context.

The sentence is also a little clunky. . .perhaps change to have 'to measured' and remove data'. These samples are a useful citation, but of course miss any modern anthropogenic sources – might be worth making this point.

We will make the changes suggested and add the point about missing anthropogenic sources

L353 Double.

Line 353. We will add 'more than double', as suggested.

L364 See my major point about anthropogenic sources.

Line 364. Yes, we should point out that this excludes anthropogenic sources. See above material that we will add.

L376. Can you also present this as an Fe solubility percentage in terms of total Fe, that would make comparison to other work easier. Same for Table 5?

Line 376. The fractional solubility estimates are given in line 338-339 and are based on an assumed total Fe content of 3.5%, and so are not tabulated.

