

Interactive  
Comment

# ***Interactive comment on “An assessment of the vertical diffusive flux of iron and other nutrients to the surface waters of the subpolar North Atlantic Ocean” by S. C. Painter et al.***

**S. C. Painter et al.**

scp@noc.ac.uk

Received and published: 3 February 2014

Response to Reviewer 1

This is an excellent paper which reports the vertical diffusive fluxes of iron and other nutrients to North Atlantic subpolar gyre. The main finding of the paper is that these fluxes represent only minor contributions to the surface waters and to the biological requirements. The oceanographic techniques are rather outside my expertise and others will have to comment on these details. My review will therefore be confined to more general aspects of the iron cycle. In this respect I find the paper to be a valuable contribution which is essentially publishable in its present form with amendments as

C8411

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



suggested below. However the oceanographic work in this field often takes for granted some assumptions which are not soundly based.

A: We thank Prof. Raiswell for his time and assessment of this paper and address his comments below.

Firstly, the use of the term 'dissolved Fe' or dFe needs to be accompanied by an explanation that much of what is measured after filtration is not aqueous species but nanoparticles and/or colloids (depending on the filter size, see comments below). There is an abundant literature on this (a recent example is Fitzsimmons and Boyle, *Geochim Cosmochim Acta* 2014). The problem is that the dFe data is usually, as here, interpreted as though chemical effects alone are responsible for the observed changes, whereas in fact nanoparticles and colloids behave quite differently for example in aggregating (which may transfer material from being filterable to being trapped) and in transforming mineralogy (which may affect leaching characteristics). Nanoparticles and colloids also diffuse more slowly (a 10 nm nanoparticles diffuses an order of magnitude more slowly than an ion). I am not suggesting that the authors attempt to deal with this problem but a few lines of caution are necessary to make the reader aware of the inherent assumptions.

A: In the context of the observations reported in this study 'dissolved Fe' or 'dFe' is taken as the measurable iron concentration following filtration through a 0.2  $\mu\text{m}$  filter (Sartobran 300 MF). This methodological detail was absent from the original submission and has now been added to the methods section (Section 2.3). The broader issue of what dFe actually represents and how changes in concentration can be interpreted however, is a particularly thorny issue as the Reviewer notes (and has recently described; Raiswell and Canfield 2012). To address this we have added the following sentence to Section 2.3 to clearly state what our assumptions are "In the following we assume the measured dFe concentration represents the concentration of aqueous Fe in seawater. This however is a simplification as the Fe pool in the <0.2  $\mu\text{m}$  size fraction is composed of aqueous, colloidal and nanoparticle species with different

BGD

10, C8411–C8418, 2014

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



physico-chemical properties (Raiswell and Canfield 2012).

Secondly, a general comment is that the oceanographic papers dealing with the iron cycle rarely adopt a comprehensive view of the processes that contribute to iron supply; references below make this point. This is not a major issue for this paper but it helps to perpetuate a very selective view of the iron cycle. Comments below are keyed to page and line numbers.

A: In focusing upon the turbulent diffusive supply mechanism in this paper we have necessarily reduced the level of detail concerning many other supply processes. This does not exclude the importance of these other processes from iron budgetary calculations and whilst we have quantified what we consider to be the major supply terms (aeolian input, convective mixing) for contextual purposes, we have not been able to fully incorporate all aspects of these and other supply terms (e.g. lateral transport) into this study; such as would be required for a full iron budget calculation. In part this is due to the different timescales over which supply processes operate, but which can be potentially very important on seasonal, annual or decadal timescales. The Reviewer is also right to raise concern over the more general and widespread simplification of the iron cycle and we address this through our responses to the comments below.

General comments: P18519 lines 18-20. The term local continental landmasses suggests a riverine source but I think the authors mean to refer to shelf sediment recycling (which is the Elrod reference). There are also more recent important references relevant to shelf recycling by Lam (Geochim Cosmochim Acta, 2012 and previous Lam papers referenced therein). There are also likely to be other sources to the Irminger Basin from Greenland meltwaters and icebergs which should be noted here. Bhatia et al (Nature Geoscience, 2013 and references therein deal with Greenland meltwater fluxes). This paper is cited later but should be introduced here, as should iceberg input which is dealt with briefly by Wadham et al Transactions Roy Soc Edinburgh) for Greenland and Raiswell and Canfield in Perspectives vol. 1 (on the EAG website). Hydrothermal inputs are also likely (see Saito et al in Nature Geoscience 2013 and

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Tagliabue et al in Nature Geoscience 2010).

A: We thank the Reviewer for highlighting these references, which are undoubtedly relevant to the matter at hand, as well as being important studies in their own right. We have modified the text of last paragraph of the introduction to incorporate them and other references as follows “Fe limitation may be alleviated following the addition of Fe from a number of different sources and through a variety of mechanisms. This can include aeolian dust deposition (Jickells et al., 2005; Mahowald et al., 2009), volcanic ash input (Watson 1997; Duggen et al., 2010), the supply of Fe from local continental shelves (Elrod et al., 2004; Planquette et al., 2007; Lam and Bishop 2008; Lam et al 2012), physical supply from the deep ocean (Watson 2001), hydrothermal input (Tagliabue et al., 2010; Saito et al., 2013) and more localised processes such as input via glacial meltwaters and iceberg carving (Statham et al., 2008; Bhatia et al., 2013; reviewed by Raiswell and Canfield 2012).

P18519 Line 22. True that aeolian supply is often considered to be the dominant supply but this view ignores the potential inputs mentioned above. A more cautious statement is required.

A: Although not explicitly stated in the original sentence we have now modified the statement to indicate that aeolian supply is not always dominant as follows “In most remote oceanic areas the aeolian supply is considered the dominant input of Fe (e.g. Croot et al., 2007) but the magnitude and even the significance of this supply term can vary regionally, seasonally and interannually (Jickells et al., 2005; Mahowald et al., 2009; Okin et al., 2011).”

P18521 line 18. What was the filter size? See comments above. Make it absolutely clear what has been measured; which will likely be a mixture of aqueous species, nanoparticulates and/or colloids. It may be best to do this on page 18526 line9.

A: In the context of the observations reported in this study ‘dissolved Fe’ or ‘dFe’ is taken as the measurable iron concentration following filtration through a Sartobran 300

**BGD**

10, C8411–C8418, 2014

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



MF 0.2  $\mu\text{m}$  filter. This information is now added to Section 2.3 (see response above).

P18524. There is a Caero in equation 3 and a CA in equation 4. Are these different? Clarify.

A: These terms are the same. We have now corrected equation 4 for the inconsistency.

P18526 line 25 on. The subsurface minima and maxima are interesting and may result from the behaviour of non-aqueous Fe species (nanoparticles and/or colloids). Take a careful look at the Fitzsimmons and Boyle paper to suggest other explanations apart from remineralisation. This behaviour reinforces my point about the difficulties in only interpreting dFe in terms of aqueous species.

A: Our interpretation was based on the assumption that the measured dFe pool was represented by aqueous Fe species. In truth, this is a simplification and does not consider the role of nanoparticles or colloidal species, both of which are likely to have been present in the  $<0.2 \mu\text{m}$  fraction. Neither did our interpretation take into account depth related changes in the relative contribution of colloidal Fe, aqueous Fe and nanoparticulate Fe to the dFe pool nor whether there was in fact any difference in the bioavailability of these species with depth. A number of recent studies (e.g. Fitzsimmons and Boyle 2014) hint at such scenarios. Although it is possible that the presence of a subsurface maximum in dFe is linked to a local accumulation of biologically inaccessible nanoparticles we consider this implausible due to the substantially higher concentration of dFe measured at the subsurface maximum, and the requirement for this accumulation to be actively maintained over timescales longer than those of physical mixing/diffusion processes which would act to dilute the signal. Under these conditions remineralisation is the most likely cause.

P18527 line 9. There are also problems because the diffusion of nanoparticles and colloids is much slower than aqueous species. Given the influence of turbulence I guess this is unimportant but see comments above.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

A: Although this is an important detail about the composition of the filtrate upon which we measured dFe it is unlikely that differences in the rate of diffusion by the various species will manifest itself as either a subsurface maximum or minimum in a profile of dFe. The constant action of turbulent diffusion, coupled with other physical mixing processes, would in the first instance make no distinction between aqueous and colloidal forms. This suggests that such maxima/minima are biologically driven but to what extent the relative ratios of aqueous, nanoparticle and colloidal forms are biologically altered in the regions of local dFe maxima/minima remains unknown.

P18528 line 11. Presumably P-rich arctic outflow refers to riverine/meltwater flow. See comments above about these sources.

A: The P rich Arctic outflow is ultimately derived from the P rich Pacific waters that flow into the Arctic Ocean. Recent nutrient mass balance calculations by Torres-Valdes et al., indicate that riverine input to the Arctic accounts for ~7% of the P exported from the Arctic to the Atlantic. Torres-Valdes, S., T. Tsubouchi, S. Bacon, A.C. Naveira-Garabato, R. Sanders., F.A. McLaughlin, B. Petrie, G. Kattner, K. Azetsu-Scott and T.E. Whitledge (2013). Export of nutrients from the Arctic Ocean. *Journal of Geophysical Research* 118, 1625-1644, doi: 1610.1002/jgrc.20063.

P18532 line 23. Scavenging or aggregation. Aggregation would material from the filtrate to the filter, see above.

A: In this sentence the word scavenging is used as a catch-all term to denote both the adsorption of dAl onto individual diatom frustules and the subsequent aggregation and sinking of multiple frustules out of the surface ocean. In other words, the term scavenging is used to denote the transfer of trace elements from the dissolved phase to the particulate phase.

P18533 line 5. Other inputs may also influence the observed seasonal changes. Inputs from shelf recycling will result from episodic re-suspension events, also there may be seasonal effects from meltwater and icebergs. Iceberg melting supplies nanoparticu-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

late Fe (oxyhydr)oxides that would contribute to dFe measurements (see Raiswell et al., *Geochem Trans*, 2008).

A: True. We now have modified the text as follows “ There was no geographical pattern behind the increases or decreases and unlike the macronutrients, which are predominately supplied from below, Fe can be resupplied from a number of sources. It is interesting that a similar pattern was not apparent in the dAl data, which suggests that the ambiguous seasonal change in dFe cannot be linked to the resupply of Fe from a single supply process (e.g. atmospheric input), and that individual stations may have been influenced to a greater or lesser extent by different supply mechanisms.”

P18537 line 5. It might be more bioavailable if the diffusive flux represented a different mixture of aqueous, nanoparticulate or colloidal species, with more of the smaller size fractions. P18538 line 1. Agreed, most likely bioavailability. See earlier comments

A: The relative bioavailability of the diffusive flux remains unknown but is, in our opinion, an important factor that should be explored further. We have revised P18537, Line 5 to include the suggestion/interpretation provided by the Reviewer as follows “More fundamentally however, there is no reason to assume the diffusive flux would be preferentially assimilated over the in-situ standing stock unless the diffusive supply were in some way more bioavailable, perhaps, in the case of Fe, as a result of differing mixtures of aqueous and colloidal species”

P18539 line 13. Yes, glacial and meltwater sources are possible, as is shelf recycling.

A: We have modified this sentence to clearly distinguish meltwater from sediments as a potential source term as follows “Only when the influence of Greenland was encountered did this trend reverse indicating the presence of a significant source of dFe to the water column from a terrestrial (via glacial meltwater; Bhatia et al., 2013) or shallow marine source (e.g. shelf sediments; Elrod et al., 2004; Planquette et al., 2007), which did not extend far into the Irminger Basin as noted in similar studies (Johnson et al., 1997; Elrod et al., 2004).”

**BGD**

10, C8411–C8418, 2014

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



P18540 line 5 to 15. A valuable point to make.

A: Thank you.

---

Interactive comment on Biogeosciences Discuss., 10, 18515, 2013.

**BGD**

10, C8411–C8418, 2014

---

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

C8418

