

Dear Editor,

In our response to 'reviewer 2', we will present our direct responses in 'bold' preceded by '>' in case of formatting problems:

1. Page 3, line 14-15 and Page 10 line 8. Wu and Luther (1995) should be cited here together with Rue and Bruland (1995) and van den Berg (1995).

> Acknowledged and addressed

2. Page 3, line 11. Wu et al (2001) should be cited.

> Acknowledged and addressed

3. Colloidal Fe is a significant portion of total dFe but has not been represented in the model. How would the colloidal Fe affect the model result?

> One could imagine that FeP is a component of colloidal Fe, but of course we do not consider any organic complexation or fast cycling of this pool. This has been suggested in some studies so we will add some text to mention this.

4. The rates of reactions involving various Fe species (kphW, kphS, kIS, kbS, kpcp and kr) are not accurately understood. What is the sensitivity of the model to range of uncertainties for these rate constants?

> The non-photochemically driven rates of iron-ligand complex formation are relatively well known for a range of ligands (e.g. Witter et al, 2000), and the dissociation rates can then be inferred from the conditional stability constants. We agree that especially the photoreduction rates of organically-bound iron kphS and kphW are still very uncertain (one of the few references is Powell and Wilson-Finelli 2003). The noon concentration of Fe(II) that we reach is very likely to scale approximately linearly with these parameters. The sensitivity to the scavenging rate has already been studied quite a bit (e.g. Parekh et al. 2004). It mostly affects the deep-sea concentration of dissolved iron and is unlikely to affect the speciation near the surface, since the rate is much lower than other rates (photochemical reduction, oxidation, ligand formation) here. It also worthwhile to note that the exact same Fe chemistry model we have used has already had its sensitivity to a number of parameters tested in previous studies (Tagliabue and Arrigo, 2006, JGR, Tagliabue et al. 2009, GBC). The text has been modified to reflect this important question.

5. The bioavailability of various Fe species, especially colloidal Fe and FeLw and FeLs, is not well understood and will influence the model result.

> The reviewer is correct here. It could be that different phytoplankton species are able to access different pools, or that all pools are potentially available but with varying affinities. We have made a discussion of this in Sec 5.4. Moreover, when we discuss the impact of speciation on bioavailability in our results, we try to consider the impact of uncertainties regarding the nature of the bioavailable Fe pool. We will nevertheless add text that reiterates the uncertainty associated with this issue and how laboratory experiments could aid in model formulation.

6. Page 10, line 24, equation 19 may have a problem. Vertical profiles of Fe-binding ligands show that the ligand concentration increases with depth similar to dFe. However, the equation 19 shows that the ligand decreases with depth like DOC. DOC is very low in the deep ocean where Fe-binding ligand concentration is very high.

> This is correct. We do have a 'background' ligand concentration that corresponds to the refractory DOC pool or the intercept of the Ligand versus labile DOC plot. We do include specific discussion of weaknesses in this parametrization in Sec 5.2, but will add more text mentioning known ligand distributions. Some more recent ligand data appears to show subsurface and near surface maxima in ligand concentrations that decrease to a 'background' minima at depth (e.g., Ibanmi et al., in press ; Thuroczy et al., 2011), which is not dissimilar to the DOC profile. Nevertheless, the reviewer is correct that a more mechanistic parameterisation of ocean Fe binding ligands is a key next step (as we mention in Sec. 5.2).

7. In general, I am not convinced that including Fe speciation in the climate model will be useful. This is because in Fe limited region, the bioavailable Fe flux to the euphotic zone is strongly influenced by upwelling

from the subsurface ocean where Fe speciation is relatively constant. Essentially all the Fe supplied to the surface ocean in the Fe-limited region is used up biologically. Thus, it is the subsurface ocean Fe flux rather than Fe speciation that controls the climate.

> In our simulations under climate change we examine the results normalised to the dFe concentration, thus we see significant changes in the speciation of the dFe pool independent of any changes in supply rate. Moreover, these changes in supply are accounted for in our model by coupling our Fe model to the global ocean biogeochemical model NEMO-PISCES. We do not posit that changes in the Fe speciation control the climate, only that climate change and ocean acidification can potentially drive a significant change in the speciation of the ocean's dFe pool at high latitudes. This change in the dFe pool's speciation could have important implications for future Fe uptake strategies exhibited by phytoplankton in Fe limited waters. A larger component of un-complexed dFe would make an uptake strategy that eschewed organic Fe in favour of inorganic Fe more competitive in the future ocean with knock effects for phytoplankton physiology and perhaps species composition.

References:

1. Wu, J., E.A. Boyle, W. Sunda, and L.S. Wen, 2001. Soluble and colloidal iron in oligotrophic North Atlantic and North Pacific oceans. *Science*. 293:847-849.
2. Wu, J., and G.W. Luther III, 1995. Complexation of Fe(III) by organic ligands in the northwest Atlantic Ocean by a competitive ligand equilibration method and a kinetic approach. *Mar. Chem.* 50:159-177.
3. Witter, A.; Hutchins, D.; Butler, A. & III, G. L. Determination of conditional stability constants and kinetic constants for strong model Fe-binding ligands in seawater *Marine Chemistry*, 2000, 69, 1-17
4. Powell, R. & Wilson-Finelli, A. Photochemical degradation of organic iron complexing ligands in seawater *Aquatic Sciences*, 2003, 65, 367-374
5. Parekh, P.; Follows, M. & Boyle, E. Modelling the global ocean iron cycle *Global Biogeochemical Cycles*, 2004, 18, GB1002
6. Ibsanmi, E., et al., Vertical Distributions of Iron-(III) Complexing Ligands in the Southern Ocean, *Deep Sea Res. II*, in press, 2011.
7. Thuroczy, C., et al., Observation of consistent trends in the organic complexation of dissolved iron in the Atlantic sector of the Southern Ocean, *Deep Sea Res. II*, doi:10.1016/j.dsr2.2011.01.002, 2011.