Biogeosciences Discuss., 4, S1125–S1138, 2007
www.biogeosciences-discuss.net/4/S1125/2007/

Biogeosciences Discussions

Interactive comment on "Iron profiles and speciation of the upper water column at the Bermuda Atlantic time-series Study site: a model based sensitivity study" *by* L. Weber et al.

L. Weber et al.

Received and published: 10 August 2007

General comments

We thank the referees for their constructive remarks, which greatly helped to improve our manuscript. We followed most of their suggestions for minor changes and further made numerous small alterations in the text based on the two reviews.

The two most important changes in the manuscript are:

- Referee ♯1 criticised that we did not include iron limitation of phytoplankton growth in our model. We now redid all model runs with a model version that includes

limitation of phytoplankton growth by iron. Details can be found below and in the the revised manuscript.

- Following a remark by referee ♯2 on the residence time of iron that suggested a comparison of particle concentrations with Deuser et al. (1990), we discovered that a unit conversion error had sneaked into our 1-dimensional model code (albeit NOT into the 0-dimensional version presented in Weber et al (2005)). This error caused inorganic particle concentrations to be a factor of 1000 too high. We regret having submitted a manuscript with a still faulty model. The error is corrected now, and the particle concentrations are in excellent agreement with Deuser et al. (1990), as they had been in Weber et al. 2005.

These two changes forced us to rerun all model experiments again and redo all analyses and figures. Luckily, these changes do not change our conclusions qualitatively, although there are of course quantitative changes. The largest changes are in: a) the estimate of the scavenging residence time, which now agrees better with conventional estimates (Section 7), and b) the magnitude of the change in colloid aggregation rate between the 0-dimensional model and the 1-dimensional model, that is required in order to bring the 1-dimensional model close to observations and to produce reasonable deep iron concentration profiles (Section 5). In the old model version, the colloid aggregation rate had to be reduced by a factor of 1000 respective to the value used in Weber et al. 2005. In the revised model version, the reduction has to be only by a factor of about 10.

The changes in model results are mostly minor, although the modeled inorganic particle concentration decreased by a factor of 1000 between the model versions. This can be explained by the fact that only the sum of biogenic and inorganic particle concentrations enter the model equations (in the expressions for scavenging and colloid aggregation). This sum on average does not change by a factor of 1000, but only by a factor of roughly 4, because biogenic particles dominate the abiotic at the BATS site

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(both in reality and in the new model runs).

We have included two new references: Schartau and Oschlies (2003) and Droop (1983). In addition we have replaced Table 5 by a Figure (Fig. 8).

In the following we list our response to the specific comments of referee ♯ 1 in detail:

Reply to specific comments by Referee ♯ 1

16. Although the authors do conclude with the statement that the strong sensitivity of the model to parameter choices means that "we are far away from understanding the influence of iron in the marine ecosystem", I think that this is a significant problem with the paper and should be addressed far more.

It is true, that the biogeochemistry of iron in seawater is very complex and not yet fully understood. The extremely low concentration of iron in the ocean and its ubiquity as a contaminant makes it difficult to measure. However, we disagree with the reviewer that this is a problem with the paper. A number of processes are known, which is combined into the present study. As we emphasised in the Introduction, the aim of this study is not to reproduce observations with a singel model run, but rather to study the consequence that specific assumptions have for the speciation, concentration and fluxes of iron, and to test whether these consequences are compatible with the few available observations. Therefore, the model outcomes are indeed suitable to investigate some less well-known parameter values and processes.

17. One of the main conclusions I drew from the paper was that the "tuning" of the model parameters to BATS data was very dependent on the physics assumptions. Some parameters used in a 0-D model version of the model (Weber et al 2005) were

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completely wrong for the 1-D version. Which then begs the question of what happens when the model is tried in a 3-D model, and how then between eddy-resolving and non-eddy resolving (especially as much of the biogeochemsitry at BATS appears to be strongly influenced by the passage of eddies). Can some of the inferences made in this 1-D version - the parameter values chosen and their sensitivities - merely be a reflection of the missing physics? In a very first attempt to address this dimensional-sensitivity: what are the results of this version of the iron/NPZD model with Run A parameters, but in the 0-D setup. Do the large parameter changes make a huge (and negative) changes to the 0-D results? It is instructive to see the difference in sensitivities shown in table 4. Possible more should be made of this and an expansion on how additional dimensions will affect these too.

We conducted a 0D model run with the parameter values of the 1D model (Run A), i.e. lower colloidal aggregation and stronger ligands. The results are similar to the 0D model runs with and without colloidal aggregation by Weber et al. 2005. The model runs differs only significantly in spring during the phytoplankton bloom. The higher the aggregation rate, the higher the export via detritus, the lower the concentrations in spring (max 25% difference in dFe concentration between the 0D model run with the initial parameter and the one with Run A parameter in spring and lower than 0.01% difference in summer). However, the concentration of dFe remained in each run in the range of observations. We did not include this result into the present paper, since a similar study is presented in Weber et al. 2005. The question what happens when the model is used in a 3-D model can only be answerd speculatively here. One has to be aware that the present model requires very short timesteps to model the fast chemical reactions, and is thus too costly to be used within larger 3D models. An intermediate model, with a prognostic part of the model for the slow variables, and diagnostic part for the calculation of the speciation of truly dissolved iron diagnostically would solve this problem, but is beyond the scope of the present study. However, we do not believe that the inferences made in the 1-D version are merely a reflection of the missing

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physics. We discussed that in Section 5 (p832, line 18ff).

18. A second mis-giving I have with the model configuration, is that possible iron limitation did not feed back to the NPZD model. The authors state that BATS is commonly thought not to be iron limited, which is why they do neglect iron limitation in phytoplankton nitrogen uptake, yet they do have iron limitation in the iron uptake by phytoplankton. More importantly, using the original 0-D parameter values they land up with very low iron (they found N:Fe ratio unacceptable): would it be as low if the biological uptake was regulated by iron.

Our decision to make the growth of phytoplankton independent from iron was based on two reasons: a) we wanted to focus on the iron chemistry alone and separate this from feedbacks through the influence on the ecosystem, and b) we thought that this is admissible, since BATS is not normally thought to be iron limited, except perhaps for nitrogen fixation, which is not included in our model anyway. The reviewer rightly points out that at least the model run using the parameter set from the 0-dimensional study by Weber et al. (2005) is inconsistent with the latter assumption. We had interpreted this run as unrealistic anyway and had thus not attempted to improve realism by including iron growth limitation. However, it is not true that the vanishing of iron in this run would disappear if biological uptake was regulated by iron, as the reviewer suggests: The biological uptake of iron in this run is negligible compared to the abiotic scavenging and aggregation processes that remove iron from the dissolved phase throughout the water column.
To clarify the potential role of iron growth limitation, we have now included iron limitation of phytoplankton growth in all model runs now. We follow the Droop (1983) approach, making the growth rate proportional to $(Q - Q_{min})/Q_{min}$ where Q is the cellular Fe:N ratio.

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19. It is not entirely clear, either, what form of iron is bioavailable. Is it Fe(III)' or Fe(II)'? - figure 3 suggests Fe(III)', but equations from Weber at al 2005 show the bio uptake coming from the Fe (II)' Is justified that only free iron is bio-available? It seems that at least some phytoplankton appear to take up FeL? Fig.2 indicates that while dFe might always be relatively high in the model, Fe (III)' and Fe(II)' are very low during parts of a 24 hour period, might the free form be limiting some parts of the day-light hours. In the appendix, iron uptake by phytoplankton is modified by iron limitation; why have this here, but not in the nitrogen uptake part of the model? Also - why use dFe and sFe in this μ_{Fe}? If only Fe(III)' is bio-available, why not use that? And why use dFe in numerator, but sFe in denominator? There needs to be further discussion and considerable clarification here. And some calculations that the assumptions (free vs ligand, no iron limitation) do not affect the results. Potentially even further runs if these do prove to be important (see specific comments).

Unlike for the macronutrients nitrate, phosphate and silicic acid, no final consensus has been reached on the species of iron directly taken up by phytoplankton. Although iron uptake in synthetic culture media varies in proportion to the free ferric ion activity and is therefore suggested to be primarily a function of the FeIII' concentration (Sunda and Guillard, 1976; Sunda, 1989; Anderson and Morel, 1982), inorganic iron species comprise only a small portion of dissolved iron in seawater. The bulk of iron speciation is instead governed by complexation to organic ligands (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther III, 1995) and the formation of colloids (Guo et al., 2000; Wells et al., 2000; Wu et al., 2001). A number of laboratory study have now demostrated uptake of organically complexed iron (e.g. Soria-Dengg and Horstmann, 1995, Hutchins et al., 1999, Maldonado and Price, 1999, 2001) through either specialized uptake sites or inducible membrane reductases. However, the availability of the different species of iron seems to depend both on the nature of organic ligands and well as on phytoplankton group (Hutchins et al., 1999). Because of this still limited knowledge, we assume that all truly dissolved iron (sFe: FeL, Fe(II)'

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and Fe(III')) is bioavailable, which might somewhat overestimate the bioavailability. μ_{Fe} only includes sFe ($\mu_{Fe} = \mu^*[\mathrm{sFe}]/(K_{Fe} + [\mathrm{sFe}])$). dFe as numerator was a simple spelling mistake. We corrected that in the paper.

20. Very little connection is made back to the NPZD model. It might be nice to know what order of magnitude the deficiencies in the NPZD model results make on the iron. How sensitive are the results to changes in the NPZD model parameters? Do these sensitivities swamp the iron parameter sensitivities? In which case this tuning the iron parameters is even more problematic.

We agree with the reviewer, that a connection back to the NPZD model would be an interesting and important study. However, the aim of the present study was to focus on the iron chemistry rather than the biology. Therefore we chose an existing well calibrated NPZD-Model, so that the nitrogen cycle is effectively independent from that of iron. That helps to analyse the sensitivity of the iron cycle to parameter changes without the feedback through changing export production. We explained that in the model description (p828). We have now redone all model runs including the role of iron limitation (see reply to comment ♯18). The model results hardly differ at all, except for the model run with the 0d parameter set. Only during spinup, differences become larger than one percent.

21. pg 825 line 3-12: several biogeochemical models (including Dutkiewicz et al 2005, Gregg et al, 2003 (DSR II, 50), Moore et al 2004 (GBC GB4028)) have included iron chemistry in their models - albeit with various simpler chemistry models - most use at least monthly dust forcing, and some even daily. Aumont et al 2006 (GBC, GB2017) has even looked at iron fertilization. I'm not sure it is entirely accurate to say that they cannot address episodic events. Certainly they do not capture diurnal variations in the way that Weber et al do. (As an aside though, it would be nice - but beyond the scope

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of this paper - to see how much of the iron chemistry of Weber et al needs to be kept to look at large scale long term processes: ie. how much are the above modelling studies missing?)

Maybe this statement was indeed a bit simplistic. The cited models (including also the Parekh et al. papers) do differentiate between organically complexed and 'free inorganic' for calculating scavenging losses. But nevertheless, the parameterizations used in these models are geared towards producing a long-enough residence time of iron that is compatible with the deep-ocean distribution of iron, and not the dynamic behaviour of iron chemistry closer to the surface. We have rephrased the sentence in the text.

22. pg 828 line 20: "without feedback through changing export production": but this has to be important to the iron cycling! If you tune model parameters to best match observations - and the observations include a biological uptake dependence - then you need to include this in your model.

See reply to comment ♯18

23. pg 829 line 11-14: not obvious what you are referring to "oceanic type B"

The transmission of light through the water column in GOTM depends on optical water types and have to be prescribed by means of choosing a Jerlov (1968) class. Jerlov (1951) synthesized observational data from surface waters and proposed three different optical water mass types based on three normal transmittance curves. Basically, the clearer the water, the lower the Jerlov Class number. Additionally two intermediate types were added (IA and IB) because a number of oceanic transmit-

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tances fell between the types I and II as for example the oceanic light transmittance in the Sargasso Sea. Based on that a global map of the oceanic water types were introduced. We mention that briefly here now.

24. pg 829 line 16-20: very badly written.

We rephrased the paragraph and checked the grammar.

25. pg 830 section 4: since the iron cycling pays particular attention to the diurnal cycle between Fe(II), Fe(III) and FeL and colloidal forms, it would be good to know how well the NPZD model captures the diurnal cycling of the ecosystem. I assume that it is important to get the hourly uptake of iron biologically as well, if these results are to be believed. (And hence also my concern that if at some point in the day plankton are iron limited, not including this in the model could be problematic).

The model as it is includes a diurnal cycling of primary production and nitrogen uptake through the dependency on irradiance. We have assumed that iron uptake is independent of irradiance, i.e. it continues throughout the night. It is true that the daily cycling of iron speciation might lead to iron uptake being limited at some point during the day, of course depending on the species taken up. However, this does not necessarily imply phytoplankton growth being iron limited, as it is not the instantaneous uptake but rather the cellular iron quota which regulates growth. As mentioned above, we have implemented a dependency of the growth rate on the internal cellular Fe:N quota, following the Droop (1983) approach. The model with this kind of dependency shows no iron growth limitation for the 'standard' set of model parameters.

26. pg 830 section 4: are you using the same parameters in the NPZD model as you

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did in the 0-D case? Or has some additional tuning been necessary here as well?

For the 1D model we used the model by Oschlies and Schartau 2005 (as stated in Section 2, p828, line 5ff). This model was calibrated against observations at BATS by Schartau and Oschlies 2003. Therefore we did not need to do any additional tuning. The 0D-ecosystem-model was based on an earlier 0D model by Schartau et al. 2001. For the 1D model the model by Oschlies and Schartau 2005 is more appropriate here, because it had already been used to study the nitrogen cycle at the BATS site in a 1D context with good results.

27. pg 832 section 5: could you specify what you are assuming as dFe here?

dFe refers to 0.4 μm-filtered samples (see Introduction, p826, line 10). Therefore dFe includes the iron forms FeII', FeIII',organically complexed iron and colloidal iron. This was not very clear expressed by us here. We defined dFe in Section 2 (first paragraph) now, and made it clearer at p832 as well.

28. pg 832 line 15-17: There could also be some significant impact of biological uptake that is, or is not taken into account?

In our model, there is no biological uptake of iron (e.g. by bacteria) below the euphotic zone. Iron is released from the remineralisation of organic matter and is lost from the dissolved/colloidal phase through scavenging and aggregation.

29. pg 833 line 5: "loss losses"

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We corrected that.

30. pg 834 line 10: Do these values compare to observations? If your model results are a little off, how will it affect your decisions here?

The modeled average concentration of particulate organic nitrogen agrees (to within the error bounds) with the values by Deuser et al. (1990, see anser to comment ♯15) in the upper 200 m. Inorganic particle concentrations are only a small fraction of the total (in the new model version after correction of our error), also in agreement with Deuser and coworkers. Lowering the inorganic particle concentrations would strengthen our conclusion that $k_C >> k_S$

31. pg 834 line 17: You could also change "R"...how sure are you about this value. Could you try change it too and see how sensitive results are to this?

The rate of iron release through remineralisation R is not a tunable parameter itself. It can only be changed by either changing the maximum Fe:N ratio in organic matter (which we have done in the paper), or by affecting the remineralisation rate of sinking speed of detritus (which would affect the nitrogen cycle of the model solution strongly, and which we therefore hav not done).

32. pg 835 and 836: section 5.3: I'm not sure that either discussion is a "justification". Yes - these are extremely unconstrained parameters - but still explain why so different in the 0-D case (would be good to run the current version of NPZD/iron in the 0-D case, with these parameter choices, and see how sensitive those results are). Since the 1-D version is so sensitive 8211; what is to say that 3-D won8217;t change these values completely again...in which case what are you really saying about these values?

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Anything?

We have rewritten the section completely.

33. pg 837 section 6: would be nice to know how diurnal cycling of the biology impacts the results of this section as well. How important is biological uptake of the Fe(III)' in the cycles you show here? could you show living-organic iron as well?

The photochemically driven cycling of iron between its different dissolved forms proceeds at rates greatly exceeding the biological uptake, as already described in Weber et al., 2005. The partitioning of dissolved iron into its different species is therefore not affected by the uptake, which however, influences the fate of dissolved iron on longer time-scales. The diurnal cycling of phytoplankton growth is represented by the model, but we have made the assumption that iron uptake is not directly light-dependent. This now becomes clear from the model equations in the appendix.

34. pg 838 line 24: "depencedependencise", pg 838 line 27: "stastablisation" - there are several similar misspellings further on through the text. Maybe a product of a file format conversion? It is in both the web view and the print version. See also 839, line 7, 840 line 10. 841 line17, 842 line 2,4 and pg 839 line 12: "ar" and "simular"

We corrected that.

35. pg 839 line 19-20: but 0.02 for Fe(III)' might be limiting.

See answer to comment ♯25

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36. pg 843 line 21: how specific to BATS is this conclusion?

The majority of dust in the water column of the Sargasso Sea is derived from Saharan dust storms and is deposited following atmospheric dust storms (Duce 1986, Jickells et al. 1998). Transport duration, conditions and processes are believed to alter the chemistry of the dust particles (Spokes and Jickells 1996, Jickells and Spokes 2001, Arimoto 2001) and therefore very specific for each location. Since the model is forced by data for the BATS site we cannot say anything about solubilities at other sites here. We mention this briefly here now.

37. pg 846 line 10: how does this affect the bio-availability of Fe?

The bio-availability is not affected by the reduction of these rates. Weber et al. 2005 already concluded that the uptake is a relatively slow process compared to the rapid iron cycling between its different forms, which mainly depends on the redox-reactivity of iron with respect to superoxide. Reducing these rates by 50% slows down the cycle between Fe(III) and Fe(II)' but does not take away the dominance of these processes, which are still up to two orders of magnitude faster here than all other processes of the iron cycle during the day. Therefore the cycling assures enough supply of iron.

38. pg 848 line 25: "to" would be better "as"

We corrected that.

39. pg 850 Section 9: How specific to the 1-d results are most of these conclusions?

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See answer to comment ♯17.

40. pg 851 appendix: might be nice to include all equations in here... save the reader having to go back to Weber et al 2005.

We see the point that having the full set of model equations together here, instead of just showing the part of the model code that is new with respect to Weber et al., 2005 and Schartau et al., 2005 would be practical for rebuilding the model. On the other hand, the full set of equation fills several pages without adding new insight. Since our model code is included in the freely available code package for the GOTM model (on `www.gotm.net`), and is therefore publicly available, by other means, we think that this is not necessary.

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Interactive Comment