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Interactive comment on "Impact of dust deposition on Fe biogeochemistry at the Tropical Eastern North Atlantic Time-series Observatory site" by Y. Ye et al.

Y. Ye et al.

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Received and published: 1 September 2009

General

We would like to thank both reviewers for the time and considerable effort they put into reviewing our manuscript. Although we do not agree with all comments by referee #1, we think that both reviewers comments were very helpful for improving the paper. Especially the review by referee #1 raises a number of points that criticize our model setup. We think that some central criticisms by the reviewer were justified and have adressed the issues raised:

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- We ran a large number of additional model sensitivity runs varying the ecosystem model parameters, in order to check how strongly our model results are affected by these choices. We also compared our parameter settings to a number of other ecosystem models for the region. The outcome is that the model results are relatively insensitive to most of the parameters, except to the phytoplankton excretion rate.
- We checked our formulation of particle aggregation, described it much more in detail in the text, and performed a set of sensitivity runs with respect to aggregation rates.
- We changed our formulation of the temperature dependency of organic matter remineralization to bring fluxes at depth more into line with sediment trap estimates.
- We performed two more sensitivity studies with respect to the remineralization rate of weak organic iron-binding ligands, and to the re-dissolution of particle-adsorbed iron.
- We included many more data to compare our model results with (including an unpublished profile of dissolved iron from the TENATSO site, thanks to Micha Rijkenberg; NIWA, New Zealand), and eliminated direct comparisons with data sets that are from outside the eastern subtropical and tropical Atlantic.
- We checked again the sources for our parameter choices, and documented them better in the manuscript.
- We extended our modeled region to the upper 1000 m of the water column instead of only the upper 400 m, to be able to better constrain weak ligand dynamics. This also necessitated that we now use a much longer spinup-period for our model runs (25 years instead of 3 years).

In consequence, all model runs were redone and most numbers in the text have changed slightly. However, almost all of our qualitative conclusions are unchanged and we still stand to every result that was stated in the first manuscript version, except to those related to the composition of sinking particulates below the mixed layer. We have also tried to make the presentation of our results clearer than in the first manuscript.

We, however, also think that some of the criticism by referee #1 is based on misunderstandings; this specifically refers to the 'calculation errors' that the referee mentions. Those misunderstandings were based on our unclear writing.

We would like to state at this point that the main aim of our model at present is not to reproduce observations that were made at a specific time as closely as possible, but rather to contribute to process understanding. This is done by implementing in the model hypotheses (e.g. on the source or life-time of organic ligands) that have been put forward, and by checking whether the model outcome is compatible with the few available observations. As more data becomes available from the TENATSO site, we hope to progress to a less qualitative approach.

In spite of the justified criticism in detail we do not agree with the general statement by the first referee that 'it is unclear that the model is valid in the first place', and we will try to make that clear in the following. Below we give a list of how we responded to each of the referee's comments.

General comments:

Were this paper to be published it would represent the 3rd version of the model. I have read the previous two papers and it seems to me that only minor modifications have been made.

The model differs from the previous ones in two major aspects: Firstly we are attempting to describe the origin and fate of organic ligands instead of just prescribing them as in Weber et al. 2007. Secondly, we are attempting to describe vertical particle

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fluxes in more detail (different classes of particles sinking at different rates, modeling of aggregation processes). Moreover rates of several processes have been adapted, in order to describe local processes better, and, in the new version presented in our revised manuscript we also take into account dust as a source of macronutrients, as suggested by the reviewer.

The current model and that of Weber 2007 (and Weber 2005 in turn) have the values for almost all parameters in common. However, the Weber 2007 model was, as was noted by the reviewers at the time, optimized for BATS. Why should we believe that all the parameters (even coarsely variable ones like zooplankton grazing rate) are the same for TENATSO? They are not and there is no basis to assume that they are.

The parameters of the ecosystem model that the reviewer here alludes to are from Schartau and Oschlies (2003), a study that used data from three different open-ocean JGOFS stations in the North Atlantic simultaneously (not only for BATS as the reviewer assumes) to find parameters for an ecosystem model for the whole North Atlantic using data-assimilation methods. They have also been used by (Zielinski et al., 2002) to model the CANIGO site in the eastern subtropical Atlantic. However, we agree that this set of parameters may not be optimal to describe the situation at TENATSO. We have therefore conducted a large set of sensitivity studies with respect to the ecosystem parameters. The details of these studies are now discussed in the paper. They demonstrate that primary and export production are not very sensitive to most parameters. Therefore, our choice of parameter value should be able to describe the average situation at TENATSO.

Data should inform models so I am unimpressed with the choices of citations that seem to show a lack of familiarity with measured values from the literature. For example, most of the references cited for particle processes date to the 1980s. There has been an enormous amount of work done since then and the authors have not adequately researched the recent literature. How can we have confidence in a model that seems not to be aware of data produced in the last 20 years? Our choice of citations results from the fact that we attempted to model aggregation processes as simply as possible, i.e. with concepts that were developed in the eighties. We are aware that more complicated and presumably more realistic model concepts exist (see e.g. the review papers by Burd and Jackson (2009); L. et al. (2004)). But given that we have no data available to constrain the parameters that a more complex model requires, and that we are interested in aggregation/disaggregation only insofar as they influence the vertical fluxes of nitrogen and iron, we have decided to keep our model simple, as in fact most biogeochemical modelers still do (Kriest and Oschlies, 2008; Gehlen et al., 2006). We have, however, checked again whether we can find more recent data to constrain the parameters of our simple model and have also performed a sensitivity analysis with respect to the aggregation rates, which is now shown in the manuscript.

References are used almost out of context to bolster a point and the same reference is not used later where it would be appropriate. For example Rue and Bruland (1995) is without question a classic paper and deserving of continued relevant citations. But their paper was a study in the Central North Pacific and, since it was largely a method development paper, the number of samples was actually quite limited. On 4311/3 the values of Rue and Bruland for free organic ligands are used as initial data for ligand concentration in the current model. However, the Rijkenberg reference cited elsewhere has actually measured this data on many more samples in waters close to the TENATSO site. Why wasn't the Rijkenberg data used in the model? There are numerous other examples where the choice of reference struck me as odd and perhaps suggesting the authors are less familiar with papers presenting data than they are with papers discussing models.

The reviewer is right that data from Rue and Bruland (1995) may not be an optimal choice as initial condition in the tropical Atlantic. However, initial conditions only determine the model results during spinup. All model results shown stem from the phase where initial conditions have been 'forgotten'. Rijkenberg et al. (2008) only measured

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surface concentration.

There are plainly errors of calculation (see detailed comments below): The value for maximal irradiance of 1978 kW m^{-2} is clearly wrong.

The name given to this model parameter is unfortunate; it is *not* a maximal irradiance, but only a scaling factor for the rate of photochemical reactions. We have renamed it to I_{ref} : reference irradiance, to avoid confusion. It is true, however, that the unit (not the value) given in the table is wrong; it should be μ E instead of W m⁻². Irradiance in the model is calculated from latitude, time, date and cloud cover (see comment further below).

Is the value for Fe(III)' scavenging rate (=2500 kg⁻¹ L d⁻¹) correct? (In Weber 2005 and Weber 2007 the value given was 25000).

In Weber et al. 2007 it was shown that the value of 25000 kg⁻¹ L d⁻¹, which was based on lab experiments by Nyffeler et al. (1984) leads to an overly rapid depletion of dissolved iron and probably should be corrected downward for open-ocean particle concentrations. The value of 2500 kg⁻¹ L d⁻¹ stems from a sensitivity study that was shown in Weber et al. 2007.

On what basis is it assumed that Fe(II)' oxidation by O2 occurs at the same rate as oxidation by O_2^- ?.

The rate of Fe(II)' oxidation by O₂ is 0.864 (μ mol L⁻¹)⁻¹ d⁻¹, whereas the rate of Fe(II)' oxidation by O₂⁻ is 864 (nmol L⁻¹)⁻¹ d⁻¹ (please note the different units of these rates).

I could not help but wonder at the utility of modeling processes at TENATSO for 1990-1995. Why not a more recent time or even a future prediction that can later be checked against measurements? For that matter I would welcome some indication of when the authors feel they might advance to even a 2D model.

As stated above, our present aim is not to reproduce observations that were made at a specific time as closely as possible, but rather to contribute to process understanding.

Although we use meteorological forcing from specific years we disregard interannual variability so far. This will become different when more data from TENATSO becomes available, and we are busy collecting more data for that purpose.

Specific comments:

4306/25 The references cited refer only to iron enrichment experiments. In this case might it be simpler to reference a single metastudy of iron enrichment experiments e.g. Boyd et al., 2007?

We have changed our citations accordingly.

4307/13 Add word: "One of the most important natural sources of iron for REMOTE marine systems. ..." And herein lays a central issue for this paper: A reader well versed with the literature about iron limitation is likely to say to themselves: "TENATSO is not remote. TENATSO is underneath the Saharan dust plume and receives so much dust and iron that one can almost imagine that even simple inorganic dissolution processes could supply sufficient iron to the biota. Why then is this model relevant and important?" The authors could do more to make this rationale clear.

What we wanted to express here is that other (e.g. riverine) sources than dust are probably unimportant at TENATSO. In that sense it is remote. Also, in spite of the large dust deposition, surface iron concentrations are relatively low in the region (e.g. Rijkenberg et al., 2008) and might be limiting to nitrogen fixers (Mills et al., 2004.). The aim of this study is to contribute to understanding the processes that determine the concentration and residence time of Fe in the region, also as a prerequisite for modeling N_2 fixation. We have rewritten the paragraph.

4307/27 NPZD not defined.

We have added a definition of the acronym.

4308/13 Why not give the spacings used instead of saying it "increases non-linearly with depth?"

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We now give a mathematical expression for the spacing as function of depth instead of a table with 100 entries.

4308/24 ECMWF not defined and the reanalysis referred to is not referenced.

We have added a definition and a reference.

4309/3 I didn't really follow how turbulence and double diffusion can be modeled in 1 dimension. Perhaps a few words of clarification here please.

The model that we use is the General Oceanic Turbulence Model (GOTM, Umlauf and Burchard (2005)), which indeed does not explicitly model the full 3-dimensional velocity fields of ocean turbulence, but describes its effects by solving equations for bulk properties such as turbulent kinetic energy using state-of-the-art turbulence parameterizations. We have clarified this in the text.

4309/4 I confess I am not very familiar with computational fluid dynamics and so I do not understand all the details of a Patankar scheme. I suspect many readers may also be in the same boat so perhaps a few words of explanation here might help. For example, in what way was the scheme modified?

We have added a few clarifying words; for a full description, the reader is referred to (Burchard et al., 2005).

4309/15 Figure 1 seems to lightly skip over the transformation from hematite (the most common oxide in Saharan dust) to Fe(III)'. See later comments about the "1% solubility" meme. I am also struck by the similarities and differences between Figure 3 from Weber 2005 and Figure 1 of the current manuscript. For the purposes of continuity it might have been easier to not change the relative positions of the boxes for "biology" and "Fe.lig".

For the solubility issue, see further below. The figure has been changed accordingly.

4309/25 What is the physical basis (or data source) to assume that the flux from the

particulate to colloidal pool is "similar" to the rate of colloid aggregation? Doesn't this assumption force there to be no accumulation of colloids? Is that valid?

There are no laboratory measurements of this rate, to our knowledge. We therefore have performed a sensitivity analysis with respect to the flux from particulate to the colloidal iron pool, which now is also described in the manuscript. The rate of this process strongly influences deep iron concentration profiles.

4310/3 The authors say that 'recent' studies have identified different ligands with different stability constants. I have no idea why this was not incorporated into the Weber 2005 and 2007 models but this is not really a new concept and has been discussed at great length even in Rue and Bruland (1995) that is cited throughout this current manuscript.

The wording here was unfortunate and was changed; we of course know that this goes back to Rue and Bruland (1995) and Van den Berg (1995). We had not included this distinction into Weber 2005 and 2007 because these papers merely prescribed total ligand concentration instead of modeling it. Here, however, we attempt to model their production and fate explicitly. We make the distinction between two ligand classes to be able to investigate the consequences of the often-made assumption that the source of these two classes is different. We have made this clear now in the manuscript.

4310/6 It seems rather excessive to need 9 references to make an uncontroversial point.

The point in the citations was to show the still very limited data-base for deep organic complexation profiles. We therefore kept the citations.

4311/1 Wedepohl actually gives 3.09% Fe in the upper crust. However, a more serious question is why not use a total measured iron content of Saharan dust or relevant soil? There are several such results reported in the literature. For example: Spokes and Jickells (1994) measured total Fe 4.8% in Saharan dust, Bonnet et al. (2004) while

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Desboeufs et al (1999) found a loess collected from Sal Island (Cap Verde) had 7.6% Fe.

We are grateful to the reviewer especially for pointing out the reference by Desboeufs at al. (1999). However, specifying availability of iron from measured total Fe in dust or loss currently cannot reduce the uncertainties because of the largely unknown value of the solubility (see next item).

4311/2 Since it appears that dust-iron solubility (to form Fe(III)') governs the total amount of iron entering the model the value for iron solubility needs to be well known. However, I do not think the references cited support the value of 1% solubility for iron: The whole point of Spokes and Jickells 1996 is to show how variable to solubility of iron from Saharan dust can be and they report a wide range of solubilities. Johansen et al. 2000 say that 0.51 – 0.56% of iron is readily released as Fe(II). Baker et al. 2006a says that the solubility of iron varies predictably as a function of grain size and give a range of $\approx 1-10\%$ in Northern Hemisphere tropical waters (and much higher in temperate waters). Baker 2006b gives $\approx 0.2\%$ solubility for the fine fraction and $\approx 2\%$ for western Atlantic stations $\approx 10^{\circ}$ N. The authors need to make a stronger case for why 1% is a better value to use than say 0.01% or 10%.

That is to say nothing of the innumerable other studies in the literature. The main conclusion I have from the literature is that the reported solubility of iron from dust covers many orders of magnitude (e.g. Baker et al., 2006a). There are multiple reasons for this and the review chapter by Jickells and Spokes (2001) in the Turner and Hunter book provides an excellent overview of the factors affecting the solubility of iron from dust, as does the work of Desboeufs, Guieu and Baker. The authors of this current manuscript could do more to demonstrate their knowledge of this situation. There also seems to be wide agreement in the literature that both the extent and rate of the dissolution of iron from Saharan aerosols, for any given location, is different for coarse and fine fractions.

Table 1. Fe solubility

author	year	dust type	solubility%
Baker, Jickells	06	Atlantic Ocean	0.5-5,mean 1
Baker et al.	06b	Saharan, Atlantic	0.5-2.5,median 1.2
Baker et al.	06a	Saharan	1.4-4.1,mean1.7
Spokes, Jickells	96	Saharan	mean 1.4
Jickells,Spokes	01	global budget	0.8-2.1

We are aware of the large uncertainties in iron solubility from dust and of the dependency on processes such as cloud processing etc. Instead of asking 'When will the observers tell us the correct value?' we have to live with this uncertainty for quite a while. 1% iron solubility is close to the most reported mean iron solubility of Saharan dust, as we show here in the following table. Because TENATSO is close to the dust source region and dry deposition is predominant, it is reasonable to take a smaller solubility or a smaller product of solubility and iron content for our model calculation.

We now show the results from a sensitivity study with respect to the combined parameter dust iron content \times solubility in the revised paper. The results support our choice of 1% solubility and 3.5% iron content.

4311/3 Rue and Bruland (1995) presents ligand profiles for the Central North Pacific. Why did the authors not to use data collected closer to the TENATSO site? For example from the Rijkenberg reference cited elsewhere, it appears that surface water ligand concentrations near TENATSO are only 25-75% that found by Rue and Bruland.

The data base for iron complexation is unfortunately still rather limited. The Rijkenberg study shows surface values only, and the study by Gerringa et al. (2006) does not distinguish between two different ligand classes. Our model assumptions result in a decrease of the strong ligand class with depth, and we have used the Rue and Bruland data only to show that this agrees qualitatively with their results. Our presentation of

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the comparison was unclear and we have reworded it.

4311/22 Why a Fe:N quota only? That is, why not consider Fe-P colimitation of N fixation as per the Mills et al reference cited elsewhere in this manuscript? (That study focused on waters receiving Saharan dust). The recent work of Baker as also explored the supply of N and other nutrients by Saharan dust.

In our present study we have attempted to focus on the iron biogeochemistry, ignoring for the moment the additional complexity brought in by nitrogen fixers, and their elevated requirements for iron. Modeling nitrogen fixation will be a next step that, requires as a first step a model for the cycling of iron. Another group in the SOPRAN project is working on diazotrophs near TENATSO: we will include nitrogen fixation in our future model, based on the results of their studies.

We added the N input by dust deposition in the updated version of our model. Chlorophyll and primary production do not change significantly.

4312/10 Re Figure 2: What do the authors make of the maximal discrepancy between the two models in June/July? Are there any measured data for comparison?

One of the two 'models' (De Boyer Montegut et al., 2004) *is* actually an analysis of measured temperature and salinity profiles to provide a climatological mean of the annual mixed layer cycle. The comparison was meant to demonstrate that our annual mixed layer cycle is close to that climatological mean, and especially that the maximum winter mixed layer depth, which is important for nutrient fluxes, is correct. A deviation between a model forced with interannually varying meteorological fluxes and this climatology by ten meters or so, especially when it concerns the summer and is not systematic, is not at all surprising and does not affect other model results.

4312/10 I didn't quite follow if this 'characteristic feature' (shallow, high-salinity) has actually been measured or is a characteristic feature of models for the site.

The tongue of high-salinity water below the mixed layer embedded between less saline

water is a well-known observational feature that has its origin is the high evaporation in the subtropics near 30°N. We have reworded the paragraph.

4312/14 I really did not follow this at all. Is it correct that the physical part of the model is GOTM? But then 'a non physical restoring term for S and T' was used. What precisely is a 'restoring term'? It seems as if this is what we used to call a 'fudge factor'. Perhaps this is justified and is necessary. It would still be a good idea for the authors to give a little more detail about the changes they made and the justification (over and above that such a 'restoring' helps produce the 'correct' answer).

The model is GOTM, as stated. We should have avoided the expression 'restoring term', which is modelers language for an additional forcing term that is proportional (with a negative proportionally factor) to the deviation between model and data, i.e. that drives the model back towards the observations if it deviates from them. The proportionality factor is chosen relatively small (the inverse of this proportionality factor is a time-scale and is 90 days in our case), in order not to interfere too strongly with the more physical forcings. One might call this a 'fudge factor', but it is justified in that it represents the lateral advection of water properties that cannot otherwise be represented in a one-dimensional model. Our explanation was clearly insufficient here.

4312/21 I am nonplussed that the authors can claim a modeled value of 0.2-0.45 μ gL⁻¹ cla-a is 'consistent' with observations of 0.06-0.7 μ L⁻¹. Plainly, the modeled values show much less variation. Does that mean the model is therefore incomplete?

We reworded the sentence with precise description of the consistence and difference between the modeled and measured data. The reviewer is right pointing out the smaller variability of the modeled data. One reason could be that we used a constant ChI:C ratio to calculate chlorophyll concentration from phytoplankton biomass. To check this, we now also calculate ChI using a variable ChI:C ratio from Cloern et al. (1995). This explains part of the discrepancy. Other factors, e.g. our simplistic ecosystem model certainly play another role.

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4313/1 I am surprised that there was 'only a weak seasonal variation' in primary production (chlorophyll). Satellite data clearly show considerable seasonality at the study site.

In the new model runs, surface chlorophyll varies by about a factor of two over the annual cycle, if calculated with a constant C:Chl ratio. Highest values are reached around February and lowest values around October. Primary production varies somewhat less, by a factor of 1.6.

4313/3 Do I understand correctly that the model calculation for primary production is 1.4 times that of the MODIS data-based estimate (660 vs. 470 mgC m-2 d-1)? This seems a poor fit to data. The data are for July 2002-December 2007. The model is for 1990-1995. Are they really comparable? If so, the authors need to explain why.

Our primary production values are indeed higher than the satellite-based estimate (which, however has a considerable error-bar), but they are lower than e.g. the value at the closest EUMELI station. Presently we cannot answer any questions on interannual variability other than in the years that we modeled.

4313/10 Equation 2 is not referred to in the text, nor are the variables explained.

Explanation and reference are added.

4313/26 Equation 3 is not referred to in the text, nor are the variables explained.

Equation 3 has now been removed.

4314/5 Again, it seems a poor fit to data if the modeled flux is 2-20 times the measured flux at similar sites. (Modeled = 50 mg Cm-2, measured between 2.0 and 12.7). The authors explore two possible reasons for the poor fit. However, might it have not been useful to adjust the model and attempt to determine which of the two causes is the more likely?

This discrepancy was the reason that we studied the effects of aggregation and of

the temperature dependency of mineralization (Q10-value) in much more detail for the revised manuscript. We show the results from these studies in the manuscript. The main reason for the discrepancy was a Q10-value of 3. Our new 'reference run' has a flux of 15 mg C m⁻² day⁻¹. We also extended the database that we compare to.

4314/12 A matter of idle curiosity only, but in what way were the different lengths of summer and winter days calculated and taken into account? (I believe that the daylengths at the solstices differ by \approx 2 hours). How was insolation calculated seasonally?

Shortwave irradiance was calculated following Rosati and Miyakoda (1988): solar altitude, declination and top-of-atmosphere irradiance are calculated from geographic latitude and local time (including seasonal variations of daylength). Irradiance at the sea surface is then calculated using monthly fractional cloud cover data from the same source as the other meteorological forcing fields. Finally, the reflection at the sea surface is calculated with an empirical fit to the relation between solar zenith angle and albedo following Payne (1972).

4314/23 While Broecker and Peng is very much a classic and prescient book, the data within are now over 30 years old and date to the very early years of trace-clean measurements. Surely a more recent source could be found? For example, Nozaki has for many years maintained a compilation of elemental profiles.

The reference to Broecker and Peng (1982) refers to the explanation what a remineralized nutrient is, not to a specific elemental profile.

4314/23 Regarding lack of DFe enrichment with water mass age: Compare with Sanudo-Wilhelmy and Flegal (2003), where NADW is postulated to add iron to Southern Ocean waters.

We are grateful to the reviewer for mentioning the reference by Sanudo-Wilhelmy and Flegal (2003). They postulated that iron in upwelled waters of the Southern Ocean may

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originate from aeolian deposition in the North Atlantic. Considering this transport with water mass, although iron has a relatively short residence time than other nutrients (Johnson et al., 1997), measured DFe profiles do not show any obvious inter-ocean fractionation in deep waters. Our wording here is not precise and has been changed in the final version of the paper.

4315/2 and Figure 3. Figure 3 includes Rue and Bruland (1995) data. This is for the Central North Pacific. What is the relevance to iron inputs by Saharan dust? What is 'Cruise POS 332'? Is this the same as that described on 4312/23 as a personal communication from Cotrim de Cahuna? If so then where are the other data for other cruises referred to?

We removed the data by Rue and Bruland (1995) from the plot of DFe profiles and put in several more local data sets. 'Cruise POS 332' is the same as described in 4312/23. During the other cruises DFe has not been measured.

4316/6 How significant or controlling is the rate of formation of Fe(III)' from deposited dust? Or even direct deposition of Fe(III)' from atmospherically processed dust?

The formation of Fe(III)' from deposited dust has often been described largely occurs within hours (e.g. Rose and Waite, 2003b) and is thus probably not rate-limiting, given the slow sinking speed of small dust particles. This does not rule out that a second fraction of iron in dust may be remineralized more slowly, leading to a release deeper in the water column. We have not explored this possibility here. Direct deposition of Fe(III)' from atmospherically processed dust is probably not an important source compared to Fe(III)' dissolved from dust particles in seawater, because TENATSO is still relatively close to the source regions of the dust, leading to little processing, and because most deposition occurs as dry deposition.

4316/14 The seasonality described here appears to contrast with the weak seasonality for primary production noted in 4313/1.

The seasonality referred to here is that of the *daily iron speciation cycle* which is mostly determined by irradiance and mixing. It is not obvious why there should be a relation to the seasonality of primary production.

4316/20 It may be a matter of semantics but here, and in many places elsewhere in this manuscript, I very much take issue with the claims like the one that 'Weber et al. (2005) demonstrated the influence of copper. . .' My reading of Weber is that the influence of copper was modeled. It is important that modelers do not forget that measured data are the final arbiter to demonstrate something. I am not comfortable with a modeled inference from one study being regarded as fact by the next generation of model from the same group. (Indeed, I also see that one of the referee interactive comments for Weber 2007 also highlighted the need to be clear about the difference between model calculations and measured data).

This was unfortunate wording. The fact that Cu influences Fe cycle is not derived from any model result, but from laboratory studies, (Voelker and Sedlak, 1995; Voelker et al., 2000). We reworded the sentence as: 'Copper redox reactions compete for superoxide with iron (Voelker and Sedlak, 1995) and thus influence the amplitude of the daily cycle of superoxide concentration and Fe speciation. Therefore, we considered the role of copper...'

4317/1 This may just be poor writing that has confused me but have I understood correctly that the authors use Cu to predict H2O2 and then go on to favorably compare the modeled inventory with the measured inventory of Steigenberger and Croot? If so then is it relevant that Steigenberger and Coot do not suggest a controlling role by copper and conclude that: 'Vertical distributions of H2O2 were strongly controlled by photo-formation and mixing processes in the upper water column. The recent irradiation history and phytoplankton activity appear to be the key sources and sinks in determining the observed H2O2 levels, with CDOM playing a minor role suggesting sunlight is the key limiting reactant in the formation of H2O2 in the Tropical and Sub-Tropical surface ocean.'

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No, the copper concentration in the model stems from field observations (Van Der Loeff et al., 1997). We agree with the cited statement that sunlight is the limiting reactant in the formation of hydrogen peroxide (we do not take into account the role of phytoplankton as a sink for H_2O_2 , though. Maybe we should). However, this does not rule out a controlling role of copper for the amplitude of the daily O_2^- and Fe redox cycle through the competition between Fe and Cu for the catalytic dismutation of O_2^- , which results in H_2O_2 . We have tried to make the role of copper clearer.

4317/4 and /11 Both sentences should begin with an article ('The').

Sentences are changed accordingly.

4317/6 and /9 It seems rather excessive to need 5 and 7 references to make these uncontroversial points.

References have been changed accordingly.

4317/12 Town (2000) (and comments) offers an alternative view point about the two classes of ligands that it might be useful to consider. (Town RM, Filella M (2000) Dispelling the myths: Is the existence of L1 and L2 ligands necessary to explain metal ion speciation in natural waters? Limnology And Oceanography 45, 1341-1357).

We agree that at least the weaker ligand class is probably characterized by a whole spectrum of stability constants rather than one (see also Hunter and Boyd (2007)). Models must simplify, though.

4317/14 If measured stability constants in Rue and Bruland are \approx 12-13 (strong) and \approx 11 (weak), why were values of 22 and 20.3 used in this model? In general I am a little uncomfortable with the reliance upon Rue and Bruland (1995). This was a very important work and I have often cited it myself. However, the study site was in a completely different ocean basin. There have been other, more relevant studies, in the North Atlantic since that time ? for example the work of van den Berg and Gerringa which are cited in this paper in other contexts.

The values in the table were the conditional stability constants $K_{L/Fe^{3+}}^{cond}$ with respect to Fe³⁺. We have now replaced them with $K_{L/Fe'}^{cond}$, the conditional stability constants with respect to inorganic Fe(III)' (sum of all the inorganic Fe(III) species) because we model Fe(III)', not Fe³⁺. This only affects the values given in the table, model calculations have always been performed with $K_{L/Fe'}^{cond}$. The new values are lower by a factor of the inorganic side reaction coefficient $\alpha_{Fe'} = [Fe']/[Fe^{3+}]$ that is estimated as 10¹⁰ at pH=8 (Hudson et al., 1992).

4317/21 It seems rather excessive to need 10 references to make an uncontroversial point.

The references show that different species produce siderophores.

4318/11 It seems rather excessive to need 8 references to make an uncontroversial point.

We reduced the references.

4319/7 This part was very unclear and I do not understand what it means to say that the ligand release rate should be so that reasonable phytoplankton growth rate can be supported by sufficient complexed iron. Doesn't this mean that the model is constructed to force it so iron-limitation can not develop?

The wording is confusing here. 'Reasonable phytoplankton growth' means comparable abundance and seasonality of phytoplankton to observations. We have not tuned the maximal ligand release rate, only made sure that phytoplankton concentration does not fall much below observed limits. We would therefore consider the rate as a first-order guess, not more. The actual rate of ligand release also depends on the phytoplankton feeling iron limitation (eq. 1 in the manuscript): no ligand is released by iron-sufficient cells. It is interesting that some production of strong ligands is required to keep modeled phytoplankton concentrations near observations (see new manuscript).

4319/14 Table 3 is referred to before any other tables. (Table 2 is not even mentioned C1748

in the text).

The tables have been renumbered.

4319/19 The authors need to more to convince me that their modeled results are 'close' to the measured data and that this is in any case relevant. Rue and Bruland report [L2T] \approx 1.5-3 nmol kg-1 and [L1T] \approx 0.4 nmol kg-1. This seems to differ from the modeled results in this paper. The shape of the Rue and Bruland profile for [L2T] is similar to that modeled for weak ligands but the Rue and Bruland measured maximum is at \approx 500m. Why use the Rue and Bruland reference? Especially since the stability constants of their ligands were so very different from the values used in this model. How is it relevant that the modeled ligand concentration in the North Atlantic is similar to that in the Central North Pacific?

We now compare to more regional measurements of organic ligand concentrations only. Depending on the remineralization rate, the profiles now come somewhat closer to observations.

4319/27 'Below 80m, strong ligands decline rapidly with depth'. This is, again, in contrast to the (irrelevant) Rue and Bruland study.

See above.

4320/1 '. . .in agreement with observations'. Which observations? Am I to understand that all the discussion comparing the model to 'observations' in fact refers to samples collected by Rue and Bruland? It is not my place to do this work for the authors but they must surely be aware that in the intervening 14 years since that paper was published that other studies have been made.

The three comments above refer to the comparison of the modeled ligand concentration to observations. We compared it with more observations and rewrote the result of this comparison. Also see the reply to the question to 4311/3.

4320/5 I found this paragraph confusing. It seems that using Q10 = 3 produces model

results that are more like the observations (though I have expressed my doubts about the validity of the observations). So surely the model should have been adjusted accordingly?

The discussion was rewritten. We now discuss the influence of the ligand remineralization rate and its temperature dependence separately and show that the remineralization rate must be relatively low, compared to average DOM. However, in a 1-dimensional model we are limited to time-scales of a few decades, since then lateral processes begin to dominate. We therefore cannot give a complete answer to the question of ligand remineralization here.

4320/25 Did I understand 4319/11 correctly to mean that oxidized strong ligands are functionally equivalent to weak ligands? Does that mean that in the model weak ligands are produced from strong ligands (as seems to be implied by Figure 6)? If this is so then from where do weak ligands pick up refractory material?

The ligands produced by photolysis of complexes with strong ligands have similar binding ability as weak ligands (see citations in paper). However, this is a minor source of weak ligands, compared to the release during remineralization of sinking organic material. This fraction contains probably the more refractory material that the referee alludes to.

4321/4 'a commonly observed value in the deep ocean'. References?

We added references.

4321/20 It seems rather excessive to need 8 references to make an uncontroversial point.

We changed the reference accordingly and kept only one review paper.

4322/8 Suggestion: Delete 'to find with' and add 'of'. The connection between size of dust grains being deposited being in the range 0.3-2.6 μ m and the link to having two size classes in the model of 10 μ m and 100 μ m escapes me. Can the authors clarify C1750

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the relationship?

The two size classes were meant to represent a 'smaller' (2μ m for dust and 10μ m for detritus) and a larger (aggregates) size class. We now distinguish with the smaller particles between dust- (only inorganic) and detritus-sized particles, in addition to larger aggregates. The whole section has been rewritten and a large set of sensitivity studies with respect to coagulation rates has been performed and described.

4322/14 Smayda 1970? Has nothing more recent and relevant been published? For example, Alice Alldredge has been active in this area for some time.

Smayda (1970) is a classic text that we think is still worth citing, although of course a large number of studies have since studied particle sinking rates, of which we cited a few here.

4322/16 The scavenging nature of sticky marine snow and organic particles in general does not seem to have been well explored here.

Our model always included the aggregation of small (inorganic and/or organic) particles with faster sinking large aggregates. We do not have an extra class for marine snow, but group them under our larger aggregate class. Maybe this was not explained well enough. We now clearly mention the role of marine snow particles in particle sinking and metal scavenging in the revised version.

4323/25 As noted, the large body of work on the properties of marine snow also shows the importance of organic aggregation.

See the reply to the former question.

4324/10 Mentions Figure 15 but last figure mentioned was only figure 11.

All the numbers of figures are changed according to the order they are mentioned.

4324/10 I suggest the authors rephrase this section to avoid giving this impression that they had not previously considered the redissolution of colloidal and particulate

material. This principle of remineralization has been known since the first depth profiles were produced. The authors however seem poorly informed about measurements made in the last 20 years.

Redissolution of particle-adsorbed iron is not yet well studied and its rate is unknown, although it is suggested in several studies as explanation for keep DFe concentration in deep waters relatively constant in spite of scavenging. This is not to say that the mechanism has not been suggested, e.g. Bacon and Anderson (1982) for Th. We therefore studied the effect of this process on DFe concentration in a series of sensitivity studies to get a more quantitative estimate of the rate.

4324/17 The fluxes in Figure 12 are absurdly precise and imply a precision that is simply not justified.

The figure has been removed.

4325/5 I'm not sure the authors have understood what 'deep' means in the context of nutrient remineralization. In my experience 'deep' most often refers to waters below the oxygen minimum; in contrast Figure 15 only has modeled results to 400m. Having said that, I would have said that once iron in any form has left the euphotic zone then - by definition - it ceases to be relevant to photosynthesis. So while a failure to reproduce features at depth calls into question other features of the model, there is no reason for the model to be extended below the euphotic zone (upwelling zones excepted).

We distinguish here the water column into the upper and lower layers with respect to different processes controlling DFe concentration: in the upper layer or surface waters photochemical reactions and biological processes are the main processes; and in the lower layer–in this context the deeper layer, some biological processes like remineralization, but mostly the physio-chemical processes like colloidal aggregation dominate. Iron availability in the euphotic zone depends on the flux of dust deposition, diffusion from the water layers below and winter mixing-up. Iron once left the euphotic zone could accumulate in deeper waters and become available for new carbon fixation by

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diffusion or mixing.

4325/10 I think that Figures 13 and 14 add little beyond the text and the other figures.

Indeed. The figures were removed.

Table 1. Is table 1 missing some units?

No.

Table 2. The change in attenuation due to chlorophyll (0.03 in Weber 2007, 0.04 in this model) did not seem to be discussed in the text. It is pure nonsense to give coagulation rate to 5 significant figures. (Equally I am skeptical that other parameters in this table can really be given to 4 or even 3 significant figures).

The value of the attenuation due to chlorophyll was a typo, it is 0.03, as before. Also, the unit was wrong in the table: it is $m^2 \pmod{N^{-1}}$, as phytoplankton is measured in nitrogen units. It is true that the number of digits for the coagulation rates were nonsense. For the other values in this table, the number of digits is mostly a result of a unit conversion: A rate of 1 s⁻¹ converts to 86400 d⁻¹. We could of course have used different units for each parameter, but this would have only created more confusion. We now mention this origin of 'exactness' in the table caption.

Table 3. The current model and that of Weber 2007 (and Weber 2005 in turn) have the values for almost all parameters in common. However, the Weber 2007 model was, as was noted by the reviewers at the time, optimized for BATS. Why should we believe that all the parameters (even coarsely variable ones like zooplankton grazing rate) are the same for TENATSO? They are not and there is no basis to assume that they are. On what basis is it assumed that Fe(II)' oxidation by O2 occurs at the same rate as oxidation by O2-? And why on Earth are these parameters listed with different units: 0.864 (?molL-1)-1d-1 and 864 (nmol L-1)-1d-1, respectively? This only serves to confuse. Where has the value for maximal irradiance of 1978 kW m-2 come from? Nearly 2 megawatts? I had previously understood that at the top of the atmosphere total solar irradiance is between 1320 and 1420 W m-2??n and that at the surface this seldom exceeds 1 kW m-2. I use NOAA functions to calculate irradiance at top of atmosphere on 21 June is about 1324 W m-2??n and at sea level ? depending on the atmospheric model and factors like ozone and aerosol optical depth ? a variable amount between 780 and 1050 W m-2?? n. That is, even if a mistake has been made by a factor of 1000 (kW for W) I still could not see how a value of even 1978 W m-2 could be justified. On the other hand, a PAR (if that is what it was) of 30 ?E m-3??n s-1 seems to suggest a total irradiance that is too low but I was not clear on how the surface area irradiance was converted to a concentration of photons per unit volume.

Explanations have been given above.

I urge the authors to check the validity of the other terms in the tables. By this stage my attention had begun to wander but I suspect other errors will be found. Fe(III)' scavenging rate 10x less than in Weber 2007 and Weber 2005. Why? FeL photoreduction has been split into strong and weak components. But in the Weber 2007 model a combined term covering total FeL photoreduction was assigned a value of 86.4 d-1 (a number conveniently related to the rates of Fe(II)' oxidation by both O2 and O2-??n and the FeL dissociation rate?).

The origin of the ubiquitous factor 86400 is a unit conversion from seconds to days. The other points have been clarified above.

Yet in this model the photoreduction rates are very different at 0.38 d-1 for FeLstrong and 7.6 d-1. Is this not a big change? Cu(II) reduction rate by O2- was 1400 in Weber 2007, changed to 182 here. Why?

The photoreduction rates for weak ligands have been estimated from the work of Powell and Wilson-Finelli (2003). We used Rose and Waite (2003a) to estimate the the ratio between photoreduction rates strong and weak ligands. The reduction rate of Cu by O_2^- depends on the degree of organic complexation of Cu. We have now added footnotes to our parameter tables stating the basis of the parameter settings.

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Axis labels and captions are in many cases too small to be read. Many captions are inadequate (e.g. see Figure 6).

We have redone all our figures in order to make them better readable and checked and rewritten some of our captions.

Final comments:

I think if I were to sum up the entire manuscript in a few words it would be to say that there is deep division between the modeling community and the experimental/ observational community. This manuscript did nothing to bridge the gap. Given the magnitude of the changes I would anticipate, I have not gone over the manuscript in any greater detail but I suspect I would have additional questions were I to do so. However, having made all these points, should the authors wish to respond, then I would be pleased to read over an amended manuscript.

We hope that the changes that we made to our manuscript will convince the referee that our model is able to help in understanding iron biogeochemistry in the oceanic region, despite all the uncertainties that remain because of the few available data and some uncertain process rates.

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