

## ***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.***

### **Anonymous Referee #1**

Received and published: 28 April 2009

#### Summary:

The paper can not be published in its current form and the authors will have to work hard to convince me that this model could ever be made fit for publication. It is not clear that the model is valid in the first place nor that the model is a significant improvement upon previous incarnations. There are calculation errors. Several assumptions are at variance with known data or are unreasonable in other ways. The authors are not familiar with the literature.

#### General comments:

Were this paper to be published it would represent the 3rd version of the model. I have

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read the previous two papers and it seems to me that only minor modifications have been made.

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, optimised 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.

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?

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.

There are plainly errors of calculation (see detailed comments below): The value for maximal irradiance of 1978 kW m<sup>-2</sup> is clearly wrong. Is the value for Fe(III)' scavenging

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rate (=2500 kg<sup>-1</sup> L d<sup>-1</sup>) correct? (In Weber 2005 and Weber 2007 the value given was 25000). On what basis is it assumed that Fe(II)' oxidation by O<sub>2</sub> occurs at the same rate as oxidation by O<sub>2</sub>-?.

I could not help but wonder at the utility of modelling 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.

Specific comments:

Here are line by line comments (page/line number).

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?

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.

4307/27 NPZD not defined.

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

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

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

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

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?

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”.

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?

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.

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

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

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4311/2 Since it appears that dust-iron solubility (to form Fe(III)<sup>3+</sup>) 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  $0.51 \pm 0.56\%$  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  $\sim 1\text{-}10\%$  in Northern Hemisphere tropical waters (and much higher in temperate waters). Baker 2006b gives  $\sim 0.2\%$  solubility for the fine fraction and  $\sim 2\%$  for western Atlantic stations  $\sim 10^\circ\text{N}$ .

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.

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.

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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.

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?

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.

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).

4312/21 I am nonplussed that the authors can claim a modelled value of 0.2-0.45  $\mu\text{gL}^{-1}$  chl-a is "consistent" with observations of 0.06-0.7  $\mu\text{gL}^{-1}$ . Plainly, the modelled values show much less variation. Does that mean the model is therefore incomplete?

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.

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  $\text{mgC m}^{-2} \text{d}^{-1}$ )? 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.

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

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

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

4314/5 Again, it seems a poor fit to data if the modelled flux is 2-20 times the measured flux at similar sites. (Modelled = 50 mg Cm<sup>-2</sup>, 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?

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 ~2 hours). How was insolation calculated seasonally?

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.

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.

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?

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?.

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

4316/20 It may be a matter of semantics but here, and in many places elsewhere in this

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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 modelled. It is important that modellers do not forget that measured data are the final arbiter to demonstrate something. I am not comfortable with a modelled 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).

4317/1 This may just be poor writing that has confused me but have I understood correctly that the authors use Cu to predict H<sub>2</sub>O<sub>2</sub> and then go on to favourably compare the modelled 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 H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> levels, with CDOM playing a minor role suggesting sunlight is the key limiting reactant in the formation of H<sub>2</sub>O<sub>2</sub> in the Tropical and Sub-Tropical surface ocean.”

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

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

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).

4317/14 If measured stability constants in Rue and Bruland are ~12-13 (strong) and

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~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.

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

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

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?

4319/14 Table 3 is referred to before any other tables. (Table 2 is not even mentioned in the text).

4319/19 The authors need to more to convince me that their modelled results are "close" to the measured data and that this is in any case relevant.

Rue and Bruland report [L2T]  $\sim 1.5\text{--}3$  nmol kg<sup>-1</sup> and [L1T]  $\sim 0.4$  nmol kg<sup>-1</sup>. This seems to differ from the modelled results in this paper. The shape of the Rue and Bruland profile for [L2T] is similar to that modelled for weak ligands but the Rue and Bruland measured maximum is at  $\sim 500\text{m}$ . 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 modelled ligand concentration in the North Atlantic is similar to that in the Central North Pacific?

4319/27 "Below 80m, strong ligands decline rapidly with depth". This is, again, in

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contrast to the (irrelevant) Rue and Bruland study.

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.

4320/5 I found this paragraph confusing. It seems that using  $Q_{10} = 3$  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?

4320/25 Did I understand 4319/11 correctly to mean that oxidised 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?

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

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

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  $\mu\text{m}$  and the link to having two size classes in the model of 10  $\mu\text{m}$  and 100  $\mu\text{m}$  escapes me. Can the authors clarify the relationship?

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.

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

Full Screen / Esc

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Interactive Discussion

Discussion Paper

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

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

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

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

4325/5 I'm not sure the authors have understood what "deep" means in the context of nutrient remineralisation. In my experience "deep" most often refers to waters below the oxygen minimum; in contrast Figure 15 only has modelled results to 400m. Having said that, I would have said that once iron in any form has left the euphotic zone then – be 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).

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

Table 1.

Is table 1 missing some units?

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 sceptical that other parameters in this table can really be given to 4 or even 3 significant

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figures).

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, optimised 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 O<sub>2</sub> occurs at the same rate as oxidation by O<sub>2</sub><sup>-</sup>? And why on Earth are these parameters listed with different units: 0.864 (μmolL<sup>-1</sup>)-1d<sup>-1</sup> and 864 (nmol L<sup>-1</sup>)-1d<sup>-1</sup>, respectively? This only serves to confuse.

Where has the value for maximal irradiance of 1978 kW m<sup>-2</sup> 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<sup>-2</sup> and that at the surface this seldom exceeds 1 kW m<sup>-2</sup>. I use NOAA functions to calculate irradiance at top of atmosphere on 21 June is about 1324 W m<sup>-2</sup> 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<sup>-2</sup>. 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<sup>-2</sup> could be justified. On the other hand, a PAR (if that is what it was) of 30 μE m<sup>-3</sup> s<sup>-1</sup> 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.

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

Full Screen / Esc

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Discussion Paper



of 86.4 d<sup>-1</sup> (a number conveniently related to the rates of Fe(II)' oxidation by both O<sub>2</sub> and O<sub>2</sub>- and the FeL dissociation rate?). Yet in this model the photoreduction rates are very different at 0.38 d<sup>-1</sup> for FeLstrong and 7.6 d<sup>-1</sup>. Is this not a big change?

Cu(II) reduction rate by O<sub>2</sub>- was 1400 in Weber 2007, changed to 182 here. Why?

## References

Each reference is followed by the page number on which it appears. It seems this is not in accordance with the reference policy described at [www.biogeosciences.net](http://www.biogeosciences.net). However, I actually found this to be useful. I would recommend the EGU consider this approach for referencing.

## Figures

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

## 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.

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Interactive comment on Biogeosciences Discuss., 6, 4305, 2009.

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