Biogeosciences

Discussions

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Interactive comment on "Manganese in the world ocean: a first global model" *by* Marco van Hulten et al.

Marco van Hulten et al.

mvhulten@lsce.ipsl.fr

Response to Anonymous Referee #3

We wish to thank the reviewer for the critical but also positive comments on our manuscript. The reviewer said that this

> approach of starting [with a] simple [model] and increasing complexity only after thorough analysis of model deficiencies is laudable. But it also means that this work is likely to be just a first step, and that more complex models will follow.

This is absolutely the idea. He or she continues:

C1

> The main victim of this approach of starting simple is that the model disregards the biological cycling of manganese, although it is known that manganese availability is necessary for oxygenic photosynthesis, and can be (co-)limiting to phytoplankton growth at times (Brand et al. 1983, Bruland et al. 1991). The authors argue that in the data they use for validating the model, there is no strong signal of uptake and remineralisation of Mn. I must admit that I am sceptical about this assumption: - firstly, is the argument to neglect of biological Mn cycling maybe biased by using primarly Atlantic data? The secondary maximum of dissolved Mn in the North Pacific, shown in Bruland et al. 1991 seems hard to explain without remineralisation of Mn in biological material, and – in addition – a slower Mn(II) reduction in the oxygen minimum. This at least is what I have gotten out of the 1-d modelling study by Johnson et al. 1996.

We now have decided to include a module for biological cycling in the model, and results of first simulations including such a biological module are encouraging. Yes, right now we are missing the secondary maximum. This is especially clear in the Pacific Ocean where there is not only a secondary maximum around 800 m, but also a higher concentration in the upper 250 m; neither are captured by our model. There should really be a study more dedicated to these issues, including indeed the uptake-remineralisation processes as well as the effect of oxygen minima into consideration. Future GEOTRACES sampling expeditions will also help in that they would be following the same quality standards as, amongst other GEOTRACES transects, the GA02. Nonetheless, there are a large number of processes and uncertainties when doing a first model. Thus, we believe that for a first global model study it is not too bad that we chose a more simple approach.

> - secondly, how consistent is the neglect of biological cycling with the magnitude of other vertical fluxes of Mn in the model? At least an estimate for the magnitude of the vertical export of Mn through biology could be obtained by multiplying Mn:P ratios in phytoplankton (Sunda and Huntsman, 1998, Twining 2013) with common estimates of global export production. The vertical sinking flux of particulate Mn

(only the precipitated form, not the non-dissolved lithogenic part) from the model could be compared to that number.

Indeed the biological module that we now have included is based on a typical or world-average Mn/P element ratio of plankton.

There are other parameterisations in this model that are less ad-hoc than they appear at first sight: The authors use a constant rate for Mn(II) oxidation and a reduction rate for Mn(IV) that switches abruptly from a high value in the euphotic zone to a low value below. Although this is qualitatively justified by the existence of photoreduction, one wonders where the values come from, until one finds in the discussion that this simple parameterization was chosen to reproduce the particulate/dissolved Mn ratio at the Vertex site. I think figure 11 and the corresponding explanation should be shifted to the model description. Instead, in the discussion, I think the authors could perhaps discuss what they think is the driving process for this reduction and whether it is likely that the Mn(IV)/Mn(II) ratio in the deep ocean is the same in different ocean basins.

Yes, the abrupt change from high to low reduction from the photic to the aphotic zone is ad hoc. In retrospect, we could have used a continuous function of depth, which would probably even gotten a higher correlation index, but the choice of the function is not constrained by the literature. (Linear in light intensity may be a good approximation.)

My last criticism concerns the parameterisation of the sinking removal of oxidised Mn; contrary to the spirit of starting a model with simple assumptions, I find this parameterisation not simple at all. At the surface and at concentrations below 25 pM, Mn particles are assumed to sink at 1 m/d. Has this value been estimated from some assumption on the size of the particles, using Stokes' law, or it it just an arbitrary choice? Most of the intially formed particles probably are so small they don't sink at all on their own and need aggregation with other organic particles to sink, but most aggregates sink quite a bit faster. The model assumes that above

C3

the threshold od 25 pM, Mn particles aggregate and sink faster, but the increasing sinking rate above the threshold is made dependent on water depth, so that it does not affect the removal of Mn near the surface. Is there any justification for the depth dependency of the sinking rate? Several biogeochemical models use a vertically increasing sinking rate for its detritus compartment, as an implicit way to account for aggregation, see e.g. Kriest and Oschlies 2010, but the absolute sinking rates for aggregates in these models are much higher than assumed here. I found the choices here quite ad-hoc and wondered how strongly the model results are affected by them.

The removal of oxidised Mn is somewhat arbitrary indeed. Most Mn probably sinks slowly with small lithogenic particles (p. 25, lines 11–15). This could not explain the strong removal rate near hydrothermal vents. One approach would be to include more species of particulate (and maybe dissolved) manganese. We chose to stick with only (observationally defined) two pools, namely dissolved and particulate manganese. This meant that we needed to set a high velocity near hydrothermal vents, but the removal needed to be small enough to maintain high surface concentrations and the (lower) background concentration. Our parameterisation works for this.

Summarizing, I think that the authors need to discuss the processes that lead to the vertical transport and ultimately removal of Mn in their model more, before the paper can be published. They have shown with their sensitivity runs that aggregagtion seems to be important for the removal of Mn from hydrothermal plumes, and that a lower threshold for this aggregation seems to be important for explaining the relatively uniform Mn background in the deep ocean. But if indeed aggregation is the main vecor of vertical transport, then one might suspect that near the surface, biological export production plays a large role in determining the vartical Mn flux, either directly from incorporated Mn, or indirectly from driving aggregation. That would lead to a much less uniform vertical transport velocity and it would be good to have an idea how much that could influence model results.

C4

In the photic zone the sinking speed equals 1.0 m/d in the model, while higher speeds can be found around and below 100 m depth. That said, there may already be some aggregation directly below the photic zone in the model, because accumulated (dissolved) Mn in that region quickly oxidises, hence exceeding the 25 pM threshold and having a higher speed than in the photic zone. This may be expected in the real ocean as well, but we cannot be sure whether our model does it in a correct way. The model suggests that aggregation would only be important in the deeper ocean.

We will address these issues in the next version of the manuscript.

Specific and minor comments

> page 3, line 3-4: My suspicion is that the good correlation between lithogenic particles and Mn may be caused by Mn inside lithogenic material, not so much by scavenged Mn. I would therefore be cautious to cite that as an evidence for that 'lithogenic particles are likely to play a significant role in the removal .. on Mn'.

Lithogenic particles contains Mn, but in Roy-Barman et al. (2005) the correlation is between the authigenic Mn concentration and lithogenic tracer concentration such as ^{232}Th in sediment. In this study, the authigenic Mn content exceeds largely the lithogenic Mn content, so that the correlation is indeed between authigenic Mn and lithogenic particles.

We will rephrase this accordingly in the new version of the paper.

> Equation 3 for the Middelburg et al. empirical formula for denitrification is incomplete, as the units of neither the denitrification rate nor the water depth are given. Probably it is metre for the latter, but for the first?

We will add the units. It is actually the logarithm of the denitrification flux; we'll make that clear in the text.

> p.4, line 17: It it on purpose that the concentration of O2 is denoted by square brackets, but that of the OH- ion by curly brackets?

Yes, this is how Johnson et al. (1996) have it. The [] is a concentration, {} activity. Since it is used only once, we will just use the words there, and not the symbols.

> In my printout of the pdf file several of the equations appear mangled, with mathematical symbols replaced by small blocks, vertical lines replaced by some dots, the vertical bracket in eq. 20 missing etc. I think this is the consequence of using the a formula editor, which relies on software-specific fonts. The formulae should be checked out not only on a computer screen, but also in a printout.

Next time I will make a print-out of the final version/proofs and check the typesetting on paper before confirming it. At first, I also thought it would be a font issue, but all fonts in the document are either standard or embedded (that's what Evince tells me). It may be a pdf library or printer driver problem. We didn't use a special formula editor, just LaTeX.

> Also, in my printout of Figure 2, all arrows are replaced with strange symbols, the ligated letters ff in 'sediment diffusion' are lost etc. I think this means that the pdf relies on the presence of some fonts that are present some type of computers, but not elsewhere. The ligated 'fl' in flux is also lost in the captions of the subfigures in figure 3.

If we cannot find (nor solve) the problem ourselves, we will ask the editors to have a look at this problem at the time of submission. Thank you for raising this issue.

Just to get the issue clear: do all these problems only occur when printing the document, or are some of them also visible when viewing the pdf file? Any other information (software used) may be of use as well.

> It is very convenient that the caption to Figure 4 marks the cruise names in the same colours as the dots within the figure, but is this feature supported in the final journal form?

Good question. They state in the instructions that it is not allowed in tables, nothing about figures/captions. We'll just see what the editor says.

> Several of the citations are incomplete, e.g. Charette et al.

We will check and update our citations (like this one) where needed.

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