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Discussions

Interactive comment on "An improved ocean model of aluminium: the effects of circulation, sediment resuspension and biological incorporation" *by* M. M. P. van Hulten et al.

Overview:

This manuscript presents results from a version of the PISCES model that incorporates the cycling of Aluminium within the ocean. It is intended as a follow-up of an earlier work (van Hulten, et al., 2013) but it was hard to find any significant differences between the current manuscript and the previous one as many of the results were reported in the earlier work. The main difference appeared to be in the inclusion of a parameterization for Al incorporation into actively growing diatoms, about which there is considerable doubt, and indeed the model was not improved by the inclusion of this parameterization. Based on an apparent negative result like this it is hard to see that the title really describes the results, as the improvements to the model and the findings

are not significantly different than from the recently published paper. Disappointingly the paper provides a poor representation of the debate concerning Al incorporation into diatom silicate, neglecting several key publications on post mortem incorporation in sediments and results from culture studies by other Dutch researchers. Indeed many key aspects underpinning the model assumptions are provided without citation, though some citations were provided in the earlier van Hulten et al. work, suggesting the latter work was rushed through submission. There is also no real discussion of how the parameterization of the PISCES model for Si and phytoplankton production may impact the ability of the model to adequately describe Al biogeochemistry - it is one thing to change a parameter for Al but if a key underlying driver is not well replicated (e.g. Si cycling in non diatom regions) and other processes are neglected (e.g. non diatom driven scavenging of Al) then no amount of tweaking the numbers may improve the model fit.

The basic problem here is that if there are any improvements to the model they are not well brought out in the main text or abstract as to what exactly they are and how they improve our understanding of the biogeochemical cycling of Al in the ocean. The resulting paper is then far too similar to the earlier published work and therefore I simply can't support publication of the paper in its present form.

General comments:

What is different from van Hulten et al. (2013)? Reading through the manuscript and in particular the abstract it was very hard to distinguish what was really new and what wasn't a slightly modified version of simulation runs from the recently published work by the same authors (van Hulten et al., 2013). This was especially so when it come to upholding the promise of the title, "of an improved ocean model for Al", as it seems that many of the changes in the parameterizations resulted in a reduced ability to replicate the West Atlantic Al data set. It felt very much like a paper trying to sell negative results as an improvement! If a work like this is to be publishable it needs to set out its stall early about what and where the significant improvements were made and to provide

an observational basis or link that support these improvements.

Al incorporation into actively growing diatoms:

The authors should be aware that there are some studies that indicate that Al is not incorporated into the silicate structures of diatoms. Indeed other researchers from Groningen could previously not detect aluminium in diatom silicate for cultures spiked with aluminium (Vrieling et al., 1999). Indeed those authors suggested that the studies which indicated that aluminium is present in frustules of diatoms were cleaned by low-temperature ashing (Gehlen et al., 2002; van Bennekom et al., 1991; van Bennekom et al., 1989; Van Beusekom et al., 1997) and this procedure may not have removed aluminium associated with organic matter, while the HNO3 oxidation method they employed did remove all the associated organic matter. Additionally recent work from groups based at Utrecht and NIOZ (Koning et al., 2007; Loucaides et al., 2012; Loucaides et al., 2010) have suggested that most of the Al found in diatom silicate in sediments is incorporated post burial. These papers indicate that the Al:Si ratio in living diatoms is most likely considerably lower than the estimates provided by the papers the model bases its assumptions on (Gehlen et al., 2002; van Bennekom et al., 1991; van Bennekom et al., 1989; Van Beusekom et al., 1997). Finally there is also related chemical evidence from work on the performance of concrete (Chappex and Scrivener, 2013), that aluminium is incorporated into silicate matrices over time. Thus it would significantly improve this work if the uncertainties of these assumptions were looked at in far more detail than they are at present.

Role of colloidal Al in Al cycling in the ocean:

Recent observational data from the Atlantic Ocean by Dammshäuser and colleagues (Dammshäuser and Croot, 2012; Dammshäuser et al., 2011; Dammshäuser et al., 2013) has indicated that colloidal Al that while it may be a small fraction of the dissolved Al pool, as seen in earlier works (Moran and Moore, 1989), it however plays an important role in controlling the removal rate and overall residence time of dissolved Al

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in the ocean. Their work strongly suggests that removal of dissolved Al is facilitated by complexation with colloidal and particulate organic carbon through a potentially reversible reaction in solution. Of course sinking particles will transport this bound Al to greater depths and ultimately the sediments. Thus the Dammshäuser et al. work strongly suggests that any model of Al cycling in the ocean should incorporate an organic complexation model for the colloidal and particulate size fractions and that this is the main process by which dissolved Al is scavenged from the ocean and not direct biological incorporation into diatom frustules (see general comments above and below).

Not all phytoplankton contain silicate:

Despite the recent finding (Baines et al., 2012) suggesting that some picoplankton also accumulate silicon in their cells it is clear that in oceanic regions where diatom productivity is low that the opal flux would be a poor proxy for the scavenging of dissolved Al. So how is Al scavenged in the oligotrophic North Atlantic under the Saharan dust plume?

How well does the model replicate biogenic silicate concentrations?

As the removal of dissolved aluminium is dependent on biogenic silica it would be extremely useful in the context of this work to see how well the model describes biogenic silica in the global ocean compared to observational data. As it appears at present that biogenic silica is scaled to primary productivity and may be potentially over represented in the oligotrophic gyres, i.e. do the nanophytoplankton also contain silicon? A better description of the basic model with regard to the primary productivity should be provided to facilitate examination of these aspects of the model.

Aluminium concentrations in bottom waters: resuspension or diffusive flux?

Resuspension of material from the sediments can be easily observed as nepheloid layers due to the changes in light scattering due to the presence of particles. These

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same particles may also scavenge dissolved aluminium from the water column despite the mixing event stirring in dissolved aluminium from the porewaters. There are almost no studies of dissolved Al in sediment porewaters, though one study in the Southern Ocean (Van Beusekom et al., 1997) does show smooth profiles that point to a diffusive flux of aluminium from the sediments to bottom waters. The diffusive flux is not considered in the present work and it may be more worthwhile to examine its influence on a global model in more detail despite the lack of data.

Technical comments: P14541 line 17. As this is a central theme to the present work the authors should at the very least provide citations in support of this statement. See also the general comment on this above.

P14541 line 20. Can the authors provide any evidence for the removal of Al by diatom production? There are a few studies (Moran and Moore, 1988a; Moran and Moore, 1988b; Moran and Moore, 1992; Ren et al., 2011) that have shown that it is part of the removal process but not the only mechanism occurring.

P14541 line 22. Once again can the authors provide some references to back their claims here?

P14542 line 7. What evidence does a modelling study (van Hulten et al., 2013) provide for this?

P14543 line 10. What other carrier phases are there? It seems biological silicate is the only one considered here. The earlier work (van Hulten et al., 2013) does mention the role of POM, CaCO3 and lithogenic particles so why not here also?

P14543 line 11. Along the west coast of North Africa, there is an apparently strong seasonal cycle in dissolved Al due to the deposition of Saharan dust (Helmers and van der loeff, 1993; Hydes, 1983; Measures, 1995; Pohl et al., 2011; Rutgers van der Loeff et al., 1997), though this region is not a major zone for diatom productivity – how do the authors reconcile this with their current scheme in which Al removal is solely via

uptake by, and the subsequent sinking of, diatoms?

P14543 line 12. The Bruland and Lohan reference is a review chapter from a text book and contains no primary data on this process and therefore should be removed.

P14543 line 21. What is the Al:Si ratios at which the dissolution of silicate begins to be influenced by Al? See also the general comment on this above.

P14544 line 27. What work are the authors referring to here? There is no citation listed and one can only assume then it is the unpublished Middag et al. work listed in the reference list. Thus there is no information provided so that the reader can check the author's claims regarding the high accuracy of this work.

P14545 line 9. See the general comment regarding the evidence for the biological incorporation of Al into diatoms.

P14545 line 17. What specifically are the 3 major changes from the earlier study (van Hulten et al., 2013)? As the circulation and biological incorporation are all considered in the earlier study, and the sediment source term was used in one of the reported sensitivity studies. As related to the general comment above it is hard to see what is significantly different about this work from the one published earlier this year.

P14548 line 14. The Lampitt (1985) work does not contain any information about Al chemistry in the sediments and thus it only has limited use here. There are works that directly address the chemistry of Al in the sediments (Koning et al., 2007; Loucaides et al., 2012; Loucaides et al., 2010). Additionally the work of Hwang et al. (2010) is appropriate here in terms of a related approach to estimate the resuspended flux of POC using particulate Al.

P14548 lines 21-25. These are the same equations as described previously for the published modelling study (van Hulten et al., 2013).

P14550 line 22. Presumably it is the pore water Si that is important here not the dissolved Si concentration in the water column? As the authors already mentioned in

the text that there are no estimates of Al flux from resuspension then can they explain in more detail how dissolved Si controls dissolved Al concentrations in resuspended material?

P14558 line 19. There are data for dissolved Al in sediments (Mackin and Aller, 1986; Van Beusekom et al., 1997) and that could be used to calculate a diffusive flux to the water column in a manner typical to that used for iron and other nutrients. See the general comment about this above.

P14560 line 1. At what level is it statistically significant? Please provide some criteria here.

P14560 line 19. Is there any experimental evidence to support the value used for the scavenging term in the present work?

P14561 line 11. This statement appears to support the findings of Vrieling et al. (1999) that Al is not incorporated into actively growing diatoms, see the general comment above. It may also simply reflect that the model requires more than two types of phytoplankton in order to simulate the processes more accurately.

P14562 lines 11/12, 16 and 19/20 Repetition - on the one hand and on the other hand...if ever there was a suspicion there was some dubious card trick going on, which hand am I meant to be watching?

P14593 Figure A1. Is this calibrated transmissometer data?

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