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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.

M. M. P. van Hulten et al.

hulten@knmi.nl

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Dear Dr. van Beusekom,

Thank you for your review. We believe that the review contains many useful points for improvement and we generally followed your suggestions. We could unfortunately not follow all of them, since several would entail a whole new research (e.g. the effect of Al on the Si cycle).

The other reviewer interpreted the title that the incorporation should improve the model, and you possibly interpreted the title in such a way as if we tested the effect of biological

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incorporation of Al on the Si cycle. Neither was the intention. Hence we have chosen a new title:

On the effects of circulation, sediment resuspension and biological incorporation in an ocean model of aluminium

1   Resuspension and dissolution.

In our paper sedimented adsorbed Al is resuspended and partly dissolved, depending on bottom $[Si_{diss}]$. You have made several critical comments and questions concerning this process. You refer to this as the major concern:

> Although the Si dependent Al release is an elegant solution to explain the Al enrichment of north Atlantic deep water, the evidence is not conclusive as pore water sources are not quantified: The latter is not taken into account although data exist that it potentially is a relevant source at least in parts of the southern Ocean. The model exercise would have been a great opportunity to discern between the two sources. In any case, the conclusion that resuspended sediments are a major Al source can only be made when the resuspension-source is compared to potential Al fluxes from pore water.

We agree that the evidence for Si-dependent Al dissolution from sediments is inconclusive. Based on theoretical arguments and the observations, we have concluded that sediment resuspension and dissolution influenced by Si is the most consistent explanation so far.

The reason for putting more weight to the resuspension instead of diffusion explanation, is the (indirect) evidence found for resuspension. This is based on observations that there appears to be an Al source from sediments where there is resuspension

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(e.g. around Grand Banks, Moran and Moore (1991), associated with deep water formation or around seafloor elevations) but not a general source from sediments when there does not appear to be resuspension. This of course does not mean that there is no diffusion flux, but the observations link near-sediment Al elevations to regions of resuspension. Hence, this is tested with the model. Other possibilities should be tested too, but this is outside the scope of this paper.

To some extent, we did test the sensitivity of sediment dissolution from the Southern Ocean compared with the North Atlantic Ocean (i.e. we *discerned* those). We presented a simulation without depending on bottom $[Si_{diss}]$ (Fig. 7) and one with depending on it (Fig. 8). This shows that the resuspension of even a relatively small supply of Al_{ads} in the Southern Ocean is too large (while the resuspension in the North Atlantic Ocean is too low) if no dependence on $[Si_{diss}]$ is introduced. We also performed a simulation with only redissolution in the North Atlantic Ocean (based on a Heaviside function of $[Si_{diss}]$), but that did not appear to give any new insights compared with our other results, so we did not put this in the Discussion Paper. (This simulation has slightly worse skill than the parametrisation based on Mackin and Aller (1986).

Furthermore, the empirical model derived from resuspension and one derived from diffusion would be structurally identical. I.e., both processes result in a flux into the bottom model layer. Since it is not possible at the moment to model the underlying processes, the Al addition from the sediment is modelled like a flux. We now made clear in the manuscript that the model is based on resuspension and dissolution but is consistent with other processes like diffusion as well. The point is that there is a significant sediment source.

Concerning the Al fluxes from pore waters, as far as we know there are no measurements of raw Al_{diss} fluxes out of the sediment. And measurements of porewater $[Al_{diss}]$ are sparse compared to the model grid. It is not possible to discern the two processes (resuspension+dissolution and diffusive flux) with our current model. We cannot completely dismiss a flux as suggested by Van Beusekom et al. (1997) and other works.

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2   Scavenging and incorporation.

About reversible scavenging you wrote:

> Furthermore, I do challenge the assumption that Al adsorbed onto (or incorporated into) biogenic opal is easily released. What is the scientific basis of this assumption? Koning et al. (2007) clearly demonstrate the opposite that Al is rapidly adsorbed onto opal and incorporated into the opal "lattice". Thus a later release of Al seems unlikely whereas an interaction with Si release is likely.

It is not clear to us whether you refer to processes in the sediment (1) or in the water column (2).

1. Sediments: The adsorbed Al is more likely to be released quickly than most other forms of Al, including biologically incorporated, post-mortem incorporated and lithogenic. These other forms of Al are within the lattice structure of the biogenic or lithogenic particles. This is why we deem adsorbed Al a more likely candidate for transformation to the dissolved form than other types of particulate Al.

Also, the Koning et al. (2007) states that a significant amount of the Al associated to diatom frustules post-mortem can be rinsed of and is thus bound to the surface.

2. Water column: In our paper Al_{diss} is reversibly scavenged. I.e. Al_{diss} is scavenged and released in the water column by a combination of decreasing and Al_{diss}, following Eqns. (2) and (3) of the manuscript. At first sight, this release appears necessary to explain the non-zero water column concentrations of Al_{diss}. This is consistent with the opal with Al_{ads} following the MOC and slowly releasing Al_{diss}. This can be seen in Fig. 1(a) and Figs. 6 and 7 where $[Al_{diss}]$ shows the 'imprint' of the MOC.

Concerning reversible scavenging in the water column, Koning et al. (2007) is of little use here, since this is a study on processes at the sediment–water interface.

Two other possibilities that may explain the observations are redissolution of incorporated Al and from lithogenic particles. Concerning the first, Al as a source from either biological or post-mortem incorporation, the Al built into the opaline lattice probably does not easily dissolve. The second alternative is that lithogenic particles in the water column release Al_{diss}. In our previous paper we suggest, based on a sensitivity simulation, that dissolution from dust below the mixed layer is negligible. However, this is based on a simulation with redissolution of adsorbed Al. Clearly, when desorption is set to zero (or a low number), subsurface dissolution of lithogenic Al would likely improve the simulation of the observations, hence confirming subsurface dissolution. Furthermore, lithogenic particles from sediments may also get into the NADW and flow southwards (Fig. 8(b) suggests this, even though the source here is sedimented adsorbed Al). Clearly, it is not certain whether Al_{ads} redissolves. Therefore, a simulation with irreversible scavenging and subsurface dissolution should be performed. This is outside the scope of this paper; it are recommendations for future work.

3 Effect of Al on the Si cycle.

You highlight the interesting effect of Al on the Si cycle:

> "Given the impact of Al on opal dissolution, this model exercise would also have been a great opportunity to test the impact of Al on the Si cycle. Although an in depth study of the Si cycle is beyond the scope of the paper, the potential impact should not have been ignored."

We agree that this would be very interesting, but feel that we cannot sufficiently constrain the process of inhibition of opal dissolution based on available observational and experimental data.

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4 Figures.

Figure quality and reduction in Figure number: Many of the Figures were too small in size to appraise all detail. Figure 3 is already shown by van Hulten et al. (2012). Fig 4 can be described in the text.

We removed Figs. 3 and 4. Concerning the quality/readability. Figures 1(a) and (b) we will align vertically, and we will try to use the full width of the page. Finally, they are vector graphics, hence infinitely magnifiable. Of course, concerning these issues, we are also dependent on the typesetters here.

5 Local remarks.

P14541, L24: Please add citation on Al/Si Interaction.

Done so, as well as added several other citations in first paragraph.

P14542, L4: Please reduce the number of citations.

Okay, we have done so.

P14542, L20: I do challenge the assumption that Al adsorbed onto opal is easily released. What is the scientific basis of this assumption? Koning et al. (2007) clearly demonstrate the opposite that Al is rapidly adsorbed onto opal and incorporated into the opal "lattice". Thus a later release of Al seems unlikely.

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In the North Atlantic Ocean near resuspended sediment (beam attenuation measured), there is an elevated $[\text{Al}_{\text{diss}}]$. This must come from the sediment. The refractory state of incorporated (either biologically or post-mortem) and lithogenic Al does not easily allow for dissolution. Of course, the entire opal may dissolve, but Al inhibits the dissolution of the opal (e.g. Van Beusekom and Weber, 1992; Dixit et al. 2001). Release from the surface of particles is therefore more likely.

Koning et al. (2007) discuss incorporation into the opaline structure and this is called *rapid* (several days), but it may very well be that desorption from opal is more rapid. Koning et al. (2007) note that the rapid incorporation occurs in pore waters. This process may actually play a role in the inhibition by high $[\text{Si}_{\text{diss}}]$. We noted this in the text.

> P14542, L 24 ff. On the other hand, van Beusekom et al. (1997) showed that southern ocean sediments are a source of diss. Al for southern ocean bottom water. This should be mentioned.

Southern Ocean sediments are a significant source of dissolved Al, i.e. values just above the sediment are significantly higher than the water column concentrations above. We have now made this more clear in the manuscript. However, these concentrations are relatively small compared to the North Atlantic Ocean, where the same amount of particles is resuspended (beam attenuation coefficient), hence the need for some inhibition in the Southern Ocean.

> P14542, L 28. Is the source of Al exclusively desorption from opal dissolution and can other sources (like redissolution of certain clay minerals) be excluded?

Since we do not precisely know what goes on in the sediment, this cannot be excluded. However, we believe that adsorbed Al is a more likely candidate to transform to the dissolved phase than the more stable clay minerals (or incorporated Al).

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P14543, L9. Another possibility removing Al is the uptake of Al by diatoms. Here
two aspects are involved: adsorption onto organic matter associated with diatom
frustules and the incorporation into the opal. The former Al may be released, but
again, the post mortem incorporation into Opal (sensu Koning et al. 2007) may be
involved.

We have included the discussion about post-mortem incorporation in our manuscript.

P14544, L24 ff. I suggest to be a bit more careful here when interpreting the model:
It may well be that the major patterns are reproduced by the model, but this does
not proof that the model is right: what is the experimental basis for the reversible
scavenging by Si_{biog}? In fact, several studies (Koning et al. (2007, and references
therein); the Al enrichment of Si_{biog} observed by e.g. Van Cappellen et al. (2002)
suggest the opposite.

Biogenic silica dissolves on its way down to the seafloor and thus Al will be released as
well and is more likely to stay in solution in a low biogenic silica / particles environment.
This is what is modelled. If $\kappa \to \infty$, then $A_{ads} = k_d S_{biog} \cdot A_{diss}$. This means that the
'partition coefficient' is proportional to the silicic acid concentration ($k_d S_{biog}$). Hence,
the 'reversible scavenging' strongly depends on S_{biog}. This needs to be the case. No
carrier for adsorbed Al, no adsorbed Al.

Furthermore, we rephrased to "are consistent with", and included a critical note.

P14545, L 6. What is the scientific basis for Al release from opal debris?

Adsorbed Al is the most likely candidate for a source of dissolved Al. Note that dis-
solution of Si_{biog} releases Al as well, according to the model (see above). We cannot
exclude other sources, but this is what can be modelled within PISCES at this stage.
Also, it at least shows that there is a significant Al source near resuspended sediment.

P14547, L 26ff. But what about clay minerals? (e.g. work by Mackin and Aller). On the time scales involved ($> 10^2$ years) this may be significant at least in the sediment and in pore water dynamics.

One hundred years may be very long compared to desorption of Al from opal. Generally timescales for sediment processes are much larger than processes in the water column. In the model we release adsorbed Al instantaneously. Of course this is not evidence for this actually happening, but it is a possibility. We now discuss clay minerals (lithogenic particles).

P14548, L3 ff. The low resolution of the model bottom layer then actually does not allow to distinguish by pore water Al fluxes of Al released by resuspended sediment. Although the authors are possibly right that no sediment Al_{diss} model is available, enough data are available to at least constrain the Al fluxes from sediments (e.g. work by Mackin and Aller, van Beusekom et al., 1997. This would allow to conclude on the relative importance of sediment resuspension.

There is no data of actual sediment fluxes, only concentrations. Nonetheless, concentrations may be used to compare with or constrain the model flux. However, data are sparse compared to the model grid. Furthermore, most sediment Al studies are not accompanied with bottom water $[Al_{diss}]$, such that no diffusive flux can be calculated.

P14549, L3 ff. One of the major concerns with the present model is that 1) Al is released proportional to the Al/Si in opal and 2) that no interaction between Si dissolution and Al uptake is included although the interaction is acknowledged and a parameterization is possible (see van Cappellen et al., 2002). Modelling this interaction actually would have been a real innovation.

1) We believe that the assumption that Al is released proportional to Al/Si in opal is reasonable. We would need convincing evidence to the contrary to apply that in our remineralisation equations.

2) Van Cappellen et al. (2002) conclude that Al incorporation has a significant effect on the solubility and dissolution kinetics of Si_{biog}. Possibly a parametrisation can be derived from this work and be implemented in our model. However, this was not the aim for our current modelling study. Therefore we only noted the effect of Al on the Si cycle, without including results of any simulations with this effect.

> P14552, L 21. Within the model the explanation certainly is right, but in the real world, it may be the other way around: low Al availability enables high Si fluxes due to a faster dissolution of opal and high opal concentrations in the sediment may effectively inhibit Al release through post mortem incorporation of Al in opal. Please comment on this.

Because of the long spin-up needed to get a quasi-steady state for Si_{diss}, and because it can have a lot of side effects to change the Si cycle, we chose not to influence the Si cycle based on $[Al_{diss}]$, but rather effectively use it as a forcing for the Al model. Hence, at this stage we only study the effect of the Si cycle on Al, not the other way around.

> P14553, L5 ff. In this paragraph, the authors acknowledge the possible role of clay dissolution. As clay minerals are not included in the model, the authors use a "trick" to allow Al release by tapping the "ads"-pool. In reality, the Si-dependent re-dissolution of clay minerals may be involved (sensu Mackin and Aller). This poses some questions behind the modeled concept that Al-desorption is influenced by Si. What is the mechanistic / chemical explanation of the modeled Si dependent Al release?

The chemical/thermodynamical explanation is stoichiometric saturation and can be found in Thorstenson and Plummer (1977). Our model does not give evidence for either the importance of redissolution of adsorbed Al, or the precise dependence on $[Si_{diss}]$. It is only a first test, the best we can do, that shows that redissolution from the sediment does occur, especially where bottom $[Si_{diss}]$ is low. Models with lithogenic particles from sediments should be developed, and then simulations can be performed showing whether using lithogenic particles as a source also works with the same or a different function of $[Si_{diss}]$.

We do not explicitly say this in the manuscript, since this would be confusing; we believe that we make sufficient critical notes throughout the manuscript, and especially the appendix, for readers to make their own choices in doing additional simulations that may confirm or reject our findings.

> P14553, L15 FF. Doesn't this imply that the Al cycle and its interaction with opal is not properly captured (Koning et al., 2007; van Beusekom et al., 1997)? By tweaking the critical value the model now seems to reflect the real Al distribution properly, but have the underlying processes been properly modeled? This of course is important when assessing the overall results/improvement of our understanding of the Al cycle.

Indeed, the underlying model is not perfect. This rather means that the Si cycle (instead of the Al cycle) is not properly captured. We tried to improve that by using a difference velocity field, but only partly succeeded.

If your comments concern more the (underlying) Al model (instead of the biogeochemistry and dynamics of NEMO), we refer to the results and discussion in Van Hulten et al. (2013) in which the underlying Al model was introduced.

> P14560, L15. The conclusion that the importance of Al dissolution from resuspended sediment is supported by the model should be discussed with more care:

No distinguishing between pore water fluxes and redissolution was made, hence no conclusive evidence is available to distinguish between both processes.

In the case you mean the distinction between diffusion and resuspension/dissolution: these are structurally the same, see answer to reviewer #1.

In the case when you mean the two-part process of resuspension and dissolution, 'pore water flux' $\propto w_s \partial A_{ads}/\partial z$, and 'redissolution' $\propto S_{diss}^{-0.8}$. The product of these terms is the parametrisation used in the manuscript (Eqns. (7) and (8)). However, no sensitivity simulations have been performed that would distinguish these two terms. We actually do present a simulation without Si dependence; does this account for your point?

> P14561, L1 ff. It was unclear to me, whether both processes (Al_{ads}, Al_{bio}) are implemented in parallel or exclusively. An alternative to Al uptake that is proportional to Si, is to model Al uptake independently from Si uptake, by assuming a Michaels-Menten type of uptake. A maximum Al/Si ratio of 0.03 seems very high to me.

We have removed the value for r_{max} of 0.03 which was an estimate based on unpublished experiments by Van Bennekom and yourself (Van Beusekom, personal communication, January 2013). In any case, it is not essential, since we have included other various values of r_{max} showing that this parameter is underdetermined (though possibly not as high as 0.03).

Adsorption and biological incorporation were included in the same simulation as separate processes. We have clarified this in the new manuscript. Only including biological incorporation would not result in a steady state, since $[Al_{diss}]$ would build up below the photic zone without any sink as there would be no removal mechanism for it.

We do not think that "to model Al uptake independently from Si uptake" is useful, though the underlying Si model does use a Michaelis-Menten uptake approach. Since Al fol-

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lows Si in uptake... possibly this may answer your question.

> P14563, L25. Rephrase: Al release from resuspended sediment (depends on both...)

Okay, reformulated.

> P14564, L10. Also pore water dynamics may potentially be important.

Yes, added this.

6 Other changes.

We have made several additional changes to the document, namely:

- Added citations that suggest there is only dust dissolution in the surface ocean.

- Replaced Fig. 2 with a more pleasant figure.

- Removed Figs. 3 and 4.

- Increased spin-up for all sensitivity simulations.

- Added five extra stations to West Atlantic GEOTRACES section, of which measurements were taken later to complete the transect.

- Redone statistics based on further spin-up and extra observations → statistical significance mostly not changed, but small changes in text were necessary. Only worsening of incorp+lower kd is not significant anymore.

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- Added more recommendations to conclusion:
  – testing of other model configurations for incorporation
  – IF incorporation realistic, THEN test effect of Al on Si cycle

- Made mathematical notation more consistent.

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