

Overview:

This manuscript presents results of the application of the MADCOW model for aerosol deposition to recent GEOTRACES data from the Atlantic. The authors expand on the original MADCOW model by varying previously fixed parameters through a combination of comparison with field data for fractional solubility and model date for residence times. While it is an interesting topic, much of the discussion reads like a summary of the earlier works and the manuscript would be better focused on providing new insights into the GEOTRACES datasets through examining how well the assumptions in the MADCOW model are adhered to. There are some question marks regarding the GA08 Al data set also as the dissolved Al values appear to be overestimated possibly due to the lack of correction for CDOM fluorescence due to the methodology that was used during that expedition. Overall this paper does a good job in adding value to existing GEOTRACES datasets and could make a very useful contribution to this field if it is revised along the lines outlined below.

General Comments:

Atmospheric fluxes – wet and dry

While the paper does a reasonable job of explaining how the fluxes were calculated it does not get into a detailed comparison with atmospheric based fluxes for which there is also data from GEOTRACES and other programs. One aspect of the current work where the atmospheric data would help decipher things is in assigning how much of the surface Al comes from aerosol flux (dry deposition) and how much from wet deposition. In this regard making the link to the precipitation fluxes for each region (Liu et al., 2012) would be beneficial in examining if this is what determine the high inferred model solubility of the aerosols or not. As the assumption of the MADCOW model is that dry deposition is the only process occurring and that in areas where wet deposition is important a higher fractional solubility is assumed. There are data for aluminium solubility in marine rain (Heimbürger et al., 2013; Losno et al., 1993), the Losno et al. (1993) paper includes several samples from the Atlantic. See also for example the impact of the Saharan air layer and the ITCZ on the relative humidity in the atmosphere (Braun, 2010). Addition of this type of analysis would greatly increase the impact of this work.

Seasonality and residence time:

A critical weakness of simple box models like the MADCOW model is that areas with strong seasonality of inputs/outputs are inadequately described when using a single concentration term to fix the inventory. Previous work has indicated that the seasonal cycle (or interannual variability) off the west African coast is on the order of 60 nM for dissolved Al (Pohl et al., 2011) and presumably the residence time is then shorter than 2-5 years first postulated by Helmers and van der loeff (1993). Indeed comparison with Fe suggests that the residence time could be much less than a year or so (Croot et al., 2004; Dammshäuser, 2012; Dammshäuser and Croot, 2012) in these high dust impacted regions.

At present there is little discussion regarding the assumptions inherent in a steady state model such as MADCOW, the focus in the paper is on the inventory size as determined by mixed layer depth and concentration and not on whether the fluxes are in balance over the time scales being investigated. In this regard there are a number of studies that have looked at the seasonality of particle fluxes of Al in the North Atlantic (Chester, 1982; Hwang et al., 2010; Hwang et al., 2009; Jickells, 1999; Jickells et al., 1984; Kuss and Kremling, 1999a; Kuss et al., 2010). With regard to the seasonality in the

Benguela region, there has been recent work looking at the fluxes from the Namib (Dansie et al., 2018; Dansie et al., 2017a; Dansie et al., 2017b) and their predominance during austral winter that is of relevance here to the question of inputs and residence times.

The challenge that arises then is how to reconcile a snap shot residence time provided by a single concentration measurement within a very active seasonal cycle. For example most sampling is in summer which while likely to be the maximum sink for dissolved Al due to enhanced biological productivity and scavenging, but also could be a minimum in atmospheric deposition leading to a residence time of weeks. Contrastingly winter measurements may have higher deposition rates and minimal scavenging resulting in longer apparent residence times (though mixed layers may be deeper also). So understanding the drivers of the fluxes in each region is probably more important than a residence time calculated from a single surface measurement.

Numerous missing references to previous work in the Atlantic:

Not sure if there was some policy by the authors not to include pre-GEOTRACES work on Al in their discussion but there are several papers of direct relevance to this work that need to be included in the discussion as they directly address some of the questions the authors raised. In particular data on surface Al concentrations for dissolved (Gelado-Caballero et al., 1996; Helmers and van der loeff, 1993; Hydes, 1983; Kramer et al., 2004; Kremling, 1985; Kremling and Hydes, 1988; Moran and Moore, 1988; Moran and Moore, 1989; Sarthou et al., 2007) and particulate phases (Helmers, 1996; Kremling and Streu, 1993; Kuss and Kremling, 1999b; Moran and Moore, 1988; Moran and Moore, 1991; Moran and Moore, 1992; Wallace et al., 1981) along with data on the wet deposition of Al (Helmers and Schrems, 1995) and Al flux estimates from atmospheric concentrations (Jickells et al., 1994; Jickells, 1999; Powell et al., 2015). I am unaware of any analytical reason to exclude these data and the same analytical techniques are still used today.

Analytical quality of the GA08 aluminium data and river discharge :

The value of 784 nM that is reported from GA08 seems very doubtful unless some other information can be provided. Such a value is above the solubility limit for Al at seawater pH (May et al., 1979) and while it is close to undiluted river values for the Congo (Dupré et al., 1996; Meybeck, 1978; van Bennekom and Jager, 1978) most samples would be presumably located at least 12 miles offshore and thus significantly diluted. The linear range for most of the analytical systems is also not that large unless the sample is diluted prior to analysis. It raises questions then about the QA/QC applied to the data. If these samples were using the standard Lumogallion method (Hydes and Liss, 1976) as described in the methods section then they should have been corrected for the natural fluorescence of the samples as was pointed out previously for the Congo plume (van Bennekom and Jager, 1978). This correction should not be underestimated as the humic fluorescence at the excitation/emission used for Lumogallion can be considerable in humic rich waters. The methods that employ pre-concentration schemes would not suffer from CDOM fluorescence.

At present the fluxes calculated for GA08 all seem to be too high because of the influence of the river plume and potentially the lack of a correction for CDOM fluorescence. The role of river inputs of Al could be compared to estimates of the riverine influence on the Atlantic (Cotrim da Cunha et al., 2007; Cotrim da Cunha et al., 2009) along with Al contents for the major rivers; e.g. Zaire river (Dupré et al., 1996; Meybeck, 1978; van Bennekom and Jager, 1978), Amazon, Orinoco (Mora et al., 2017) and Niger.

Al composition of dust – the D term in the equation:

The 8% value that Measures and Brown used in the original MADCOW was mentioned in the text but I could not find anywhere what value the authors decided to use (should be around 2.69 mmol/g⁻¹ if 8% Al by weight and 26.981539 is the molecular weight for Al) and if they varied this according to region. If it is constant then the term could be incorporated into the S term to reduce the model variables. How valid is the assumption that it is constant? Could not some of the variability in the S term be related therefore to variation in the D term if other studies made the same assumption? At the very least the value used should be included somewhere in the text. Some explanation of how this was handled in the current work would be most illuminating!

Specific Comments:

P4 line 20: (sp) The chemical reagent is known as **Lumogallion**, not Lumogallium.

P4 line 33. For consistency the dissolved Al concentrations should be in $\mu\text{mol m}^{-3}$.

P5 line 1. There is no explanation of what value is used for the D term in the equation. The other terms are explained in sections 2.2.1 – 2.2.3 but not the D term. If it is constant it could be included then in the S term.

P5 line 7. This is a very large value $\Delta\sigma_\theta = 0.125 \text{ kg m}^{-3}$ to use for determining the mixed layer depth as more recent work have shown that using smaller constraints $\Delta\sigma_\theta = 0.03$ coupled with $\Delta T = 0.2^\circ \text{ C}$ provides a better estimate (de Boyer Montégut et al., 2004), this is in fact the threshold that is used in the Argo mixed layer climatology as cited in Holte et al. (2017). Thus it would be beneficial if the same criteria was used for the observed mixed layer depths to have a consistent approach. The problem with using a value $\Delta\sigma_\theta = 0.125 \text{ kg m}^{-3}$ is that can seriously overestimate the mixed layer depth in high latitude areas leading to an increased inventory and longer residence time.

P5 line 24. The authors should also be aware of work modelling the fractional solubility of aerosol Al (Han et al., 2012). It would therefore be prudent to include this work in the discussion and compare to the field data of Baker et al. (2013).

P6 line 2. The residence time is a key variable in the version of MADCOW employed in this work and so it should be fairly well constrained. As the authors note the original version of MADCOW had the residence time fixed at 5 years along with the fractional solubility at 8% in order to simplify the calculations as changing one would impact the other. In the current approach it should be noted that the Han et al. (2008) work also includes many of the works that were not included in the citation list (see the general comments above) and these works were used to inform the residence times. It is also worth pointing out to the reader that Han et al. (2008) used a fixed mixed layer depth of 50 m and a constant solubility of 5% so this needs to be directly stated in the current manuscript with regard to how the values might compare.

P6 line 10. The modelled residence times will include advection and mixing to an extent, but the use of a fixed solubility and mixed layer depth will also induce some key differences for the regions examined in the present work. This likely explains why the residence times are longer in the Han et al. (2008) work than in others as for many locations, the

underestimation of the solubility and the overestimation of the mixed layer will both work to increase the estimated residence time.

P7 line 9. See the general comment above regarding this extremely high value of dissolved Al.

P8 line 12. There is a considerable amount of surface data for this region and compiling it all in one place may reveal more about the seasonal timings of the dust flux to this region and the aluminium response. See the general comment above regards other works that have data for this region.

P8 line 21. Not all of these studies attribute it to wet deposition, as the ITCZ acts partially as a barrier to the transport of the dust so the highest values are typically associated with direct dust deposition (Ravelo-Pérez et al., 2016; Tsamalis et al., 2013). Though precipitation is enhanced along the boundary between the ITCZ and the Saharan air layer (SAL) (Wilcox et al., 2010).

P9 line 2. From where does the Al rich upwelled waters come from? Al profiles normally decrease with depth (scavenged profile) so this needs to be explained further as it would have then be more likely to be resuspension of Al rich particles close to the shelf rather than a direct upwelling source.

P9 line 3. Do you mean an increased number of particles or that they were *enhanced* in some other fashion? Larger? More sticky?

P9 line 4. See the general comment on this above.

P9 line 8. (sp) reported

P10 line 2. A strong control of the fractional solubility is the relative humidity/hygroscopicity of the particle as this controls the pH, aerosol acidity (Keene et al., 2002).

P10 lines 22 and 24. This isn't a calculated result though, it is an estimate from a comparison with the work of Baker and colleagues.

P10 line 27. See the general comment about relating the fractional solubility to the precipitation or relative humidity levels in the atmosphere for these regions.

P11 line 8. It would be useful to see a plot of the residence times (as a 2D map or property-property plot) to see how they look on spatial scales and in relation to primary productivity if it is the main loss term for Al in the mixed layer.

P11 line 33. It should be pointed out that statistically there are no differences between the values estimated here and those by Mahowald et al. (2005). So speculation on why the Mahowald is over estimated is somewhat spurious.

P13 line 25. The more northerly flux values are likely underestimated as the residence time used is too long as it is likely in reality, days to weeks (see discussion about this above). This is an important point as the MADCOW model should work well where the Al fluxes and concentrations are the highest.

P14 line 2. Most likely – it clearly overestimates the fluxes when most of the Al is from the river.

P14 line 12. See the general comment above about relating the seasonality of the dust fluxes.

P14 line 25. So how do samples collected in the Pacific and Indian oceans tell us anything about deposition to the South Atlantic? Please explain this sentence more clearly.

P15 line 12. ...lack of an island site...

P15 line 16. It is great that AI is measured on GEOTRACES cruises but this does not make this approach using MADCOW any stronger as the majority of the development of this type of work was done pre-GEOTRACES.

P15 line 21. Which IDP 2014 or 2017 – both are citeable now.

P15 line 23. For the Atlantic there are a number of north-south transects for AI and so some sort of seasonal signal is probably already possible and should be examined in the current work.

Figure 2: Please state in the caption the climatology range used here, is it over an annual cycle?

Table S5: The residence times used in this study are significantly shorter than what has been used previously in the MADCOW model (see above) and they are now on the same time scale as seasonal phytoplankton turnover so does this mean the residence time for AI can be scaled to productivity rather than input fluxes?

Figure S4: The figure and the legend for this figure don't match up and there is no explanation of what the circles represent. While it is easy enough to conclude that the circles may represent discrete measurements at stations, the contoured data isn't explained and clearly does not share the same colour scale as the circles as the lowest value on the colour scale is blue and there is no blue in the contoured data. This figure needs to be fixed and explained better prior to acceptance.

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