Interactive comment on “Impacts of dust deposition on dissolved trace metal concentrations (Mn, Al and Fe) during a mesocosm experiment” by K. Wuttig et al.

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Received and published: 14 February 2013


As indicated in the paper, atmospheric inputs are a crucial pathway for metals and nutrients to the surface ocean. Despite decades of research there are still important questions to be answered about the mechanisms involved in release of elements from particles, their changes in form and their impact on ocean ecosystems. Here a novel approach has been applied through the addition of dusts to mesocosms in a follow up experiment to DUNE-1. Whilst several of the authors are experienced in metal analyses in marine systems and the methods used are well covered, I do have some significant issues with the discussion. In particular “processes” are frequently postulated to explain the observations, but most of these are unsubstantiated and lack any real evidence from the current work to support the ideas put forward, or are not clearly argued.

RESPONSE: We thank reviewer #2 for the helpful comments which significantly helped to improve the quality of our manuscript. Regarding this major concern of the reviewer, some significant changes have been made in the discussion of the revised manuscript. Most of the changes are explained along the detailed answers to the reviewer. The major changes are presented here: Proposed changes: 1. We’ve taken out the total trace metal data (ETAAS) and therefore the sections 2.2.5 and 3.4 and put this information into the SI. This implies that we also changed section 4.1 and took out the part in which we discussed these trace metals like Zn, Cd and Cu and in section 4.2 the explanation why we do not further discuss these additional trace metals. As we are only talking about dissolved trace metals, we took out all the d’s in front of the Fe, Mn and Al.

2. We improved the written English.

3. We enlarged section 4.3 slightly to explain the temperature difference better.

4. 4. We have rewritten the explanation of the calculation of the fractional solubility (please see reviewer #1 for detailed information) and added an equation for a better explanation (fig1).

5. 4.3.2 the Al loss rates were compared to the Chl-a inventories (from the HPLC data) (Giovagnetti et al., 2012) instead of (Ridame et al., in prep.) which gives a good correlation and strengthens our statement that dAl was lost by scavenging on biogenic particles.

6. Section 4.4: we refer to Bressac et al. (in prep. this issue) – we send the review-
ers a confidential version of the manuscript. We worked on this section and a better discussion.

7. Concerning the particular case of dissolved Fe, we added the measured FeL data (by CSV after Croot and Johansson (2000)) which show an increase iron binding ligands concentration after the addition of dust supporting the idea developed in the DUNE Project that the effect of two successive seedings can induce different responses in terms of iron dissolution.

Major omissions limiting the interpretation to my mind are: 1) Particles appear very important yet whilst there is information on the particle distribution in a separate paper (Bressac et al.), links of these particles with the fate of metals in the system are very tenuous. I could see no mention of why the metals associated with the particles collected in the trap were not analyzed (e.g. using a mild leach) to see if surficial metals had indeed increased during the period of the mesocosm deployment. Also the involvement of organic phases in generating sinking particles refers to a second Bressac et al paper but this is not even submitted yet it appears, and thus it is not possible to follow up on ideas presented.

RESPONSE: One of the difficulties in an integrated experiment like the DUNE-2 experiment is that most of the data collected are interdependent for their discussion. However, it is impossible to put all the information into every manuscript. For this reason the DUNE community has decided to submit a special issue on the entire experiment with cross referencing to the different manuscripts. The article by (Bressac et al., this issue) will be added as a confidential version and be soon submitted to the special issue in BGD, allowing the potential readers to have access to the particle distribution in the mesocosm during the experiment. Nevertheless, we agree with the reviewer that some information on particles might be important for the present manuscript. The major trends on particle dynamics in the mesocosms described in (Bressac et al., this issue) will be more precisely discussed in the present manuscript. Concerning the analyses of associated metals on particles collected in the traps, we would like to draw attention to the fact that this type of analysis represents a real analytical challenge in the configuration of this experiment. The DUNE-2 dust additions represent a large flux of lithogenic material in the mesocosms. Indeed, if we consider the case of aluminium during DUNE-2, for example, the maximum loss of dissolved aluminium (Al) observed is of 300 $\mu$mol m$^{-2}$. The amount of dust particles added to the mesocosms is $10 \text{ g m}^{-2}$ which represents 15000 $\mu$mol m$^{-2}$ of particulate aluminium (based on the elemental composition of the added dust). The particulate Al represents 50 times the expected Al that might be scavenged on these particles. In this condition, a mild leach would have dissolved a small fraction of particulate aluminium which we could discriminate from scavenged Al. For this reason, we consider that estimating scavenging through trap collected particulate analysis is not a valuable approach in this case.

2) I see no information on biomass or number of organisms (either autotrophic or heterotrophic), another potentially very important class of particle present– the only mention of biota is to a separate paper, information from which is not given here, and the Ridame paper has not even been submitted as yet according to the citation. No information is shown to directly implicate biota with removal of metals from solution.

RESPONSE: We agree with the reviewer that no information on biomass was given in the manuscript. In the revised manuscript, we have used the HPLC data presented by Giovagnetti et al. (2012) in order to estimate the role of biomass on trace metal scavenging (see response to no. 11). Moreover, in order to estimate the Fe uptake some information on bacterial abundance will be added to the revised manuscript in section 4.3.2.

3) There is very limited information on the physical structure of the seawater column in the mesocosm, and any mixing processes occurring. This is relevant for understanding the distribution of dissolved metals in the mesocosm that may have been released /removed after release, and variability within the mesocosm. Mixing is apparently occurring (p 13878 line 20) but what is the impact on the metal distributions and what causes this mixing? Is the lateral water column structure within the mesocosm re-
ally uniform, or are there lateral concentration gradients that are not discussed? Also p13879 l1-5 talks of marked changes in physical conditions over the first few hours “likely impacted particulate export dynamic” - how?? This is not at all clearly explained, and does not relate readily to the rest of discussion on structure.

RESPONSE: Denman and Gargett (1983) show that mixing occurs due to solar insolation and wind. We assume that during the mesocosm experiment the primary driver of mixing in the mesocosm is temperature, because the mesocosm protects against mixing due to the wind friction. Moreover once the mesocosms are closed, salinity changes might be limited and we assume that density differences within the mesocosms are mainly driven by temperature. Due to the risk of contamination, no vertical profile with a CTD was made within the mesocom. Instead fixed temperature sensors (all plastic) were deployed at different depths in order to measure temperature (see Guieu et al. (2010)). Therefore we chose to use the only available physical and continuously measured parameter, temperature difference, as proxy for the mixing in- and outside the mesocosms. Changes in this proxy of mixing are described on page 13873 of the manuscript. See below for details that have been added to the revised manuscript.

Concerning the lateral water column, the extension of the mesocom was only (P13862 L20-22) 2.3 m of diameter. This means that there was only very limited space for lateral mixing. We assumed that the lateral gradients within the mesocosms were negligible.

Text changes: “In fig.5(a), the calculated temperature difference between the surface and the bottom of the mesocosm is plotted (0 – 10 m). Indeed the temperatures measured at four depths (0, 3, 6 and 10 m) inside and outside the mesocosms are the only available physical parameters measured during the entire experiment. The temperature difference between 0 and 10 m measured inside the mesocosm is therefore used as an indicator for mixing or stratification. If there was little or no temperature difference between 0 and 10 m, we interpreted this as an indication that the water column in the mesocosm was well-mixed. We assume that the more significant the temperature difference, the more the mesocosm was stratified. The proxy illustrated that the experiment can be separated into four periods: a relatively well-mixed mesocosm during the first 96 h; a stratified water column from 96 to 180 h; a mixed water column again until 240 h; a stratified water column until the end of the experiment. The main difference between the two dust additions was that the first occurred in a well-mixed water column and the second one in a stratified one.”

Examples of where I was not convinced by the claims of knowledge of processes occurring are: p.13876 3-4 “The complex processes that control the fractional solubility (of Fe) are clearly shown here”. All that is actually shown is that there is variability in dissolution between batch additions, and removal is variously ascribed to “biological utilization” (no evidence given for this) ..“could correspond to scavenging”- which processes specifically are unambiguously and rigorously demonstrated to be occurring? I do not see any information for this, particularly as apparently no particles were analyzed. Further unsubstantiated ideas are given on page 13879. Are we really any better informed about what processes are occurring as a result of this work relative to DUNE 1??

RESPONSE: As mentioned earlier, we agree with the reviewer that some “claims of knowledge” in the discussion were not always rigorously demonstrated. However, concerning “the complex processes that control the fractional solubility (of Fe)”, we believe that our study provides new information that complements the earlier study made during DUNE-1. In the revised manuscript, we have more precisely demonstrated that biological utilization is negligible (see response to no 11). If the Fe loss is not explained through biological uptake, Fe must have been scavenged on the mesocosms surface or on sinking particles. Even if we are unable to make chemical analyses on particles to demonstrate scavenging (see earlier comment), during DUNE-1 some evidence of scavenging have been demonstrated by a modeling study (Ye et al., 2010). This study was not focusing on new proof of this scavenging but on the effect of a second dust addition. We show that the 2nd dust addition induced a transient dissolution, supported by an increase in iron binding ligands (new data are reported in this revised
manuscript to support this). We therefore demonstrated that iron is governed by much more complex processes than Mn or Al. For all these reasons, we believe that this study is clearly a step forward after the DUNE-1 experiment.

Some other important features are not explained as far as I can see. Thus for Mn second seeding the highest dMn is very close to surface (<5m) then by next sampling events, the Mn at depth is relatively uniform. Now is this a result of mixing of water within the mesocosm (see point 1 above; infers very effective vertical mixing going on) or due to particles falling and continued release of Mn, in which case what happens to the high surface concentrations??? These points are not really answered or addressed in the paper.

RESPONSE: This is a valid point and we need to explain this feature in more detail in the discussion (in 4.3.2). It is true that the highest Mn values were observed very close to the surface after the 2nd seeding and this can be explained by the strong stratification within and outside the mesocosms when the 2nd seeding took place. Mn is released mostly instantaneous from the dust or due to H2O2 (not measured) and, due to the strong stratification, we observed a strong accumulation of Mn in the surface layer where the dust was added. The values at 5m started to increase 24-48h after the 2nd seeding when the mixing (3rd period) had started again. We then observed lower concentrations in the surface, but as the water column in the mesocosm mixed higher concentrations were observed, first at 5 and then at 10m depth.

Overall I came away with view that key processes were not rigorously examined. The interpretation was not helped by much potentially useful information being not accessible in unpublished manuscripts (and not presented or used here) and weak arguments being used to support pet theories. I think this manuscript has some good data but it needs a major rewrite with additional detail and information (e.g. particle concentrations, what is happening with the bacteria and phytoplankton) to test ideas presented. It is no use having key information in other unpublished manuscripts when it is needed here for the interpretation. Overall more focus and better presentation of arguments to support ideas presented are needed.

RESPONSE: As mentioned earlier, we agree with this comment of the reviewer. We hope that the significant changes in the discussion and the submission of a new manuscript (Giovagnetti et al., 2012) in the special issue and Bressac et al. (this issue) as a confidential version for the reviewers and soon submitted will convince the reviewer that our dataset contributes to the comprehension of the impact of atmospheric deposition on trace metal chemistry in the ocean. We explicitly added FeL data into our manuscript for a better comparison and discussion of the results and we compared the Mn data to bacteria. From the Chl-a (HPLC) data (Giovagnetti et al., 2012) we calculated the inventories in the mesocosms and found a correlation to the Al loss rates and added fig. 6 in the revised manuscript to show this.

Specific points: 1. 13864 line 20 brackets need rearranging.

RESPONSE: In the revised manuscript, the brackets have been rearranged.

2. 13865 7-9. Were these Mn analyses done directly on the SW or after some pre-concentration?? Later in the methods it says that other elements were measured using solvent extraction prior to ETAAS, including Mn. It needs to be made to be made clear how the non malachite green method Mn was measured. Thus material lines 7-11 13867 needs to be inserted in earlier section discussing Mn ananlysis.

RESPONSE: The section for the ETAAS-Mn was moved to the Mn-FIA section and information about these two Mn-measuring methods were ded for a better differentiation.

3. 13865 15 should this not be < 1 nmol/L??

RESPONSE: This has been corrected in the revised manuscript.

4. 13866 Wavelengths rather different to the ones used by Hydes and Liss – any reason for this

RESPONSE: Yes, this is a slight variation to the wavelength used by Hydes and Liss
This is due to the better resolution on modern fluorometers today and this is the wavelength with the maximum fluorescence.

5. Presumably the first and second dust additions were identical in terms of mass added? (it does not explicitly say this at the moment)

RESPONSE: Yes, the amounts were the same P13858 Line 12: “Two consecutive artificial dust deposition events, each mimicking a wet deposition of 10 g m 2 of dust, were performed during the course of this DUNE-2 experiment.”

6. What is the physical mixing within the mesocosms or is it totally stratified and particle fall and subsequent release the only mechanism for transfer of Mn to deep part of mesocosm? See comments above.

RESPONSE: This connects to mixing and fig. 5. We worked on section 4.3 for a better explanation of the thermal stratification which occurred twice during the experiment – at the end of the 1st seeding and in the 2nd 24h after the 2nd seeding and again towards the end of the 2nd seeding experiment. At this time the mesocosms were thermally strongly stratified with 6 °C difference between the surface and 10m and this can be seen in fig. 6(a). Bressac et al. (this issue) show that the particles accumulated in the upper 2 m of the mesocosms directly after the 2nd seeding and at the time when the mesocosms were thermally stratified. In the case of Mn we worked on a better comparison between Mn and bacteria in section 4.3.2 and changed it to: “However, for Mn there was no appreciable difference in the loss rate after the first and second additions of dust, suggesting that the loss of Mn was not affected by uptake or adsorption to phytoplankton. Scavenging of Mn by particles requires the oxidation of Mn(II) prior to particles loss, as Mn(II) is only weakly complexed or adsorbed to particles (Yeats and Strain, 1990; Sunda and Huntsman, 1987). Abiotic oxidation of Mn(II) is normally considered to be too slow to account for the adsorbed loss rates and instead it is strongly believed that bacterial oxidation is the major pathway in the ocean (Morgan, 2005; von Langen et al., 1997). During this experiment bacterial numbers were relatively constant throughout the experiment in all mesocosms suggesting that the Mn oxidation rate was relatively constant (Pulido-Villena et al., this issue). The dissolved Mn loss rates observed here are equivalent to 0.35 0.5 % per day of the dissolved Mn pool, which is in the range of rates (0.2 1.5 % per day) observed in other oligotropic regions (Moffett, 1997). It is also likely that a diel cycle in Mn oxidation was occurring, due to photo-reduction of MnO2 via reaction with humics or photo-produced H2O2, and potential photo-inhibition of Mn oxidizing bacteria, as has been observed in coastal waters and the Sargasso Sea (Sunda and Huntsman, 1988, 1990). However analysis of diel cycles is beyond the scope of the present work. ”

7. 13870 line 8-9 Syntax needs some work here.

RESPONSE: This has been corrected in the revised manuscript

8. 13872 line 3 metals plural.

RESPONSE: This has been corrected in the revised manuscript.

9. Argued that very rapid release important to follow yet first samples after addition only 12 H in?? A significant amount of release and scavenging could have happened by this point.

RESPONSE: True, it would have been great to have had samples every 3-4h directly after each off the seedings, but unfortunately this wasn’t possible due to logistical reasons. The mesocosms were in remote area, but this also meant that it was more than half an hour of boat drive between the mesocom the station with the containers to work in. A lot of the samples needed quick treatments and it was necessary to go back as quickly after each sampling as possible.

10. Why are dissolution and scavenging processes approximated to a linear relationship to give rates? In just about any dissolution experiment I have seen in the literature you have a curve with rapid initial release followed by slower changes.

RESPONSE: We appreciate the reviewer’s comment which allows us to clarify things
on the approach we used in our manuscript. We did not represent scavenging rates, but only dissolution and loss rates, with the expectation that scavenging is part of the overall loss term. Under this terminology, uptake for phytoplankton growth is not considered scavenging, as scavenging is typically defined as adsorption onto sinking particles, and uptake into active cells is thus not considered as scavenging but is still a loss from the dissolved phase.

We based our linear approach to the dissolution rate on earlier work (Wagener et al., 2008) that showed dissolution could be modeled as two linear dissolution processes. The 1st one has a steeper slope and then the 2nd linear process reveals a flatter slope. In our experiment, at the time scale we sampled we assume that we only see the second slope and therefore the whole process is essentially linear. Our dissolution rates therefore are a minimum estimate for the overall rate. It is not possible in a multiple mesocosm experiment to obtain a dataset that could resolve the dissolution rate process more than this and so the principle of Occam’s razor applies here and we don’t try to fit 3 or 4 points to a higher order curve for which we have no data at timescales longer than a week and it is clear there are other processes occurring in the water column.

The curved dissolution rate graph that the reviewer suggests is typical of flow through experiments in which a fresh solution constantly flows over the aerosol solution. There are many examples in the literature for this; e.g., (Desboeufs et al., 1999). A variant on this is the semi-continuous flow through reactor (Wu et al., 2007) which uses small volumes of water in contact with the aerosol for a fixed time and then replaces with a fresh solution for the next time point. This method also typically gives a curve with an initially rapid dissolution and then a slower dissolution as the experiment proceeds, such a curve can be fitted with either two linear curves or in some cases an exponential of the form \( A = A_{\text{max}}(1-e^{-kt}) \), where \( A_{\text{max}} \) is the max amount dissolvable, \( k \) is the dissolution rate constant and \( t \) is time. In a recent study, using the same approach as Wu et al. (2007), but much shorter dissolution times (minutes rather than hours), near linear increases in concentration with time were found (Aguilar-Islas et al., 2010).

In fixed volume solutions, in which aliquots are removed with time, the data is also often fitted to an exponential curve as noted above, though a recent study (Shi et al., 2011) using this approach also indicates that over the first 6-20 h the dissolution rate their data could be estimated by two linear rates; a fast initial rate occurring over the first hour or so and a slower rate over the rest of the time – analogous to the findings of Wagener et al. (2008). Shi et al. (2011) also examined other model forms to describe their data.

11. 13877 line 8 Correlations of Al with Chlor were also found by : : :” No correlations of Al and Chlor are given here

RESPONSE: We agree with the reviewer that this sentence was inappropriate. During DUNE-2, we observe that the loss rate of Al is increasing when the inventory of Chl-a in the mesocosm is increasing. When plotting the loss rates of Al against the Chl-a inventory in the mesocosms, we observe a significant correlation. In the revised manuscript, this correlation is presented on a new figure based on the Chl-a data from companion manuscripts in the special issue. This supports the idea developed in this manuscript that the higher loss rate of Al observed after the second dust addition is linked to the increase of biogenic particles in the mesocosms. These observations are in agreement with Moran and Moore (1988) study where a decrease of dissolved Al concentration is observed after a bloom of phytoplankton. The section concerning this part of the discussions has been changed in the revised manuscript to: “During DUNE-2, an increase of chlorophyll-a in the DUST-Mesos is reported by Giovagnetti et al. (2012). These increases in Chl-a inventories correlate well with the increases in Al loss rates (see fig. 6) suggesting that this could explain the observed significant change in the loss rates for Al is linked to the amount of biogenic particles that might scavenge the Al. Correlations of the relation between Al scavenging and Chl-a increase were also described by Moran and Moore (1988). However, this is not observed for Mn which had similar loss rate after the first and the second addition of dust, indicating that
Mn was not appreciably lost by scavenging on biogenic particles.”

12. Confusing - Wagener paper refers to DUNE1, how can you relate biological activity in the DUNE2 experiments (which presumably the first sentence refers to) when no data/information is given on biological activity? If the chlor a is important it should be reported here as well as Ridame (note this manuscript has not even been submitted yet!).

RESPONSE: We agree with the reviewer and added some information to this section. The reason why we compared with the DUNE-1 iron uptake is because we considered that this estimation is in any case an overestimation of what happened during DUNE-2 and is therefore indicated here to demonstrate that iron dissolution could sustain biological activity. The estimation of biological uptake of Fe during DUNE-1 was based on an increase of Chl-a concentration from 0.10 µg L−1 to 0.25 µg L−1 and bacterial abundance 0.5 10⁶ to 1 10⁶ cell mL−1 in the first 48 h following the dust addition (See Wagener et al, 2010). Based on elemental ratios in microorganisms cells, an iron uptake of 500–1000 nmol m−2 d−1 has been estimated. During DUNE-2, in the 48 hours after the dust addition, the Chl-a concentration increased from 0.07 µg L−1 to 0.10 µg L−1 after the first addition and from 0.12 to 0.15 µg L−1 after the second addition. The bacterial abundance does not show significant increases after both additions. For these reasons, we estimate that iron uptake by microorganisms following both dust additions during DUNE-2 is lower or equivalent to DUNE 1. More details have been added on this point in the revised manuscript.

13. You need a reference to say that this Fe is indeed “adequate” to relieve Fe limitation and is this relevant here in the Med where apparently the system is primarily N (unpublished Ridame paper) or P limited.

RESPONSE: Here again we agree with the reviewer that the formulation was confusing. This part of the Mediterranean is not Fe limited. We just wanted to prove that the transient dissolved iron increase induced by dust particles after the second addition could support the phytoplankton growth induced by the addition of dust. This section has been corrected in the revised manuscript.

14. Figure 5. Units for inventories needed.

RESPONSE: Units have been added in fig. 5 (µmol m−2)


Pulido-Villena, E., Baudoux, A.-C., Obernosterer, I., Catala, P., and Guieu, C.: Enhanced carbon remineralization by the microbial food web after dust deposition: results from a mesocosm study, Biogeosciences Discuss., this issue.


Sunda, W. G., and Huntsman, S. A.: Diel Cycles In Microbial Manganese Oxidation And Manganese Redox Speciation In Coastal Waters Of The Bahama-Islands, Limnol.


Interactive comment on Biogeosciences Discuss., 9, 13857, 2012.
Case 1: 1st addition

\[
\text{FracSol}(%) = \frac{\text{DM}_{\text{max}}}{\text{DM}}
\]

Case 2: 2nd addition

\[
\text{FracSol}(%) = \frac{\left| \text{DM}_{\text{max}} \right|}{\text{DM}}
\]

Where \( A \) is the surface area of the mesocosm and assuming it is a perfect cylinder, \( t \) represents the time since the last dust addition.

Fig. 1.