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

This manuscript reports findings from a dust fertilization mesocosm experiment conducted in the oligotrophic Mediterranean Sea. The study charted the changes in dissolved Mn, Al, and Fe concentrations over time following two dust “seedings”. The results are used to calculate dissolution rates, loss rates, and aerosol solubility. In general, there is value in the dataset but I have serious issues with both the presentation
of the data and the support offered for many of the conclusions. The structure and writing is confusing and could benefit from careful revision by the senior members of the authorship.

RESPONSE: We thank the reviewer for their appreciation of our dataset. We have worked extensively on our scientific writing, structure, especially the discussion and conclusions to seriously improve this manuscript in response to the valuable comments. Large sections in the discussion were rewritten for the revised manuscript, two figures added and 1 deleted (fig. 4 the resolution and the parts corresponding to it).

General Comments: I found the manuscript relied heavily on referencing previous work, particularly concerning the first mesocosm experiment DUNE-1, when describing this experiment. Readers should not have to search for other papers in order to gain a basic understanding of the experimental set up. Further, comparisons between the two studies are not especially helpful. Much of the text on P13862-13863 concerns this sort of a comparison. The space would be better utilized to more completely describe the methods employed during DUNE-2. The manuscript also placed too much reliance on citations of companion manuscripts that are still in preparation. While this is somewhat of a necessary evil in large, collaborative projects, our ability to interpret the findings in Wuttig et al. is hampered considerably. For example, an increase in biomass reported in Ridame et al. (2012) is cited to support a change in dAl loss rate. Because Ridame et al. (2012) in not available, the reader is unable to follow up on this discussion and no supporting data is reported here.

RESPONSE: We find the reviewer's comment here slightly bizarre in that it is standard practice for articles to refer to previous work and in particular to refer the reader to earlier work using the same approach for the in depth method description. Furthermore we completely disagree with the reviewer’s statement that comparison between DUNE-1 and DUNE-2 is not especially helpful, quite the contrary we believe that as these are the only two studies of their type that have been performed it is absolutely imperative
that they are compared directly. We also note that later comments by the reviewer also heavily contradict their own assertion stated above as the reviewer seeks to link the work done in DUNE-1 and DUNE-2 in their specific comments on our work. The Chl-a (by HPLC) data is published by now by Giovagnetti et al. (2012) and we added fig. 6 to our manuscript in which we show that the Al loss rate is correlated to the Chl-a inventories of the mesocosms (for more information please see reviewer#2).

I do not think that the use of contouring in Fig 1-3 is appropriate. Contouring implies knowledge of the dissolved concentrations over times and depths that were not sampled and I do not think there is sufficient data to interpolate over these missing data. What are the assumptions made by the software to calculate the missing values? Are the values assumed to change linearly between two data points? Is that a reasonable assumption? This issue is most clear in Fig. 3 because of the missing dAl values (C1 for example). No data is plotted in much of C1 because there are no data points at the surface or at depth and the software is unable to interpolate between a data point and “no value”. Why should we believe the software’s calculated values in other instances of missing data? Also, from these figures it is apparent that dissolved metal concentrations were not measured within 12 hours prior to the second seeding. It would seem that we do not truly know what their concentrations were prior to the second addition.

RESPONSE: The concentrations did not change over the last 3 days before the 2nd addition of dust was performed. Therefore it was decided to use this point as the starting before the 2nd seeding. This decision goes back to logistical problems and we think that we achieved good data coverage. Therefore we used one of the standard contouring programs. We used an optimal Delaunay triangulation and gridding of Cartesian data (http://gmt.soest.hawaii.edu/gmt/html/man/triangulate.html). We are aware that contouring might implicate things or missing data points as it interpolates, but this is a point that applies to nearly every work. Moreover, we have taken care to have some black dots on these figures which represent the samples in order that the reader can clearly evaluate what is “interpolation” and what is “data”. We decided to
use this standard feature as we think that it shows the differences, changes and the relationships better than if we had used plots with single points.

Specific Comments: P13858 Line 13: How does the addition of dust to the mesocosm mimic wet deposition?

RESPONSE: It was an addition of evapocondensed dust dissolved in MilliQ water (MQ), sprayed onto the surface of the mesocosms and therefore mimicking wet deposition. For the changes in the revised manuscript and further explanations please see reviewer #1. 

P13863 Line 9 describes the dust as being “cloud processed”, although what that means is not made clear (Guieu et al 2010a should be cited). I do not think that the dust seedings mimic wet deposition at all. During wet deposition, dust particles are carried through the sea surface microlayer by the momentum of the precipitation. Further, dust in wet deposition is bathed in mildly acidic water which will likely effectively increase the initial influx of soluble trace metals. This process introduces readily soluble and dissolved trace elements directly to the water column. Dust deposited by dry deposition (or seeding) will be exposed to the complicated chemistry of the microlayer prior to incorporation into the surface waters. Is 10 g m-2 a reasonable dust flux?

RESPONSE: This has been changed and Guieu et al. (2010a) has been cited in this context. The seeding was performed in 2010 exactly as in 2008. We politely disagree with the reviewer and think that we were mimicking wet depositions. The evapocondensed dust was dissolved in MQ and sprayed onto the surface of the water column in the mesocosms with an all plastic gardenspray. Then the dust was carried through the water column. The originally collected soil which we used was sieved and prepared with mild acids to mimick the midly acidic conditions of a wet deposition. Guieu et al. (2010a) show that 10 g m-2 is a reasonable dust flux as in the Mediterranean easily dust fluxes up to 22 g m-2 have been observed (Bonnet and Guieu, 2006;Guieu et al., 2010b;Ternon et al., 2010).
P13860 Line 3-10: This sentence runs on and would be clearer if rewritten.

RESPONSE: For the revised manuscript, this sentence was broken down into two parts: “Indeed, in addition to atmospheric factors controlling the inherent solubility of the metal in the particle (size of the particles (Baker and Jickells, 2006), mineralogy (Journet et al., 2008), chemical composition (Sedwick et al., 2007)), there are a number of factors that can be important once the particle is deposited in seawater. These factors can be e.g. the initial concentration of dissolved metals in seawater (Liu and Millero, 2002; Mendez et al., 2010), photochemical processing (Fe(III) to Fe(II)) (Zhuang et al., 1992) and lability in the atmosphere and in seawater (Spokes and Jickells, 1996), but also specific chelating substances like for Fe (Gledhill and Buck, 2012; Wagener et al., 2008).”

P13861: The chemistry of Fe should be discussed in addition to that of Mn and Al.

RESPONSE: For the revised manuscript the chemistry of Fe was also discussed shortly.

P13862 Line 7-13: The objectives do not read as such. They need to be clear and concise. For example: 1) To assess the impact of dust seeding on dissolution and loss rates. 2) To quantify these processes.

RESPONSE: We agree with the reviewer and the objectives have been changed to: "This paper presents the dissolved trace metal stocks of Fe, Mn and Al during the DUNE-2 experiment. Based on the revised experimental strategy after the DUNE-1 experiment, the specific objectives of this study are (i) to assess dissolution and loss rates of these trace metals after the addition of dust and (ii) to quantify the processes involved on different time scales."

P13862 Line 24: What is meant by “...the water column was preserved.”?

RESPONSE: This was changed to “retained” and explained in the revised manuscript.

P13863 Line 6: How far away from the mesocosms was the collection of the OUT C8219
samples?

RESPONSE: The outside (external reference point for the control mesocosms- this is also now explained better in the revised manuscript) samples were taken approximately 10 m away from the installed mesocosms. It was like a quadrangle with one corner for the 3 control mesocosms (tied together), the 2nd for the 3 dust seeded mesocosms, the 3rd for the optical mesocosms and the 4th for sampling the samples outside all of these 7 mesocosms to get some data for a comparison to exclude contamination.

P13863 Line 8-9: How do water masses “settle”?

RESPONSE: This was changed to “equilibrate” in the revised manuscript.

P13863 Line 13-15: A more thorough description of the seeding process is needed. How was the dust introduced to the surface?

RESPONSE: This was changed to: “The two consecutive seedings were performed with each 41.5 g of evapocondensed Saharan dust that was dissolved in Milli-Q and sprayed onto the surface of the mesocosms. This corresponded to a realistic, high wet deposition of 10 g m \(^{-2}\). The first seeding took place at t0, the second at t166.”

P13863 Line 16-24: Were discrete samples collected for each trace metal? Were samples collected for each metal at every sampling time? There appears to be missing data in some of the figures and the reader may wonder why this is.

RESPONSE: Yes, discrete samples were taken for each trace metal (TM, Fe, Mn and Al) and for every other parameter. Therefore it sadly wasn’t possible to take every sample at every time point. This had logistical reasons, some were lost due to for example machines going crazy, blockages etc. Also we were limited in bottles in some cases. Also please see reviewer #4.

P13865 Line 15: <1 nmol l\(^{-1}\)?

RESPONSE: This was corrected in the revised manuscript.
P13867 Line 13-20: The codes are confusing and this description does not aid the reader. I suggest devising a simpler coding scheme and perhaps presenting that information in a table to help clarity.

RESPONSE: The codes were simplified and better explained in the result section: “The nomenclature for samples of the DUNE-2 experiment is as follows: dust seeded mesocosms D1, D2 and D3, unseeded control mesocosms C1, C2 and C3 and the sampling point outside the mesocosms. Samples were taken at 0.1, 2.5, 5.0, 7.5, 10.0 and 12.5 m depth. The time “tx” is expressed in hours (x) since the first dust addition and in parentheses “tx(y)” the time (in h) since the second dust addition. The samples outside the mesocosms were taken as an external reference point to the control mesocosms and the concentrations are not reported in the figures, but are available in the supplementary information.”

P13867 Line 25: It would be clearer to present the concentrations of dMn rather than the change in concentration.

RESPONSE: This was changed to make it more obvious in the revised manuscript.

P13867 Line 9-18: This paragraph is very difficult to follow. It might be clearer to simply discuss the trends in concentration change rather than the specific values at a given time and depth.

RESPONSE: The paragraph was simplified and the sentences shortened.

P13868? Need to simplify this section

RESPONSE: This was changed to make it more obvious in the revised manuscript.

P13869 Line 21: “…pretty uniform…” is not a useful descriptor.

RESPONSE: This was changed in the revised manuscript to constant.

P13869 Line 24: Why was Al not measured for 72 hours? What was the sampling schedule and why was it not the same for each of the trace elements?
RESPONSE: This happened due to the logistical scheme to and on Corsica and for Al there is always the problem with non-contaminating sample bottles for dAl. As dAl was not measured directly on Corsica, but back in Kiel, we only had a certain amount of clean bottles for Al and had to decide directly there which were taken. Afterwards we would have loved to have every time point sampled.

P13870 Section 3.4: Is this section necessary? There is no further discussion of these metals.

RESPONSE: the paragraph 3.4 was eliminated from the revised manuscript as it is of no relevance for the other three dissolved trace metals. Therefore also 2.2.5 was shrank down to only the Mn measurement for the validation of the Mn-FIA data (which was then moved to section 2.2.2). Also section 4.1 was therefore shortened to make the discussion have more of a leitmotif. But as the data is important as baseline data and for comparison reasons, the values are still given as supplementary information to the paper.

P13870 Line 17: How were concentrations determined to be “significantly” different? Comparing the values in Table 2 shows that the differences were often >10% and as much as 50%.

RESPONSE: In Table2 in the revised manuscript the $1\delta$ is shown. Yes, as significantly different >10% was used, which was here more than twice the precision.

P13872 Line 7: What does “…the closest value was used for the extreme values” mean?

RESPONSE: This was changed in the revised manuscript to “values at the extremes (surface and bottom)”.

P13872 Line 19-21: The concentration differences among the sampling resolutions only occurred in D2 and not D1. Is this significant?

RESPONSE: The temperature was only measured for 1 mesocosm which we calcu-
lated the mixing/stratification from. Therefore if one of those two dust seeded mesocosms was more similar stratified (like C1 where the temperature sensors were installed) and the other one not, this might lead to this slight difference. We still think that this is significant.

P13872 Line 27-29: How does Figure 4 show this? This is no small point as one might expect a great deal of response within the first 24 hours following seeding. How do these observations compare with previous experiments?

RESPONSE: We took out fig. 4 out of the revised manuscript and the corresponding text as we only had two dust seeded mesocosm to do these calculations and comparisons, but the responses for the three different calculations in the first 24 h after the 2nd seeding were not entirely the same for D1 and D2 and therefore a clear statement is not possible.

P13873 Line 11: How was temperature measured? Perhaps this is addressed in Guieu et al. (2012) manuscript but how was the determination of mixing versus stratified made? Is a temperature difference of 6 °C sufficient to inhibit mixing?

RESPONSE: The temperature was measured by installed temperature sensors inside one mesocosm and outside the mesocosm as described in Guieu et al. (2010a). Bres sac et al. (this issue) show the temperature variations 20-27.3 °C) with temperature sensors installed in the mesocosms and explain nicely how the thermal stratification was induced due to hot air temperature and a subsequent sudden heating of the surface waters. This happened twice- at the end of the first seeding period and continued in the beginning shortly after the second seeding and at the end of the experiment. By comparing our calculations (we carefully revised the written explanation for this) to their results and the resulting particle load in the stratified surface waters, it can be clearly observed that our approach with assuming that a difference of 6 °C in 10m water column is stratified, is valuable.

P13874 Line 25-28: The description of the dissolution percentage equation is unclear.
The equation must be clearly described with special attention paid to the denominator as this is particularly unclear. The implied rationale for this equation is that any increase (the authors chose the mean inventory change over the time of the experiment) in the inventory of a metal relative to the control is due to the dissolution of that metal from the added dust. Based on the values in Table 3, the authors do not use the “percentage of each element added with dust” but rather the amount of element added (in $\mu$mol m$^{-2}$) assuming a particular chemical composition of dust (e.g. 2.31% for Fe which is assumed based on a previous study).

RESPONSE: We have written the calculation (fig.1) as an equation and rephrased the explanation to: “The fractional solubility of an element from dust particles in seawater is commonly expressed as a percentage. For a given element at a given time, the fractional solubility is the ratio between the amount of an element dissolved from dust in seawater and the total amount of this element introduced with the dust particles. Here, the solubility of each element from the added dust is estimated at the time point when the inventory of this dissolved element in the mesocosms is at its maximum after the dust addition. The amount of the dissolved element introduced by the dust is estimated as the difference between the inventories in the dust seeded and the control mesocosms. The total amount of the element introduced by dust is estimated from the amount of dust introduced to the mesocosm and the elemental composition of the dust used (Guieu et al 2010). It is important to note that in the case of this experiment, using the difference of the inventories between dust seeded and the control mesocosms to estimate the dissolved amount, allows us to avoid taking the changes in dissolved concentration observed in the control mesocosms during the experiment into account. The dissolved concentration changes in the control mesocosms are independent from the added dust and must therefore not be taken into account in the solubility calculation. This is an important difference with classical abiotic batch protocols where the amount of dissolved element is estimated from the difference in concentration before and after the dust addition.”
P13875 Line 1-2: This sentence is unclear.
RESPONSE: This sentence was rephrased.

P13875 Line 3: What estimation?
RESPONSE: This sentence was changed in the revised manuscript to: “An estimation was made for each dust addition even if the inventory had not reached the CONTROL-Mesos value again after the first addition. Values of fractional solubility are reported in Table 3.”

P13876 Line 3-5: I do not think that anyone in the marine aerosol community would disagree with this statement but I also do not think that this study brings us any closer to resolving the “complex processes that control the fractional solubility”. The authors only report one solubility estimate (0.12%) for Fe which would imply that is the absolute value for “cloud processed dust” as devised for this experiment. The authors do not make a compelling argument that their method is any more realistic than the unnamed laboratory methods and their values for all three trace metals fall within the ranges found in the literature. Ignored in this commentary is that much of the literature includes data from trans-oceanic cruises which sample a broad combination of aerosols resulting in the “fractional Fe solubility spread” cited here. In my estimation, the authors appear to be confounding the modeling community’s tendency to apply one (or more) aerosol Fe fractional solubility estimate to their models of global soluble Fe deposition with the actual reports of aerosol solubility from the field.

RESPONSE: We thank the reviewer for their comment and agree with them regarding the mixture of aerosol types that are typically encountered in oceanic cruises but don’t agree that our one value implies this is the absolute value for ‘cloud processes dust’ as that is clearly not what we stated in the manuscript. We believe that the mesocosm approach is more realistic to estimate the fractional solubility: This method allow to reproduce the settling of dust particles through the water column and the particle-particle interactions that can occur during settling. For this reason, we think it is an important
result to see that for Mn and Al the fractional solubility estimate in this study is in the same range than estimated during laboratory experiments. Concerning iron, we show in this study, that in the conditions of the DUNE experiment, no fractional solubility is observed at the daily scale after the first addition of dust because of scavenging whereas but the second addition is followed by a transient increase in dFe. This is a clear evidence of the importance of the "biogeochemical state" of the water mass were the dust particles settle. In the revised manuscript, this hypothesis is supported by iron binding ligand measurements. Furthermore we have more faith in the modeling community as we know through contact with many of them that they are aware of these issues and are trying to incorporate more realistic parameterization of fractional solubility into their work, however they are, as usual, limited by the computational costs and more likely in this case the lack of a scientific consensus on how to parameterize these processes.

P13816 Line 18-27: Returning to the issue of whether the mesocosms were indeed stratified, this text seems to indicate that there was mixing occurring. “...the inventories...the same when integrated over the entire mesocosm”. This observation would imply that stratification was not an issue as does “...the overall rate of dissolution seemed not to be affected by the mixing of the water column...”

RESPONSE: The presence of a significant (> 1 °C) vertical temperature gradient in the mesocosm can only occur when the water column is stratified as salinity does not change appreciably upon addition of the simulated wet deposition and there are no other inputs that will alter seawater density as the mesocosms had rain covers. Thus a return to conditions where there is no gradient indicate mixing events; from convective overturn or wind induced mixing. It is clear from figure 5 that period of stratification and strong mixing occurred throughout the duration of the experiment. As we stated in the manuscript, stratification did seem to play a role immediately after the 2nd addition in terms of phytoplankton abundance and concentrations of trace metals but it did not appear to impact the dissolution of the dust overall. In simple terms the same amount of dust was dissolved into a smaller volume due to stratification.
P13876 Line 25: What is meant by “dilution of the dissolved elements”? Did a rain event dilute the mesocosm?

RESPONSE: There was no rain event impacting the contents of the mesocosms, the dilution referred to here is in reference to the mixing of the metals derived from the dust into the whole mesocosm. In this way they are effectively diluted into a larger volume of water. The reviewer is also referred to the previous response.

P13877 Line 4-5: Is dAl not scavenged by non-biogenic particles as well? Were the particles in the sediment trap characterized?

RESPONSE: We agree with the reviewer that dissolved Al scavenging on non-biogenic particles cannot be completely excluded. However in the revised manuscript, a correlation between Al loss rate and chlorophyll-a stocks is added, in order to illustrate that biogenic particles are the main driver of Al scavenging. Concerning the characterization of Al scavenging on the sediment traps particles we refer the reviewer to the response we made to reviewer #2: "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 µmol m-2. The amount of dust particles added to the mesocosms is 10 g m-2 which represents 15000 µmol 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."

P13877 Line 12-29: There is too much comparison with DUNE-1 which only serves to
muddle the discussion. Both particle scavenging and loss to the mesocosm walls are mentioned as possible causes for dFe loss after the first seeding. The former could be tested by analyzing the chemical composition of the particles collected in the sediment trap. In this case, the comparison to DUNE-1 is instructive. There was not dFe loss in DUNE-1 which would suggest that loss to the mesocosm walls was not occurring as presumably DUNE-1 and DUNE-2 used the same materials for the mesocosms. Why would adsorption suddenly become an issue? Further, an increase in the dFe inventory was observed following the second seeding. Would adsorption to the walls not still be occurring? There would also be similar rates of particle scavenging...it is likely that ligand production is acting to enhance the effective Fe solubility within the mesocosm.

RESPONSE: We only partially agree with this comment of the reviewer. Comparison with DUNE-1 is warranted here as it is the only similar experiment performed to date with regard to examining the chemical composition of the particles, the reviewer is referred to the previous comment. Concerning the wall adsorption, we agree with the reviewer that same material was used during DUNE-1 and DUNE-2. As indicated during the DUNE-1 experiment (Wagener et al. 2010), even if wall adsorption cannot be completely excluded, we believe that this process is certainly irrelevant due to the surface to volume ratio in these large mesocosms. We have rephrased this part of the discussion in order to state more clearly that wall adsorption is certainly not the major process that explains the loss of Fe in the mesocosm.

P13878 Line 17: Should this be Fig. 5a?
RESPONSE: This was changed in the revised manuscript.

P13879 Line 1-4: The evidence for stratification needs to be strengthened to be made more compelling.
RESPONSE: See the earlier response above.

P13879 Line 4-6: “. . .the removal of particulate metals and the adsorbed or scavenged
metals they contain” Who is they?

RESPONSE: “These findings are important in the present context as they represent the removal of particulates and the adsorbed or scavenged metals they contain.” They = these findings.

P13879 Line 14-16: The optical data is not shown here rendering this statement meaningless and the reader has not means to assess if the settling of large particles (what size?) played a small role in scavenging.

RESPONSE: “Combining the optical data with the dissolved trace metal data suggests that the larger dust particles sunk out quickly but played a small role in scavenging both Mn and Al from the water column, as release processes dominated at that time.” (Bressac et al., this issue)

P13879 Line 16-18: What size is a small particle in this context?

RESPONSE: In this context, small particles range from the colloidal to the nanophytoplankton size range.

Table 1: This table appears unnecessary as the “other trace metals” are only fleetingly mentioned in the

RESPONSE: This was changed in the revised manuscript. The table was moved to the Supplementary Information for additional information and to show that there was no contamination in the mesocosms and as a valuable additional trace metal dataset for the Mediterranean.


Mendez, J., Guieu, C., and Adkins, J.: Atmospheric input of manganese and iron to C8230


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

\[
\text{FracSol}(\%) = \frac{\max \left\{ A \left( \left[ \sum_{j} B_j \right]_{t_{z}} - \left[ \sum_{j} B_j \right]_{t_{a}} \right) \right\}}{\sum M_{t_{z}}} \]

Case 2: 2nd addition

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.