

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.

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) is not available, the reader is unable to follow up on this discussion and no supporting data is reported here.

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.

Specific Comments:

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

P13860 Line 3-10: This sentence runs on and would be clearer if rewritten.

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

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.

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

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

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

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

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.

P13865 Line 15: $<1 \text{ nmol l}^{-1}$?

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.

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

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.

P13869 Line 21: "...pretty uniform..." is not a useful descriptor.

P13869 Line 24: Why was dAl not measured for 72 hours? What was the sampling schedule and why was it not the same for each of the trace elements?

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

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% .

P13872 Line 7: What does "...the closest value was used for the extreme values" mean?

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

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?

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 $\mu\text{mol m}^{-2}$) assuming a particular chemical composition of dust (e.g. 2.31% for Fe which is assumed based on a previous study).

P13875 Line 1-2: This sentence is unclear.

P13875 Line 3: What estimation?

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.

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...”

P13816 Line 25: What is meant by “dilution of the dissolved elements”? Did a rain event dilute the mesocosm?

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

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.

P13878 Line 17: Should this be Fig. 5a?

P13879 Line 1-4: The evidence for stratification needs to be strengthened to be made more compelling.

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

P13879 Line 14-16: The optical data is not shown here rendering this statement meaningless and the reader has no means to assess if the settling of large particles (what size?) played a small role in scavenging.

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

Table 1: This table appears unnecessary as the "other trace metals" are only fleetingly mentioned in the manuscript. Why are Mn, Al, and Fe not included here? Does "Date and hour" refer to the collection time?

Table 2: Is the uncertainty one (two?) standard deviations? Why are there no uncertainties for the measurements outside of the mesocosm?

Table 3: "Difference of inventories Average DUST-Mesos minus average CONTROL-Mesos ($\mu\text{mol m}^{-2}$)" should be shortened.

Table 4: Is a linear dissolution rate the correct choice?

Figure 1-3: I have previously mentioned my misgivings regarding the appropriateness of applying contouring to this data. Additionally, the gray lines signifying the dust seeding are quite faint and difficult to see. Also, the sampling gaps should be addressed as these further weaken the power of contouring.

Figure 5: What do the error bars show?