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## ***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.***

**K. Wuttig et al.**

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Biogeosciences Discuss., 9, C5641–C5643, 2012 www.biogeosciences-discuss.net/9/C5641/2012/ © Author(s) 2012. This work is distributed under the Creative Commons Attribute 3.0 License. Biogeosciences Discussions 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.

Anonymous Referee #1 Received and published: 13 November 2012 The submitted manuscript deals with a dust addition mesocosms experiment conducted off Corsica in the W Mediterranean. The work follows dissolved Fe, Mn and Al concentrations

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over time following dust additions. In additions, the work calculates solubilities and discusses scavenging. This is a very nice piece work which deserves publication. However, my main concern with the submitted manuscript is the poor quality of the written scientific text, and the structure of the paper. This paper requires a number of iterations by the team of authors before resubmission. The team has a number of highly experienced scientists and these should be able to get this manuscript into shape. I have made a number of comments on the manuscript, and these are listed below. However, I have not much commented on the scientific phrasing of the results and discussion sections. I will leave it to the authors to improve these.

RESPONSE: We thank referee #1 for the helpful comments and the recommendation for publication. We worked on clarifying and improving the discussion section and the structure of the paper. To improve the written scientific text, the senior scientist carefully revised the manuscript and especially the discussion and figures. Large sections in the discussion were rewritten for the revised manuscript and the manuscript written by native speakers. Two figures were changed. The resolution figure and part in the discussion was eliminated from the revised manuscript, but a figure on the evolution of the FeL data (and the dFe arithmetical corresponding means at 5m depth) was added. The second added figure is to show a better comparisons with the biomass. This means that we used the Chl-a data (HPLC) (Giovagnetti et al., 2012) and calculated the Chl-a inventories and compared these to the Al loss rates. We observed a correlation ( $R^2=0.6049$ ) and show this correlation in the new fig. 6.

P 13858. Line2. Dust also supplies trace elements which are less abundant in rocks.

RESPONSE: We assume here that the reviewer is actually referring to anthropogenic aerosols. In our work the dust was sourced from arid soils which are derived solely from mineral rocks and thus contain the same elemental composition as the rocks.

P 13858. Line 5. Residence time is not directly related to speciation.

RESPONSE: We politely disagree and note that the reviewer provides no citation to

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back their statement but there are plenty in support of a relationship between residence time and speciation. Soluble elements have long residence times and insoluble elements do not (Hunter and Boyd, 2007). The insoluble elements Al, Ti and Zr are for example abundant in rocks, but significantly lower in seawater, because of their hydrolysis chemistry and their strong tendency to adsorption and removal by particles (i.e. scavenging). Due to these reactivities the insoluble metals are quickly removed from the ocean (Sohrin and Bruland, 2011).

P 13858. Line 12. The method section indicates that the dust was added as a dry substance. Hence we are not dealing with wet deposition!

RESPONSE: The actual process of the seeding with evapocondensed dust is described in (Guieu et al., 2010) (P13862 Line 16). We used exactly the same procedure mimicking 2 consecutive wet depositions. For clarification in the text we changed the following sentences in the method section: P 13863 Line14, original sentence: “The seedings with 41.5 g of artificial dust to the surface of the mesocosms correspond to a realistic, high wet deposition of 10 g m<sup>-2</sup>. “ It was changed to: “For each of the two consecutive seedings 41.5 g of evapocondensed dust was dissolved in Milli-Q and sprayed with an all-plastic spray bottle onto the surface of each of the mesocosms. This corresponds to realistic, large wet depositions of 10 g m<sup>2</sup>.”

P 13859 Line 16 ‘Due to the elemental composition of the earth crust, the flux of dust particles constitutes a major source of trace metals to the surface ocean (Duce et al., 1991).’ This sentence is awkward and does not mean much. Rephrase.

RESPONSE: This and the next sentence were changed to: “In addition to macronutrients (phosphorus and nitrogen) transported by dust particles, it has been suggested that the response of biota might be (partially) controlled by trace metals brought to the surface ocean with dust particles (Duce et al., 1991).”

P 13860. ‘.....and availability in the atmosphere and in seawater (Spokes and Jickells, 1996),.....’ Availability of what.

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RESPONSE: Availability was replaced by lability.

P13861 line 28: a key issue with oxidised Mn species is their insolubility, with the reduced form being soluble.

RESPONSE: The original sentence was changed (see below). Original: “On the other hand, Mn is a bioactive metal with a complex chemistry in seawater: While Mn(II) is not thought to be organically complexed, dissolved Mn(III) and Mn(IV) organic species are possible, but have not yet been observed in oxygenated seawater.”

Changed to: “On the other hand, Mn is a bioactive metal with a complex chemistry in seawater. While most of the Mn exists as the soluble Mn(II) which is not thought to be organically complexed, dissolved Mn(III) and Mn(IV) organic species are possible, but have not yet been observed in oxygenated seawater. Soluble Mn(III) is rare in natural waters because it hydrolyzes and precipitates as Mn(III) oxides or disproportionate into Mn(IV) oxides plus Mn(II) (Nealson et al., 1988;Stumm and Morgan, 1996).”

P13862: The objectives are so convoluted that they are not very useful.

RESPONSE: This has been rewritten for the revised manuscript: “This paper illustrates the three dissolved trace metals (Mn, Fe and Al) inventories during the DUNE-2 experiment. Based on the revised experimental strategy after the DUNE-1 experiment, the specific objectives of this study were: 1) To assess the impact of dust seeding on dissolution and loss rates. 2) To quantify these processes. 3) To evaluate the scavenging and/or biological utilization versus dust dissolution of after dust addition on different time scales.”

P 13862, line 19: conservation instead of preservation

RESPONSE: This has been corrected in the revised manuscript.

P 13862, line 20: what is a typical summer oligotrophic condition?

RESPONSE: Changed to “In June 2010, seven trace metal clean mesocosms were

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deployed in the bay of Elbo in the preservation area of Scandola near Corsica (42.374° N, 8.554° E) during typical oligotrophic summer conditions. Marine oligotrophic areas, also described as low nutrient, low chlorophyll (LNLC) areas are typically defined by a chlorophyll-a content of less than 0.1 mg m<sup>-3</sup> (Carr et al., 2006; Longhurst et al., 1995). (Giovagnetti et al., 2012) showed that during the DUNE-2 experiment the chlorophyll-a content always remained below this threshold even after the seedings. Their initial chlorophyll-a concentration was 0.02 – 0.03 mg m<sup>-3</sup>.”

P13862, line 21: entirely instead of purely

RESPONSE: This has been corrected in the revised manuscript.

P 13862, line 24: what does it mean that the water column was preserved?

RESPONSE: This has been corrected in the revised manuscript to: “In each mesocosm, the total seawater volume was 52 m<sup>3</sup> and the water column was retained.” When the mesocosms were put into the water and the transparent outside cover pulled down, we tried not to disturb the water column (by, for example, divers). Before closing the mesocosms, they were left open for 24h to let the water masses equilibrate with the outside water masses. As we have shown with the external reference point outside the mesocosms : The initial conditions when the experiment started were the same for the dust seeded mesocosms, the control mesocosms and the outside sampling site.

P 13863, line 7: how do water masses settle?

RESPONSE: This has been corrected in the revised manuscript to: “After deploying the mesocosms, they were left open for 24 h in order to let the water masses equilibrate. After closing the mesocosms, t<sub>0</sub> was sampled then the mesocosms were seeded.”

P 13863: this sentence does not make much sense: ‘Sampling for dissolved trace metals was conducted using 0.2 m Sartobran filter cartridges (Sartorius, Germany) adapted to a Teflon<sup>TM</sup> diaphragm pumping system and then the samples were directly collected into the corresponding bottles’

RESPONSE: This has been corrected in the revised manuscript to: "Sampling was performed with a Teflon<sup>TM</sup> diaphragm pumping system. For dissolved trace metals, samples were filtered through 0.2  $\mu$ m filter cartridges (Sartorius Sartobran filter capsule 5231307H5, Germany)."

P 13864, line 13: so to what pH were Fe and Al samples acidified?

RESPONSE: This has been corrected in the revised manuscript to: "The filtered samples for dissolved trace metal analysis were directly acidified on-land with Q-HCl to pH 1.7 under a class 100-laminar flow bench."

P 13864, line 15: I was not sure Kiel has clean rooms rated class 100. It is class 1000 or 10000.

RESPONSE: There are a number of class 100 clean rooms at GEOMAR in Kiel. The one used in this study (Westufer) is TÜV certified ISO class 5 = class 100 in the older nomenclature.

P 13864: you mean a diode array spectrophotometer

RESPONSE: We politely correct the reviewer as we did not mean diode array spectrophotometer, but as we wrote a variable wavelength spectrophotometer.

P13865, line 15: you mean < 1nM?

RESPONSE: This has been corrected in the revised manuscript.

Results: the description of the data format should be with the appropriate table. At present it is incomprehensible; it needs a rewrite.

RESPONSE : We agree with the reviewer that the explanation of the labeling was inappropriate in this section of the manuscript. In the revised version of the manuscript, the detailed explanation of the sample labeling will be part of the metadata file submitted with the complete data file in the supplement to the manuscript.

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Table2: what was the standard deviation: one or two sigma? Also, is there an standard deviation associated with the outside measurements?

RESPONSE: The error presented with the mean values in this table corresponds to the standard deviation (one sigma) calculated on the values at 5 meters in the 6 mesocosms directly after their deployment. This will be mentioned in the footnotes of the table in the revised manuscript. An unique sampling point existed outside the mesocosms where the non-mesocosm control samples were collected. For this reason, no standard deviation is associated with this value.

Page 13871: the Fe values by Boyle are better to be removed. They were obtained before ultra clean trace metal sampling/analysis for Fe.

RESPONSE: We assume the reviewer is referring to the work of Sherrell and Boyle (1988) that we cited in the manuscript. If so, we would like to politely point out that the value of 53 nM is for total Fe and includes a substantial amount of particulate Fe suspended in these waters. As Professor Boyle was one of the original developers of ultra clean trace metal sampling in the late 1970's we believe the reviewer assertion is unwarranted. We also note that the reviewer does not provide an alternative reference in support of their inference that the Boyle data is anomalous. Nonetheless we change our sentence to: "(Sherrell and Boyle, 1988) report a limited set of data for total and dissolved Fe in the western Mediterranean. They found maximal values in the core of the Atlantic inflow jet in the Strait of Gibraltar of 53.0 nmol kg<sup>-1</sup> total Fe, dissolved Fe was only 30% of this value indicating a high particulate load. Outside this plume of Fe, surface total concentrations were around 5 nmol kg<sup>-1</sup>."

P 13872: consider discussing the outcomes of the inventory calculations first, before discussing the advantages of the higher sampling resolution.

RESPONSE: This section and the corresponding figure was completely removed from the manuscript.

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P13874: why calculate the solubility from the difference between the control and dust mesocosm inventories. An alternative option would be to use the inventory of the dust mesocosm just prior to dust addition.

RESPONSE: We partially agree with this comment of the reviewer, as we note that a key assumption, which appears validated here, is that the control and dust mesocosms had the same inventories prior to the dust additions. The reason why we made the choice of calculating the solubility based on the difference between dust seeded and control mesocosms instead of the difference between values prior to the dust addition and after the dust addition in the dust seeded mesocosms comes from the “philosophy” used to design the experiment. Due to presence of organisms in the mesocosms, biogeochemical changes are observed within the mesocosm even if no dust is added. For this reason three control mesocosms were deployed. The observations in the dust seeded mesocosms can be “corrected” from the changes observed in the control mesocosms in order to estimate the changes due to the dust addition only. Based on this “philosophy”, we decided to calculate the solubility from the difference of inventories between the dust seeded and the control mesocosms.

We consider that our set of data justifies this calculation method. For example, in the case for iron, a clear decrease in concentrations has been observed both in the dust seeded and the control mesocosms directly after the first dust addition. The reason of this decrease is unclear, but it is in any case independent of the dust addition. Calculating the solubility with the inventories in the dust seeded mesocosms just before the dust addition would have given completely different (even negative) results, but these results would not be representative of the effect of the dust addition only. A short section will be added concerning this point in the revised manuscript as mentioned in the next comment.

P 13874: the description of the calculation of the solubility is awkward, if not wrong.

RESPONSE: We agree with the reviewer that the description of the solubility calcu-

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lation was unclear, however it was not incorrect. This description has been rewritten as following: “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.”

We had assumed the reviewers would be at least familiar with the concept of fractional solubility (we refer the reviewers to Baker and Croot (2010) for more details if this is not the case). In this work the fractional solubility is calculated from the dissolved inventories as follows:

Case 1: 1st addition- see fig.1 please.

Case 2: 2nd addition- see fig.1 please. 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.

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(see the revised manuscript for a full explanation of this equation).

P 13879: : : the residence time of dFe in surface waters is strongly influenced by Saharan dust deposition: : :'. Explain which way the residence time was influenced: shortened?

RESPONSE: A sentence was added in the revised manuscript: "Our observations are consistent with field studies from the Atlantic Ocean which have shown that the residence time of dFe in surface waters is strongly influenced by Saharan dust deposition (Croot et al., 2004), while that of Mn and Al are much less so (Jickells et al., 1994; Jickells, 1999). In the case of dFe in the surface waters Croot et al. (2004) showed that the fractional mean residence time was shortened as a result of high Saharan dust fluxes."

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$$FracSol(\%) = \frac{\max \left\{ A \left( \int_z^0 \left| \mathbf{M}_{DM} \right| dz \right) - \left| \int_z^0 \left| \mathbf{M}_{DM} \right| dz \right|_{t=43} \right\}}{\Sigma M_{Dust}}$$

Case 1: 1<sup>st</sup> addition

$$FracSol(\%) = \frac{\max \left\{ A \left( \int_z^0 \left| \mathbf{M}_{DM} \right| dz \right) - \left| \int_z^0 \left| \mathbf{M}_{DM} \right| dz \right|_{t=43} \right\}}{\Sigma M_{Dust}}$$

Case 2: 2<sup>nd</sup> 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.