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Comment

***Interactive comment on* “Effects of dust deposition on iron cycle in the surface Mediterranean Sea: results from a mesocosm seeding experiment” by T. Wagener et al.**

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General Comments:

This manuscript presents valuable data on the effect of dust deposition on iron cycle in surface waters of the Mediterranean Sea. The unexpected results of a dust event resulting in a decrease of dissolved Fe, rather than an increase, due to abiotic scavenging are very interesting. The experiments were well executed and the data analysis and calculations are sound. I found the discussion very insightful and focused. In general the manuscript is well written. There are a few sections that need further clarification (see comments below), especially how certain calculations were made and some of

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the methodologies.

RESPONSE: We thank Referee #2 for his encouraging and constructive comments and criticisms on the manuscript.

Specific comments: Introduction Page 2801, line 29. A reference is needed after 'dissolution processes'.

RESPONSE: A reference to the article by Baker and Croot [2010] has been added. This article performs a review of the processes that occur when atmospheric particles are in contact with seawater with particular attention to dissolution processes.

Materials and methods

Page 2802, line 15 to 20. It would be helpful to indicate the depth of the mesocosm here (12.53 m, correct?). This number is necessary to calculate the biological demand of Fe in the mesocosms (page 2811).

RESPONSE: As described in Guieu et al. [2010], the bottom of the mesocosm is conic and therefore two depths can be considered: The depth of the cylindrical part (12 m - the entire length of the cylindrical part of the mesocosm is 12.5 m from which 0.5 m are out of the water at the surface) and the depth of the sediment trap (14.2 m - 12 m plus the 2.2 m of the conical part). This information has been added to this paragraph.

Page 2803, line 4. The dust addition should be normalized to the volume of the mesocosms, so that the dust addition in the mesocosms and the batch experiments can be compared. According to my calculations, the addition to the mesocosms was 0.789 mg/L [41.5 g / (52 m³ x 1000 L/m³)].

RESPONSE: The amount of dust added normalized to the mesocosm volume (theoretical concentration) has been added to the revised manuscript. However, it will be explicitly mentioned that this corresponds to a purely theoretical concentration obtained assuming that the added particles are homogeneously distributed over the entire volume of the mesocosm. As illustrated on figure 5b, this is not the case since particles

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are settling through the water column and the gradient of concentrations is changing continuously with time.

Page 2803, line 7. Please include more information about how the aging of the dust particles was accomplished. Adding something like “The protocol for aging the dust particles reproduced the photochemistry and the pH gradients & ionic strength normally observed during cloud processing of dust.” would be useful to the reader.

RESPONSE:As suggested by referee #2, following sentence has been rephrased in the revised manuscript : “Dust was obtained through a mechanical treatment of soils from a dust source areas in southern Tunisia to obtain fine particles and further physico-chemical treatment in the laboratory in order to mimic the pH gradients and the incorporation of organic material normally observed during cloud processing of dust (see Guieu et al., 2010b for details).”

Page 2804, line 9. Please include the porosity of the cellulose acetate filters.

RESPONSE:This information has been added to the revised manuscript.

Page 2805, line 5-15. It would be helpful to have some additional details here. For example, was the dust added to the ‘bottle’ experiments also diluted in Milli-Q water, as done for the mesocosms (see page 2803, line 6)? Why was the dust addition in the bottle experiments 5mg L⁻¹, while that in the mesocosms was 0.798 mg L⁻¹? The authors should justify their chosen additions of dust, 5mg L⁻¹ in in the ‘bottles’ vs. 0.798 mg L⁻¹ in the mesocosms. I am surprised that the difference between the two is almost an order of magnitude. Is it possible that this difference might have somehow affected the outcome of both experiments regarding the solubility of Fe?

RESPONSE:Concerning the protocol for the “bottle” experiments: The dust added to the bottles was also first diluted in Milli-Q water and then added to the seawater following the same protocol described in Wagener et al. 2008. This has been added to this section of the revised manuscript. We chose a concentration of 5mg.L⁻¹ for the bottle

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experiments because it is a standard concentration that we have used in former studies (Wagener et al., 2008). This concentration corresponds to the mixing of the added particles within the first two meters of the water column. As discussed before, due to the settling of the particles through the water column of the mesocosm, the concentration of particles in the mesocosm is time and depth dependent (horizontal variation may certainly also exist). On the contrary, “bottle” experiments are perfectly homogeneous batch reactors where a constant concentration can be defined over time. We think that the observed differences between “Bottle” and “mesocosm” results are caused by this important difference between both experimental approaches rather than by a concentration issue. These points have been further stressed in the discussion of the revised manuscript in the section 4.4.

Page 2805, line 14. It would be helpful to have estimates of surface area to volume ratio for the ‘bottles’ vs. the mesocosm experiments. This may be handy in the discussion.

RESPONSE: The surface to volume ratio is 251 m⁻¹ for bottles and 1.82 m⁻¹ for mesocosms. This difference has been underlined in the discussion on the protocols used for iron dissolution measurements in section 4.4 of the revised manuscript.

Results

Page 2806, line 17-18. What do the authors mean by “Variability among the replicates was more important in [pFe] than in [dFe].” ? Do they mean variability was higher?

RESPONSE: This sentence has been rephrased : “Variability among the replicates was higher in [pFe] than in [dFe].”

Page 2806, line 23. There is a typo here. It reads “The mass of particulate iron [dFe] per sample...” It should be “[pFe]” instead of “[dFe]”.

RESPONSE: This has been corrected in the revised manuscript

Page 2807, line 16-17. The authors should justify discarding samples with high [pAl]. Why is it ok to discard samples with high Al content?

RESPONSE: The four samples which were discarded correspond to the highest particle concentration encountered directly after the dust seeding. This could correspond to the formation of dust aggregates with organic matter which could slightly change the Fe/Al ratio of the collected particulate matter. The following sentence has been added in the revised manuscript: “The slopes of both correlations are significantly different. However if the four samples with [pAl] concentrations higher than $30 \mu\text{g}\cdot\text{L}^{-1}$ are discarded in the water column dataset, the slope (Fe/Al ratio) is 0.53 and hardly differs from the ratio in the sediment trap. These four samples correspond to the higher particulate concentrations encountered directly after the dust addition. The formation of dust aggregates with organic matter at this time could have slightly changed the Fe/Al ratio of the collected particulate matter. The Fe/Al ratio of the dust introduced for the fertilization is 0.56 ± 0.06 [Guieu et al., 2010b]. ”

Page 2807, line 22-25. I found this paragraph very hard to understand. The legend in Figure 4 is better. Please modify this paragraph to make it clearer. Maybe the authors should include a little equation. There are too many ‘between’ in the sentence, so it is hard to see what they are exactly comparing or dividing. For example, in line 25, after reading it a couple of times, I realized that “...measured before the addition of dust particles to the batch reactor” refers to the filtered seawater. Why not make the sentence more concise and precise?

RESPONSE: This paragraph has been rewritten and an equation defining ($\Delta[\text{dFe}]_{72\text{h}}$) has been added to the revised manuscript.

Discussion

Page 2809, line 2. Replace “submitted” with “subject”

RESPONSE: This has been done in the revised manuscript

- Page 2809, line 6-8. The quoted, highest Fe:C ratio for phytoplankton was originally presented in Brand 1991 manuscript. This manuscript thus should be cited after the

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number.

RESPONSE: This has been done in the revised manuscript

- Page 2809, line 23 & 25. Please indicate units in parenthesis.

RESPONSE: This has been added in the revised manuscript

- Page 2811, line 19. I calculated the phytoplankton Fe demand based on their reported Fe:C ratio (400 $\mu\text{mol Fe per mol C}$), a C:chl a ratio of 100 g/g (typical of Fe-limited phytoplankton), and a depth of the mesocosm of 12.53 m. According to my calculations, the phytoplankton demand is in the order of $\sim 3100 \text{ nmol Fe d}^{-1} \text{ m}^{-2}$. It would be helpful for the authors to be more explicit about their calculation. They could simply put the calculation in brackets at the end of the sentence. Again, I am not sure that citing Veldhuis et al 2005 is the most appropriate, given that the title of the Veldhuis manuscript is on picophytoplankton. What kind of phytoplankton community composition did they have in the mesocosm? A sentence with this info would be helpful. The authors can then justify using a Fe:C typical of diatoms, or picoeukaryotes, cyanobacteria....

RESPONSE: We agree with Referee #2 that the calculations were not detailed enough in the former manuscript. The main idea was to make an estimation which appeared to be reasonably overestimated in order to compare with the measured loss of dissolved iron. Here is the detailed justification of the calculation: No data on phytoplankton community composition are available for this experiment. However, based on pigment measurements on samples collected two days after the end of the DUNE-1-P experiment, picophytoplankton appeared to be the dominant group in the study site (C. Brunnet Pers. Com.). We therefore used the values reported in Veldhuis et al. [2005] for pico-phytoplankton. The Fe/C ratio values reported in this paper for pico-phytoplankton are smaller than $0.01 \mu\text{mol.mol}^{-1}$. We voluntarily used the much higher value reported in Brand 1991 in order to be sure to overestimate the iron requirements. The value reported in Brand 1991 as the high average value is a molar Fe/P ratio of 0.01. Based on Redfield ratio of 106, this would correspond to a Fe/C molar ratio of

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ca. 10⁻⁴. For C/Chla ratio we chose a higher ratio than recommended by referee #2: 10 mol.g⁻¹. Here is the detailed calculation Chlorophyll increase in the first 48 hours of the experiment: 0.15 mg.m⁻³ Chlorophyll increase per day integrated on the 0-5 meter layer: 0.375 mg.m⁻².d⁻¹ Equivalent Carbon increase 3,75 mmol.m⁻².d⁻¹ Fe consumption due to chlorophyll increase 375 nmol.m⁻².d⁻¹ This has been detailed in the revised manuscript

- Page 2811, line 21. I also calculated the heterotrophic bacteria Fe demand using a Fe:C of 9.1 μ mol Fe per mol C, and a C quota of 2.6 fmol per cell. My calculation is close to that presented here (mine 77 vs. the authors' 55 nmol m⁻² d⁻¹).

RESPONSE:Here is the detail of the calculation for the heterotrophic bacteria iron demand in the 0-5m layer based on a Fe:C ratio of 44 * 10⁻⁶ (Value proposed by[Tortell et al. 1996] for bacteria in a iron rich culture) and a C quota of 2 fmol.cell⁻¹ (ca. the double of the value proposed by [Fukuda et al., 1998]). Cell number increase in the first 48 h of the experiment at surface 5*10⁵ cell.mL⁻¹ Cell number increase in the first 48 h of the experiment at 5m 0 cell.mL⁻¹ Cell number increase per day integrated on the 0-5 meter layer 6.25*10¹¹ cell.m⁻².d⁻¹ Equivalent Carbon increase 1.25*10⁻³Å mol.m⁻².d⁻¹ Fe consumption due to heterotrophic bacteria 55 nmol.m⁻².d⁻¹ This has been detailed in the revised manuscript

- Page 2812, line 13-15. This information should also be placed in the legend of the pertaining figure.

RESPONSE:A short explanation on the defined parameters has been added in the figure 5 legend. Moreover, as recommended by Referee #1, this sentence will also be placed earlier in the manuscript when the figure 5 is first introduced.

- Page 2814, line 9-13. It is not clear to me how “scavenging of colloidal Fe on dust particles or the re-precipitation of soluble Fe favored by the presence of an important amount solid particle after the dust seeding” can increase Fe solubility. Shouldn't this decrease Fe solubility? Please clarify.

RESPONSE: The hypothesis presented here is that, due to the dust addition in the mesocosms, dissolved iron has been lost from the water column through scavenging of colloidal iron onto dust particles or through re-precipitation of soluble iron favoured by the important amount of particles. In the batch experiments, new iron is then added through dust particles and, in the DUST-Meso batch experiments, a part of this added iron could be stabilized in the form of soluble or colloidal iron because some iron had 'disappeared' before. This would explain the relative increase of [dFe] in DUST-Meso. This sentence has been rephrased as following in the revised manuscript: "The dust addition into the mesocosms induced the scavenging of colloidal iron onto dust particles or the re-precipitation of soluble iron favored by the important amount of particles . After addition of new iron by dust particles in the batch experiments, stabilization of new iron in the form of soluble or colloidal iron could then take place and would explain the relative increase of [dFe] in DUST-Meso."

Figures

Figure 5. I am confused about the t_0 loss in panel B. How are they calculating the loss term at t_0 , this calculated loss is relative to what? Are they just reporting the values of [dFe] and [pFe] before the dust addition? This should be clarified in the legend and the graph itself. Also, the font in the figure symbols of all the graphs is too small and hard to read.

RESPONSE: By definition, the loss term of dFe is the difference between the concentration in the control and the dust mesocosm. At t_0 , the small loss term is due to the natural variability in dFe profile. Panel A of figure 5 shows that, at t_0 , the differences in dFe are not significant between control and dust, but they still induce a small loss term. A sentence has been added to the legend of figure 5 in order to explain this point: "At t_0 , the dFe_stock_loss is due to natural variability in dFe profile in CONTROL-Meso and DUST-Meso.". The font of the figure symbols has been improved.

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