

## ***Interactive comment on “Particulate trace metal dynamics in response to increased CO<sub>2</sub> and iron availability in a coastal mesocosm experiment” by M. Rosario Lorenzo et al.***

### **Anonymous Referee #1**

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Review comments for Biogeochemical Discuss Particulate trace metal dynamics in response to increased CO<sub>2</sub> and iron availability in a coastal mesocosm experiment Authors: M. R. Lorenzo, M. Segovia, J. T. Cullen, and M. T. Maldonado

This manuscript reports a particulate trace metal data set in controlled mesocosm experiments which conducted in the Raunefjord. Four conditions were prepared for the mesocosms and particulate trace metal concentrations were measured during *Emiliana huxleyi* blooming which induced by artificially. The authors claimed that they found the results that marine particle trace metal is highly dynamic, positively correlated with phytoplankton biomass, influenced by growth requirement, and strongly affected by

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changing CO<sub>2</sub> level and Fe availability.

Generally, the topic of the change of particle trace metal during the marine environment changing such as Ocean acidification (OA) and different Fe availability is very interesting for ocean biogeochemists. I believe the data set is valuable in this field. I feel that, however, authors need to regard more about how they can present their data set to induce conclusion above, which they claimed in conclusion section in this paper. The present contents of this manuscript are not well organized for presenting their data set to conclude the claimed conclusions.

General comments In construction of this manuscript, "results" section is not constructed only by result, and "discussion" section is not well explained by this study's result (data) ("Discussions" are only like a review of previous knowledge). I recommend that authors should re-construct and re-organized whole part of the manuscript. "Results" section should be used some "Figures" for presenting their data. It makes more easily to understand for readers. "Discussion" section should be related more to data from this study, including which data induce which conclusion more clearly.

The effect of CO<sub>2</sub> did not follow a clear trend in this study, as authors mentioned in the text. The effect of controlled Fe availability by DFB addition/non-addition to phytoplankton bloom is also not clear. How authors induced these their claimed results is not clearly understandable for readers. For discussion OA influence, I think authors should focus on to show "How particle trace metal concentrations and its ratio changed by CO<sub>2</sub> concentrations" by more well presented their own data set. For Fe availability, they need to discuss that "did DFB addition influence positive/negative to Fe availability?". It depends on natural dissolved Fe concentrations. Additionally, authors should show more clearly about relationship between Fe availability and *E. huxleyi* bloom response, with figure etc. It is very difficult for readers to understand the relation only from the "Tables" number. DFB addition inducing more dissolved fraction of TM is artificial response. This is different story from Fe bio-availability. Important for bio-availability is how much free Fe exist under each condition. As one of author well know that DFB-Fe

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uptake by phytoplankton need very complexed mechanisms. Authors should discuss more detail about this part.

Specific comments Line 86: Authors describe “a bloom of the coccolithophorid *Emiliana huxleyi* was induced in a mesocosm experiment”. This manuscript described time variation of particle trace metal parameter on Day 12 (d12), d17, d21. It is better to show the bloom development and termination in each mesocosm, with particle trace metal concentrations and other data, by Figures. This is more helpful to readers for understanding what was occurring in the each mesocosm. Authors can show such as cell number, chlorophyll a, POC, nutrients conc. for basic information for background of this study. If it is already reported, part of this can be cited from published work.

Line 116-117; 171 Table 2 etc: Authors described that “The biological and chemical variables analyzed were phytoplankton abundance and species composition, dissolved Fe and Cu, nutrient concentration, and particle trace metals concentration”. They only show these data in Tables. Figures which present time variation are easier for readers to understand the data variation during the experiments. Please prepare Figures. I can imagine the particle trace metal data was only collected on d12, d17, d21. But for grasp biological response and chemical environment change, sampling should be done more frequently. If authors have more frequent data for nutrient, cell number for *E. huxleyi*, etc, it should be plotted to the Figures.

3. Results Line 170- , 3.1 Biological and chemical characteristics during bloom., 178-181: Authors described time changing of “diatom” with nutrient concentrations. Authors should make a plot of “day since day0” vs “diatom cell number”, vs “pigment”, vs “*E. huxleyi*” and vs “nutrient concentrations” in each mesocosm. It is helpful for reader.

Line 188-189, 3.2: Authors described “The only metal that showed a time-dependent decrease in its particulate concentrations was Fe. . . . .” “dMetals”, “pMetals”. These also should be appeared by figures.

176: Authors described “An increase in dFe was observed in all treatments between

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day 7 and 17.”. In Table 2, there are no data from d7, it should be appeared in the Table 2. And d17 LC-DFB data is decrease. So “all treatments” in this sentence is not correct.

Line 195-196: Authors indicate that “high CO<sub>2</sub> had negative impact on particulate Fe” and “Cd concentrations were also inversely affected by CO<sub>2</sub>”. These parts are difficult to understand which data indicate this fact.

Line 197-198: Authors described “All other elements (P, Co. . . . . these two factors was clear (Table 5)”. Please explain how clear as like Cd description in previous sentence. Only showing Table 5 is not enough explanation to reader.

For “3. Results” section, all subtitle is not well organized. Some contents can be compiled to one (For example, 3.1 and 3.2 can merge for “biological chemical response in mesocosms”. And particle trace metal variation in different treatment in 3.2, 3.3, 3.4 can merge to one section.

Title and contents of subsection in 3.6 and 3.7 are part of “discussion”.

4. Discussion Line 247-248: “Our results demonstrate that in the studied fjord, particulate Ti and Fe concentrations were dominated by lithogenic material.”. Authors need explanation how they judged this. The explanation is appeared in section 3.6 result (actually this is discussion). Please indicate clearly “this data is shown in Figure 1”.

Line 248-250: “In contrast, particulate Cu, Co, Mn, Zn, Mo and Cd concentrations were correlated with P concentrations, as well as phytoplankton biomass, suggesting strong biogenic influence on their distribution (Table 6)”. Authors need explanation how they judged this. The explanation is appeared in section 3.7 result (actually this is discussion). Please indicate clearly “this data is shown in Figure 1”. Only showing Table 6 is not kind for reader. This part is overlapped to 4.2 section. It should be in to 4.2 section with detailed explanations with Tables and figures.

Line 251-252: “Changes in CO<sub>2</sub> and/or Fe levels affected total particulate and biogenic

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metal concentrations for some metals.” This part of results is not well presented in manuscript overall. Authors should regard to present some figures which can compare particle and biogenic metals concentrations among each treatment.

Line 255-263, 4.1 Efficacy of the oxalate-EDTA wash removing lithogenic trace metals from particles: First half part of this section is should be move to “results”. Especially from line 260-263, “In general, the concentrations of Fe and Co in the particles were decreased the least by the oxalate wash (by ~ 25%), while Mo and Pb concentrations were decreased the most (by ~70%). The concentrations of particulate Cu, Zn, Cd and Mn were reduced by 50% by the oxalate wash. As shown previously (Sanudo-Wilhelmy et al. 2004), the oxalate reagent also removed extracellular P (by ~20%).”.

Line 282:” Me:P ratios we measured in the particles are similar to those of natural phytoplankton assemblages (Ho, 2006) and of *Emiliana huxleyi* cultures (Ho et al., 2003).”. If authors want to compare their filed data to previous reported data by Ho, 2006, and Ho et al., 2003, authors should show the previous study’s number with their data on to Tables or Figures with citation. Otherwise, authors just state “similar” to natural plankton but did not show any evidence.

Line 311-312, 319-320: “Interestingly, we also found a putative ZIP-transporter gene. ZIP-transporters are....., such as tRNA synthetase, reverse transcriptase, metallo-carboxypeptidase, ABC-Zn-transporter and CDF-Zn-transporter.”. If authors want to say “we found”, they should show their data and discuss with using their data. If this “gene part” is part of other study, they should cite the other study appropriately. This discussion section is very strange for this aspect. It is written like author’s original data for this study.

Line 329- : Discussion on Cu:P should construct by using their data, what their data’s characteristics, what their data indicate, what is authors claim from the data, which previous knowledge supports their claims. This section 4.2 is like just a review of other papers.

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Line 344: “The Cd:P were significantly lower than those found in phytoplankton and *E. huxleyi*.”. Reader can not understand clearly which data they compared. Is this sentence mean that “The Cd:P were significantly lower than those found in individual phytoplankton and *E. huxleyi* which was reported by previous studies (Ho, 2006, Ho et al., 2003)”?. If so, they should show the comparable data from previous study.

Line 377: “The decrease in particulate Fe might have been due to enhanced solubility of Fe- oxides at low pH.”. The author should show scientific basis. They have to show relation between pFe and PH in each treatment.

Line 378: “the concentration of the elements P, Co, Zn, Mn and Mo were influenced by CO<sub>2</sub> and Fe levels”. Which data indicate those results? Authors should present with their dataset.

Line 380-381: “where the addition of DFB resulted in higher dissolved Fe, and optimal pH enhanced *E. huxleyi* growth.”. Authors should present this relation, between dissolved Fe, pH and *E. huxleyi* growth, with figures which are constructed by their dataset.

5. conclusion remarks Please consider for my “general comment”. It is necessary to describe more specifically what was understood in each argument (claim) a)-d).

Authors should present what are difference/similarity of their data among four mesocosms treatment more clearly, and what they can find from the difference/similarity? How they induced the conclusion of this study form the difference/similarity? This aspect is not clear overall in this manuscript.

Others Authors used “pFe”, “particulate Fe”, “particulate iron”, “dFe”, and “dissolved Fe” in the text. They should use same words through the manuscript.

End of review.

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