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Interactive comment on “Effect of ammonium input over the distribution of iron in the seawater and the phytoplankton in a mesocosm experiment in a North Patagonian fjord” by N. Sanchez et al.

Anonymous Referee #2

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by Sanchez, N., Ardelan, M. V., Bizsel, N., and Iriarte, J. L.

This manuscript followed the iron (Fe) distribution during a 22 day mesocosm experiments in brackish and marine water in a North Patagonian fjord. Different amounts of ammonia were added to the mesocosms to simulate the artificial nutrient enrichment (here ammonia) introduced by fish farming in fjord ecosystems. Fe was divided into total Chelex labile, dissolved Chelex labile, DGT labile, total particulate Fe, and fractionated Fe, divided into size fractions between 2-10 μm , 10-20 μm , and 20-140 μm . The scientific background is of high interest and important to project man made changes of the fjord ecosystem at the coast of Chile. However, for my opinion the presented trace metal data set is very unsteady. Important things that should be taken always into

C6185

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account in the method section are missing, such as a detailed sampling procedure, measurement of reference materials (CRM's, SAFe, GEOTRACES). I am sure that the authors were working with best knowledge. However without these important facts the presented data and the made results in the discussion section are inconclusive. Due to that I recommend major revision for this article. Please find my major points below.

Materials and Method

Page 13743: Line 12- 17: Please explain in more detail the fjord hydrography. How low was the Salinity in the surface layer and below! I presume that the pycnocline was right between the brackish and deep waters at ~ 5 m. Would be nice to have a plot that shows T,P,S, O₂ (very important for the redox sensitive trace metal Fe) in the fjord. What was the average depth of the fjord? This all should be mentioned when planning to extrapolate the results to fjord waters.

Page 13743: Line 19-25: It is really hard to understand what was exactly done, please rewrite. "Seawater was pumped to a 33 L container via a peristaltic pump deployed both on a peer. The collected water was then distributed equally to 1m³ mesocosms." I have several questions here: When you work on trace metals, such as Fe, was the hose and the 33L container acid washed. Were the 1m³ tanks cleaned too? Were the mesocosms closed after filling, or were they left open. When open how much additional fresh water was introduced by rain? Why was the water not prescreened? A lot of more details should be mentioned here to trust your data! Also, how much Fe was in the fjord (without pumping, ect.), that could at least used to quantify the amount of added by the sampling procedure!

Page 13744: Line 1-15: Nutrient solutions were cleaned, and received from where, also the acids and the ammonia/acetic acid?

Page 13744: Line 14: "nutrient concentration" there is no concentration in Table 1; just some strange rates! Please correct the table, see comments for Table 1.

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Page 13744: Line 17: How the water samples were collected on the raft? Any standard seawater was run?

Page 13745: Line 2ff: What was the pH of the buffer solution, and the final seawater solution? Was the filtration performed before the addition of Chelex or afterwards. It is not very clear from the text. The seawater chelex matrix was transferred into a column with a frit? Replace “Milli-Q” by “deionized 18.2MOhm cm water”! Am I correct that when you collect the TFeCh fraction also other particles (e.g., inorganic sediments introduced by filling the tanks) were collected during column separation? Grade of used acid?

Page 13745: Line 20ff: UP: Ultra pure? How was the gel/resin and the HNO₃ separated from each other? Did you transfer all added HNO₃? When 4mL 3M HNO and 4mL MQ are added together you end up with 8mL 1.5M HnO₃!

Page 13746: Line 12: Washed with deionized water!

Page 13746: Line 22ff: Any recovery test for the Chelex performed? Results

Page 13747: Line 3ff: I don't see any errors for TFe and DFe. Please include in Fig. 2. I was reading earlier that the experiment was conducted for 22 days, but just 8 days are shown, why? However, I'm not sure what the labile TFeCh is telling you! It is just a leach of the particulate fraction, or when you collect the Chelex with the particles suspended then you do a leach with the HNO₃ later in the lab, right. So, I'm really concerned what kind of total fraction we are talking about here! Similar problems I have with the labile DFe fraction. Some organically complexed Fe won't be scavenged by the Chelex at pH8. Especially the strong ligands will compete. Any numbers of how much was in the real dissolved Fe fraction.

Page 13747: Line 21ff: With respect to the wide scattering of FeDGT I don't see any trend! With respect to the difficulty of the procedure DGT, I personally would also take contaminations into account? Or why should be the DGT Fe concentration higher than

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Discussion Paper

the labile dissolved? I also do not see the need for that technique since fluxes are important for sediments for instance, but in the water column. Probably of interest at the pycnocline, but other than this?

Page 13747: Line 2ff: TFe and DFe values in Figure 3b and 3c represent the final concentration or the average over all days?

Page 13748: Line 12ff: The particulate samples were collected when (after 22 days?)? First you talk about average concentration which is fine deciding between brackish and seawater, but from my point it is also of interest how the particulate Fe fraction evolved? By combining PFe and Chl/POC you show that the intracellular ratio changes from the beginning towards the end of the experiment. However, I have no idea what the PFe:Chl to Chl diagram is telling us and which idea it supports! Have you thought about an terrestrial particulate Fe fraction (sediment resuspension etc. that were sucked into the mesocosms when filling)

Page 13748: Line 25ff: I do not understand that sentence. When Fe concentrations of all size fractions are added together then we end up with PFe, or? I do not also understand what we learn from the mean total PFeSF what we have not learned already from PFe!

Page 13749: Line 7: Seawater is decreasing!

Page 13749: Line 9-18: It is really hard to understand that paragraph, since the following section is dealing especially with the size fraction. Better to put all the size fraction results in one paragraph! Page 13749: Line 23: What happened with Fig. 7. Page 13750: Line 2ff: Last sentence should come earlier in the paragraph. Would increase the chance to understand the ratio better.

Page 13750: Line 12ff: Rewrite “A long time, . . .” It sounds like a fairy tail.

Tables

Table 1: As I understood correctly you added every third day macro nutrients to the

C6188

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mesocosms. Here you show a rate per day. Be more consistent and state that you added nutrients every third day. For that reason numbers should be stated in target concentrations. Column mesocosm, should read “1 and 6”, “2 and 7”, etc. Otherwise, people might think from mesocosm 1 to 6.

Table 2: Fe Concentrations?

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C6189

