

**Title:** A comparison of biogenic iron quotas during a diatom spring bloom using multiple approaches

**Authors:** King et al.

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*General comments:* This manuscript presents the first exhaustive comparison of field-based plankton iron quotas determined with three different, but well established methods. This study took place during an in situ phytoplankton bloom in the subtropical Pacific Ocean off the coast of New Zealand. The data presented are of very high quality, and are nicely discussed in the manuscript. The corrections applied to the data are well thought out. The manuscript is well written. This manuscript would be a very significant contribution to the field of Fe biogeochemical cycles. I thank the authors for taken the initiative to complete this nice study. This research was long overdue and would be greatly appreciated by the scientific community. My comments below are meant to improve this, already excellent, manuscript; as well as to clarify some parts of the manuscript.

### **Materials and Methods**

*page 9387, line 6.* Somewhere in the manuscript, maybe right here, the authors should define the light levels of their sampling depths (30 and 60 m). Since the bottles for the determination of Fe:C using radioisotopes were incubated at 30%  $I_0$ , it would be nice to see how this light intensity compares to the depth were the phytoplankton were originally collected from.

*page 9387, line 10.* Something is not right in this sentence; it reads "Each filter was then individually washed with oxalate reagent to remove both extracellular Fe (Trovar-Sanchez et al. 2003). " Either add the other element that is removed with the oxalate wash, or remove "both".

*page 9387, line 12.* Where is this trace metal clean seawater from? Is this chelexed, artificial seawater Aquil? Or is this seawater from a HNLC region? Do you have the background Fe concentration? This is not important for the washes of the  $^{55}\text{Fe}:$  $^{14}\text{C}$  ratios, but it will be important for the washes of the particulates collected on filters for the ICPMS-based Fe:C/Fe:P determinations.

*page 9388, line 9-12 & page 9389, line 10-15.* According to the methods described here, the ICPMS filters were treated with the oxalate wash to remove extracellular Fe. Does this include some lithogenic Fe? If it does, then the ICPMS Fe data is overcorrected for lithogenic Fe, as the oxalate wash would remove some lithogenic Fe, and the ICPMS Fe data is then corrected using a crustal Fe:Al ratio (that assumes no oxalate wash). Is like the data are corrected twice for lithogenic Fe, one using the oxalate wash, and another one using the crustal Fe:Al ratio. The authors should include some discussion about whether the oxalate wash also removes extracellular Al. If the oxalate wash removes to the same extent extracellular Al and Fe, then using the crustal Fe:Al correction after the oxalate wash would be fine, as the two elements are affected equally by the wash.

### **Results**

*page 9393, line 19.* It would be helpful to know what mediated the decline of the phytoplankton bloom? Was it Fe limitation, Si limitation and/or light limitation (due to deepening of the mixed layer)? A sentence here with some insights from the authors would be helpful.

*page 9394, line 16.* Please add “Oxalate-washed” at the beginning of the sentence “Total P-values by ICPMS...”

*page 9395, line 5-7.* It is also worth noticing that the total C uptake rate on day 266 was relatively low compared to this study range (3.9 to 8.8 E-7  $\mu\text{mol C } \mu\text{g chl a}^{-1} \text{ h}^{-1}$ ), so probably fast Fe uptake rates combined with low C uptake rates account for the elevated Fe:C ratios on day 266.

*page 9395, line 8-10.* I will rephrase the sentence as “The results from day 266....were driven largely by higher DFe at this depth, *which probably resulted in faster Fe uptake rates, since the ambient DFe were well below the half saturation constant for Fe uptake (4 nM Fe', Maldonado et al. 2001)*”. The present statement is misleading, as it is true that higher DFe will lower the specific activity of the radiotracer but this should not affect your calculated uptake rates, as they were corrected with the daily ambient DFe concentrations. To clarify this, please also add “daily” after “and” in *page 9387, line 16*, where you described how Fe uptake rates were calculated using ambient DFe.

*page 9395, line 2-4 & page 9396, line 8-10 & Figure 2 and 3.* In general, the radioisotope and ICPMS derived Fe:C ratios showed a trend of higher ratios for the 30 m samples than the 60m samples. Can the authors provide an explanation for this? In terms of Fe quotas and light availability, I would have expected the opposite, higher Fe:C at lower light (60m).

*page 9396, line 14-16, & 26.* Why does lithogenic Fe become more important as size increases? I would have expected the opposite, as smaller particles would have a higher surface area to volume ratio for Fe to adsorb to them. Is this telling us that the lithogenic Fe and Al in this region is mainly comprised of large particles? Is this typical of lithogenic Fe and Al? A reference here supporting the findings of the present study would be useful. Or is this due to the oxalate wash used in this study? Did the oxalate wash get rid of most of the lithogenic/extracellular Fe in the small particles but not on the larger size particles?

*page 9397 and 9398, section SXRF Fe quotas.* In this section there is no discussion of the Fe:C ratios derived using this method. This is worth a sentence here. For example, I found interesting that the Fe:C converted values (using the in situ 133 mol C: mol P ratio), ranging from 17-56, were similar to the ratios I calculated (using the Fe:P and the typical Redfield ratio of 106 mol C:1 mol P), ranging from 21-70. It seems that in general the Fe:C derived using biovolume C may underestimate the ratios. This is briefly mentioned in the discussed.

## **Discussion**

*page 9398, line 25.* Include “oxalate washed” before “total ICPMS-determined BFe:P...”

*page 9399, line 1.* After “...ICPMS-determined BFe:POC” a parenthesis should be added to specify that the POC was not derived from the ICPMS but from the CHNS elemental analyzer.

page 9399, line 12. Do you mean 273 instead of 274? There are no data for day 274.

page 9401, line 15. Why do you limit the discussion of  $^{14}\text{C}$  uptake here to the photosynthetic picoplankton? So far in this paragraph you are discussing Fe:C ratios in general, so why narrow this discussion to the picoplankton. It seems as if a sentence describing Fe:C ratios in the small size fraction is missing here. However, in general the data presented in Table 3 do not support that the Fe:C ratios were the highest in the 0.2-2  $\mu\text{m}$  size fraction, so I am not sure this discussion is necessary here. I would simply mentioned that the 0.2-2  $\mu\text{m}$  size fraction Fe:C ratios include Fe uptake from the heterotrophic and autotrophic bacteria, but only C uptake from the autotrophic bacteria, so the Fe:C ratios in the smallest fraction might be an overestimate of the true ratios of the 0.2-2  $\mu\text{m}$  phytoplankton.

page 9402, line 13-15. The most useful information for the reader here is by how much did you increase the ambient DFe as a result of the  $^{55}\text{Fe}$  addition. According to my calculation, the  $^{55}\text{Fe}$  addition increased the ambient DFe by 1.33 and 7.6 fold. I would change the sentence in line 13-15 to incorporate this information.

page 9402, line 17-18. I do not agree with this statement. See my previous comment for page 9395, line 8-10. The result here is due to higher DFe which results in faster Fe uptake rate.

page 9402, line 20. Replace “affect” with “enhance”

page 9402, line 23. “...in which phytoplankton were observed to be Fe-limited..”. Can you provide  $F_v/F_m$  for the phytoplankton in these days? This could support your statement on the Fe limited condition of the phytoplankton on day 272 and 275.

page 9403, line 1-5. The key here is that the Fe addition should be as minimal as possible to avoid changes in the ambient (and speciation) Fe concentration. If this is achieved, the cells will be in their steady-state, and the Fe and C uptake rates should reflect the in situ uptake rates. As a result the ratio of this rates should be the steady-state Fe:C phytoplankton ratios. Adding Fe bound to an organic ligand is one way to achieve this, but the Fe and the organic ligand concentrations added, as well as the organic ligand of choice need to be carefully thought out.

page 9403, line 25. It is ok to use the Fe:Al ratio of the crustal material to correct the data even if dissolution occurs, the key is that the dissolution of both Fe and Al needs to occur and to the same extent. This complements the comment above, see page 9388, line 9-12 & page 9389, line 10-15.

page 9406, line 14. Here would be a good place to include information about the dissolution of Fe relative to Al in lithogenic particles? In the cited manuscript, do the author report % of solubilisation of Fe relative to Al?

page 9406, line 26-27. It is not clear what this last sentence is describing. Is it describing data from the present study or data for the *Trichodesmium* study/es? Please modify the sentence to clarify.

page 9408, line 28. days 265 and 276 are not included in Table 1. Is this a typo here? According to Table 1, the highest DFe were found on days 263, and 266, and maybe also 273 and 275.

page 9410, line 10-11. Adding  $^{55}\text{Fe}$  bound to an organic ligand could be suggested here, as a mean to not disturb the system.

page 9410-9411. Given this beautiful data set, which include Fe:P and Fe:C, I think the authors are in a unique position to comment on what is best to normalize biogenic Fe data. I believe a paragraph should be included on the pros and cons of using P or C.... This is especially important for the ICPMS data, as the remineralization of organic C and P is different in the water column. This should be discussed somewhere here.

## Tables

*Table 2.* The numbers reported in this table under the heading “chl a % of total” need to be multiplied by 100 in order to reflect true %. This comment also applies to Supp. Table 2, 3, and 4.

*Table 3.* More information is needed in this legend. Please include “oxalate-washed, ICPMS determined” before “BFe:P..”

*Table 5.* Spell out LS at the beginning of the legend.

*Table 7.* I would include some advantages and disadvantages here about what it is used to normalize the Fe data for each one of the three methods. Normalization is clearly more problematic for the ICPMS derived data. In the radioisotope method I would emphasize the need to carefully design the additions of Fe (with or w/out an organic ligand) to not disturb the steady-state condition of the phytoplankton.

## Figures

*Figure 1.* In this legend nothing is said about significant differences between 30 and 60m. Is this because there are no significant differences? If so, please mention it at the end of the legend.

*Figure 2.* I am assuming that the data presented in Panel A were corrected for ambient DFe concentrations so these are the Fe:C ratios derived from radioisotope experiments. I will change the Y-axis label in Panel A to “ $\mu\text{mol Fe}:\text{mol C}$ ” instead of “ $\mu\text{mol }^{55}\text{Fe}:\text{mol }^{14}\text{C}$ ”. Also the Y-label of Panel B should be changed from “ $\mu\text{M Fe uptake h}^{-1} \mu\text{gchl a}^{-1} \text{L}^{-1}$ ” to “ $\mu\text{mol Fe } \mu\text{gchl a}^{-1} \text{h}^{-1}$ ”. Similarly, the Y-label of Panel C should be changed from “ $\text{M C uptake h}^{-1} \mu\text{gchl a}^{-1} \text{L}^{-1}$ ” to “ $\mu\text{mol C } \mu\text{gchl a}^{-1} \text{h}^{-1}$ ”. This comment also applies to the legend of Supp. Table 3

*Figure 3.* Emphasize “oxalate washed” ICPMS based BFe:P...

*Figure 5.* In order to see better the SXRF and radioisotope derived Fe:C ratios, please change the Y-axis range in Panel A from 0-30 to 0-25 and in Panel B from 0-200 to 0-150. In the legend insert “total” after “Comparisons of..”

*Supplementary Table 3.* I would change the units of the legend in this table in order to remove all these E-6, E-7 or E-8 next to the numbers. For example instead of reporting  $2.3\text{E-6 pmol Fe } \mu\text{g}$

$\text{chla}^{-1} \text{h}^{-1}$ , report 2.3 amol Fe  $\mu\text{g chla}^{-1} \text{h}^{-1}$ . Similarly, for the C instead of reporting  $1.6 \text{ E-7 } \mu\text{mol C}$   
 $\mu\text{g chla}^{-1} \text{h}^{-1}$ , report 0.16 pmol C  $\mu\text{gchla}^{-1} \text{h}^{-1}$ .

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