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Interactive comment on "The effect of organic matter (OM) quality on the redox stability of OM-Fe association in freshwater sediments" *by* Nana O.-A. Osafo et al.

Anonymous Referee #2

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This manuscript examines organic matter-Fe interactions in freshwater sediments with the goal of better understanding the fate of these organic matter-Fe associations. Interest here stems, in part, from recent work examining the "rusty iron sink" for organic matter preservation in sediments. This is an important area of research and I think there may be some interesting data here. However, the manuscript is too speculative in too many places, and a number of aspects of the work need additional clarification. For these reasons, this manuscript will need extensive revisions before it be reconsidered for publication.

One of the big problems I have with this manuscript is that it discusses processes

associated with iron redox cycling, but there is no evidence of such processes in the profiles presented here. For starters, virtually all depth profiles show no change with depth (especially given the associated error bars), and so I see no evidence, for example, of DOM or Fe solubilization in association with the processes proposed here. There is also no background information about the sediments to help interpret these profiles. For example: Are the bottom waters of the reservoir oxygenated, seasonally anoxic or permanently anoxic?; If there is oxygen in the bottom waters what is the oxygen penetration depth in the sediments, and does it vary seasonally?; What are the concentrations and depth profiles of dissolved iron in the sediment pore waters? With this kind of information one could begin to estimate where the sediment redox boundary is, which is critical for understanding the basic aspects of iron redox cycling in these sediments, and which could then aid in the interpretation of these results.

Listed below (by line number[s]) are some more specific concerns I have.

1. (71-3) – These are results and don't belong in this section. Also what does "more stable" mean?

2. (76) – Why is the bulk scheme mentioned, since as far as I can tell all of the data discussed here comes from the sequential extraction procedure.

3. (78-) – I may be missing something here, but this sequential extraction scheme does not make sense to me. As I read the text, BD1 extracts Fe that is redox active, then BD2 next extracts iron that is redox stable, and then OH1 next extracts iron that is redox active and finally OH2 extracts iron that is redox stable. If these are sequential extractions and BD1 does not remove all (or most) of the redox active iron why, for example, does any redox active iron escape extraction during BD2 (which is the same as BD1 just longer) to then be extracted by OH1? What am I missing here?

4. I'm trying to compare this extraction scheme to others I am a bit more familiar with (e.g., Goldberg, et al. 2012. Chem. Geol. 296, 73-82; Poulton and Canfield 2005. Chem. Geol. 214, 209-221) and am having trouble understanding how NaOH extracts

iron oxides. Related to this, it's also not clear to me if any iron is actually extracted in the OH extractions – no data is presented.

5. The concept of redox "active" versus redox "stable" is a bit misleading. All iron oxides will undergo reductive dissolution, but the rates will vary by quite a bit (see, for example, Table 4.1 in Raiswell and Canfield (2012, Geochemical Perspectives 1, 1-220)).

6. The vast majority of the comparisons made later on in the paper are between the BD1 and BD2 phases (see, for example, the concluding remarks starting on line 247), thus I am further confused by where (and how) the OH extractions fit in here.

7. (137) – Differences in DOC concentration in the BD1 versus BD2 extracts do not necessarily imply differences in OM affinity for these different iron pools. For starters, there is more iron in the BD1 pool so there are presumably more potential iron oxide binding sites for DOM. That may be the simplest explanation for these DOC differences.

8. (154) – By averaging the results from the 4 cores you are implicitly assuming there is no spatial variability in the sediments along this sampling transect. However, here the authors talk about variations along this longitudinal profile (although no data are shown to support this assertion). Nonetheless, you can't have it both ways. If there is longitudinal variability among the cores you shouldn't be averaging the depth profiles and in fact, by doing so you may be obscuring real depth trends in each core.

9. (210 – 215) - This is far too speculative and not well supported by the data. Components C1 and C2 may include quinones that can react with iron oxyhydroxides and this may release DOM that may be biodegradable. Yet the profiles presented here show no evidence of this. Likewise, C3 may be non-redox active and may be irreversibly bound to the iron phases, but I see little to really support this assertion. The points made here in the text are also made in the Abstract (lines 20-21) and the Conclusions (lines 233-6), and are, in my opinion, presented in far too definitive a fashion, given the data presented here. Furthermore, generalization of this speculation to the "rusty iron sink" (line 236) is very premature (at best).

10. The differences between the fluorescence characteristics of the DOM associated with the different iron phases is intriguing, but in the context of all of the other issues I have with this manuscript, it's hard for me to be know how to interpret their significance.

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