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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.

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We appreciate the insightful comments offered by the reviewer. Her/his thoughtful review will certainly help us in shaping the manuscript for its intended publication. We are also grateful to the reviewer for noting interesting data in the study. We take the concerns of the reviewer about the data being speculative very seriously and seek to use this opportunity to clarify all those concerns kindly raised by the reviewer. Answers to comments from reviewer One of the confusing sections in the current iteration of the manuscript is that explaining the extraction scheme, the question of redox labile and redox "stable" phases of iron. We admit the lack of clarity in the form that the

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Discussion paper

extraction scheme was structured in the manuscript. This is to be modified for the sake of clarity. We will seek to clarify it to the best of our ability and hopefully that would clear the doubts the reviewer has enlisted. Firstly, it should be noted that the organic matter (OM) associated with iron (Fe) phases are in particulate and not dissolved form. As the OM-Fe is said to even withstand episodes of anoxia. Also, it is true that all Fe oxyhydroxides would be differentially reduced, however, it is not just the rate of dissolution that differs, but also the degree of dissolution in terms of the percentage dissolved. This points to the fact that some phases are metastable, whiles others are more labile. That was the essential deduction from the result of the extraction scheme implemented. It basically modified the original extraction scheme where the bicarbonate dithionite (BD) is used to dissolve all reactive minerals in a single step reaction over 2 hours. As noted by Jan et al. (2015), few minerals dissolve completely after about 10 minutes, whiles most of the minerals of concern dissolves within 2 hours. Hematite, however, does not dissolve completely even after 6 hours, implying that the usage of a single step extraction scheme overestimates the impact of dissolution of Fe oxyhydroxides. In consequence, a sequential extraction discriminating Fe phases which are more redox labile was considered necessary given that other phases are redox "stable". From such approach, one could infer the impact of dissolution of Fe in the environment. Eusterhues et al., 2014 noticed that in both abiotic and biotic mechanisms, the rate of OM-Fe dissolution and the proportion of the Fe dissolved differs but are comparable. Based on this foundation we characterized the associated OM to understand which quality of OM are associated with the different phases of Fe and discussed it in the light of published and well cited studies. To the issue of the bottom waters: the reservoir used as a natural laboratory is a dimictic system with spring and autumn turnovers. Sampling was done on a longitudinal transect from the inlet to near the dam. Aside the inlet, the other three sampling sites are anoxic over a period. Anoxia is established at the inlet depending on the conditions of the year. Also, the morphology of the base in the reservoir doesn't follow a progressive increase of depth along the longitudinal profile, but an irregular one, hence it is not that prudent to

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Discussion paper

analyse the data in the longitudinal perspective. With regards to the differences in the DOC and Fe dissolved by both BD1 and 2 there is a clear difference in their means, we admit the standard deviations diminishes the effect of the differences between BD1 and BD2 and this is due to the morphology of the system. Below, we answer specific questions from the reviewer.

Specific comments

R2Q1 (71-3) -These are results and don't belong in this section. Also, what does "more stable" mean?

A1. We have moved this to the results section and "more stable" is a mistake should read "remain constant in the first 2 cm of the vertical profile".

R2Q2 (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.

A2. It was mentioned to stress why sequential extraction discriminate Fe oxyhydroxides in terms of their redox lability and "stability". Bulk extraction data was placed in the supplementary section.

R2Q3 (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?

A3. We thank the reviewer for pointing out the confusion. BD1 and BD2 are the only extractants that dissolves reductive Fe. OH1 and OH2 do not dissolve Fe at all especially after the BD extraction. It rather dissolves mainly aluminium (Al) oxyhydroxides. Hence the Fe concentration profiles were from BD extracts. There is no data for Fe

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Discussion paper

dissolved by NaOH because Fe is not extracted by NaOH extractant. Yes, classically all Fe would be dissolved but it is also a fact that some oxyhydroxides as well as OM-Fe associations are metastable as shown by the data in Eusterhues et al., 2014; Jan et al., 2015.

R2Q4 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.

A4. NaOH extractant did not dissolve Fe after BD1 and 2. This fraction was not aimed at dissolving OM associated with Fe. The purpose of the NaOH step is to obtain a full spectrum of DOM to determine the quality of OM associated with Fe (see also A6 below).

R2Q5 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)).

A5. That is true all iron oxides will dissolve, however, the experimental dissolution done in the laboratories with strong reducing agents like BD correspond to longer time scales in the environment. Hematite, even after a period of 6 hours did not dissolve completely. As a result, some Fe oxides are termed metastable and based on that they can be in the environment even in anoxic conditions and would not dissolve completely.

R2Q6 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.

A6. As stated in A3 and A5(above), NaOH did not dissolves Fe. The NaOH was used

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Discussion paper

to have a full spectrum of DOM, for determining the quality of OM associated with Fe. We could also move the NaOH data into supplementary if deemed prudent during the revision.

R2Q7 (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.

A7. Our understanding is that BD1 dissolves Fe oxides which are active compared to that of BD2. Also, Fe oxides dissolved in BD1 had comparatively larger surface areas which favours sorption affinity compared to BD2. We thank the reviewer for the suggesting that there might be an alternative explanation for the differences observed for DOC yields in BD1 v BD2. These will be further reasoned in the next iteration of our manuscript.

R2Q8 (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.

A8. We thank the reviewer and appreciate the opinion about the handling of the data. However, we would like to more clearly state, again, that the data was not discussed in a spatial perspective as we are not especially concerned in characterizing the site, but using the sediments from this natural lab for interrogating the OM-Fe association and its fate in general.

R2Q9 (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)

A9. We really appreciate the comments from the reviewer and appreciate where the difficulty may be leading to the comment. The extractant used for the dissolution of Fe oxyhydroxides is a reducing agent. The redox lability and “stability” were assigned to how fast and the proportion of the Iron oxides that will dissolve in the event of a reducing condition as detailed in the general comment section. Now to directly answer the question; As we have stated in the General comment, Fe dissolved in BD1 are usually redox labile those dissolved in BD2. The quality of OM associated in DOM was ascertained to explain how these qualities could be an influential factor in making a phase of the Fe oxides more redox labile than the other. The observed FDOM components have been extensively studied. The shuttling of electrons between Fe oxides and associated aromatic OM have also been studied. It is based on this literature that we discussed our findings, that the identified quality of OM selectively dissolved in the BD1 fraction plays a role the redox lability of Fe phase as established that, such quality of OM enhances the dissolution of the Fe oxyhydroxides. Whiles the protein-like component comparatively doesn’t enhance dissolution of Fe explains why they are associated with the Fe phases which are redox "stable".

R2Q10 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.

A10. We thank the reviewer for giving value to the fluorescence characteristics of the DOM associated with the different iron phases. Clarifications that in our view will help

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in interpreting the significance will be included in the revision of our manuscript.

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