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Discussions

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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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General response

We appreciate the thorough work by the reviewer, and we share in the concerns raised. We hope our response would help put the study in perspective and thus bring clarity to the study and the reviewer. The study considered works which has been done so far with both synthetic and natural samples in terms of the association of Organic matter (OM) and Iron (Fe) oxyhydroxides (OM-Fe). From those studies, there were disparity in concluding which of the OM quality is selectively preserved by Fe. The study used a sequential extraction scheme which mainly shows form of OM quality

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Discussion paper

associated to a corresponding Fe oxyhydroxide and discriminate Fe in terms of its redox lability and "stability", since we thought that could play a role in the selective preservation of OM-Fe and is missing in literature reviewed so far. Thus, the quality of OM associated with the redox "stable" Fe are therefore the selectively preserved on a longer time scale. We would like to point out that the data for this study was not discussed in the light of spatial gradient. The only time that was used, was to explain the variations in Fe concentrations in the study. The study was mainly more on qualitative and mechanistic means of OM-Fe associations from 4 cores. In terms of the conclusion, the main conclusion was to show that non-humic quality of OM are preserved on a longer time scale compared to humic components and this can be seen when a sequential extraction scheme is used instead of a bulk extraction, which doesn't necessarily differentiate redox labile Fe from redox stable Fe in natural environmental samples. Also, we acknowledge why the reviewer interpretated the extraction as water, acid, base. However, we would like to state clearly that none of the extraction was done in an acidic medium. The dithionite was buffered to a circumneutral pH as seen in Table. 1 and the supernatant was only acidified after extraction to keep the Fe in dissolved form. With reference to OM-rusty sink in connection with changing of the climate, that was meant as an implication of this knowledge, for instance the thawing of permafrost soils that become water-saturated and reducing. Also, the main OM sources of a system could be used to predict how susceptible they could be in the mineralization of OM in producing greenhouse gases.

Specific response

R1Q1 The introduction is very short and very specific, and it is unclear what the broadly interesting knowledge gaps are, and whether the study addresses fundamental knowledge gaps or hope to confirm known patterns with a simpler approach

A1. We thank the reviewer for pointing out concerns with the introduction. We take seriously the concerns of the reviewer. For clarity sake, the introduction sought to show the work done and the different conclusions as in the quality of OM been selectively

preserved. The reasons we assigned to this was due to the heterogenous nature of OM and hence the approach used in studying could be what is leading to the disparities in conclusion. Also, we concluded that none of the studies so far considered the different redox lability of Fe in their study. To that effect our work sought to use a sequential extraction scheme which discriminate in terms of redox labile and redox stable Fe which in our opinion is lacking in the studies so far.

R1Q2 Section 2.3: More details are needed to appreciate the chemical treatments, and what they mean for adequate interpretation of the results. I acknowledge that a reference is provided, but at least the reasoning behind the treatments is needed in this manuscript to understand the coming results. This is important because there is barely any difference among cores (or this is not shown), and from surface to bottom of the cores; most of the variation comes from across treatments.

A2. The main purpose of this extraction was to estimate OM associated with reactive Fe oxyhydroxides of different redox lability which is achieved using the Bicarbonate dithionite extraction sequentially. Water and sodium hydroxide were included to estimate the full spectrum of the OM quality and concentration. There are some changes in individual cores but not shown as the data was treated as replicate.

R1Q3 L100: I did not understand this sentence, and what the reference actually refers to

A3. The original study was conducted on water samples and not on any chemical extraction. However, the study cited used it in applying to both water and alkaline extracts hence used as a justification in using it in applying same in our study.

R1Q4 L102-104: I did not understand what was done

A4. From L102-104, it is established that Fe influences the absorbance at 254 nm on the UV-VIS spectra hence the need to correct that effect. To do that, absorbance at 254 nm of different concentrations of Fe which reflects that of the study was measured

and a calibration curve was plotted from that.

R1Q5 L109: But does not pH affect fluorescence?

A5. We thank the reviewer for this question. We must say from all studies cited so far fluorescence were measured within the scale of pH our study was conducted (pH = 2-13). Presence of metals like Fe quench fluorescence and reducing the pH to 2 eliminates the effect of quenching by metals (Poulin et al., 2014) cited in study.

R1Q6 Paragraph at L131: There is a huge difference among treatments, but without further explanation of what they mean, in the Methods, it is hard to appreciate these findings

A6. We appreciate the concern of the reviewer and would improve the clarity in the next stage if it will go further.

R1Q7 L154-156: Where is this coming from? No result, or description of the cores was provided to appreciate this statement

A7. Under sampling section (L 68), we stated that the cores were sampled on a longitudinal transects which varied in Fe concentration. Hence this was an explanation to the variation of Fe concentration of the mean.

R1Q8 Section 3.2.1: This section is too superficial and is barely interpreted R1Q9 3.2.2: same

A8&9. We admit this data wasn't discussed thoroughly this is because there isn't much to say than what have been said.

R1Q10 3.3: Here the authors go at length in describing the PARAFAC components, with a level of details that greatly differs from previous sections. I believe the idea is to interpret how specific components may mean a particular chemical composition, which is then used in the following section to interpret associations with Fe, but the ideas are not explicitly connected in my opinion; there is a leap in the level of information pro-

vided by the optical approaches in section 3.3 vs the detailed chemical interpretation provided in section 3.4. For example, on what basis, specifically, can you conclude the following: "The structure of both C1 and C2, however, possesses a redox behavior that makes their reaction with Fe-oxyhydroxide reversible leading to the solubilization of the DOM or both Fe and DOM, with the latter subsequently being biodegradable (Burdige, 2007; Keil and Mayer, 2014).". I am not saying that this interpretation is wrong, but I believe that there is not enough information in the manuscript that supports this interpretation based on the authors findings.

A10. The components C1 and C2 have been thoroughly reviewed by (Ishii and Boyer, 2012) and has been cited in the study. This was from an original study by Cory and Mcknight 2005. These were interpreted as reduced and oxidised quinones respectively. The quinone moieties have been established to be taking part in the shuttling of electrons. It was on such basis the data was discussed.

R1Q11 L223-225: I do not think these studies have identified C3 specifically (at least they are not presented in Table 1), so this wording is misleading

A11. Yes that is true, they didn't identify C3 as none of those studies used fluorescence, but they identified non-humic components/aliphatic components which is C3 in this study. In fact, in the study by Lalonde et al., 2012, the authors described the component as rich in sugars and proteins. They were cited in the general sense of non-humic quality type of OM. "We also analysed the isotopic composition (δ13C and δ15N) and elemental composition (molar ratio of carbon to nitrogen) of the bulk organic matter and the iron-associated organic carbon fractions of all sediment samples. In most cases, we find that OC-Fe is enriched in 13C (δ13C increases by 1.762.8%; Fig. 2) and nitrogen (C:N decreases by 1.762.8) relative to the rest of the sedimentary organic carbon pool, whereas d15N shows little or no fractionation (Supplementary Figs 1and 2). Natural organic compounds rich in 13C include proteins and carbohydrates25, which are rich in nitrogen and/or oxygen functionalities that favour the formation of inner-sphere complexes with iron." (Lalonde et al., 2012) "We discovered that

hematite preferred to sorb more aromatic organic matter as a result of inner-sphere coordination and other interactions, but the aromatic carbon-rich organic matter was more susceptible to the reduction release. These results have important implications for the biogeochemical cycle and stabilization of carbon. First, we provided evidence that iron-bound, non-aromatic carbon was more resistant to reduction reactions, which can preserve aliphatic organic matter." (Adhikari et al., 2015)

R1Q12 L228-229: What is "appreciable time", and why is it important? Also, it is weird to end the discussion saying that in the end we are not sure what is going on hence more studies are needed, I would suggest concluding on a more "positive" note in terms of your main contributions to this topic.

A12. We thank the reviewer for his advise and concerns raised. "Appreciable time" used here is in relation with processes in natural systems. For instance, episodes of anoxia and oxygenation as well as possibility of resuspension do take place. The oscillation of anoxia and oxygenation influences the Fe crystal structure over a period and as well the possible diagenesis of the OM would influence the fate of the OM-Fe. In laboratory experiments devoid of such processes which occurs in the natural environment as in the case of the study cited would probably lead to a different interpretation of the fate of OM-Fe in such study.

R1Q13 The conclusion overall is interesting to read, but I found it unsupported by the results and insufficiently developed in key places of the manuscript. I suggest using sentences from the conclusion as key points (maybe paragraphs topics) that guide the development of the introduction and discussion

A13. We are grateful to the reviewer for the recommendations. They will be studied and effected in the revised version of the manuscript. We also are convinced our conclusions are supported by our data discussed so far.