

Interactive comment on “Flocculation of dissolved organic matter controls the distribution of iron in boreal estuarine sediments” by Tom Jilbert et al.

Anonymous Referee #2

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This is a paper on the removal mechanisms of Fe to sediments in the riverine-estuarine transition of a long riverine estuary on the Eastern Baltic Sea and the effect of this removal for the corresponding iron diagenesis in the underlying sediment. The key message of this paper, if I understand this right, is that riverine Fe is removed by flocculation in the riverine-estuarine transition of the Eastern Baltic Sea. These results are similar to the Fe story presented in Yu et al (2015) Chemical Geology in another Finnish estuary. The flocculation occurs as an organic Fe complex.

These results are based on the interpretation of Mössbauer spectra, which revealed an unknown Fe phase that was neither well-crystallized silicate, magnetite, nor ferrihydrite. The inference is therefore not direct, but indirect, and that is a major shortcoming.

In the underlying sediments of the outer estuary and the Baltic Sea, Fe accumulation

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occurs as different phases than in the riverine part, where more crystalline Fe hydroxides occurred than in the distal part where organic Fe dominates.

In principal I believe some of the story, e.g., the organic-Fe transport and rapid removal in the estuary. But I failed to see how the results translate into different diagenetic Fe processes in the sediment.

In particular, I felt that the story on the anaerobic oxidation of methane by iron was underdeveloped. While this is an impressively large data set from many stations, much of the potential novelty hinges upon the interpretation of the Mössbauer data. The combination of Mössbauer/extraction data call for a major reinterpretation of the operational Fe extractions, in particular of a re-assessment of the dithionite extraction as an organic Fe phase. This has large ramifications for many published papers and the authors need to be very careful in their assessment and interpretations.

I would like the authors to address and comment on a number of questions I have:

Why do you not present Mössbauer spectra of riverine material, dissolved and particulate? This would be most interesting to see.

Why do you claim that hydroxylamine-extracted Fe occurs as Fe^{2+} , when hydroxylamine is a strong reducing agent? No information on prior oxidation state is possible using this extraction method.

Why do you not even consider or discuss the extraction of Fe_{ox} phases with dithionite? This is well known. Not all Fe may be organically associated to the same extent throughout the transect and not necessarily as Fe^{2+} , because dithionite is also a reducing agent.

In your table or on the Mössbauer spectra you should show the patterns for Fe_{ox} or FeS_2 phases to convince the reader that the composite spectrum is not influenced by these phases.

The Mössbauer spectroscopy standardization and reference spectra are not explained.

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It is not clear why your conclusion is that the phase must be an organic Fe²⁺ phase. If it is ferrihydrite associated with organic matter, what kind of association is this?

Is there a possibility that the unknown spectrum is an amorphous Fe-silica phase?

Why is it that there are hardly any changes in Fe speciation at Station D, although the S content changes so significantly and therefore likely the concentrations of FeS and FeS₂?

What is the major Fe carrier down the river, i.e., what is the speciation of Fe in river and estuarine water?

How much is associated with the organic fraction – how much is present as ferrihydrite – what is the exact molecular association?

Figure 5 figure caption and left figure panel don't agree. The caption reads Fe²⁺/Fe_T, the other Fe³⁺/Fe_T ratio.

Figure 6: The down-core operational Fe profiles don't exactly make sense in light of the pronounced changes in S content with depth at Station A. At least, the 100% scaling makes it difficult to associate the species changes with the S concentration changes.

I recommend to show the Fe species as concentrations, e.g., as summed bars totaling to the actual Fe concentration. That would help at least for comparing the data of Station A. The Fe species do not correspond at all to the sulfur concentrations. How is this possible, if FeS/FeS₂ forms? My conclusion would be that the dithionite-extracted species seem to be associated at least partly with some FeS/FeS₂. This needs to be accounted for.

p.14 l.25: I think the authors mean 'isotopically depleted'

p.16, l.16-17 Fe-Si amorphous phases; FeS mackinawite-like material?: Why Fe²⁺, could also have been Fe³⁺?

p.17, l.1-5 hydroxylamine hydrochloride is a strong reducing agent suggesting that the

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Fe could have been reduced by the extraction. I would also like to see a transect plot of DOM and POM.

p.18. Are the salinity differences significant enough to impact the Fe-S system? I don't think so.

p.18 l.24 what do you mean by background rates: How are these background rates? Aren't these the major reactions? What about sulfate reduction rates and coupled oxidation of sulfide by ferrihydrite?

The anaerobic oxidation of methane by iron is often invoked these days, but to argue for this process there has to be good direct evidence. I am sure the authors are aware that AOM also can be coupled indirectly to reduction of iron oxyhydroxides through sulfide oxidation, but cannot be distinguished easily without performing specific experiments. Concentration profiles alone are not enough. The authors should refrain from inferring that AOM by iron is a major process controlling deep iron diagenesis when they have not addressed sulfide oxidation processes. They do not even present DIC data to support their assertion. In addition, should this process occur, it is easy to assess the quantitative significance by assessing the methane flux and the required removal of Fe to account for methane oxidation.

Along these lines, generally there is also too little discussion on sulfide oxidation coupled to iron reduction in the surface sediments. These organic-rich sediments likely have very low oxygen penetration depths of a few mm. Based on many other studies in estuarine systems, it is likely that anaerobic degradation processes such as sulfate reduction commence in the first centimeter. This makes it possible that FeS phases already occur in the topmost cm, and that not only iron reduction, but co-existing iron and sulfate reduction take place in the topmost cm.

Finally, although the authors do very well in describing the bathymetry of this estuarine system, they fail to associate the bathymetric features with the current transport/hydrography and the resulting particle transport and accumulation. For example,

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Station D likely must be influenced by saline water transport upstream, which is the only explanation to explain the higher bottom salinities. Therefore, inshore/upstream transport of organic material and of Fe has to be considered for the deep depressions. In addition, Station D, being the deepest station of the inner estuary, is clearly a particle trap of fine-grained material, also of organic material. As such, the focusing and accumulation of material here may override the estuarine mixing signal the authors have as their overriding study target. Stations C or E may be more informative in this context. Do the authors note the same signals at stations C, D, and E?

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