

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

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Review of BG-2017-181

With interest I have read this manuscript, in which the authors explore the role of salinity-driven flocculation of DOM and dFe in controlling the settling and diagenetic fate of riverine Fe along a salinity transect in a Baltic Sea estuary. The authors suggest a key role for flocculation in transferring Fe(III) in the form of Fe(III)-OM complexes and Fe(III) (oxyhydr)oxides from the water column to the sediment. Moreover, the Fe-OM pool is relatively stable and this Fe does not seem to participate in the “normal” reductive diagenetic pathways in organic-rich sediments. The manuscript is well-written, well-structured and an interesting addition to the flourishing research field of Fe-OM

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interactions in marine and terrestrial systems.

Together with this review, I have uploaded an annotated pdf document with all my questions and comments. Below, I highlight the main questions that arose while reading the manuscript.

1. On a technical note: If I understand correctly, relative errors for all solid-phase analyses were calculated from replicate analysis of “regular” (powdered) reference materials. I wonder whether this gives relative errors that are also representative for analysis of suspended material on filters. As far as I am aware, such samples are somewhat harder to process and I am curious to know if the authors can comment on how/whether they specifically assessed analytical precision and accuracy associated with filter samples (or why not).

2. There is no information provided on which standards were analyzed with Mössbauer spectroscopy (or whether reference spectra collected previously were included) and how the selection of (number of) standards for LCF was performed. The LCF fitting routine was only explicitly mentioned in the caption to Fig. 5; it should also feature in the main methods section. The key statement “Quantification of iron-bearing phases and iron oxidation states is based on relative subspectral areas” may be expanded a bit (as it is to some extent in the notes of Table 3). Overall, the procedure of obtaining relative proportions, including that of the “undocumented” Fe phase (in my opinion an awkward term, perhaps “unknown” is more appropriate?), should be more clear, as this phase plays a rather crucial role in the manuscript. Goodness-of-fit is also an important parameter in this respect, as it is basically the (areal) mismatch between the fit and the actual spectrum that is used as a measure of “undocumented” Fe. I think it would be good if all (relevant) reference spectra (perhaps including likely candidates that were not present such as siderite) are clearly presented (they are somewhat hard to discern in the current Figure 5: perhaps a stack plot with offset would work).

3. The authors assign the “undocumented” Fe phase fully to complexes of non-

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sulfidized Fe(II) with organic matter (p 12, L 17-19). They base this on the study of Yu et al. (2015), who found Fe(II)-OM phase “to be a major component of sedimentary Fe in a nearby boreal estuary.” In the Yu et al. study, OM-complexed Fe(II) was identified by Fe X-ray absorption spectroscopy using standards of Fe(II) and Fe(III) complexed with organic matter. As far as I could see, no empirical data in support of the assumption of OM-Fe(II) is provided in this manuscript. Because the Fe(II)-OM phase plays such an important role in the discussion, I wonder whether the authors can further substantiate their assumption that all the “undocumented” Fe, that could not be assigned to their (to the reader unknown) library of standards, was present as Fe(II)-OM? It should be clear exactly which Fe phases could be ruled out based on LCF with reference spectra. Some more focus on which spectral features could not be explained by the available reference standards, and how these may point to OM-associated Fe, would also be welcome. In the absence of a “smoking” gun, perhaps some more consideration should be given to the fact that OM-Fe(II) may not necessarily account for all “undocumented” Fe (to what extent do fitting uncertainties play a role?). In particular, the authors may want to address the validity of extrapolating Mössbauer data (key for assigning Stage 3 and 4 Fe to OM-Fe(II)) for the uppermost sample (0-1 cm) to the whole sediment record (up to 60 cm) at all sites (see also Comment 7).

4. p 14, L 13-19. The authors attribute the excess removal of Fediss relative to DOC to “preferred association of Fe with higher molecular weight compounds, which are more sensitive to flocculation (Asmala et al., 2014) or a mechanistic enhancement of flocculation by the presence of Fe (Forsgren et al., 1996).” Firstly, the second mechanism deserves some explanation (it now implies enhancement of flocculation of Fe by Fe?). Secondly, as the authors also observe a ferrihydrite signal in their Fe flux to the sediment, could flocculation of Fe independent of DOM -> POM dynamics play a role in the removal of Fe from the water column (driven by salinity, pH, perhaps DO)? The authors mention that “Flocculated material in the oxic estuarine water column is likely present as Fe (III) partitioned between organic-Fe (III) complexes and ferrihydrite (Neubauer et al., 2013).” (p 16, L 20-21). Changes in surface charge of Fe(III) particles due to

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adsorption of ions at higher salinity may also affect the solubility/flocculation of Fe(III) particles?

5. The reasoning behind the conclusion “that flocculation of DOM to POM in the estuarine environment may provide the second fraction of POM detected in the N/CPOM and $\delta^{13}\text{CPOM}$ data.” is somewhat unclear to this non-expert in that field (Fig. 3 and 4 and section 5.3). The authors state that the POM signal in surface waters is dominated by phytoplankton and therefore DOM-POM transitions cannot be discerned in N/CPOM vs $\delta^{13}\text{CPOM}$ plots. In fact, the N/CPOM vs $\delta^{13}\text{CPOM}$ signature of surface water-DOM from a previous study plot in the field of C3 plant material, suggesting that phytoplankton is not an important component of surface water DOM? I found this in itself surprising, as I would expect the DOM to be impacted by decomposition (POM \rightarrow DOM) of fresh algal material. The POM data from deeper waters from this study plot towards the C3 plant signature. The authors use this trend as an indication that the second OM source besides phytoplankton, i.e. C3 plant material, is transferred from DOM to POM through flocculation. I wonder whether the POM N/CPOM vs $\delta^{13}\text{CPOM}$ trend with water depth cannot also be determined/impacted by magnification of the C3 signal in the POM reservoir below the phytoplankton-dominated surface waters? I guess this strongly depends on the “rapid remineralization of fresh phytoplankton material during settling” (p 15, L8-9) which would remove the phytoplankton signal from POM and DOM and the persistence of the phytoplankton POM signal.

6. p16, L18-27. The authors interpret dithionite- and oxalate-extractable Fe as OM-Fe(II), and state that this is formed in the water column rather than the sediment. As far as I can see, this is again based on the findings of Yu et al. (2015) for a nearby boreal estuary. It may be good if the authors highlight data from this study or further literature besides Yu et al. (2015) in support of the conclusion that OM-Fe(II) is exclusively formed in the water column and is not of diagenetic origin.

7. p 17, L 4-7. The maximum accumulation of ferrihydrite in a (seasonally oxygen-depleted) “pit” of Station D is interesting, in that redox shuttling apparently causes

maximum accumulation Fh (the most labile and easily reduced Fe(III) phase) in the surface sediment (Fig. 6), where H₂S already seems to accumulate (Fig. 7). Striking is also the persistence of Stage 1 and 2 Fe (“ferrihydrite”) with depth through sulfidic depth intervals at Station D and to a lesser extent Station J. Could ferrihydrite perhaps be only part of the answer? The authors assign all Fe extracted by Na acetate at pH 4.5 to ferrihydrite, while this mineral is very slow to dissolve at that pH. Iron monosulfide was not specifically quantified in this study, could the presence of FeS help explain the Na acetate-extractable Fe pool and the persistence of Stage 1 and 2 Fe with depth? Egger et al. 2014, ES&T, mention that FeS in Baltic surface sediments is extracted in Stage 1 and especially Stage 2 of the same Fe extraction scheme as used in this study. The Mössbauer data indicate abundant superparamagnetic Fe(III) at Stations A and to a lesser extent Station D, but these are data from the uppermost sample (0-1 cm) that was in contact with bottom water O₂ that was still ~ 75 % (Station A) to 30 % (Station D) of saturation, eyeballing Fig. 1. FeS persistence far below the zone of H₂S accumulation may be unlikely (unless the system is very dynamic and far from any steady state). This zone, characterized by abundant Fe²⁺ but no sulfide, is often associated with formation of reduced Fe minerals such as vivianite and siderite. Could these also be present here and extracted in the low pH Stage 1 and 2 of the extraction scheme? The fact that these phases were not observed in the Mössbauer data from the surface sample does not rule out their presence at depth. Overall, some more words (beyond “seasonally oxygen depleted”) can be spent regarding the steadiness of a geochemical state with apparently co-occurring “Fh” and H₂S accumulation, and the nature of Fe extracted from anoxic non-sulfidic and sulfidic sediments during Stages 1 and 2 of the Fe extraction scheme.

I look forward to enjoying the revised version of this manuscript.

Kind regards, Peter Kraal Utrecht University, Department of Earth Sciences-Geochemistry

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Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2017-181/bg-2017-181-RC1-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-181>, 2017.

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