

Interactive comment on “Organic Iron Complexes Enhance Iron Transport Capacity along Estuarine Salinity Gradients” by Simon David Herzog et al.

The response to the referees comments are structures as follows: (1) comments from referees, (2) *author's response and author's suggested changes in manuscript (italic)*.

Response to comments by referee #2:

The authors present new data characterizing iron speciation in Scandinavian rivers together with Fe stability experiments aiming at estimating Fe transport across the salinity gradient to reach oceanic waters. While the work about Fe speciation seems rather well described and of high quality (for a non-specialist like I am), the work about Fe transport across the salinity gradient deserves more attention in my opinion. In addition, the authors seems to excessively generalize their findings. For instance the first sentence of the abstract is about 'open marine waters', while the most saline sample analyzed here has a salinity of 25 (seawater has a salinity of 35). Moreover, most studied rivers (7 out of 8) flow into the Baltic sea (typical salinities of 5 to 10) that is not proper seawater. Finally, the manuscript really lacks quantification (the authors state that fluxes could be 'significant' but no quantification is provided). The topic is extremely interesting. I recommend publication in Biogeosciences only after the points below have been addressed.

Nice to hear that the topic is found to be interesting and that we are given the opportunity to address points raised. As the comments above are further elaborated by the referee in the list of major points, we respond and describe suggested changes to each specific comment below.

Major points:

1. Excessive generalization of results obtained mainly along the Baltic Sea. Authors should make clear from the title and abstract (and discussion and conclusion) that their study is regional, mainly along a sea with especially low salinity, and based on lab experiments (for the transport capacity).

Thanks for this comment. Our intention was not to suggest that our results can be generalized to all systems, but rather to put the topic in a general context. While the systems we work in are indeed atypical given the low salinity in the Baltic Sea, the general response of riverine Fe to increasing salinity is likely to be comparable in other regions. The response is probably more influenced by the water chemistry of the rivers than the salinity gradient, considering that the loss of Fe from suspension appear to occur at salinities below 15. Nevertheless, it is important that the results are not overstated and that the reader is not misled about how far conclusions can be drawn. We have gone through the manuscript with this in mind and suggest the following changes:

*In the abstract we clarify the geographical region in which the study is performed: “In this study, we directly identified, by X-ray absorption spectroscopy, the occurrence of these two Fe phases across **eight boreal rivers draining into the Baltic Sea**, and confirmed a significant but variable contribution of Fe-OM in relation to Fe (oxy)hydroxides among river mouths.” Moreover, we removed the reference to marine waters in the concluding sentence of the abstract: “This study suggests that boreal rivers may provide significant amounts of potentially bioavailable Fe **beyond the estuary**, due to organic matter complexes.” We also*

clarify that Fe transport capacity was assessed by lab experiments: “The stability of Fe to increasing salinity, **as assessed by artificial mixing experiments**, correlated well to the relative contribution of Fe-OM, confirming that organic complexes promote Fe transport capacity.”

In the introduction we also clarify the geographic region of the study and the fact that the rivers drain into the brackish Baltic Sea: “To this purpose, we sampled eight river **mouths that drain at the Swedish coast into the brackish Baltic Sea.**“

The low salinity, particularly of the northern Baltic is now explicit in the Discussion “In the **low-salinity mixing regime present in the northern Baltic (Bothnian Bay)**, aggregation may occur without significant sedimentation (Forsgren and Jansson, 1992).”

Finally in the conclusion: “This would suggest that high and rising concentrations of Fe from boreal rivers (Kritzberg and Ekstrom, 2012; Björnerås et al., 2017) may indeed result in increasing export of bioavailable Fe **to the Baltic Sea** and open waters, where it may limit N-fixation and primary production (Stal et al., 1999; Stolte et al., 2006; Martin and Fitzwater, 1988).”

2. Lack of quantification of the potential Fe source the authors talk about (L 23 'potentially bioavailable Fe' from rivers) compared to other Fe sources to the surface ocean. The authors should provide estimations of the different Fe sources to the ocean, so that the reader can make an opinion about the significance of the source discussed in the present paper compared to other sources. This is necessary to support for in-stance the 2 following sentences (L13-14 and L 23-24 below). - 'Rivers discharge a notable amount of Fe ($1.5 \times 10^9 \text{ mol yr}^{-1}$) to coastal waters, but are still not considered important sources of bioavailable Fe to open marine waters' - 'This study suggests that boreal rivers may provide significant amounts of potentially bioavailable Fe to marine waters beyond the estuary, due to organic matter complexes.' The authors should remove assertions such as 'Fe loading from boreal rivers to estuaries is increasing substantially [...] this is a finding with major implications' (L 35 - 40) if they cannot present data showing that river dissolved Fe stabilized by organic ligands is indeed a significant flux compared to others for the surface ocean.

Thank you for this comment. In our view, the first sentence of the abstract is there to provide a general context. The elaboration on quantifying different sources as suggested by referee#2 is complex and would require more text than can be fitted into an abstract. Furthermore, the increasing Fe loading from boreal waters will likely have major implications also if not stabilized by organic ligands. Studies have shown that Fe of riverine origin is a phosphorus sink in coastal sediments, for instance. The reasoning is that what the specific implications may be depend on the fate of Fe across the salinity gradient.

3. The core of the paper, in my opinion, reside in the fact that 2 main characteristics are studied, 1) Fe speciation and 2) Fe transport capacity, and that these 2 characteristics are compared to each other. However, while the first point, Fe speciation is well de-scribed in the ms (notably with 3 figures), the transport capacity experiment is hardly presented in the main part of the ms (data are almost only shown in the supplementary materials), so that the reader cannot really make an idea about the validity of the author assertions. This is really a problem, because all the work about speciation is much less useful (at least in the presented context), if the transport capacity experiments are not validated. I believe that much more attention should be given to this part of the paper, with a proper discussion about the validity of

the experiments, especially using the in situ data. In the main part of the ms, not in the supplement.

In the original submission, the Fe transport capacity was presented in Figure 5 and Table 2 of the main manuscript, and the comparison of in situ Fe concentration along estuarine salinity gradients and theoretically estimated concentration based on the artificial salinity experiments were presented in Figure S3 in the supplementary information. In response to the above comment, we suggest to move the latter Figure into the main manuscript and expand the discussion on the validity of the artificial mixing experiments. For suggested text addition see response to comment 5 below.

4. Unfortunately, from what is shown in the supplement, I am not convinced that the mixing experiments do simulate accurately what would happen in situ. My opinion is that this dataset is insufficient to validate the transport capacities illustrated in Fig. 5 for instance. At least the authors should try to estimate error bars on the transport capacities (Table 2) and on the concentrations presented in Fig. 5.

It is important that mixing experiments are initiated as soon as possible after sampling, to make sure that Fe speciation is not altered. Moreover, the number of samples that can be included and processed in the experiment within a reasonable timeframe after sampling, is limited by centrifugation capacity. In the trade-off between running experimental replicates at a few selected salinity levels and including a wide gradient with many levels of salinity, we chose the latter, as we believe this provides more information. The consistency in the gradual loss of Fe in suspension with increasing salinity is in itself a validation of the Fe transport capacity measured at high salinity. We agree that the artificial mixing experiments are unlikely to capture exactly the loss of Fe along the natural salinity gradient, where for instance photoreduction may play a role, as well as the occurrence of organic matter of marine origin which may interact with riverine Fe and influence its behaviour. We also agree that these limitations should have been clearly recognized. Indeed, the experimental setup we apply capture the response of riverine Fe to increasing salinity in isolation. For suggested text addition see response to comment 5 below.

5. They should also mention that organic matter of oceanic origin (not reproduced in the lab mixing experiment) may also take part to the process.

We agree that this should be mentioned. The following text addition is suggested to better describe the strengths and weaknesses of the artificial mixing experiments:” Results regarding Fe transport capacity derived from the artificial seawater mixing experiments were in good agreement with the estuarine transects sampled. Theoretically calculated Fe concentrations, based on Fe loss in artificial seawater mixing experiments with river water and the dilution factor, showed only minor deviations from Fe concentrations measured in the Gullmar Fjord. For the Öre estuary on the other hand, measured Fe concentrations were somewhat higher than the theoretical calculations (Figure S3). In the low-salinity mixing regime present in the northern Baltic (Bothnian Bay), aggregation may occur without significant sedimentation (Forsgren and Jansson, 1992). This has been observed in the plume of nearby River Kalix, and was hypothesized to result from a high organic component of the aggregates, where low specific density may lead to transport of these aggregates far away from the river mouth (Gustafsson et al., 2000). Thus, the centrifugation used to efficiently separate aggregates in the mixing experiments, may overestimate estuarine particle loss in this context. Despite the agreement between measured and theoretically estimated Fe concentrations, the artificial mixing experiments are unlikely to capture all processes that affect the loss of Fe along the natural salinity gradient. In the estuary, photoreduction may affect Fe speciation and affect its fate, as well as the occurrence of ligands produced by marine biota which may also influence the behaviour of riverine Fe. Indeed, the artificial

mixing experiments capture the response of riverine Fe to increasing salinity in isolation, and how that depends on Fe speciation.”

6. In addition, I think that the comparison between the 2 characteristics (speciation, transport) is also not sufficiently presented and described. L 245-247 'For the river mouth samples, the Fe transport capacity at 35 salinity correlated positively with the Fe speciation ratios (CN Fe- 245 C /CN Fe-Fe : $r = 0.675$, $p = 0.023$; LCF ratio:0.78, $p = 0.005$). Further, Fe transport capacity at 35 salinity were negatively correlated to pH ($r = -0.730$, $p = 0.007$)' and L 291-293 'The positive correlation between the contribution of Fe-OM (as determined by XAS) and Fe transport capacity (determined in artificial mixing experiments) adds a direct support that organic complexation of Fe is enhancing the stability across salinity gradients.'. I think that if the authors could provide a graphical representation of these correlations, this would be much easier for the reader and more convincing.

Thanks for this input. To follow this advice, we suggest the addition of a figure to the supplementary that visually demonstrates the relationship between Fe transport capacity and the contribution of Fe-OM (as determined by XAS).

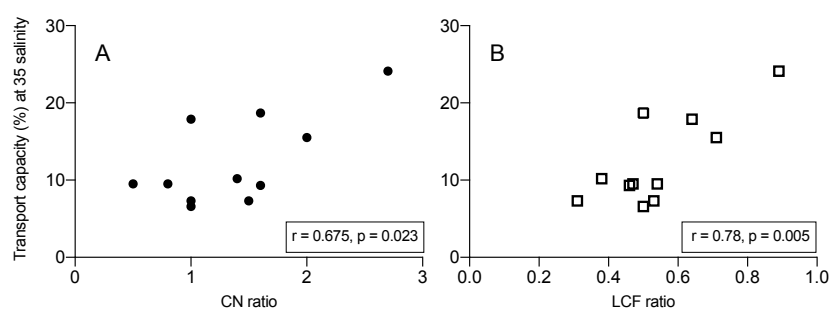


Figure S5 Relationship between Fe transport capacity at 35 salinity and relative contribution of organically complexed Fe as assessed by the CN-ratio (A) and LCF-ratio (B).

Minor points

7. Throughout the ms, the Fe phase the authors are talking about is not always clear. For instance, L 14 'the vast majority of riverine Fe', it seems that this is about dissolved Fe, but it is not mentioned. What's about particulate Fe ? Same for L 12. '1.5x10⁹ molyr⁻¹'. For what phase ? etc. L 13-14. 'Rivers discharge a notable amount of Fe (1.5x10⁹ mol yr⁻¹) to coastal waters, but are still not considered important sources of bioavailable Fe to open marine waters'. This is not totally true in my opinion, because, since papers such as Radicet al 2011 or Labatut et al 2014, remobilization of particulate iron river discharges is presented as a major source. This comment is related to the preceding one.

While size distributions are not a focus of this manuscript - organically complexed Fe and Fe (oxy)hydroxides are overlapping in size and can span from dissolved to particulate – we have gone over the manuscript to avoid unclarity as to the Fe phase referred to. Moreover, it is correct that iron that has settled to the sediment may be remobilized. While we cannot elaborate on this in the abstract, we have included this in the introduction: “Moreover, benthic release of Fe and subsequent lateral transport, was recently found to be a significant source of dissolved Fe to open marine waters (van Hulst et al., 2017).”

8. L47. 'fraction of riverine Fe remaining in suspension'. A discussion about the phases involved would help clarify the ms. what about colloids, very small particles etc.

This comment has already been address (see above).

9. L56 'aggregates'. Check English

Thanks – corrected.

10. L63. XAS. Define

Thank you for pointing this out the abbreviation will be written out: "The Fe speciation of all river samples was characterized by X-ray absorption spectroscopy (XAS)."

11. L86. 'cold'. What temperature?

The samples were stored in cooling boxes with freezing blocks during transport to keep the water from warming, This will be clarified: "Samples were stored cold and dark in a cooling box with freezing elements until return to the lab."

12. L 128 'were according'. Check English

The phrasing has been changed and reads now: "... was performed according to ..."

13. L283. FeTC. Define.

Thank you for pointing this out, FeTC has been replaced by "Fe transport capacity"

14. L 378. ' the increases in Fe discharge is also likely to alter e.g. P retention in coastalsediments'. Again, this assertion should be supported by quantification.

The sentence has been removed based on a comment by referee #1 (Comment 56).