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Biogeosciences Discussions

Interactive comment on "Organic Iron Complexes Enhance Iron Transport Capacity along Estuarine Salinity Gradients" *by* Simon David Herzog et sl.

Anonymous Referee #2

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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.

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).

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 instance the 2 following sentences (L13-14 and L 23-24 below). - 'Rivers discharge a notable amount of Fe (1.5x10 9 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.

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

Minor points

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 mol yr-1'. For what phase ? etc.

L 13-14. 'Rivers discharge a notable amount of Fe (1.5x10 9 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 Radic et 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.

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.

L56 'aggregates'. Check English

L63. XAS. Define

L86. 'cold'. What temperature ?

L 128 'were according'. Check English

L283. FeTC. Define.

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

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