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Discussions

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

Anonymous Referee #1

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Review of Organic Iron Complexes Enhance Iron Transport Capacity along Estuarine Salinity Gradients by Simon David Herzog, Per Persson, Kristina Kvashnina and Emma Sofia Kritzberg. Briefly, the manuscript presents the use of X-ray spectroscopy for the characterization of iron species in freezed-dried samples collected in a range of Scandinavian rivers ending in the Baltic Sea (except one in the Skagerrak). The study is complemented with mixing experiments with artificial seawater to imitate natural estuarine processes. The research group has a broad experience in the use of this specific technique and has published a series of interesting paper on iron speciation in Baltic rivers. The paper is a fine piece of work and brings forward many interesting conclusions about iron transition in riverine waters of boreal rivers. I really wish the authors would extend their area of study and produce similar works in rivers from other areas

covering catchments of different characteristics. I also think the authors should start collaborations with other groups that could provide other analytical techniques due to the limitations of the analytical approach shown in their work for species quantification. Overall, this is a very interesting work that brings a lot of qualitative information about the wide range of iron speciation that can be found in fairly similar estuaries. The manuscript supports the recent hypothesis that iron can scape high latitude estuaries in a percentage substantially higher than previously thought. The data has good quality and increases our understanding of estuarine processes. I recommend its publication after moderate revision mainly based on the need to increase the revision of literature (especially of literature referred to other analytical techniques) and improvable description of Fe changes under the increase of salinity. Sampling handling should be polished but I do not think this invalidates the manuscript. I have a few major concerns (nothing cannot be fixed): Data cooking is quite complicated and in principle very difficult to evaluate for an external reviewer and takes a few arguable assumptions. In principle, I have no doubts about the skills of the authors about this process. However, the result is a series of values without any indication of uncertainty or variability. This is a major issue in this kind of studies and in the few number of their papers I went through to prepare this review, there is no indication/description/estimation of the uncertainty associated to the values presented. I would appreciate a paragraph where the topic is addressed for a non initiated in the use of X-ray spectroscopy. So the reader can have an idea of the confidence can be given to the numbers presented in tables. It is also clear that trends obtained with different variables match but it is not clear how pecentaged of org/inor compare using different ratios. My second concern refers to the description of iron estuarine processes during the discussion. At the end of the discussion there is an approach to the real complexity of processes but in the first 3 sections there are oversimplifications. Example: "complexed Fe (Fe-OM) can "survive" the salinity gradient, while Fe (oxy)hydroxides are prone to aggregation and selectively removed". No possibility of FeO(OH) remaining in solution, OM is always described as a unique species where the real case is an extraordinary heterogeneity, ternary FeO(OH)-OM are only considered to the end of discussion, fulvic vs humic , OM flocculation and precipitation, etc. I wonder how ternary phases FeO(OH)-OM would show in the WT contour plots. Would those separate on its components or create a third patch? Third, the use of artificial seawater for mixing experiments. This is an interesting experiment here to see the effect of ions but it is expected that marine OM plays a role in all these processes. So no surprise that the empirical transport parts ways from the "theoretical" value. The experiments presented here are perfectly valid and offer interesting results but the possibility that marine OM plays a role is not considered in the discussion. Fourth. There is a lot of literature not considered in the introduction. We have information about the fate of iron ligands in estuarine waters from recent work with voltammetric techniques (Buck, Lohan et al. 2007, Laglera and van den Berg 2009, Bundy, Abdulla et al. 2015, Su, Yang et al. 2015, Su, Yang et al. 2016, Yang, Su et al. 2017, Su, Yang et al. 2018). Fe transport is not specifically calculated but can be inferred from data. It is not about citing them all but at least acknowledging their existence and the hypotheses included. There is also interesting mixing work done on iron transport capacity with isotopic labelled iron (Krachler group) (Krachler, Jirsa et al. 2005, Krachler, Krachler et al. 2015) that is not referred. The manuscript relays too much in X-ray and partitioning techniques and does not cite the existence of other analytical approaches; it should include them in my opinion. There is also a recent paper that is much on the direction of this paper where it is determined the concentration of iron specifically bound to humics inclluding a profile of humic-rich Arctic waters (Sukekava, Downes et al. 2018).

Specific and minor comments:

Title: the title is generic and seems to be referring to global processes. The authors made a good effort sampling many rivers and repeating samplings in different seasons. The problem is that all rivers are from a small geographical region and refer to similar catchments, have similar conditions and end in the same regional sea. This is related to my opinion that the authors should use this interesting analytical approach in rivers from other locations. I think that the title should conceal the relevance of the study to

the area where it can be applied. I suggest "Organic Iron Complexes Enhance Iron Transport Capacity along Salinity Gradients of Baltic Estuaries". Fe speciation is not clearly defined as Fe transport is. Fe speciation sometimes refers to organic vs inorganic species and sometimes relates to the oxidation state of iron. My advice is to use organic speciation (or perhaps overall speciation) when org vs inorg is discussed and redox speciation when the Fe(II)/Fe(III) is discussed. How different noise in Fig 3 spectra translates in uncertainties at the time to report: example Helge river Abstract Lines 16-17. Example of oversimplification. All FeO(OH) precipitates and Fe-OM survives. Please add "a fraction" of the organically complexed …………. I never heard of a study that suggest that all organic Fe "survives" the estuarine transit. Low-order stream? Not sure what is the meaning of the expression. Introduction: 28 iron is the fourth most abundant element in the earth crust and mantle, on earth it is possibly the most abundant element. 29 systemS. Please give range. I am not sure whether the authors refer here to freshwater systems or fresh and seawaters. 33 please add reference (Liu and Millero 2002). This is the main work on iron solubility in seawater and this paper is dedicated mostly to seawater. The Lofts paper is dedicated to freshwater. This paper should be the reference to discuss solubility 38 "suggesting that Fe export from soils are increasing." Check grammar, export is increasing

40 the Fe requirement in coastal waters is high but since it is not limiting I do not know if it plays a key biological role 48 "much higher than generally observed". This phrasing accepts several interpretations. I think the authors mean higher than predicted from prior works (the reference to 95% precipitation)

50 "Fe in natural waters is known to occur in two main phases, mononuclear organic complexes (Fe-OM) and Fe rich Fe (oxy)hydroxide colloids associated with chromophoric organic matter (Breitbarth et al., 2010;Hassellöv et al., 1999;Andersson et al., 2006)." In my opinion this is oversimplification, as it reads it seems that CDOM only can be found associated to Fe(OH)O and not forming soluble complexes. Electrochemical measurements have proved that fulvic and humic components of CDOM

bind iron forming complexes that can migrate freely to the electrode, i.e.: mononuclear (van den Berg and Laglera works on humics). This phrasing also assumes that associated to FeO(OH) there are no non coloured substances. This interpretation comes from the cited paper that include a peculiar description of iron complexation in rivers: "iron transport in rivers is associated with two types of carrier phases (besides detrital particles), an oxyhydroxide phase with associated CDOM (chromophoric dissolved organic matter, mostly consisting of humic acids) and an organic carbon (fulvic) phase (e.g. Lyv′en et al., 2003; Andersson et al., 2006)." From Breitbarth etal 2010). There is a huge body of literature that proves that fulvics belong to the CDOM fraction of DOM. Actually, the oversimplification that is found in the first 3 sections of this manuscript is diluted in the discussion section and there is a recount of the real complexity of the problem. Please rewrite this paragraph. 56 found "in" aggregates

Materials and methods 83 I am going to give a piece of advice to the authors for future work. Do not sample by hand in estuaries unless you have a system to open the bottle once it is at depth. Dipping an open bottle across the surface opens the possibility to collect a lot of surfactants and floating debris from the surface microlayer. I saw samplings ruined by this strategy. Fair paragraph at 90. I am interested in the concentration factor and should be included. Line 90 is a bit tricky because speciation here is obtained from the physical and not chemical properties of the sample (centrifugation=size partitioning prior to analysis). The warning is interesting because later on the manuscript the authors try to argue about the form of FeO(OH) crystallization. 94 how was the pH meter calibrated? TRIS or NBS solutions? Section 2.2. No problems with the approach. However I strongly recommend that for future studies they either obtain cleaner reagents or consider to remove metals from their working solutions. 150 nM Fe is a huge contamination and could interfere with some of the mixing experiments (obviously, the speciation of this contamination is different to the speciation of the sample). Please convert the blank concentration to mg Fe /L since this is the unit used throughout the paper. 110 24 h is a good compromise but has to be put into context. From (Liu and Millero 2002) work on Fe solubility in seawater "In our first series of measurements, we examined the solubility as a function of time. The results of iron solubility over 4 days at pH 3 and 8 are shown in Fig. 1. The iron concentrations decreased significantly from 3 h to 1 day and continued to decrease. After 1 week, the solubility did not decrease significantly. These results agree with our work in NaCl (Liu and Millero, 1999) and Kuma et al. (1996) in seawater. The subsequent solubility measurements were conducted with an equilibration time of at least 1 week. Our results represent the quasi-equilibration with iron solubility with particle size greater than 0.02 mm. Such a definition is in accordance with those of Byrne and Kester (1976a) and Kuma et al. (1996, 1998a,b). It may take several years for the solid to reach equilibrium (Schindler et al., 1963). The causes for the decrease in the solubility of Fe(III) with time has been recently been examined in more detail by Kuma et al. (1992, 1996, 1998a,b)." Please make a back of the envelop calculation about the fraction that is not removed in 24 h (I agree should be small) and cite Liu and Millero work. Also consider that with longer equilibrium times (as those residence times verified in estuaries, FeO(OH) aging could shift crystallization.

111 why 3000 rcf for 8 h?????? there is no bibliography attached as justification. What is approximately the size you discriminate? 2.3 Was any reference material analysed? Or at least in a previous work using exactly the same analytical settings? This is always required for oceanic studies. 118 problem with measuring pH with an electrode with a single calibration at changeable ionic strength. Again, how was this electrode calibrated? 2.4 and 2.5 I congratulate the authors for the degree of detail used to describe the analysis and data treatment steps. Again, the only thing I missed is a rough estimation of the uncertainty associated to the technique (specially the complex data treatment of the signals). 125 recorded? 140 Here I have a question. What is he concentration of Fe(III) added per mg of SRFA? Several recent reports state that the actual complexation is in the order of 15 nmol Fe per mg SRFA (Yang, Su et al. 2017, Slagter, Laglera et al. 2019). It could be that if iron was added greatly in excess, it was partially chemically bound and partially attached with other type of weaker interaction. I think a short explanation is important and future work could help to elucidate these

binding capacities reported by voltammetric methods. 175 please rewrite “were close to saturated with dissolved oxygen (85 – 118%)”. 178 was this higher pH caused by biological or geochemical processes? 180 oxygen saturation suspiciously low. Was the temperature effect properly accounted for? This paper would greatly benefit of some sort of visual library (supplementary file?). Not clear from the text whether ferrihidrate and goethite show exactly the same contours 190 what compounds? Humics or mononuclear ligands? 193-198. Not sure tables S1 and S2 are correctly cited. Not in order for sure 208- it is clear there is a good correlation between the CNFe-C/CNFe-Fe and LCF ratios but my question is, are values comparable? Please add an statistic or visual comparison (for instance, if values of two different analytical approaches to the same parameter are close, the correlation should have slope close to one and Y-axis close to zero). 227- Are the authors referring to the Helge river here? In Helge pH is not low and O2 is not low 233-238 this paragraph is very difficult to evaluate without a rough idea of the uncertainty of the approach. Since the technique clearly struggles with quantification (although fantastic for qualitative analysis of multiple species) I would recommend for future work the combination with other speciation techniques. It could be that correlations have been hindered by the low number of data and uncertainty. 3.3 243 high removal but here the point would be, the remaining concentration is high or close to seawater concentrations in the Baltic sea (not reported here)? 243-244 This is very surprising and requires further discussion. Fe precipitation is usually the consequence of coprecipitation with organic phases after flocculation of organic matter (mostly humics) due to the increase of the ionic strength that cancels the negative charge of organic matter at natural pH (addition: this is discussed further in the discussion section but still. . ..). This is something described since Sholkovitz/Boyle papers. Therefore, the lack of OC precipitation is very surprising and not a result that mimics natural conditions. Here the authors need to elaborate much more in this result. If the experimental procedure somehow precluded the flocculation/coagulation of organic matter, then the precipitation of Fe was severely underestimated. This is for me the most worrying result in the manuscript. 251-252. This should have not been

done like this. Seawater has a minimum pH of 7.8 (function of course of temperature and salinity and local biochemical conditions); the perform of dilution experiments with pH at the high saline end member as low as 7.1 is not realistic. The authors should had forced the pH to realistic values ∼8. This could have modulated the precipitation of species during mixing experiments. 4. 265 I would rephrase to “in contrast to the thermodynamic modeling suggested by (Wällstedt et al., 2010) for these systems that predicted a dominance of ferrihydrite (≥97 %).”. This prediction is subjective and depends in the parameters fed to the SHM model. I think that other research group could had obtained different results with the same model. Actually, I could not find the DOM concentration used in that specific paper.

268 I had concerns about the preservation of the redox speciation during sample processing but the result of Figure 3 is very revealing of the power of the analytical approach here. Kudos to the authors. Again, I would recommend for future work support from other ex-situ techniques more suited for quantification (spectrophotometry or chemiluminescence). 284 I do not think Sholkovitz was ever supportive of reduced Fe aggregation in any type of estuary independently of its latitude. The Powell paper shows complete iron precipitation (Figure 1). The idea of effective iron transport off high latitude rivers and humic rich streams was first put forward (to my knowledge) by Krachler and coauthors and it is deeply discussed in a recent review (Muller 2018). 285 “DOC was little affected by increasing salinity as previously observed (Linkhorst et al., 2017;Herzog et al., 2017).” This assertion is against prior observation by Sholkovitz, Boyle and other authors (I referred to this before), please discuss this finding and discrepancies among authors if exist or refer to the type of estuaries were this specific behaviour was observed. 289 these authors do not argue that the whole iron complexed to organic matter survives the estuarine transition. It is a bit more subtle although not against findings in this paper. The assertion is that against prior reports that sustained that all Fe coprecipitates with OM, a significant percentage of iron bound to DOM (in some works they specify to humic substances) “survives” estuarine mixing. Laglera and van den Berg argue that coprecipitation takes place down to a Fe/humics ratio

when both stabilize (or “learn to survive” if we continue with the metaphor). I advise rephrasing this section correcting the interpretation of prior literature and putting it into context with findings in this work. 294-295. First I would remove Sander’s reference since this is a description of interactions at pH 4 under complete protonation of carboxylic groups. At pH 7-8 negative charges are dominant. 296-298. This is not exactly the common description of the estuarine transition of DOM and their interaction with inorganic iron. As cations increase and neutralize the surface groups of DOM, repulsion forces decrease and DOM starts flocculation. Many non charged colloids (such as Fe colloids) get trapped during this formation of bigger aggregations and coprecipitate eventually. Basically, the result is the same described in the paper but the authors suggest independent precipitation and the literature is full with text about combined precipitation. Actually, FeCl3 addition for organic matter coprecipitation and removal is a common procedure used in water treatment plants. 306 this assertions ignores a whole body of literature. Iron speciation at the concentrations found at the saline end member of estuarine is available after cathodic voltammetric methods (Stan van den Berg, Kristen Buck, Loes Gerringa, Han Su and many others). With those methods it is possible to measure the iron ligand concentrations and concentration of humic substances. It is true that it is not clear whether those methods may discern between stable Fe oxyhidroxydes and Fe-OM complexes but the reported ligand concentrations in excess of iron concentration can only be ascribed to the presence of organic ligands. It would be fair to do a short summary of findings and add to the discussion that organic ligands in excess of iron concentrations have been found by this technique. 310-315 there is a factor not considered. In the estuary, there is production of iron ligands by biota that could be used to explain why dissolved Fe in the estuary was higher than the predicted after experimentation with ligand free seawater. 323-324. Please add reference to Liu and Millero 2002. Some of the observations here could be easily predicted. 340. there could be other Fe(II) sources. For instance, at higher flow conditions probably there is more turbidity and less light penetration limiting Fe(II) photoproduction. Let alone biological production of Fe(II). The subject is very complex. 360 which amounts? 370 this sentence has to be toned bown. First, this study is carried out in rivers which impact is never going to reach iron limited areas. Second, the number of iron limited areas in high latitudes of the northern hemisphere is not so extended (areas of the Bering Sea and perhaps after bloom in the Northern Atlantic). Third, the two studies referenced mention Arctic rivers, which are completely different catchment areas to those presented here since those are affected by permafrost melting. Not because there are iron limited areas and Fe from Baltic rivers is expected to increase, the Arctic Ocean is going to be fertilized. 377. I would remove last sentence. Although possible, it is very speculative and brings the focus out the main topic of the paper. Is there a first column missing in table S1?

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