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Interactive
Comment

# *Interactive comment on* “Factors influencing the dissolved iron input by river water to the open ocean” *by* R. Krachler et al.

**R. Krachler et al.**

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We would like to thank the two referees for their comments.

Author comment to RC S248, Anonymous Referee #2:

“The paper would benefit from a discussion of potential changes to the stream before it reaches the estuary.” - In the water column of the river, transformation and removal of fulvic-iron complexes during transport may occur. However, the predominantly biological refractory character of riverine fulvic acids has repeatedly been reported, so the degradation of fulvic acid -like substances is expected to occur mainly from solar irradiation. Precipitation of fulvic acid-bound iron may occur when the polyvalent cation ($Al^{3+}$, $Ca^{2+}$, $Mg^{2+}$) content increases which might cause precipitation of bridge-bonded complexes. Another mechanism of iron removal is scavenging of fulvic-iron complexes by suspended inorganic or organic particles. The half-life of DOM in river water depends on its specific structural properties as well as on the limnological characteristics of the river, i.e. stream chemistry, turbidity, residence time of water, climatic conditions, and hydrological dynamics. However, at least in unpolluted rivers, a large fraction of the terrigenous iron-binding DOM will reach the estuary unchanged.

"Is there any evidence from in situ mixing studies that rivers with more wetlands in the watershed have less Fe loss in estuaries than those with fever wetlands?"- To our knowledge, the role of wetlands in Fe delivery to the ocean has not been systematically investigated by in situ mixing studies. However, a very large number of investigations showed a significant positive relationship between iron and DOC concentrations in river waters. It is known that, in soils, the elements susceptible to dissolution and leaching loss to rivers are in the following order: Ca$>$Na$>$Mg$>$K$>$Si$>$Fe$>$Al. Accordingly, in most soils, iron is more or less insoluble. Only three types of soils - histosols and gleysols (bog/wetland soils) and podzols (boreal forest soils) - are of importance with respect to iron dissolution processes and leaching loss to rivers. In these soils, iron dissolution mechanisms have been found to be closely linked to oxygen-limited conditions due to water saturation and to the formation of humic and fulvic acids. Enhanced humic and fulvic acid concentrations in river waters are linked to catchments with high proportions of peatland (Aitkenhead J.A., 1999, Hydrological Processes 13 (8), 1289-1302; Elder J.F. et al., 2000, Wetlands 20 (1), 113-125). Accordingly, rivers with more wetlands in the watershed are expected to have significantly higher iron concentrations and higher fulvic acid concentrations than those with fewer wetlands. Recent studies (Waite T.D., 2003, Marine Chemistry 84 (1-2), 85-103; Linnik P.N., 2003, Analytical and Bioanalytical Chemistry 376 (3), 405-412) suggest that organic complexes between iron and terrigenous fulvic acids in river water may be quite strong, and will have a major effect on the iron solubility in estuaries, which is in accordance with the results of the present study.

Author comment to RC S294, Anonymous Referee #1:

"The study did not measure fulvic acid concentrations or analyze organic iron compounds." - Our results show clearly that the iron transport from land to sea is significantly influenced by DOM which is contributed by peat bog water. In order to understand the processes of iron export from terrestrial ecosystems to the ocean in detail, in future investigations, the simultaneous determination of concentration and structure of the relevant organic iron complexes will be performed using HPLC and NMR methods.

“It is stated that error bars for iron transport capacity were estimated to be 3% but it is not clear how the error bars were estimated.” -The error bars refer to the iron concentrations. Depending on the counting time, the error of analysis of iron concentrations was between 1,5% and 3%.

“The paper mentions that dissolved iron concentrations in the water from the bog-draining stream were higher than the iron-hydroxide solubility level.”- The solubility of Fe(III)-hydroxide in oceanic water has been determined by Kuma et al., 1996 (Limnol. Oceanogr. 41, 396-407). Solubility measurements in seawater indicate a total dissolved inorganic Fe(III) concentration on the order of 0.1 nmol L-1. Fe(III) species will dominate in oxic waters with very low equilibrium concentrations of Fe(II) species. The results of the present study suggest that the solubility of peat-bog derived organically complexed iron in seawater is at least three orders of magnitude higher than the iron-hydroxide solubility.

Interactive comment on Biogeosciences Discussions, 2, 537, 2005.