

Interactive comment on “Increasing iron concentrations in surface waters – a factor behind brownification?” by E. S. Kritzberg and S. M. Ekström

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General comments

Based on Swedish river monitoring data and a laboratory experiment, this manuscript deals with the causes of increased water colour in these surface waters. Special emphasis is put on the possible impact by iron. The topic is within the scope of Biogeosciences and the manuscript is well written, technically sound and well organized with some few exceptions (see technical comments). However, the data presented and conclusions based on them need some improvements (see Specific comments). Hence, I consider the manuscript suited for publication in Biogeosciences after major revision.

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Specific comments

1. Page 12288, line 14-15: Why just industrial emissions? Since 1972, the municipal and industrial sewage treatment has improved tremendously, greatly reducing the emissions of COD (BOD) and phosphorus (P). The latter affects the autochthonous production of OM probably affecting the time series of COD and TOC especially in the more populated parts of southern Sweden. In this region, agriculture is also an important source for P due to leaching and erosion, potentially affecting the aquatic primary production and OM trends. Hence, the manuscript should be complemented with P concentration levels (Table 1) and trends (Table 3) and the results should be commented on in the discussion chapter. Could the different trophic levels and partly different OM origin explain the differences between northern and southern Sweden?

Page 12296, chapter 4.1: Discuss the effects of sewage treatment improvements and the production of autochthonous OM coupled to P concentration levels and trends.

2. Page 12289, line 14-15: Fe and Mn are since 1994 analyzed with ICP-AES or ICP-MS and before that it was AAS (flame). The websites below describes the analytical methods (in Swedish)

<http://www.slu.se/sv/fakulteter/nl/om-fakulteten/institutioner/institutionen-for-vatten-och-miljo/laboratorier/vattenkemiska-laboratoriet/vattenkemiska-analysmetoder/jarn-och-mangan-med-aes/>.

<http://www.slu.se/sv/fakulteter/nl/om-fakulteten/institutioner/institutionen-for-vatten-och-miljo/laboratorier/vattenkemiska-laboratoriet/vattenkemiska-analysmetoder/metaller-i-vatten-icp-ms/>

In the discussion chapter, comment on whether the shift in analytical method has any important influence on the Fe trends.

3. Page 12290, line 16: "...Casual relationships...were tested..." How do you know (or show) that they are casual? Change wording.

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4. Page 12292, line 11-12: The expression "...relative rate of change..." is not defined. Does it refer to z-scores or any other type of normalized data? Define!
5. Page 12293 and elsewhere: You use the expression amount when it actually refers to the concentration. Look this over throughout the manuscript and change where appropriate.
6. Page 12299, chapter 4.3: I miss comments which refer to the articles by Löfgren et al. (2010) and Löfgren and Zetterberg (2011) showing that the DOC concentrations in soil water of mineral soils are generally decreasing in southern Sweden (L&Z 2011) and that the effects of Fe on the DOC concentrations in soil water is negligible compared with Al (L et al. 2010). In those articles you also find references on DOC trends in soil water in other parts of the northern hemisphere. The referred articles strengthen your hypothesis that organic soils such as peat lands are important for the water colour trends.
7. Page 12299, lines 20-23: The river mouth concentrations of Fe do not reflect the acidity status in the discharge areas where Fe is leached into the surface water system. Hence, the conclusion is dubious and should be removed. It could be expected that Fe(III) as well as Al(III) is leached into headwaters as water soluble Fe-humus complexes formed in the riparian soils (cf. Löfgren and Cory 2010 and references therein). Influx of Fe(II) is of course important, but does not necessarily have to be the whole truth.

Technical comments

- A. Page 12287, line 28: "In this study we address the direct causes...". Change "direct" to "potential" or something similar.
- B. Page 12288, line 2 (and Abstract): Even though it is defined in Material and methods, it should be clearly defined already here that it is data from the national Swedish river monitoring dataset that have been used. Add the same information in the Abstract.

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- C. Page 12288, line 12: The web address has changed to <http://webstar.vatten.slu.se/db.html>
- D. Page 12289, line 9: Add "...SWEDAC accredited..."
- E. Page 12291, line 6: The title "3.1 Water colour and concentrations of Fe and organic matter" would be a better title and in agreement with the title of chapter 3.2.
- F. Page 12291, line 15 and 21: Add % after the values 0.8 and 0.5, respectively.
- G. Page 12293, line 21: Add % after the value 1.2.
- H. Page 12294, line 9: Change to Bothnian.
- I. Page 12297, line 28: Change "that" to "than".
- J. Table 3. Add "ns" (non-significant) or something similar where appropriate.
- K. Figure 4. In the legend, add information on that each point represent single river.
- L. Figure 5. In the legend, add that TOC is from 1987.

References

- Löfgren, S. & Cory, N. 2010. Groundwater Al dynamics along boreal hillslopes at three integrated monitoring sites along a sulphur deposition gradient in Sweden. *J. Hydrology* 380:289-297. doi: 10.1016/j.jhydrol.2009.11.004.
- Löfgren, S. Gustafsson, J.P. & Bringmark, L. 2010. Decreasing DOC trends in soil solution along the hillslopes at the two IM sites in southern Sweden – Geochemical modelling of organic matter solubility during acidification recovery. *Sci Total Environ* 409:201-210. doi:10.1016/j.scitotenv.2010.09.023.
- Löfgren, S. & Zetterberg, T. 2011. Decreased DOC concentrations in soil water in forested areas in southern Sweden during 1987-2008. *Science of the Total Environment* 409:1916-1926. doi:10.1016/j.scitotenv.2011.02.017

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