

***Interactive comment on “DOC-dynamics in a small headwater catchment as driven by redox fluctuations and hydrological flow paths – are DOC exports mediated by iron reduction/oxidation cycles?” by K.-H. Knorr***

**K.-H. Knorr**

kh.knorr@uni-bayreuth.de

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Author response to the editor's comment and to reviewers' comments

Dear Brian Bergamaschi, dear Simon Bottrell, dear reviewers,

I thank you very much for the constructive reviews and the summary of the reviewer's suggestions. I am convinced that I provide a revised version that will meet all the raised issues. Below, I outline my responses and intended changes for a revision of the manuscript.

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“Reviewers suggested to one degree or another that alternative explanations exist for the observed trends in export - the simplest explanation being changes in hydrology (Reviewer 1).”

I fully agree with the reviewers that changes in hydrology may successfully explain changes in DOC. The named references were indeed helpful to strengthen this point in the revised version. As I intended to write this manuscript as a bridge between hydrological and biogeochemical approaches of the observed DOC increase, I really acknowledge all the named additional studies that I may have overlooked or did not adequately consider so far. One point I would like to make here and that was maybe not clearly made in the current version, is that changes in hydrology (i.e. as named in the manuscript “increased wetness”) could also affect reducing conditions within the wetland and thereby increase DOC release from reductive dissolution of mixed iron/organic matter phases. Nevertheless, regarding available discharge data, there is no clear trend over the last 2 decades, as also stated in Lischeid (2001). I will include a graph of the discharge time series from 1988-2008 in the revised version, including a LOWESS trend line. Using the same LOWESS parameters as for the solute data, there is a weak increase in LOWESS discharge in the time span from 1988 to 1995-1998, while there is no further trend or possibly a slight decrease in the subsequent years until to date. Therefore, especially the stronger increase of DOC in the last 10 years is not matched by a trend in discharge. While highest peaks in the discharge occurred in the mid to late 90s, peak concentrations of DOC seem to further increase thereafter. In the revised version, I will add these considerations about changes in hydrology and also mention the observed lack of changes in discharge.

“Reviewer 3 expresses this as a need for some experimental data to back up the observed trends.”

I can understand the doubts of Reviewer 3, as there is no explicit manipulation to test the hypothesis. Only a manipulation experiment within the wetlands has been carried out, where we studied the effect of increased drought and rewetting (see manipulated

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water table levels in experimental plots D1, D1 compared to controls C1, C2 as depicted in Fig. 4). Although this drying/wetting experiment within the wetlands clearly demonstrated the parallel dynamics of DOC and iron, I agree that a further mechanistic study would be desirable. I will definitively work on this issue in due time and I will hopefully report on progress on the hypothesis in a forthcoming study. In this study, my main intention was to make use of a large dataset of time series and porewater data and to derive an alternative hypothesis for DOC mobilization processes. To point out that this study wants to seek for support of this new hypothesis, the title was written as a question. I hope that Reviewer 3 could agree on my main intention of the study that definitively does not want to seek support for the failure of other hypothesis, but provide an additional idea to stimulate a discussion and further mechanistic studies, including appropriate manipulations. However, I will certainly improve the discussion about alternative hypothesis for the revised version.

“Reviewer 3 points to the idea that the central hypothesis should be further tested using stoichiometric calculations to assess if the observed changes in iron concentration could account for the changes in DOC.”

This is indeed an interesting point that I also tried to work on. Some thoughts are outlined in the following: Ratios of Fe/DOC in the pore waters are mainly between 0.02 and 0.06 (i.e. dissolved Fe is 2-6 % of DOC concentrations), which fits well with the observed Fe/OM ratios of the solid peat, especially in the uppermost layers rich in Fe and yielding high DOC concentrations upon wetting (Blodau et al., 2008). Iron is thereby (at least in the uppermost peat) the dominant metal, followed by Al (about 50 % of Fe) (based on XRF and digestion data for Al and Fe, respectively; Al data unpublished). In the porewater, Fe and Al make up approximately the same proportion of total ionic strength. This brought me to two conclusions: firstly, as effective flocculants there is only iron and aluminum to interact with DOC, secondly, iron is of those two the element affected by redox transitions and could explain the relationship to redox dynamics (Fig. 4). I do not want to exclude that there are more effects involved: e.g.

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reducing conditions (Fe, but also SO<sub>4</sub> reduction) lead to increases in pH, thus further increasing DOC solubility. Many studies of DOC and iron/aluminum interaction were carried out in mineral soils or using high concentrations of iron/aluminum oxides that do not occur in organic soils (as just to name a few very recent studies: Eusterhues et al., 2011; Mikutta and Kaiser, 2011; Schneider et al., 2010). Therefore, I found it difficult to discuss this more intensively. In the discharge, the Fe/DOC ratio decreases to about 0.006 to 0.008, meaning a preferential loss of iron (assuming that this is not only due to dilution). Based on a simple mass balance, a precipitate with about Fe/DOC 0.05-0.07 should form, which is again quite similar to what was observed in the uppermost peat layers. Interestingly, there is also no significant change in the Fe/DOC ratio since 1988 until to date, meaning that the increase is parallel. Nevertheless, I agree that the interaction with iron is probably not be the exclusive mechanism and accompanied by e.g. changes in pH, ionic strength, precipitation of oxides (aerobic) or sulfides (anaerobic), and ongoing DOC production stimulated by electron acceptor turnover. Therefore, I will include a few numbers on stoichiometric ratios and improve the clarity of the discussion towards what I have outlined above. I hope that this is somehow answering the issues addressed by reviewer 3. Otherways I will be open for any further suggestions.

“The manuscript would be strengthened by addition of discharge (Reviewer 1) and nitrate data to figure 1. A figure showing the location of site and layout of the sampling at the site would also be useful.”

These figures will be included

“The manuscript would benefit greatly from careful editing as there are many editorial and language issues that interfere with clarity”

I will carefully revise the text to improve clarity. I thank for the corrections already mentioned by the reviewers.

Additional points raised by the reviewers:

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Reviewer 1: "I don't agree with the statement that the most streams that have shown increased DOC concentrations are rich in peat. This finding has been across the all types of catchments"

This was indeed a misunderstanding, the reviewer is of course correct and I will revise this statement.

Reviewer 2 (Simon Bottrell): "If the S cycle dominates then dissolved ferrous iron concentration can decrease under reducing conditions (due to precipitation of FeS, as more sulfide is produced by sulfate reduction than Fe<sup>2+</sup> is produced by iron reduction) and increase during oxidation (as FeS is partially oxidized to sulfate plus dissolved ferrous iron) [. . .] Indeed, as pollutant S loadings decline there may be a transition from S-cycle dominated systems to Fe-cycle dominated systems!"

I thank Simon Bottrell for this comment. I was also thinking of these mechanisms, however, I did not include these thoughts in the current manuscript not to make it too complex or also (for the second part) too speculative. However, as I see that this is indeed interesting to the readers, and as it fits exactly with what I have thought during writing of the manuscript, I will include a short note on this issue.

Reviewer 2 (Simon Bottrell): "How do you know that DOC and iron were "eliminated" rather than diluted? Can you compare to more chemically conservative species – e.g. chloride?"

I indeed tried to compare iron and DOC fluxes with conservative tracers. However, there is unfortunately little difference in appropriate tracers. Shallow groundwater within the wetland does not substantially differ in <sup>2</sup>H and <sup>18</sup>O so that these tracers can only be used to identify event water. Also chloride concentrations provide little information, as there is partly interference with salt loads from a nearby road, an effect that lingers on even during summer. So my current interpretation is based on the observation during stormflow conditions most water originates from the riparian wetland areas (Lischeid et al., 2007), and for this water the dilution by rainwater can be estimated using the

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stable isotopic composition. A clear separation of groundwater is probably not possible based on the current dataset. Nevertheless, colleagues investigated iron and trace element exports from the catchment in more detail, analyzing also colloidal phases (E. Neubauer and others, unpublished data). Their data shows that there is a considerable formation of Fe(III) and NOM colloids during the transition into the streamwater. From my point of view this would support the oxidative "elimination" of Fe and NOM in transition into the streamwater. This point clearly merits more research and will be addressed in our future work.

Reviewer 2 (Simon Bottrell): "A difference between sulfate trends in summer and winter is noted in the caption. Maybe this deserves more comment in the text."

I will add a comment on this in the text.

Reviewer 3: "An example from the literature of DOC sorption to hydrous metal oxides (McKnight et al. 1992, ES&T) is a special case where metals are elevated in an acidic stream so that the concentrations of DOC and Fe are similar. That is not the case in the catchment studied by Knorr so stoichiometric calculations need to be considered and used to constrain the potential for DOC removal based on the Fe concentrations present."

As noted above, I will include some stoichiometric considerations on Fe/DOC ratios. A major difference between this study and the study of McKnight et al is, however, that here there is a redox transition from pore water to surface water, from Fe(II) to Fe(III). Based on the observations in the pore water, high concentrations of ferrous iron do not seem to decrease DOC solubility. Nevertheless, if such pore water is sampled under oxic conditions and iron is allowed to precipitate, there is a considerable loss of DOC in the sample. Moreover, if we work in the lab with humic acids, we may add substantial amounts of ferrous iron into the solution without significant formation of precipitates, while the addition of ferric iron leads to rapid precipitation of humic acid and iron (Libbecki and Dziejowski, 2008). Therefore I see a strong support for a mechanistic

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link here, although the reviewer is right that within the context of a wetland this should be backed up by experimental studies. I hope to do this in due time.

Reviewer 3: "Changes in pH and temperature could certainly increase DOC concentrations, but I do not see in this manuscript a compelling case that supplants the study of Monteith et al. 2007 published in Nature linking increases in DOC with changes in acid deposition and ionic strength as a leading explanation for the phenomenon across a broad spatial scale."

As outlined on page 12967, line 14 – page 12968, line 2 I wanted to outline an additional factor that needs to be considered when DOC is primarily exported from wetlands, dominated by reducing conditions. In wetlands, sulfate addition may have a rather stimulating effect on decomposition, increasing also pH during reduction, thereby possibly enhancing DOC production and export. I did not intend to disprove the hypothesis and findings of Monteith et al. (2007), but rather provide another hypothesis that is following the observed biogeochemical process patterns within wetlands. I agree with the reviewer that the mechanistic links need to be better elucidated by experimental manipulations in the future.

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