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Biogeosciences Discussions

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

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General comments: This paper represents an interesting advance in our understanding of DOC dynamics in freshwater systems and is supported by a significant new dataset that has been subjected to detailed and rigorous analysis. The author brings to the fore the impact of redox-controlled element cycles in wetlands and their interaction with hydrology in controlling DOC export. These cycles are driven by a series of processes that are interlinked in complex ways but the author is careful in attempting to distinguish cause and effect. The work is well presented and clearly expressed, so I have only a

few relatively minor comments. Specific comments: P12954 Lines 3-6. This is only one take on the possible redox drivers for these elements. 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 Fe2+ is produced by iron reduction) and increase during oxidation (as FeS is partially oxidized to sulfate plus dissolved ferrous iron). Exactly these relationships were observed in wetland pore-waters by Bottrell et al. 2007. As far as I can see this does not, of itself, invalidate the interpretation you advance for your data, but it does imply that there will be situations where the controls on Fe cycling and interaction with DOC may be very different to those that you describe. It will be interesting to see which type of behaviour is dominant across different types of catchment. Indeed, as pollutant S loadings decline there may be a transition from S-cycle dominated systems to Fe-cycle dominated systems! I think this needs to be dealt with here and maybe later where it may impact your discussion/findings. P12966 Line 13. How do you know that DOC and iron were "eliminated" rather than diluted? Can you compare to more chemically conservative species – e.g. chloride? Or have you already done this? – if so make clear here. Figure 5 and caption. A difference between sulfate trends in summer and winter is noted in the caption. I think it likely that this is due to seasonal differences in the dominant processes in the wetland sulfur cycle – i.e. sulfate uptake by plant growth in spring/summer and release to pore-water by plant decay/humification in the winter (see Bartlett et al. 2009 who show that these processes can dominate S processing). Maybe this deserves more comment in the text. Technical corrections: P12959 Line 9. Please be specific about when the Fe/SO4 correlation is positive and when it is negative. P12960 Line 1 and line 13. Beginning (not "begin"). P12960 Line 14. Maybe you mean "somewhat" rather than "somehow"? References cited: Bartlett, R., Bottrell, S.H., Coulson, J.P., Lee, J. and Forbes, L. (2009) 34S tracer study of pollutant sulfate behaviour in a lowland peatland. Biogeochemistry 95, 261-275. Bottrell, S.H., Mortimer, R.J.G., Spence, M., Krom, M.D., Clark, J.M. and Chapman, P.J. (2007) Insights into redox cycling of sulfur and iron in peatlands using high-resolution

diffusive equilibrium thin film (DET) gel probe sampling. Chemical Geology 244, 409-420.

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