

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

Anonymous Referee #3

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The manuscript by Knorr asks the question of whether DOC exports from a small headwater catchment are mediated by iron reduction/oxidation cycles. While this data-rich study provides detailed analyses of correlations among constituents within various water sources in the catchment, all of the work is descriptive. With no experimental manipulations to address the question the manuscript ends where it began - with speculations about the mechanisms controlling DOC concentrations. The suggestion that DOC concentrations are controlled by the flocculation of carbon in concert with iron oxidation and the subsequent dissolution of flocculated iron and the release of carbon

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under reducing conditions is intriguing. 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. Further, the drivers that control iron speciation in wetlands, primarily hydrology and oxygen content, can be invoked as drivers that control organic carbon concentrations without any mechanistic link. There is a need for experimental studies to assess the strength of these linkages, and determine whether biotic reactions and/or abiotic reactions are involved. The suggestion that the long-term changes in DOC concentrations may be the result of “...increased wetness as a result of changed precipitation patterns” is certainly plausible, but no data are presented for either historic changes in precipitation or an expansion of the wetlands within the catchment in support of the idea.

The presentation of data on the temporal variation of numerous analytes within the catchment waters is valuable. 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.

The manuscript is generally well written. There are a few instances where edits are needed -12957 line 17 (at a pH rather than an pH); and other instances where the English should be modified – 12969 line 4 (...adjacent streams pointed out... could be replaced by something a little less anthropomorphic ...our observations of opposing relationships of DOC...adjacent streams underscore the importance...).