## Dear Editor and Reviewer 1,

We thank Reviewer 1 for their thorough and constructive review of our manuscript and the positive feedback that the "study is novel and the experimental observations are well performed" and that the manuscript is "suitable for publication." We plan to provide a full response to this review once we have received all of the reviews and the Editor's decision.

In the meantime, we wish to address the reviewer's comments that "the paper does not fit well to the HESS audience as this audience is less focused on analytical geochemistry." The scope of HESS includes "the role of physical, chemical, and biological processes in the cycling of continental water in all its phases, including dissolved and particulate matter, at all scales." Along these lines, "biogeochemical processes" is a subject area for the journal. The manuscript type we submitted (technical note) is for papers relating to "experimental and theoretical methods and techniques which are relevant for scientific investigations within the journal scope."

This technical note provides new methodological insights for the interpretation of fluorescence spectroscopy data (excitation-emission matrices, EEMs) in groundwater samples containing significant Fe<sup>2+</sup>. Fluorescence spectroscopy techniques and EEMs are frequently applied to characterize dissolved organic matter and biogeochemical processes in a wide range of continental waters.

To support our argument that the manuscript falls within the scope and readership of the journal, we have provided a references list on the following page containing six articles published in HESS that include dissolved organic matter characterization using EEMs. Additionally, because HESS is an open access journal, the article will be able to reach the widest possible audience compared to traditional subscription-based geochemistry journals.

We are currently preparing a separate manuscript focused on full geochemical characterization of groundwater and sediments across the saline-freshwater gradient at the Kidd 2 site, where the groundwater sample used in this technical note was collected. In this follow-up paper we will show that the highly elevated  $Fe^{2+}$  is observed due to reductive dissolution of iron oxide minerals via organic matter oxidation. The results of this technical note are required to interpret the fluorescence spectroscopy measurements in the context of the wide range of  $Fe^{2+}$  concentrations observed at the site (10 to 300 mg/L). We decided to publish this technical note separately to allow the site characterization paper to be more focussed.

Thank you again for your helpful review. We look forward to providing a full response to your comments.

Sincerely, Cara Manning on behalf of coauthors Kun Jia, Ashlee Jollymore and Roger Beckie

## **References:**

Bernal, S., Lupon, A., Catalán, N., Castelar, S., & Martí, E. (2018). Decoupling of dissolved organic matter patterns between stream and riparian groundwater in a headwater forested catchment. *Hydrology and Earth System Sciences*, 22(3), 1897–1910. https://doi.org/10.5194/hess-22-1897-2018

Bernard-Jannin, L., Binet, S., Gogo, S., Leroy, F., Défarge, C., Jozja, N., et al. (2018). Hydrological control of dissolved organic carbon dynamics in a rehabilitated *Sphagnum* dominated peatland: a water-table based modelling approach. *Hydrology and Earth System Sciences*, 22(9), 4907–4920. <u>https://doi.org/10.5194/hess-22-4907-2018</u>

Broder, T., Knorr, K.-H., & Biester, H. (2017). Changes in dissolved organic matter quality in a peatland and forest headwater stream as a function of seasonality and hydrologic conditions. *Hydrology and Earth System Sciences*, 21(4), 2035–2051. <u>https://doi.org/10.5194/hess-21-2035-2017</u>

Graeber, D., Goyenola, G., Meerhoff, M., Zwirnmann, E., Ovesen, N. B., Glendell, M., et al. (2015). Interacting effects of climate and agriculture on fluvial DOM in temperate and subtropical catchments. *Hydrology and Earth System Sciences*, *19*(5), 2377–2394. https://doi.org/10.5194/hess-19-2377-2015

Pennino, M. J., Kaushal, S. S., Mayer, P. M., Utz, R. M., & Cooper, C. A. (2016). Stream restoration and sewers impact sources and fluxes of water, carbon, and nutrients in urban watersheds. *Hydrology and Earth System Sciences*, *20*(8), 3419–3439. https://doi.org/10.5194/hess-20-3419-2016

Shatilla, N. J., & Carey, S. K. (2019). Assessing inter-annual and seasonal patterns of DOC and DOM quality across a complex alpine watershed underlain by discontinuous permafrost in Yukon, Canada. *Hydrology and Earth System Sciences*, *23*(9), 3571–3591. https://doi.org/10.5194/hess-23-3571-2019