

Response to Reviewer 2.

This study focuses on applying machine learning to endmember mixing analysis of weathering chemistry in subsurface groundwater flow paths. They apply an NMF scheme and train it on syntactic data generated using a multivariate normal distribution of log-transformed stream water chemistries. The NMF is then applied to 3 measured stream water samples to delineate mixing proportions. The study is well presented and written, the SM is seminal to the understanding of the study and holds the key details for the optimization of the NMF. The main finding is within the sensitivity of the reaction to the groundwater flow paths which are unknown, yet they control the concentration relation between the components and therefore they are controlling the overall chemistry. In a way, these flow paths are a spatial localization of the reaction in space and time, due to the seasonal effects, as shown here. I found the paper very interesting, well written, and clear and supports the publication of the study, yet the main missing part that is not discussed here and must be added is a discussion on the how.

We thank the reviewer for their thoughtful summary, reviewing our work, and for their support in publishing our work. Below are responses pertaining to your questions of “how”.

How does the NMF manage to capture the effect of the subsurface groundwater flow paths? What is the additional mechanism that is deciphered by the NMF? The spatial and temporal effect of the subsurface groundwater flow paths must be captured in a meanfield way by the NMF, and this is not clear how it managed to do so and what was the missing mechanism.

NMF determines patterns in datasets. As domain scientists, we then interpret those patterns in the context of our system. For example, at Shale Hills, the patterns derived by NMF show that one endmember of the stream chemistry has high $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}]$ and $[\text{Mg}^{2+}]/[\text{SO}_4^{2-}]$ ratios. Using our prior knowledge, we recognize that water that flows deep at Shale Hills predominantly dissolves carbonate (i.e., calcite and ankerite) and pyrite. It is important to know that NMF does not “know” anything about flowpaths, it only derives the patterns that we are interpreting as flowpaths.

In the past, scientists have used their domain knowledge to define endmembers for EMMA and our new approach uses domain knowledge after the endmembers have been derived by NMF. The main idea behind our interpretations is that mineral reaction fronts commonly separate in the subsurface (Brantley et al., 2017); therefore, different flowpaths dissolve different minerals, and patterns of these mineral dissolution reactions can be detected using NMF.

We thank the reviewer for the comments, and we will expand the discussion in sections 3.2 and 3.5, as well as add information for where we think NMF could and could not be helpful. For example, in section 3.2, we will add: “The dissolution of different minerals along these flowpaths lead to patterns in stream chemistry that our NMF model discerns and separates the signals. If mineral reaction fronts are not separated in the subsurface, different flowpaths might not be separated by NMF; however, Gu et al. (2020) shows that separation of reaction fronts is common in shale watersheds.”

Reference:

Brantley, S. L., Lebedeva, M. I., Balashov, V. N., Singha, K., Sullivan, P. L., & Stinchcomb, G. (2017). Toward a conceptual model relating chemical reaction fronts to water flow paths in hills. *Geomorphology*, 277, 100-117.

I agree with referee 1 remarks 5 and 6, do clarify the mathematical components with a mathematical expression.

We agree with the reviewer and we have updated the text to reflect the changes. Please see the response to reviewer 1 for full derivation of the mathematical expressions outlined in remarks 5 and 6.