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Response to review of Hubert Savenije

Erwin Zehe et al.

Author comment on "Preferential pathways for fluid and solutes in heterogeneous groundwater systems: self-organization, entropy, work" by Erwin Zehe et al., Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2021-254-AC1, 2021

We sincerely Hubert Savenije (HS) for his thorough and encouraging assessment of our manuscript. We also thank him for the highlighted edits, which we will happily include in the
revised manuscript.

We agree that the interplay of dissolution and precipitation of minerals such as silicate or carbonate rock, and the related local feedbacks on saturated hydraulic conductivity, will certainly affect and change the distribution of entropy and power in fluid flow (and in flow of
chemicals). Aspects of dissolution and precipitation and their feedbacks on hydraulic conductivity, flow patterns and chemical transport are currently addressed in hess-2021-238
by Edery et al. (in review 2021). A precondition for dissolution of e.g., carbonate, is to maintain a local "saturation deficit", i.e., the actual carbonic acid concentration in relation to
the pH must be lower than the local equilibrium concentration established by the pH. Such
local reaction-limited conditions arise if the low pH is funneled towards the preferential flows
and is not distributed homogeneously over the inlet. This is expected to happen in high conductivity regions, where preferential flow occurs, and one could imagine that these regions
grow preferentially due to the dissolution (maybe even backwards as rill systems) and establish a more connected drainage network. Precipitation requires exactly the opposite conditions: local oversaturation of carbonic acid relative to the pH, because the concentration
is larger than the equilibrium concentration. This could happen upstream of "low conductivity
bottle necks" or perpendicular to the preferential flows, which might imply that conductivity,
locally, declines even more.

Overall, this could imply that preferential pathways become more preferential, while local bottle necks become even more "narrow". Such a system could, overall, still evolve to a more
organized dynamic behavior and we agree with HS that the key to assess this is to

include
molar entropy " but also free energy differences associated with the chemical reactions and
chemical energy fluxes associated with chemical transport " into the entropy and energy balances.

We will reflect on these aspects in the conclusion and outlook section of the revised manuscript; we are currently working on them as a continuation of our study and that of Edery et al. (in review 2021).

Reference:
Edery, Y., Stolar, M., Porta, G., and Guadagnini, A.: Feedback mechanisms between precipitation and dissolution reactions across randomly heterogeneous conductivity fields, Hydrol. Earth Syst. Sci. Discuss. [preprint], https://doi.org/10.5194/hess-2021-238, in review, 2021.