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Interactive comment on "Crossing hydrological and geochemical modeling to understand the spatiotemporal variability of water chemistry in an elementary watershed (Strengbach, France)" *by* Julien Ackerer et al.

Anonymous Referee #2

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The study 'Crossing hydrological and geochemical modeling to understand the spatiotemporal variability of water chemistry in an elementary watershed' by Ackerer et al. presents results from coupled hydrological and geochemical reactive transport models of a small watershed. The authors find that observed 'chemostatic' behavior is controlled by seasonal patterns of subsurface transit times and suggest that simple geometric representations of mineral surface areas may be sufficient to match lab and field measured effective rates. While I find this study promising and potentially interesting to a broad community of researchers, I believe there are some significant issues with the

authors' methodologies and conclusions that merit major revisions or resubmission. It is possible that I have also misunderstood some of the technical issues, as the authors do not provide adequate description of the modeling and validation methodologies, as detailed by Referee #1.

First, I'd like to echo comments offered by Referee #1 — this manuscript needs a much more detailed description of the geochemical modeling including in depth descriptions of rate parameterizations, reaction pathways, kinetic rates, and equilibrium constants used. As it stands, it is hard to contextualize any of the presented results. Additionally, there have been other studies which combine fully distributed hydrologic models with geochemical reactive transport code that should be acknowledged.

Flowpath Modeling: From what I can piece together, the back-trajectory simulations provide subsurface flow path lines that all originate at the boundary of the watershed domain. If the hydrologic model simulates subsurface/surface water connections as described, why aren't flowpath origins distributed evenly across the land surface? It seems the authors provide a quick fix to this situation by assigning an even distribution of inputs along a flowpath, but this step and its necessity should be described in more detail. In particular, this situation is characterized as 'realistic' in the beginning of the discussion, but from my understanding, other codes such as ParFlow / SLIMFast back trajectories would not need this fix because they predict the origin of waters across the land surface.

Additionally, from the diagram in Fig 5, are the measured soil solutions taken as inputs into the modeling domain? If so, it would be extremely useful to see where these fall relative to the C-Q plots in Fig's 8 and 10. What is particularly important is seeing what soil concentrations are relative to precipitation concentrations. In other words, does a significant amount of solute generation occur in soils, and if so, is that being represented in the model at all? My understanding is that it is not, which could also be one of the primary causes of observations of chemostatic Na behavior at CS1 as mentioned in more detail below. What proportion of overall solute generation from

precipitation to spring is missed by not representing soil processes?

Model Validation: As far as I can tell, the primary validation for the model is a qualitative matching of modeled v. observed solute concentration patterns across discharge. This seems fine in general to me (though would be strengthened by some level of statistical analysis); however, the implications of this matching appear oversold. Specifically, the fact that model results match observations only means that this particular combination of parameters and subprocesses (water transit times, mineral surface areas, assumed reaction networks and associated kinetic and thermodynamic constants) combine to get the right answer, but that does not validate each individual subprocess. In other words, there is the problem of equifinality: if the hydrologic model is consistently underestimating transit times, for example, then the model could still match results by overestimating dissolution/precipitation rates. Without some independent validation of water transit times (i.e. seasonal water isotope variability, tracers), the authors cannot conclude that each individual process is accurately represented. This issue needs to be discussed, particularly w/r/t Section 6. As I read it the model-data match is used to independently validate (1) water transit time simulations; (2) the fact that bedrock waters don't need representation; (3) mineral surface areas and kinetic rate constants; (4) the specific representation of clay solid solution series (which is not adequately described) — in my mind these conclusions are not sufficiently supported without independent validation of these sub-processes.

Also echoing Referee #1, it would be useful to include more description of the C-Q dynamics – both in the introduction and in the analysis. Specifically, Si seems much less chemostatic than Na, particularly at CS1. Why is this and why does it also happen in the model? Are Na concentrations diluted until they reach observed soil concentrations (i.e. point above) in which case does its representation in the subsurface even matter?

Small point is that the authors consistently characterize precipitation and drought events as 'important' without context.

I also agree that figures would benefit from formatting to make them more readable – particularly y-axis labels of concentrations.

Lastly, and in general, these subsurface transit times seem relatively fast which may make sense for such a small catchment system. However, how does this compare to measured transit times in other catchment systems (for example as a function of watershed scale)? In other words, how applicable are the conclusions that chemostatic behavior here reflects far-from-equilibrium hydrologic controls to other areas?