

April 2d, 2019

To: Pr. Jan Seibert
Handling Editor -HESS

Re: Answers to the reviewer comments: Manuscript HESS-2018-609 " Crossing hydrological and geochemical modeling to understand the spatiotemporal variability of water chemistry in an elementary watershed (Strengbach, France)" by Julien Ackerer et al.

Dear Editor,

We appreciate the efforts the reviewer has invested in our manuscript, which resulted in a set of revisions. Please find attached the a pdf with the answers to the reviewers' comments in red, to distinguish them from the reviewers' comments. If required the revised manuscript with the changes marked in red can be send for your kind consideration.

We are grateful to the reviewer for providing stimulating comments and advices to improve the initial version of the manuscript.

Yours Sincerely

François Chabaux, for the authors
University of Strasbourg
UMR CNRS 7517 – LhyGeS
1, rue Blessig
67000 Strasbourg – France

Answer to Reviewers

Answer to Reviewer 2:

Anonymous Referee #2

Received and published: 19 February 2019

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.

The revised manuscript brings now more details on the modeling and validation exercises. The hydrological modeling and its validation are presented in lines 200-222, and a new table giving the initial and adjusted parameter values of the hydrological simulations has been added (table 2). Clay minerals and secondary phases are detailed in lines 255-262, lines 270-273, and lines 712-720. The whole geochemical database and the geochemical modeling parameters (minerals, reactive surfaces, thermodynamic and kinetic constants, clay solid solution end members, etc.) have been reassembled as supplementary material associated with the revised manuscript (tables EA10-EA13). We also refer to the recent work by Ackerer et al., 2018, concealing detailed information on the KIRMAT model (line 716).

Recent works coupling hydrological and geochemical models, including ParCrunchFlo (Beisman et al., 2015) and PHIM (Li et al., 2017) are now cited in the Introduction of the revised manuscript. The general content of these studies is presented at the end of the Introduction, which also allows us to better raise the points that give originality of our contribution compared with these previous works (lines 110-121).

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.

The backtracking of a particle, which ended in coordinates (x, y, z) at time t consists in following particles through flow fields with reversed directions. The stream lines drawn by this procedure indicate the time (prior to t) at which a particle passed at a given location or entered the flow field. In the case limiting the backtracking to various successive subsurface flow fields, no stream line will reach the surface, with the exception of distorted flow fields generated by a continuous massive infiltration at a few locations in the system. It must also be raised that the studied watershed with its steep slopes mainly generates gravity driven flow from top hills to valleys, which renders steam lines extending from the boundaries of the domain to the stream. To observe stream lines originating

from various locations over the watershed, one should proceed with a forward tracking (with the velocity fields in their actual directions) following particles initially spread over the surface of the system at a given time t , and then moved by the successive velocity fields posterior to t . Our Modeling tool NIHM allows for this forward tracking but the results are not that sought to condition geochemical interactions in the subsurface. We seek the various flow paths and associated travel time distributions in the subsurface that are collected at point locations in the domain where water chemistry is monitored. It is far easier to proceed with a backtracking technique initiating the (back) travel of particles from the sampled points and the sampled times of geochemical data.

Other codes such as ParFlow/SlimFast with a three-dimensional approach to the subsurface compartment could eventually backtrack particles up to the land surface in the case discussed above of a massive local infiltration area. In the case of gravity driven flow along slopes associated with widespread infiltration from the surface, almost all backtracked stream lines should also reach the boundaries of the system. That being said, it is right that backtracked stream lines, irrespective of the code employed, do not inform on the elementary water flux conveyed along each lines. They also do not distinguish between the time a particle passed at a given location and the time the particle entered in the subsurface at this location. Therefore, extracting transit time distributions from backtracked stream lines implies that these distributions are an approximation that gives exactly the same weight to all the times retrieved along all the stream lines. This approximation goes with uniform elementary water fluxes along each line and uniform inlets from the surface. Proceeding differently would imply to solve a transport equation in transient flow regime and for transient source terms, a cumbersome procedure probably resulting in as much uncertainty as backtracking for a poorly known hydrosystem only conditioned by the stream flow rates at the outlet of the system.

With regard to geochemical modeling, it is right that the calculations assume uniform inlets of soil solutions along the subsurface flowlines and spatially homogenous water-rock interactions within the watershed (rephrased in lines 307-310). These assumptions are supported by the good agreement between measured and modeled solute concentrations (this study), and the comparison between regolith profile data and water chemistry data (Ackerer et al., 2016).

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?

The deepest soil solutions are that used as inputs into the modeled subsurface compartment. This is clarified in lines 284-287. The concentrations in soil solutions are presented in figures 7, 9, 11, and 12. In the case of the Strengbach catchment, soil solution concentrations are by far higher than precipitation concentrations, and the aim of this study is to grasp the hydro-geochemical processes that occur in the subsurface between soil solutions and spring or ground waters. Modeling what occurs between precipitations and soil solutions would imply to cope with another scale of

investigation, relying upon precise modeling (the cm scale, or less) of transient unsaturated flow coupled with reactive transport.

Since the soil solutions are injected into the modeled subsurface, the chemical temporal variability of these solutions and its impact on the water-rock interactions are accounted for in the modeling exercises. This point is better specified in lines 290-293. It is worth noting that the impact of the soil solution chemistry on spring waters is detailed in Ackerer et al., 2018.

Na concentrations are much higher in spring waters than in soil solutions (figures 7, 9). The Na concentrations in spring waters are obtained from a combination of an initial load in soil solutions, primary mineral dissolution (albite), and Na incorporation into clay solid solutions. There is no solute generation in spring waters missed by our approach, as the deepest soil solutions aggregate the surface processes, then they enter the aquifer, and water-rock interactions within the aquifer are modeled via KIRMAT.

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.

More information is now available regarding the hydrological model validation (lines 200-222). Regarding the solute concentrations, the validation is simply performed by checking that modeled concentrations are close to chemical data up to the addition of eventual analytical uncertainties on measures.

We underline that the hydrological modeling is performed independently and before any geochemical simulation. If the hydrological model were set up to significantly underestimate water transit times, a correct reproduction both in fluctuations over time and amplitude of the water flow rates at the outlet of the watershed would not be possible. The fact that the flow rates are well reproduced over the whole hydrological context between 2010 and 2015 supports the idea that the water transit times inferred by NIHM are realistic. This point is mentioned in lines 695-701.

The fact that the chemical composition of waters is well captured indicates that the combination of geochemical parameters and water transit times in KIRMAT is able to generate realistic reaction rates. This is rephrased in lines 683-686. We simply emphasize that non-modified kinetic constants and geometric reactive surfaces form a combination able to reproduce the evolution of water chemistry in the catchment (line 686-690). It is right that eventual equifinality between parameters in any model might result in multiple solutions fitting observed data. In that sense, we cannot assert that each single geochemical parameter is set up at its right value. But we support the idea that the inferred set of geochemical parameters produces realistic reaction rates, and is relevant for this kind of geochemical studies (lines 683-686).

We agree that a comparison of our results with water isotope variability could be interesting, even if the seasonal variability of isotopes content might be not accurate enough to be faced with the short transit times that characterize the watershed. It is reminded that the steep slopes of the subsurface compartment generate rapid and very transient flows mainly controlled by the variability over time of hydro-meteorological inlets and the wet versus dry character of some portions of the system. In any case this comparison is beyond the scope of our study, but a sentence has been added to suggest that seasonal variability of isotopes could be informative (lines 718-720).

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?

The introduction has been modified to reintroduce this notion of concentration-discharge relationships (lines 60-69). We explain that these relationships are mainly qualitative and do not substitute to quantitative evaluations for which the coupling between hydrological and geochemical modeling is an important new step. This feature is also reminded later in the discussion (lines 660-666).

Na concentrations in spring and piezometer waters are higher than in soil solutions (see figure 7 and 9). Na concentrations in spring and piezometer waters cannot be explained by a simple dilution. A gain of Na load occurs in subsurface waters because of the dissolution of albite minerals. The relative response of each chemical element to a change in water discharge is also associated with the initial soil solution concentrations, the nature of primary minerals leached by waters and the degree of incorporation of the element in the clay solid solutions. Na is only provided by one single primary mineral (albite) and is weakly incorporated into clays. Si is provided by several primary minerals (albite, biotite, K-feldspar...) and strongly incorporated in clay minerals that are characterized by varying precipitation rates with hydrological conditions. These points explain why the response of solute concentrations to hydrological changes is variable for each element. This is now specified in lines 401-408.

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.

It is now clarified that these important flood and drought events are defined with reference to the maximum and minimum flow rates at the outlet of the watershed (line 346-347).

The figures 7 to 11 have been improved in the revised manuscript (better organization of axes and titles). The plots are now individually labeled (e.g., 7A, 7B, 7C, 7D) and quoted as such in the main text to improve readability (example in lines 684, 691). Error bars are drawn in the figures and their interpretation is given in the captions.

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?

Yes, the small size of the watershed, but mainly the small storage capacity of the aquifer (thickness less than 10 m) and the steep slopes generating gravity driven flows, induce short water transit times. This is rephrased in lines 370-371. The chemostatic behavior is in our study explained by short transit times, precipitations (and thus percolations of soil solutions) regularly distributed over time and space and few mixings of waters from contrasted origins. There is no reason to suggest that our conclusions could not extend to systems with similar dynamics. This is clarified in lines 725-727.