

Answer to Referee 1

Anonymous Referee #1

Received and published: 19 February 2019

Highlights: The study presents a coupled hydrological + reactive transport model capable of characterizing the hydrogeochemical variability in a small watershed in France, (Strengbach). This model is composed of a depth-integrated and spatially-distributed NIHM model and Kinetic Reaction and MAss Transport KIRMAT reactive transport model. The principle results of these numerical simulations can be summarized as follows: (1) chemostatic behavior is a direct consequence of water transit times and, thus, hydrologically controlled; (2) small k reactivity constants + reactive surface areas are the only parameters necessary to constrain water chemistry.

This study represents a nice contribution to catchment modeling efforts in merging characteristically separate hydrologic and reactivity models together in order to better understand chemical and hydrological subsurface dynamics. However, it would seem there is some general omission of the rich variety of reactive transport simulation capabilities now available and in application to hillslope – watershed scale weathering and solute fluxed. Further there is a lack of clarity regarding which parameters are adjusted in the model and in order to match the discharge data, the functional form of the rate expressions and the treatment of solid solutions, all of which must be clearly articulated in order to ensure reproducibility. Finally, the paper needs substantial revision in terms of writing, organization, and formatting. Thus, I suggest major revisions.

We agree that a few recent studies geared towards the coupling between hydrological and geochemical approaches (e.g., Beisman et al., 2015; Li et al., 2017) could be duly acknowledged. Therefore, the introduction has been slightly modified to underline some of these works, and also to better emphasize the points that give originality to our present contribution (lines 110-120).

We also answered to Rev #1 who claimed for improved clarity regarding the adjusted parameters in the models. The fitted parameters employed in the hydrological model to match observed discharge data at the outlet of the watershed are provided in lines 200-222. A new table also gathers the initial and adjusted values of parameters in the hydrological simulations by NIHM (table 2). The treatment of solid solutions is better explained in lines 255-273. Additional geochemical data and the values of geochemical parameters used for reactive transport simulations are now reported in tables supplied as supplementary material including: minerals, reactive surfaces, thermodynamic and kinetic constants, and clay solid solution end members (tables EA1-EA13).

Abstract Line 22: “over” rather than “for the next decades” Line 36-37: Unclear what the authors mean when stating “vary from approximately 1.5 to 3 months from floods to drought events.” Lines 43-45: Unclear what the authors mean by “low surfaces”? What range of surface areas would be considered “low” for this study (I think based on Table 2, this is between 0.026 m²/g – 1.420 m²/g)? Why only “low surface areas”? What about the influence of secondary mineral precipitation (that leads to the formation of high surface area phases)? Lines 48-50: This sentence doesn’t say anything new. I think that the “process-based” approach to characterizing water chemistry is something that everyone is doing. The key goal for our reactive transport models is to better characterizing those water transit times, especially between the variably saturated subsurface and deep groundwater. Either way, I think the authors need to wrap up this abstract with a final sentence that states what is so unique about their hydrogeochemical models that separates it from the rest.

These points have been modified or rephrased to improve clarity (lines 25, 38-41). The range of values spanned by "low" surface values is now given line 47. It is also explained that the secondary minerals precipitated in the simulations are clay minerals (lines 265-266). Precipitation of other secondary minerals such as carbonates, amorphous silica, hematite, etc., have been envisioned. But in view of the hydro-climatic context prevailing at the Strengbach catchment, these secondary minerals did not precipitate in the various simulations performed (lines 270-273). The end of the abstract has been partly rewritten to better point out the originality of our modeling approach (lines 47-52).

Introduction General comment: Introduction looks fine, but a couple points are missing that could help provide a fuller context for this study. In particular, the authors discuss concentration-discharge relationships in the abstract, but fail to return to this topic in the introduction. I think discussing C-Q relationships and their use as a diagnostic tools to understand subsurface reactivity and transport is a key context for arguing why an integrated hydrologic + RTM model is necessary. Specific comments: Lines 56-58: ‘That results. . .’ I don’t understand what this sentence is trying to say. What “results from”, exactly? The challenge of estimating the repercussions of climate change to the overall hydrological cycle? I suggest that this sentence be re-phrased for clarity. Lines 90-95: also water quality issues. . . Lines 104: I think there is something missing between the sentences “ A new step is therefore necessary. . . “ and “This is the aim of this work, which combines for the first time in this manner. . .”. This is a key area in which the authors omit acknowledgement of important and current studies that have sought to combine RTM with hydrological models – for instance, ParCrunchFlow (Beisman et al. 2015), PHIM (Li Li & Sue Brantley), DHARA (Kumar).

The introduction has been modified to mention the concentration-discharge relationships as a tool to qualitatively inform on subsurface reactions and transport, these mechanisms being then quantitatively re-handled via coupled hydrological and geochemical models (lines 60-69). Some points are also rephrased for the sake of clarity (lines 57-60).

We acknowledge that a few recent works coupling hydrological and geochemical models were omitted. Those relying upon ParCrunchFlow (Beisman et al., 2015) and PHIM simulations (Li et al.,

2017) are now quoted, while the introduction was slightly modified to present their content (lines 110-113). This rewriting also better mentions where to find the differences in our contribution compared with these previous works (lines 113-120).

Site presentation and data acquisition Line 141: with a sampling frequency sufficient to cover the entire range of water discharges. . . rather than “allowing for covering the entire range of water discharges. . .”. Also it’s unclear what this phrase means. Do the authors refer to daily data? Hourly data? Important to be specific on this point as it has critical implications for the model. Line 160: presented in this study rather than presented in the following”. Line 164: “chemical data . . . presented in Table 1”. The authors’ mention (line 145) that soil solutions were also sampled and provide citations to Gangloff et al. 2014 and Prunier et al. 2015 for the dissolved major cation concentrations. This is useful, but it would be better to have that information directly included in Table 1 in addition to the spring water data. Further, it is unclear if the resolution of the geochemical data is on a yearly-scale or monthly-scale, etc. based on the data presented in Table 1. It’s also confusing based on the C-Q plots in Fig. 8 and Fig.10 where there seems to be more data points presented for the CS1 and CS2 springs than 12 points shown in Table 1. This needs to be cleaned up. In general, it’s good practice to present the entire geochemical dataset to the reader (it can be included in a supplementary table if necessary).

These suggestions have been accounted for in the revision of the manuscript (lines 151-153). It is now better specified that the geochemical database collects histories with a monthly resolution, some additional data being also available from specific sampling campaigns (lines 151-158). To avoid trimming the main text with large tables, the data from soil solutions are presented as supplementary material in tables EA6-EA7. It is also clarified in the captions of figures 8 and 10 that the data points can be found in table 1 and in supplementary table EA1. The complete geochemical dataset employed in our study is provided as supplementary tables (EA1-EA9).

Modeling methods Line 167: remove “acquisition of” Line 188: “Water exchange” rather than “the water exchanges” Line 190-198: What parameters in the model are tuned to match the discharge data?? This must be clearly articulated to ensure reproducibility. How is it determined whether the water discharges are correctly reproduced? Is this done purely by visual comparison or is a statistical approach or some threshold of reproducibility (within a 90-95% confidence interval for instance) utilized? Line 225: What is the form of the chemical rate law used in the KIRMAT code? Is it based in Transition State Theory? Line 228: How does the model track the clay solid solution composition with time?

These suggestions have been taken into account in the revised version. Notably, a paragraph has been added to state how the hydrological model is run to match the discharge data at the outlet of the system (lines 200-222), and which indicator is used to assess the matching between model outputs and data (KGE: Kling Gupta efficiency coefficient, lines 217-219). A new table also gives the parameters used in the NIHM simulations (table 2). Additional information on the KIRMAT model is available. It is specified in the Section on methods (lines 249-252) that KIRMAT is based on the Transient State Theory; clay solid solutions are better depicted (lines 255-262). We also refer to the previous work by Ackerer et al., 2018 where additional information about KIRMAT is available.

Results Line 343: remove “that”

Discussion Line 489-490: Clarify whether the change in reactive surface area is monitored through time as the primary minerals dissolve. Depending on how the chemical rate law is defined (again this must be reported), a change in surface area has a first order control on net dissolution rates ($R = kA (Q/K - 1)$; where k = rate constant, A = reactive surface area, Q = activity quotient, and K = equilibrium constant). So being able to monitor this evolution in surface area with time is important. Also, is secondary mineral precipitation included in the simulations? I know that the composition of clays are tracked in the model through a solid solution, but it's not clear if secondary mineral formation is tracked as well. This is an important component that needs to be addressed since secondary mineral precipitation would also impact net dissolution rates.

“That” in line 343 has been removed.

The previous discussion of lines 489-490 has also been clarified. Reactive surface areas were monitored over time for primary minerals (lines 267-268), which showed that, within the short timescale of the simulations, the change in surface areas were negligible (lines 268-270). More information on secondary minerals and clay minerals are provided lines 255-262 and lines 271-273. It is worth noting that these points are now presented in the methodological Section 3, as they are related to the settings of the reactive transport model.

Line 513: What are the values of the “standard” kinetic constants that were used in these simulations? These constants (and references to the associated studies from which they came from) should be shown in Table 2 (or maybe another table) for the primary minerals – there is absolutely not a set of ‘standard’ values that everyone uses. Without all this information included (as well as an explanation of the impact of secondary mineral precipitation), the rest of this section is too speculative.

New tables are available as supplementary material to detail all the thermodynamic, kinetic constants and other geochemical parameters that are used in the modeling tasks (tables EA10-EA13). References to studies associated with the elaboration of these tables are also quoted in the supplementary material. More information on secondary minerals is provided in lines 255-262, lines 270-272, and also in lines 712-718.

Lines 641 - 645: OK, only now the authors clarify that the reaction rates are based on transition state theory and discuss the influence of secondary mineral precip. But, this is far too late in the paper. This needs to be addressed much earlier, preferably in the “hydrological methods’ section.

Lines 646- 648: There is no evidence provided that supports the author’s argument that a clay solid solution precipitated at equilibrium can generate reasonable precipitation rates. Maybe the authors could present the numerically generated precipitation rates along with precipitation rates found in the literature in a table?

These points are now clarified but presented earlier in the manuscript. The fact that a clay solution precipitated at equilibrium can render reasonable precipitation rates for the Strengbach watershed

case was previously discussed in Ackerer et al., 2018 (in section 6.2). To avoid useless repetition, the interested reader is referred to this recent work for more details (line 716).

Conclusion: Overall a bit long, it could be shortened a bit without losing the key points of this study.

Figures Figures 7-11 look like they have been quickly made in excel with little formatting done. I strongly suggest that the author take the time to improve these plots and properly format and organize axes, legends, and titles. I also suggest labels in each plot A, B, C etc. and reference to these specific panels in the text (i.e Fig. 7A, Fig. 7B, etc.) to make it easier for the reader. Additionally, error bars should be shown for the measured concentrations (and a description of what the error bars represent, 1SD, 2SD, etc.). This would help justify the author's assertion that the KIRMAT simulations agree with measured concentrations.

The conclusions have been slightly trimmed (lines 729-748), but it was found difficult to shorten them more. The figures 7 to 11 have been improved (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 lines 669, 676). Error bars are drawn in the figures and their interpretation is given in the captions.