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Pr. Jan Seibert
Handling Editor – Hydrology and Earth System Sciences (HESS)

Dear Editor,

The new revised version of the manuscript we have submitted for publication to HESS (Manuscript HESS-2018-609) has been uploaded with this file.

Please find below the answers to the reviewer comments along with a marked-up manuscript version showing the changes made.

We hope that the new version sent with the letter and the different answers to the reviewer’s comments make the manuscript suitable for publication in HESS.

Yours Sincerely

François Chabaux, on behalf of the authors.

Reply to Reviewers – Third round of revisions

Reviewer 1:

The authors have comprehensively addressed previous comments. in particular, the manuscript has been improved with more precise language about novelty of the work, in-depth discussion on concentrations, rates, and transit time, and the positioning of this work in the context of other existing work. I support the publication of the manuscript.

Reviewer 2:

General Summary: This study presents the application of a coupled hydrological—reactive transport model capable of characterizing monthly to annual scale hydrogeochemical variability in Strengbach, a small granitic headwater catchment in France. The model proposed is composed of both a depth-integrated and spatially-distributed NIHM hydrologic model and a Kinetic Reaction and Mass Transport KIRMAT reactive transport model. Although there are several combined hydrologic + geochemical models that have been developed in the literature, this particular model has some unique features that make it quite appealing in application to watershed scales. One feature in particular is the low-dimensional approach to the hydrologic model, which consists mainly of combining vadose and saturated zones into a single subsurface compartment that can be modeled as a simple 2-D layer. Reducing the "dimension" of the hydrologic model has significant advantages in that it reduces the complexity of solving numerically for both unsaturated and saturated flow and the computational costs. This is not the first study to take such an approach, but it is novel in that it's one of the first studies to combine this "non-dimensionalized' hydrologic model with a fully realized reactive transport model. This model was further validated with field data where independently constrained water transit times through the hydrological simulations were used to accurately predict observed geochemical variability.

General Comments: This last round of revisions has shown large improvements to the overall quality of the manuscript and I thank the authors for their efforts. In light of the corrections that have been made by the authors, I believe that this article is now suitable for publication granted that certain minor modifications are made beforehand. I suggest the authors try to concentrate more on what these model simulations tell us about the catchment dynamics in Strengbach and how this build on findings from other studies of this catchment. As one of the other reviewers noted, Strengbach is a well-studied catchment and, thus, articulating how the results from these novel hydrological + reactive transport models provides a (large?) step forward in our understanding of the Strengbach catchment in particular would boost the impact of this paper in my opinion. While I think it is good to explore what these findings might mean at a global scale or in comparison to other similar catchments, it shouldn't be the centerpiece of the present conclusions; rather it should be used as motivation for conducting similar types of studies in other catchments in the future.

We updated the section 6.2 discussing the implications of this work for the Strengbach watershed in particular (lines 641-689). More information is available on how our results propose a new step to validate several hypotheses made by previous studies conducted in the Strengbach watershed (i.e. Viville et al., 2012; Pierret et al., 2014; 2018; Pan et al., 2015; Ackerer et al., 2016; 2018; Chabaux et al., 2017; Weill et al., 2017). The modeling work first emphasizes the key role of times of water-rock interactions (lines 647-661). The modeling work also reveals that the spatial distribution of the weathering processes is relatively homogenous within the catchment (lines 662-672). This latter point explains the previous observations of similar chemical fluxes in the stream, springs and regolith profiles (lines 669-673). In addition, our results bring the important conclusion that the hydrogeochemical functioning of the watershed is properly simulated by water circulations in the very shallow subsurface (saprolitic aquifer, lines 674-689). The contribution of waters circulating in the deep fracture network of the granitic bedrock is not necessary to explain both the dynamic of the stream and the chemical composition of springs (lines 674-689). The independent flow paths feeding the springs are also confirming hypotheses from previous isotopic studies (lines 683-689). Finally, section 6.2 underlines how this study improves the understanding of the Strengbach headwater catchment.

However, we believe that it is important for the conclusion of the manuscript not being too much "Strengbach centered", with the meaning that many headwater catchments could behave as we show. This incline us to let room in the conclusions for general implications that our study suggests (lines 787-807).

Additionally, I found quite a bit of spelling and grammar mistakes as I was reading through this latest version of the manuscript. There are also areas where I still believe the writing can be paired down. I strongly urge the authors to address these issues before publication.

We corrected the last mistakes and reduced slightly the text where it was feasible (e.g., section 6.2). Some repetitions between sections regarding "Results" and "Discussions" have been removed (e.g., between sections 6.2 and 4.2, lines 712-724).

Specific Comments:

Lines 36- 37: “explains why transit times span much narrower ranges of variation than that water discharges.” Does this statement apply to Strengbach specifically or is this a more general observation? Please provide citations for the latter.

This finding is a result from our modeling work and is specific to the Strengbach watershed. This is clarified in line 40. The point is that flow over the catchment is mainly controlled by gravity (the slopes) irrespective of the local pressure head gradients. As an example, 1 or 7 m of water-saturated thickness (and therefore of pressure head) in the system does not really influence water velocity when the elevation gradient is of 30%. This renders water velocities almost invariant over time, with pressure heads simply being an indicator of stored water. Water storage highly fluctuates, with consequences on volumetric fluxes and on instantaneous stream discharges, when water velocity fluctuations are smooth.

Line 50: remove “the” in “ effects of the ongoing climatic changes…”

Done line 52.

Lines 87- 89: How the flow is treated in a dimensionally reduced hydrologic model should be quickly added here. Even the explanation that was provided to one of my comments in the last round of revisions is suitable as shown below:
“NIHM solves subsurface flow via an integrated Richards equation …”

We added this information in the text lines 91-94.

Lines 607-610: Is the model able to track the areas of maximal clay formation in the catchment and how this varies between wet and dry seasons? This would be very useful information to complement the predicted areas of max dissolution rates proposed by the model.

Yes, the model is able to track the clay formation rates and the clay compositions along the flow lines. Clay formation rates are slightly higher at the upstream tips of the flow lines, where the dissolution rates of primary minerals are also higher. With the seasonal variability of the extend of flow lines (flow lines extending up to the crests during wet periods and retracting to middle elevations during dry periods), the clay formation rates are maximal near the crests during floods but maximal at middle elevations during dry periods. We added this information lines 469-475. We moved this part dealing with primary mineral dissolution and clay formation rates in the section on results (lines 469-475), as this result is a direct conclusion of the modeling task.

697-699: Yes, but only on a monthly to annual timescale resolution. It would be interesting to see if this model can replicate observed water chemistry in more high frequency daily or hourly geochemical datasets during major flooding events.

Yes, the modeling exercise in this work is definitely dealing with monthly timescale data, even though hydrological simulations, due to the variability of rainfalls events, infiltration and stream flow velocities sometimes use very short time steps (sometimes less than 15 min). Testing our modeling approach with high frequency geochemical data would be an interesting new step for the future. But this exercise is currently infeasible because hourly collected geochemical data for the Strengbach spring waters are lacking.

Line 713: Be specific in regard to the explanation of this thermodynamic equilibrium, which is (I think) the primary mineral dissolution reaction. I think I found this elsewhere throughout the manuscript.

We underline here the difference between the chemical equilibrium state of the water as in the sentence: ” It is also important to emphasize that the simulated chemical compositions of waters remain far from a state of chemical equilibrium with respect to primary minerals.”(lines 756-757), and the way to handle precipitation of clay minerals in the KIRMAT code as in “a clay solid solution precipitated at the thermodynamic equilibrium is able to generate reliable water chemistry (this study) and realistic clay precipitation rates (more detail in Ackerer et al., 2018)” (lines 765-768).

The precipitation of a clay solid solution at thermodynamic equilibrium means that no kinetic data are used for the clay solid solution end members. Only the thermodynamic constants log(Ki), log (Qi/Ki) are used for the precipitation of the clay solid solution end members (supplementary table EA13).

With these model properties, spring waters remain far from a state of chemical equilibrium with respect to primary minerals, resulting however in correctly captured geochemical composition of spring waters (lines 765-768). The overall clay precipitation rates are also realistic compared with the determination of clay mass fractions in regolith samples (lines 765-768, details in Ackerer et al., 2018).

Lines 727-729: “…spatial and temporal variability in flow paths is a key process to explain C—Q relations” I would add for this particular catchment.

We added “in this type of headwater catchment” in line 783. Our results support that this finding is probably applicable for other headwater catchments in a similar context.

Lines 748-752: “…good estimate of the reactive surface within the natural environment” is a little too broad. While I agree that this geometric approximation of the minerals is most likely a better approach in the models, I don’t think you can generalize these conclusions to the “natural environment”. In this case, for this particular catchment, these estimated low surface areas along with the rate constants did provide good replications of the observed geochemical data. This might also be the case for other similar granitic headwater catchments, but not perhaps the case for volcanic or karstic systems.

We agree, “natural environment” is a probably a too large perspective. We replaced “natural environment” by “in this type of granitic catchment” to be more specific (lines 805).

Figure 8: The axes for the H4SiO4, Na+, K+, and Mg2+ should really be shown here in mmol L-1, rather than mol L-1 that way it’s easier for the reader to see the variability.

All our figures are using mol/L, making that we prefer to keep the axes in mol/L for consistency. But we updated the variation ranges of the axes to improve readability (figure 8).

Reviewer 3:

This work is of great interest and provides new insights in coupling hydrological and geochemical processes at watershed scale. The authors explore the development of a dimensionally-reduced model coupled with a reactive transport model. The modelling approach is validated by field data collected in springs and piezometers at wet and dry periods, which allows for the investigation of the spatial and temporal variability of transit times and reaction rates. The authors conclude on a hydrological control on the chemostatic behavior of the watershed, due to fairly constant transit times despite highly varying flow dynamics. The conclusions of the paper thus strongly rely on the hydrological model simulating a low variability of water transit times, from which the geochemical model logically simulate a low variability of geochemical concentrations. To my point of view, a more detailed description of the hydrological model is needed to strengthen the confidence in the results (see specific comments). I recommend moderate revisions before publication of this interesting work, mainly because information is missing in the method section and because the study would gain from a more detailed analysis of the results.

We updated this new version of the manuscript and we provide more details on the hydrological modeling (section 3.1). In particular, the way the depth-averaged hydraulic conductivity is calculated is detailed in lines 267-273. We also remind that the topic of the present work is not aimed at hydrological modeling with low-dimensional approaches, and that specific publications dealing with the features and the development of the hydrological model NIHM are quoted in lines 202-204 (i.e., Pan et al., 2015; Weill et al., 2017; Jeannot et al., 2018). We reorganized parts of the manuscript to slightly reduce the text when feasible, and we moved a few parts from the section devoted to discussion to the section on raw results for clarity (lines 712-724, section 6.2 to 4.2). A deeper interpretation of the implications associated with our main findings concerning the Strengbach catchment is also proposed in lines 641-689.

Specific comments:

Figure 1. Please add a x scale.

Done in figure 1.

l. 175 refer to Figure 1

We refer to figure 1 line 185.

METHODS

l.179 A lot of geochemical data seem available, both for springs and piezometers, but only some of them are used to validate the models. Why are you only using some of the available data? The model would be improved with a validation on all available data that span a long period of time. And if not, the authors should justify why they use only a limited part of their dataset and how they chose the data used.

The overall geochemical database for springs and piezometers is available in supplementary tables EA1-EA9, and the modeled samples are given in table 1. The caption of table 1 has been updated to clarify that the table only reports on samples used for the NIHM-KIRMAT modeling task. It is not possible to run the NIHM-KIRMAT coupled approach on the overall and vast geochemical database (see supplementary table EA1-EA9) because of computation time (hundreds of samples). In addition, trying to exploit the whole database, would probably blur the message conveyed by this study and stating that a reliable but parsimonious geochemical modeling can rely upon a lose coupling with a hydrological model via streamlines and water transit time distributions. It can also be argued that the geochemical database, started 30 years ago, as most long-term databases started monitoring things without prior knowledge on how the monitored system was working! The authors of the present contribution sorted the data according to their revisited interpretation of the catchment.

That being said, for each date, 10 flow lines are backtracked per site by the code NIHM. After this step, a significant number of KIRMAT runs are performed to generate the mean water chemistry delivered by each flow lines. This approach is possible for a reasonable number of interesting dates and samples, not for all the database including hundreds of samples. Rather than modeling all the samples, we selected a reasonable number of dates that are covering the whole range of hydrological conditions in the catchment (table 1).

l.200 “The exchange of water between the surface and subsurface flows are addressed via the hydraulic head differences between the compartments.“ A hydraulic conductivity value of the interface between the two compartments must be also considered. Which value was used? Was it calibrated or fixed? Please clarify.

It has been clarified in line 209-213 that water exchange between the surface (streams) and the subsurface compartments depends both on the thickness and the hydraulic conductivity of the interface layer. This interface layer has the classical physical meaning of riverbed layers that are not the aquifer on the one hand, and not the free flowing water of the river on the other hand.

The hydraulic conductivity of the interface has been calibrated. The feature has been added in the form of values reported in table 2 and mentioned in the text in line 214-226.

The model parametrization paragraph needs clarification and additional precisions.
- "several zones of heterogeneity" please refer to the Figure

Done in lines 220-221.

- Please specify all parameters instead of "other parameters" l.206 for clarity

Done in lines 223-226.

- I guess the aquifer thicknesses given Fig. 2 correspond to the values obtained after the calibration. If so, please be specific on the figure or in the legend. Also add in the legend that the grey lines show the mesh grid of the hydrological model (if it is the case).

Done in figure 2 caption.

- The hydraulic conductivity is calculated using with the Van Genutchen model (which involves parameters such as the saturated hydraulic conductivity, n and alpha), and therefore is a result of the simulations at the grid size, is it correct? I don't think it is clearly said in the paper.

It has been emphasized in lines 391-396 that the hydraulic conductivity is calculated in NIHM (thus, at the so-called grid-size, by relying upon the empirical Van Genuchten equation to define the effective conductivity compared with its saturated upper bound).

As the temporal variability of the hydraulic conductivity is an important point of this study, I think a very clear explanation of how the depth-integrated hydraulic conductivity is calculated would make it easier for the reader to follow the logic. Fig.6, do the red colour (highest hydraulic conductivity) correspond to the value of the calibrated saturated hydraulic conductivity? If yes, it might be worth saying it, as it shows that the subsurface compartment is fully saturated at high flows.

A short explanation regarding the inference of the depth-integrated hydraulic conductivity has been added in lines 267-273.

The red color in figure 6 indicates that the depth-integrated hydraulic conductivity is higher than 6.1E-5, while the saturated hydraulic conductivity of most of the catchment is 8E-05. This also means that areas at 6.1 E-5 are saturated over almost the whole local thickness of the aquifer. This has been specified in the main text when discussing Fig.6 (lines 400-403).

- How is the calibration realized? Which algorithm was used? Could the authors add some uncertainty estimates on the calibrated parameters?

More precisely, the procedure relied upon a simple Monte-Carlo approach (detailed lines 214-2328) testing various configurations of the system because automatic inversions for integrated hydrological models are not available for the moment (though some advertisements are available in the literature, but not followed by effective inversions exercises). NIHM is in the process of being associated with adjoint-state calculations to perform automatic inversions via descent-direction methods and multi-scale parameterization. A task not straightforward at all when catchments react very differently to subsurface flow, surface routing and diffuse runoff according to their geometrical, geological, topographical and meteorological settings. After multiple exploratory calculations, it was shown that that the most sensitive parameters were the depth of the substratum, the saturated hydraulic conductivity, and the porosity. This is why these are the only parameters that were not defined as uniform values over the catchment. Uncertainty estimates on model parameters are unavailable, or more precisely, would be flawed by the Monte-Carlo approach. Each solution does not converge the same way, and bounds on parameters mix models that have not been conditioned the same way. Getting estimates of parameter uncertainties via Monte Carlo approaches would require converging algorithms as for example Monte Carlo Markov Chains (MCMC). Unfortunately, these algorithms applied to a complex system would also require more than 100,000 direct simulations for being statistically meaningful, something infeasible for the moment.

- The hydrological model over the whole catchment is calibrated only on the discharge time series located at the outlet of the catchment. Do the authors have other hydraulic data they could use to strengthen their calibration, such as piezometric heads or spring discharge rates? If not, I am worried that equifinality might not be negligible, which also points for a serious estimation of parameter uncertainties and/or sensitivity analysis (see previous comment).

There are no other continuous discharge rate measurements at the catchment for the simulated period (period which goes with that of available geochemical data on outcropping springs), but there are some boreholes. Unfortunately, these boreholes have been drilled deep enough (60 m) to intercept a few fractures in the bedrock (under the substratum of the shallow subsurface aquifer, made of soil plus saprolitic rock, simulated by NIHM). This renders the water levels monitored in these open boreholes unable to reflect hydraulic pressure heads in the active shallow porous aquifer of the catchment simulated by NIHM. This has been emphasized in lines 274-289. Geochemical investigations also show that deep borehole waters are not connected with effective subsurface flows feeding the springs and streams (Chabaux et al., 2017; Pierret et al., 2018).

Equifinality is the curse of any modeler, irrespective of the mass of data to condition the model. In some cases, increasing the mass of data can also favor equifinality. In the present case, flow over the system is mainly constrained by the steep slopes (i.e., elevation gradients) of the catchment, thus rendering the water saturated thickness mainly as an indicator of storage and not of water velocity (via pressure head gradients). There obviously exist equifinalities in the model proposed, but they hardly affect water velocities which are very similar for various model configurations, provided those configurations generate transient water storage compatible with the good fitting of the stream flow rate. We are now in the process of completing the third round of review, with more than 6 different reviewers involved, and 18 months past initial submission! We did not stay arms down during that period and tried to improve the hydrological conditioning by introducing local MRS (magnetic resonance sounding) data. Those are sensitive to the vertical distribution of water contents in the subsurface. Introducing these data slightly modified model outputs mainly on the storage capacity distribution (porosity of active aquifer layers) but did not change the transit and residence time distributions and their weak variability over time. A paper has been published on the topic (Weill et al., 2019, Water 2019, 11(12), 2637; https://doi.org/10.3390/w11122637), but we ignore whether or not we can mention it, as it was proposed and accepted after submission of the present work. That being said, a few words have been added in the manuscript to better emphasize the feature that transit times (which are here the main hydrological output for geochemical modeling) are mainly conditioned by the steep slopes of the catchment (lines 274-289). The paper in Water is also quoted (line 761, but can be removed on request). A conditioning on MRS data (Weill et al., 2019, water content distribution) slightly modified the model but without incidence on the overall distribution of flow paths, their variability, and the associated transit time distributions. This is more precisely emphasized in lines 274-289 but can be removed on request.

The hydrogeochemical modelling strategy presented Figure 5 deserves more details. For each flow line, how much is “several”? What is the value of the “constant distance along the flow line” that is used?

We used a constant space step of 1m along the flow lines. This distance refers to the distance between regularly distributed inlets along a stream line where the soil solutions percolate into the aquifer. This information is given lines 333-335. ‘Several’ therefore refers to a variable number of simulations, as this number is specific to each flow line. For example, a flow line with a length of 100 m is discretized into 100 cells of 1 m. 100 KIRMAT simulations will be performed along the flow line as illustrated in figure 5. The integrated chemistry of waters at the sources is the arithmetic mean of all the solute concentrations given by the 100 KIRMAT runs.

Do the boxes drawn Figure 5 correspond to the grid of the NIHM model or not?

No, the boxes in Fig. 5 represent the grids of the reactive-transport code KIRMAT. But 1D simulations with KIRMAT are performed along the flow lines previously determined by the hydrological model NIHM (lines 327-329). We updated the captions of figures to make this all clear.

KIRMAT simulations were performed for different flow lines independently and then mixed at the outlet of the flow lines, if I got it correctly (Figure 5). The mixing could also occur all along the flow line, each percolated soil water mixing with the water coming from the upstream “box”. Would the results be different?

Both types of mixing are employed, a mixing of water chemistry simulated at the outlet of independent flow lines (as the consequence of diverse flow paths feeding the outcropping sources) and a mixing as presented in Fig. 5. The latter states that along a single flow line, water chemistry is the mix of water that entered the subsurface system (i.e., the flow line) at various points upstream. Because each flow line is associated with a 1m space step injection locations, one can consider that the whole process corresponds to percolations along the whole flow line. The point is that the water flux entering at each location along the flow line is unknown. Calculating at the outlet of the line an arithmetic mean is equivalent to state that percolation of soil water is uniform along the line. This assumption is supported by the modeling results but also by observations of similar geochemical fluxes from stream, springs and regolith profiles (lines 662-673, Viville et al., 2012; Ackerer et al., 2016; 2018).

What is the justification for no mixing between flow lines within the subsurface compartment?
With the physics of Darcian flow in continuous media, the stream lines cannot intersect. Mixing of solutes between lines could only occur by diffusion, which is undoubtedly less efficient in an advection-dominated problem than the spreading generated by taking means of ten independent stream lines (and which could also correspond to solute spreading due to heterogeneous velocities and flow paths).

RESULTS

l. 320 Where are the results of the water velocities?

Results of the mean water velocities are presented figures 7A, 7B, 10A, 10B, 11A and 11B. We also describe these results in section 4.2.

l. 328 Please specify which characteristics of the flow lines you consider similar (geometric characteristic? length, position…), as the velocity along the flow lines for instance differ from given dates (4.2). Maybe not talking about water velocity along flow lines in this paragraph might be less confusing.

We detailed that for the sites located on linear or slightly convex slopes, all the characteristics (geometry, flow rates, transit times) of the different flow lines that feed each site are comparable for a given site and for a given date (lines 378-380).

l. 341 “or parameters” Parameters should not change under transient conditions as they have been previously calibrated, right?

Yes, we removed ‘or parameters’ because this expression was confusing. We mean here: hydraulic variables (lines 392).

l. 344 Please describe the driving factors of the spatial and temporal change in the simulated hydraulic conductivity. How much is this result related to the geometry of the watershed (small thickness, steep topography…)?

This point is detailed lines 416-429. Spatial variability of the saturated hydraulic conductivity is associated with zones of various thicknesses (some degree of alteration in the saprolitic aquifer) and that fact that low storage capacity, no contributive zones, and rapid draining downward are conducive to dry crests with smaller effective conductivities. Variations over time are mainly associated with the water content in the system. With NIHM calculating effective mean conductivity values over the aquifer thickness, temporal variations of the effective conductivity depend on both hydro-meteorological forcing and the geometry (mainly the thickness) of the aquifer layer.

l. 385 refer to Figure 7

Done line 452.

Figure 7. Where do the uncertainty bars come from in the KIRMAT simulated concentrations? Please, clarify what you mean by “induced” in the legend. A priori it could not be induced by the hydrological model as uncertainties are not taken into account. Is it only coming from the propagation of soil solution uncertainties?

Yes, the uncertainty bars take into account the propagation in the KIRMAT simulations of analytical uncertainties from pH and chemical concentrations measured in the soil solutions. This is now clarified in the figure captions.

Figure 8. The CS1 geochemistry was simulated at 6 different dates, but we cannot tell which of the observation blue point corresponds to each simulated orange point on the Figure. This information is

needed to assess the reliability of the modelling. Maybe using different colors, please link each simulated point to the corresponding observation point.

The figure 8 is already relatively heavy and we avoided to overload it with additional color codes. Instead, we added in the caption of table 1 the information relative to the different dates used for the hydrogeochemical modeling. In the caption of figure 8, we refer now to Table 1 for the dates, chemical data and water discharges of the modeled samples. We also refer in the caption to the supplementary material EA1 for the overall geochemical data. A visual comparison between simulated and measured concentrations is also available in figures 7C, 7D, 10C, 10D, 12A, 12B and 13.

Figure 9. and l. 403-405. The sentence is quite vague. The authors chose to present the differences between elements in a figure, which is very interesting. But then their explanation for the differences remain very vague and not specific to any element. Could the authors expand on the geochemical mechanisms yielding to the different C-MTT relations?

This point is clearly detailed in the discussion section in lines 725-746.

PZ3 and PZ5 piezometers. You already specify paragraph 4.2 that, such as for CS1 and CS3 springs, single flow lines can be used, so you can shorten the first part of the section. Maybe this section could be merged with the previous one as the approach and the results are similar.

We slightly reduced the text in the section 4.2.

CS2 and CS4 springs. Same comment as above, you can probably shorten the justification of the scattered flow line distributions as it is a repetition of paragraph 4.1.

We also slightly reduced the text in this part.

DISCUSSION

Have the standard kinetic constants used here been determined on minerals all coming from the Strengbach catchment? Then would you recommend to use site-specific kinetic constants to account for local aging effects?

No, the standard kinetic constants are coming from studies dealing with minerals from various origins (see table EA12 in supplementary material and references therein, lines 299-300). All these minerals are from natural rocks and were collected in the field, but are not from the Strengbach catchment. Simulations performed with these kinetic constants are able to capture spring chemistry while respecting water transit times, this is why we conclude that relevant aging effects are potentially included in these kinetic constants (lines 628-632).

I am not sure if Figure 13 brings anything new. It might be more interesting to show the distribution of dissolution rates over the catchment.

The figure 13 simply brings a general overview of modeled concentrations along an elevation transect PZ5, PZ3 and CS1 in the watershed. It is not possible to show the distribution of dissolution rates over the catchment, precisely because dissolution rates in our parsimonious geochemical modeling approach are only determined along the backtracked flow lines reaching the sampled sites. That being said, these sites are representative of the various flow patterns over the system, and their variability over time.

The discussion on the chemostatic behaviour would gain from a more concise and straightforward argumentation. Some repetitions with the result section could be avoided. For instance, the whole paragraph describing changes in the simulated hydraulic conductivities, in water velocities and in mean transit times should not be detailed as much or details should be moved to the result section 4.2.

Yes, we reduced slightly the text in this section (lines 712-724). We reduced the discussion section dealing with the general chemostatic behavior and moved some text and examples in the results section 4.2.

Lines 693-699 aim to justify the modelling approach and results (same holds true for the discussion on the clay solid solution), which could be moved elsewhere for clarity. I would advise to refocus the whole paragraph only on the discussion on the potential origins for the chemostatic behaviour.

Here, we underline that the choice of the clay solid solution and the question of the distance to chemical equilibrium for waters are key points in discussing the origin of the chemostatic behavior (see the discussion section 6.2 in Ackerer et al., 2018). The choice of clay minerals and the way to handle clay precipitation is major regarding the acquisition of the water chemistry (see discussion in Godderis et al., 2006; Maher et al., 2009; Ackerer et al., 2018 for example). Clay minerals and clay precipitation rates play a role in controlling whether or not chemical equilibrium occurs along the flow lines, and thus, if chemostatic behavior is explained by chemical equilibrium or not. This is why highlighting the relevance of our clay mineral assemblage and clay precipitation rates is important in this section concerning the chemostatic behavior (lines 763-768). It is worth noting that, within another round of reviews, one of the reviewers asked us to be very picky regarding the two points mentioned above.

References:

Goddéris, Y., François, L. M., Probst, A., Schott, J., Moncoulon, D., Labat, D., & Viville, D. (2006). Modelling weathering processes at the catchment scale: The WITCH numerical model. *Geochimica et Cosmochimica Acta*, *70*(5), 1128-1147.

Maher, K., Steefel, C. I., White, A. F., & Stonestrom, D. A. (2009). The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence, California. *Geochimica et Cosmochimica Acta*, *73*(10), 2804-2831.

Crossing hydrological and geochemical modeling to understand the spatiotemporal variability of water chemistry in a headwater catchment (Strengbach, France)

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Abstract

Understanding the variability of the chemical composition of surface waters is a major issue for the scientific community. To date, the study of concentration-discharge relations has been intensively used to assess the spatiotemporal variability of the water chemistry at watershed scales. However, the lack of independent estimations of the water transit times within catchments limits the ability to model and predict the water chemistry with only geochemical approaches. In this study, a dimensionally reduced hydrological model coupling surface flow with subsurface flow (i.e., the Normally Integrated Hydrological Model, NIHM) has been used to constrain the distribution of the flow lines in a headwater catchment (Strengbach watershed, France). Then, hydrogeochemical simulations with the code KIRMAT (i.e., KInectic Reaction and MAss Transport) are performed to calculate the evolution of the water chemistry along the flow lines. Concentrations of dissolved silica (H_4SiO_4) and in basic cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) in the spring and piezometer waters are correctly reproduced with a simple integration along the flow lines. The seasonal variability of hydraulic conductivities along the slopes is a key process to understand the dynamic of flow lines and the changes of water transit times in the watershed. The covariation between flow velocities and active lengths of flow lines over changing hydrological conditions reduces the variability of water transit times and explains why transit times span much narrower variation ranges than the water discharges in the Strengbach catchment. These findings demonstrate that the general chemostatic behavior of the water chemistry is a direct consequence of the strong hydrological control of the water transit times within the catchment. Our results also show that a better knowledge of the concentration-mean transit time relations (C-MTT relations) is an interesting new step to understand the diversity of C-Q shapes for chemical elements. The good matching between the measured and modeled concentrations while respecting the

water-rock interaction times provided by the hydrological simulations also shows that it is possible to capture the chemical composition of waters using simply determined reactive surfaces and experimental kinetic constants. The results of our simulations also strengthen the idea that the low surfaces calculated from the geometrical shapes of primary minerals are a good estimate of the reactive surfaces within the environment.

1- Introduction

Understanding the effects of ongoing climatic changes on the environment is a major issue for the coming years. The global increase of temperature is expected to affect the hydrological cycle at a large scale, and providing a precise estimation of its repercussion on the evolution of soils and on the chemistry of waters remains difficult. This challenge results from the wide diversity of hydrological, geochemical, and biological processes, and of their coupling, that operate at the Earth's surface (e.g., Gislason et al., 2009; Goddéris et al., 2013; Beaulieu et al., 2012; 2016). Up today, the study of concentration-discharge relations (C-Q relations) has been intensively used to assess the coupling between hydrological and geochemical processes at the hillslope or watershed scales (Godsey et al., 2009; Kim et al., 2017; Ameli et al., 2017; Diamond and Cohen, 2018).

C-Q relations are acknowledged to integrate critical zone structure, the hydrological dynamics and the geochemical processes of watersheds (Chorover et al., 2017). Recent studies debated to which extend the chemical variability of waters is explained by a mixing of different water sources (Zhi et al., 2019), the chemical contrasts between deep and shallow waters (Kim et al., 2017), the variability of transit times (Ackerer et al., 2018) and/or seasonally variable flow paths (Herndon et al., 2018). It is clear that a good knowledge of the water flow paths and of their seasonal variability is an important new step to better constrain the water transit times within catchments, and then, to correctly understand the temporal fluctuations of the composition of waters. Modeling such variability of water flow paths and water geochemical composition would require further development of modeling approaches able to combine hydrological and geochemical processes (e.g. Steefel et al., 2005; Kirchner, 2006).

Recent efforts in hydrological modeling were conducted to develop spatially distributed approaches that better consider the interplay between surface and subsurface processes (e.g., Gunduz and Aral, 2005; Kampf and Burges, 2007; Camporese et al., 2010). Due to the complexity of flows in the hydrological processes, many modeling approaches are based on the full resolution of Richard's and Saint Venant equations to correctly describe the interactions between stream, overland and subsurface waters (Kampf and Burges, 2007). These approaches have shown their ability to capture the hydrological functioning of various watersheds, knowing that the full resolution of Richard's and Saint Venant equations requires long computational times and faces calibration and parameterization difficulties (Ebel and Loague, 2006; Mirus et al., 2011). Questions have been raised regarding the optimal complexity of the equations that are needed to correctly treat the hydrology of catchments in their surface and subsurface compartments with reasonable computation times (Gunduz and Aral, 2005).

Low-dimensional models have attracted growing interest because they represent an interesting compromise between equation complexity, computational time, and result accuracy (Pan et al., 2015; Hazenberg et al., 2016; Weill et al., 2013; 2017; Jeannot et al., 2018). The reduction of dimensionality is mainly associated with a subsurface compartment (including both the vadose and the saturated zones) modeled as a two-dimensional layer. Some low-dimensional models, as the one employed in this study, can solve subsurface flow via an integrated Richard's equation, meaning that flow and transport processes are integrated over a vertical direction or a direction normal to bedrock, and manipulate averaged (integrated) hydrodynamic properties. This type of low-dimensional approach recently demonstrated its ability to reproduce the results from fully dimensioned approaches in small catchments while reducing computational costs (Pan et al., 2015; Jeannot et al., 2018). Nonetheless, the water transit times calculated from these depth-integrated models are rarely confronted with the water-rock interaction times inferred from hydrogeochemical modeling of water chemistry in watersheds.

For its part, the understanding of the hydrogeochemical functioning of the critical zone has been significantly advanced by the implementation of reactive-transport laws in geochemical modeling codes (Steefel et al., 2005; Lucas et al., 2010; 2017; Goddéris et al., 2013; Li et al., 2017). These developments allow for considering a variety of processes, such as flow and transport processes, ion exchanges, biogeochemical reactions, and the interplay between primary mineral dissolution and secondary mineral precipitation (Moore et al., 2012; Lebedeva and Brantley, 2013; Ackerer et al., 2018). Reactive transport models have been used to explore a wide variety of scientific issues, including the study of global atmospheric CO_2 consumption by weathering reactions (Goddéris et al., 2013; Li et al., 2014), the formation and evolution of soil and regolith profiles (Maher et al., 2009; Navarre-Sitchler et al., 2009; Lebedeva and Brantley, 2013), and the variability of water quality and chemistry in the environment (Lucas et al., 2010; 2017; Ackerer et al., 2018). However, these approaches usually rely on a simple 1D flow path through a regolith column or along a hill slope to model flow in the system (e.g. Maher, 2011; Moore et al., 2012; Lucas et al., 2017; Ackerer et al., 2018). 1D reactive-transport models are useful to discuss the key processes involved in the regolith formation and in the acquisition of the water chemical composition, but these models cannot consider the complexity of the flow trajectories in watersheds, and hence, its effects on the water chemistry.

A new step is therefore necessary for the development of hydrogeochemical modeling approaches that are applicable at the watershed scale and are able to integrate the complexity of the water flows and the diversity of the water-rock interaction processes. Recent efforts have been undertaken in the direction of merging hydrological and geochemical codes, with for example, the parallel reactive transport code ParCrunchFlow (Beisman et al., 2015), or the coupled hydrogeochemical code RT-Flux-PIHM (Bao et al., 2017; Li et al., 2017). As an alternative to fully dimensioned codes, this work proposes an original low-dimensional approach, with relatively short computation times and applicable at the watershed scale. This study is combining for the first time in this manner the results from a hydrological low-dimensional (depth-integrated for the subsurface) but spatially distributed model (NIHM) with a reactive-transport model (KIRMAT). The combination allows for simulating over time and space the flow trajectories, the flow rates, the weathering reactions, and the evolution of the water chemistry within a headwater system, the Strengbach catchment.

This catchment is one of the reference observatories of the French critical zone network (OZCAR), where multidisciplinary studies, including hydrological, geochemical and geological investigations, have been performed since 1986 (“Observatoire Hydrogéochimique de l’Environnement”, OHGE; http://ohge.unistra.fr; El Gh’Mari, 1995; Fichter et al., 1998; Viville et al., 2012; Gangloff et al., 2014; 2016; Prunier et al., 2015; Pan et al., 2015; Ackerer et al., 2016; 2018; Beaulieu et al., 2016; Chabaux et al., 2017; 2019; Schmitt et al., 2017; 2018; Daval et al., 2018; see also Pierret et al., 2018 for an updated overview of the Strengbach watershed).

2- Site presentation and data acquisition

The Strengbach catchment is a small watershed (0.8 km²) located in the Vosges Mountains of northeastern France at altitudes between 883 and 1147 m. Its hydroclimatic characteristics can be found in Viville et al. (2012) or in Pierret et al. (2018). It is marked by a mountainous oceanic climate, with an annual mean temperature of 6 °C and an annual mean rainfall of approximately 1400 mm, with 15 to 20% falling as snow during two to four months per year. The snow cover period is quite variable from year to year, and may not be continuous over the entire winter. The annual mean evapotranspiration is of approximately 600 mm, and the annual mean infiltration (no significant surface runoff observed) of approximately 800 mm (Viville et al., 2012). The watershed is currently covered by a beech and spruce forest. The bedrock is a base-poor Hercynian granite covered by a 50 to 100 cm-thick acidic and coarse-in-texture soil. The granitic bedrock was fractured and hydrothermally altered, with a stronger degree of hydrothermal overprinting in the northern than the southern part of the catchment (Fichter et al., 1998). The granite was also affected by surface weathering processes during the Quaternary (Ackerer et al., 2016). The porous and uppermost part of the granitic basement constitutes an aquifer from 2 to approximately 8 m thickness. In the Strengbach watershed, the major floods and high-flow events usually occur during snowmelt periods at the end of the winter season or in the early spring. By contrast, the low-flow periods commonly happen at the end of the summer or during the autumn. Several springs naturally emerge along the slopes (figure 1). The watershed has been equipped with several piezometers and boreholes since 2012, those being located along the slopes on both sides of the watershed (figure 1 in Chabaux et al., 2017).

Spring waters have been regularly collected and analyzed since 2005, with monthly sampling supplemented by a few specific campaigns to cover the complete range of water discharges in the watershed. Piezometer waters have been collected only during specific sampling campaigns over the period 2012-2015, and, as for the spring waters, these sampling campaigns cover different hydrological conditions from wet to dry periods. The soil solutions were collected with a monthly frequency on the southern slope at a beech site (named HP) and to the north at a spruce site (named VP; figure 1; more details in Prunier et al., 2015). For all the collected waters, the concentrations of the major dissolved species and the pH were determined by following the analytical techniques used at LHyGeS (Strasbourg, France) and detailed in Gangloff et al. (2014) and Prunier et al. (2015). Discharges of water from the springs were measured during the sampling campaigns, as were the water levels within the piezometers.

The mineralogy and the porosity of the bedrock have been studied in detail in previous studies (El Gh’Mari, 1995; Fichter et al., 1998). On the southern part of the catchment, the weakly hydrothermally altered granite (named HPT, figure 1) is mainly composed of quartz (35%), albite (31%), K-feldspar (22%) and biotite (6%). It also contains small amounts of muscovite (3%), anorthite (2%), apatite (0.5%) and clay minerals (0.5%). On the northern part of the catchment, the lithology is more variable, with the presence of gneiss close to the crest lines and the occurrence of hydrothermally altered granite on the rest of the slopes (El Gh’Mari, 1995, figure 1).

The hydrological, geochemical and petrological data obtained from these field investigations are the basis of the modeling exercise presented in this study. More precisely, this study is based on hydrogeochemical data from 2005 to 2015 for waters from four springs of the southern part (CS1, CS2, CS3 and CS4) and one spring of the northern part (RH3) of the watershed (figure 1). Hydrogeochemical data obtained over the period 2012-2015 for two piezometers (PZ3, PZ5) of the southern part of the watershed are also studied (figure 1). The overall hydrogeochemical database is available as supplementary tables (tables EA1 to EA9). The specific chemical data from spring and piezometer waters modeled in this study are reported in table 1.

3- Modeling methods

The modeling developments presented in this study represent a new step in the efforts undertaken to constrain the mechanisms controlling the geochemical composition of surface waters and to understand their spatial and temporal variations at the scale of headwater mountainous catchments (Schaffhauser et al., 2014; Lucas et al., 2017; Ackerer et al., 2018). The main innovation of this present work is to couple a spatially distributed and low-dimensional hydrological model with a reactive transport code to constrain the spatiotemporal variability of chemical composition of waters. To the best of our knowledge, this is the first time that such a coupling between low-dimensional hydrological and hydrogeochemical modeling approaches has been attempted in this way at the watershed scale.

3-1 Hydrological modeling

To assess the water flows in the watershed, several simulations were performed with the hydrological code NIHM (Normally Integrated Hydrological Model; Pan et al., 2015; Weill et al., 2017; Jeannot et al., 2018). This code is a coupled stream, overland, and low-dimensional (depth-integrated) subsurface flow model developed at LHyGeS and already tested in the Strengbach watershed (Pan et al., 2015). The stream and overland flows are described by a diffusive-wave equation, and the subsurface flow is handled through an integration (in a direction normal to bedrock) of the unsaturated-saturated flow equation from the bedrock to the soil surface (Weill et al., 2017). The exchanges of water between the surface and subsurface flows are addressed via a first-order exchange coefficient involving the thickness and the hydraulic conductivity of an interface layer (e.g., the riverbed, for interactions between surface routing and subsurface compartments), and the hydraulic head differences between the compartments (Jeannot et al., 2018).

Regarding the hydrological simulations, NIHM was used with only its stream flow and subsurface flow compartments activated, the Strengbach catchment having never evidenced diffuse two-dimensional surface runoff or subsurface exfiltration over large areas. In addition, and because of the steep slopes, the stream flow process revealed almost insensitive to the roughness and Manning's parameters of the riverbed, which were set to usual values for very small streams of mountainous landscapes. By contrast, the parameters of the subsurface were adjusted in NIHM through a calibration-validation process. Several zones of heterogeneity (figure 2) were defined based on field observations (Ackerer et al., 2016; Chabaux et al., 2017). In each of these zones, the saturated hydraulic conductivity, the depth of substratum, and the porosity, were set to uniform values. Other parameters (the residual water content, the specific storage, the Van Genuchten coefficients n and α, and the saturated hydraulic conductivity of the interface layer between the groundwater compartment and the surface compartment) were set to uniform values over the whole catchment (table 2). The thickness of the aquifer that was used for the simulations varied from 2 m near the main crests to up to 8 m in the middle of the watershed (figure 2), in agreement with the data obtained during the recent geological investigations and drilling campaigns undertaken at the catchment (Ackerer et al., 2016; Chabaux et al., 2017). The uniform precipitations over space applied at the surface of the catchment are drawn from data of the pluviometric station located at the highest elevation of the watershed (site PA, figure 1). The hydrological model NIHM was then run over a first time period (years 1996-1997). By a Monte-Carlo approach, the parameters were “randomly” sought to improve the fitting between the observed and simulated flow rates at the outlet of the catchment (table 2). The fit was quantified by the root mean square error (RMSE) and the Kling-Gupta efficiency coefficient (KGE; Gupta et al., 2009), applied to the outlet flow rate of the stream, which is the only reliable and always available hydrological variable monitored in the system.

Once the best fit was obtained, the model was then run over another time period (2010-2015), but without changing the parameters anymore, and the quality of the fit was re-assessed for this new time-period with the KGE and RMSE. Figure 2 shows the result for the 2010-2015 time period. Once the water discharges were correctly reproduced at the outlet, a backtracking approach was used to constrain the origin of subsurface water exiting the system at prescribed locations, and the spatiotemporal variability of the flow lines within the watershed. To back track the water particles, the velocity fields calculated by the NIHM model were inverted in their direction, and the locations of the backtracked particles were saved at each time-step. A daily time-step was used for the backtracking, as a compromise between computational efforts and a refined description of the transient velocity fields. A schematic representation of the backtracking approach is given in figure 3. This methodology allows for constraining the flow lines that bring waters for a given time and at a given position on the catchment. This information is of major interest to determine the origin of the spring and piezometer waters. It is shown at the catchment scale, that flows are mainly driven by gravity in association with the steep slopes of the watershed, the latter being almost evenly drained over its whole surface area (figure 4). For each water sampling area, ten flow lines that bring water to the location of interest were determined (figure 4), together with a few features of the flow lines, including: local velocities, mean velocities, and length of the flow paths.

It is worth noting that NIHM is a depth-integrated model for its subsurface compartment where flow is simulated over a 2D-mesh and under the assumption of an instantaneous hydrostatic equilibrium in the direction perpendicular to the substratum. Therefore, times calculated along the backtracked streamlines correspond to a date, x days before arrival, at which a water particle entered the subsurface or passed at a given location along the streamline. Streamlines calculated via backtracking and reaching sampling sites only consider flow in the subsurface compartment and are conditional to an arrival date at a prescribed location. As backtracked streamlines are not associated with mean water flux values, the transit time distributions drawn from streamline calculations are only an approximation of the actual transit time distributions.

It should also be noted that, knowing the water head at a given location, the assumption of an instantaneous hydrostatic equilibrium over the direction perpendicular to the substratum directly renders the associated water pressure over the whole aquifer along that direction. Then, since the water pressure, saturated hydraulic conductivity, porosity, residual water content, and Van Genuchten coefficients are known, the Van Genuchten equation can be integrated numerically, which gives to NIHM the possibility to calculate local depth-integrated hydraulic conductivities over the direction perpendicular to the substratum.

With a conditioning of NIHM limited to the reproduction of the stream flow rates at its outlet, it can be questioned on the reliability of the solution, equifinalities in model outputs being usually all the more present that few data are available to condition the model. The point is that there is no other reliable information on flow patterns, and for example, the few boreholes available (mainly drilled for rock core sampling) are deep enough to intercept a few fractures in the bedrock (under the bottom of the aquifer simulated by NIHM). This renders the water levels monitored in these open boreholes unable to reflect hydraulic pressure heads in the active shallow porous aquifer of the catchment. Nevertheless, the steep slopes of the catchment are the main feature conditioning water velocities, thus rendering transit times (the variable of interest for a geochemical study) very stable over time, irrespective of hydro-meteorological conditions and current head pressure in the system. After the present study was completed, NIHM was employed at the Strengbach to simulate water content distributions with the aim to mimic data from magnetic resonance sounding (Weill et al., 2019). The model was slightly improved in terms of storage and its variability over space, but the modeled distribution of flow paths, their variability, and the associated transit time distributions remained unchanged.

3-2 Hydrogeochemical modeling

The simulations of the water chemical composition along the flow lines were performed with the hydrogeochemical KIRMAT code (KInectic of Reaction and MAss Transport; Gérard et al., 1998; Lucas et al., 2010; Ngo et al., 2014). KIRMAT is a thermokinetic model derived from the Transition State Theory (TST, Eyring, 1935; Murphy and Helgeson, 1987) that simultaneously solves the equations describing geochemical reactions and transport mass balance in a 1D-porous medium. The mass transport includes the effects of one-dimensional convection, diffusion and kinematic dispersion. Chemical reactions account for the dissolution of primary minerals and oxido-reduction reactions, in addition to the formation of secondary minerals and clay minerals. Thermodynamic and kinetic data for the primary minerals are available in supplementary materials (tables EA10, EA11 and EA12).

The clay fraction is defined as a solid solution made up of a combination of pure clay end-members. The clay end-members are defined on the basis of X-ray diffraction analyses of clay minerals present in bedrock samples collected in the field (Fichter et al., 1998; Ackerer et al., 2016; 2018). They consist of K-Illites, Mg-Illites, Ca-Illites, Montmorillonites, Na-Montmorillonites, K-Montmorillonites, Ca-Montmorillonites and Mg-Montmorillonites (supplementary material table EA13). During the hydrogeochemical simulations, the clay solid solution is precipitated at thermodynamic equilibrium and its composition varies over time, depending on the evolution of the water chemistry and the bedrock mineralogy (Ackerer et al., 2018). This multicomponent solid solution reproduces the impurity of the clay minerals formed during low-temperature water-rock interactions (Tardy and Fritz, 1981).

The KIRMAT code also includes feedback effects between mineral mass budgets, reactive surfaces, and the evolution of bedrock porosity (Ngo et al., 2014). The reactive surfaces of the primary minerals were calculated by assuming a simple spherical geometry for all the minerals, and the mean size of the minerals was estimated from the observation of thin sections from bedrock samples. During simulations, clay mineral precipitation and the evolution of the reactive surfaces of primary minerals are tracked together with chemical processes and water chemical composition. Given the short time scales reported by the hydrological simulations (monthly timescale), changes in the reactive surfaces of primary minerals over the simulation time were negligible. Precipitation of other secondary minerals such as carbonates, hematite or amorphous silica was also tested, but these minerals were not formed given the saturation states calculated in the geochemical modeling (supplementary table EA14). Secondary mineral precipitation is therefore controlled by clay mineral formation. The KIRMAT code has already been applied in geochemical modeling of alluvial subsurface waters (Lucas et al., 2010) and surface waters (Lucas et al., 2017; Ackerer et al., 2018).

For this study, the modeling strategy is adapted from Ackerer et al. (2018) to consider the new transit time constrains provided by the hydrological code NIHM. To capture the chemical composition of the spring and the piezometer waters, numerical simulations were performed along the subsurface streamlines that were determined through the backtracking approach. A sketch of the hydrogeochemical modeling strategy is provided in figure 5. For each streamline, several KIRMAT simulations were performed with different starting positions along the active part of the line. The starting positions represent the locations at which the soil solutions percolate through the subsurface shallow aquifer. These starting positions are spaced with a constant lag distance of 1 m along the subsurface streamlines, which results in a sub-continuous percolation of solutions along the whole length of the lines. The deepest soil solutions collected to the south at the beech site (HP) and to the north at the spruce site (VP) were considered representative of the soil solutions for the southern and northern slopes of the catchment, respectively. The data of soil solution chemistry used in this study are available in Prunier et al. (2015) and in supplementary tables (tables EA6 and EA7). These soil solutions integrate the surface processes occurring before water percolation into the weathered bedrock (regolith). Because the soil solutions can be injected into the aquifer at various times, the temporal variability of the soil solution chemistry and its impact on the water-rock interactions along the flow paths are accounted for in the modeling approach.

Data related to the regolith properties, such as the mineralogical compositions, the mineral reactive surfaces and the thermodynamic and kinetic constants are given in Ackerer et al. (2018) and in supplementary tables (tables EA10 to EA14). Mineral phases are assumed homogeneously distributed over the regolith layer. By following this strategy, the simulations that consider soil solutions percolating at the upper part of the catchment reflect the chemical evolution of waters with long path lengths and long transit times within the aquifer. By contrast, shorter path lengths and shorter transit times are associated with the percolation of soil solutions that occurs in the vicinity of the sampling locations (figure 5). Because the springs or the piezometers collect waters from different origins and with various transit times, integration along each water flow line was performed. The aim of the integration is to determine the mean chemical composition resulting from the mixing of the waters characterized by variable transit times (figure 5). The integrated chemical composition of the waters provided by a given flow line is calculated by taking the arithmetic mean of the solute concentrations calculated by the succession of the KIRMAT simulations along the flow line (figure 5). This arithmetic mean reflects a simple full mixing of uniform water fluxes along a stream line irrespective of the short or long transit times. In other words, the geochemical simulations are based on the hypothesis of spatially homogenous water-rock interactions along the flow lines. The soil solutions are assumed to percolate uniformly within the aquifer and are then conveyed along the slopes by uniformly distributed masses of water until reaching the sampling locations. When needed, the eventual calculation of water chemistry exiting several stream lines reaching a sampling location accounts for the spreading associated with various flow paths, spatial variability of water velocities and related travel times.

4- Hydrological modeling results

4-1 Spatial variability of the flow lines

The results provided by the hydrological code NIHM show that to the first order, the Strengbach catchment is well drained and that the topography exerts an important control on the flow line distribution (figure 4). Along the hillsides presenting linear or slightly convex slopes, the water flow lines show simple characteristics. The flow paths are nearly parallel, and the water velocities are similar along the different flow lines on this type of hillside. The water velocities tend to increase when moving downstream, with slower velocities near the main crests and higher velocities on the steepest parts of the hillsides. The waters collected along this type of hillside are therefore characterized by small variability of transit times. This is the case for the CS1, CS3 and RH3 spring waters located on the southern and northern parts of the catchment (figure 4). This is also the case for the piezometers PZ3 and PZ5 in the southern part of the watershed (figure 4). For the sites located on linear or slightly convex slopes (CS1, CS3, RH3, PZ3 and PZ5), all the characteristics of the different flow lines that feed each site are therefore comparable for a given site and for a given date.

By contrast, in the vicinity of the valley and in the topographic depressions, the hydrological modeling indicates that the flow line characteristics are more variable. Because flow lines coming from different hill-sides can feed a topographic depression, mixing of different flow lines with variable flow paths and contrasted water velocities can occur at these locations. The waters collected in valleys or in topographic depressions are therefore characterized by a higher variability of transit times. This is the case for the CS2 and CS4 springs, which are located in a depression, in the axe of the small valley, and surrounded by slopes with various orientations, and a complex flow line distribution (figure 4). For these two springs, the characteristics of the different flow lines can be different for a given date.

4-2 Temporal variability of the flow lines

Hydrological modeling under general transient conditions can render the evolution over time of water flows in the watershed but also of other hydraulic variables. As an example, after an important rainfall event (30/03/2010 in figure 6), snapshots of the integrated hydraulic conductivity (modeled via the Van Genuchten formulation) in the subsurface and simulated by NIHM at the scale of the mesh size show increasing values with decreasing elevation in the watershed. The same observation holds for conductivities during drought periods (see 29/11/2011, in figure 6). Provided that the hydraulic head gradient is largely dominated by the topography and therefore almost constant over time (figure 6), the water velocities are increasing along the flow lines from crests to valleys, irrespective of the wet versus dry hydrological periods. However, it is noticeable that wet periods are favorable to a large extension in the valleys of high values of depth averaged hydraulic conductivity indicating that the aquifer is locally almost completely saturated from bottom to top (e.g., values of 6.5×10^{-5} ms^{-1} in figure 6 for a saturated bound at 8 10^{-5} ms^{-1}).

For the CS1 spring, the mean flow velocities along the flow lines vary from approximately 1 m/day to 7 m/day between the severe drought of 29/11/2011 and the strong flood of 30/03/2010 (figures 7A and 7B). These events correspond to the annual minimum and maximum flow rates at the outlet of the Strengbach watershed. For the same dates, the mean velocities vary from 2 – 12 m/day, 1 – 4 m/day and 1 – 9 m/day for the springs CS2, CS3 and CS4, respectively. The variations from drought to flood are very similar for the piezometer waters, with velocities in the ranges 2 – 10 m/day and 2 – 12 m/day for the PZ3 and PZ5 piezometers, respectively. The RH3 spring located on a steeper part of the northern slopes exhibits flow velocity variations from 5 to 20 m/day from dry to flood conditions.

In addition to the flow velocity variations, the hydrological simulations also reveal variability in the lengths of the active parts of the flow lines. For illustration, the active parts of the flow lines are reduced from 160 m to 110 m from the flood to the drought events for the CS1 spring (figures 7A and 7B). Such variability is triggered by the particular seasonal variations of the hydraulic conductivities within the catchment. After important precipitations, high water content and large integrated hydraulic conductivities (sometimes up to the saturated bound) are simulated in the vicinity of the crests and all along the small valley of the catchment (figure 6). During periods of drought, the simulations indicate a strong decrease of hydraulic conductivities close to the main crests and much smaller variations at mid-slopes (figure 6). The crests rapidly dry out, whereas the areas at mid-slopes still supply some water to the stream network. These contrasting hydrological behaviors result from the differences in aquifer thickness and water storage between the crests and the other parts of the catchment (figure 2). Thin aquifer, flow divergence and absence of feeding areas prevent large water storage on the crests, in opposition to mid-slope parts with much thicker aquifers and the presence of feeding areas upstream. This particular pattern simulated for the hydraulic conductivities implies that the active parts of the flow lines extend up the main crests during important floods, whereas they are limited to mid-slopes after a long dry period.

The consequence of this hydrological functioning is to moderate the seasonal variations of the transit times of waters, as the active lengths of flow lines vary simultaneously with water flow rates. Calculations indicate that for the spring and piezometer waters collected in this study, the mean transit times of waters only vary from approximately 1.75 to 4 months between the strongest flood and the driest conditions. Notably, these short subsurface water transit times are explained by the small size of the catchment and the steep slopes.

5- Hydrogeochemical modeling results

5-1 CS1 and CS3 springs (southern slope)

The CS1 and CS3 springs emerge on the same slope and drain the same rocks. Their hydrological behavior is also very similar in terms of flow lines and water transit times. The interesting consequence of the simple flow line distribution for these springs is that a single flow line can be considered as representative of all the flow lines that are feeding the spring, irrespective of the hydrological conditions. Hydrogeochemical simulations were performed along a single flow line for different hydrological periods using the methodology illustrated in figure 5. The case of CS1 spring is used below to highlight the main results obtained from this approach. For the strong flood of 30/03/2010, the KIRMAT simulations modeling the waters coming from the vicinity of the spring and characterized by short transit times produced too much diluted solutions, whereas the waters coming from the main crests were too much concentrated to reproduce the spring water chemical composition. However, after an integration of all the waters arriving at CS1 with the different transit times employed for the simulation, the resulting geochemical composition correctly reproduces the chemical composition of CS1 spring water at this date (H_4SiO_4, Na^+, K^+, Mg^{2+}, and Ca^{2+} concentrations, figure 7D). A similar conclusion is obtained for the important drought of 29/11/2011. Again, geochemical integration of all the waters arriving at CS1 along a water line but with different transit times correctly reproduces the chemical composition of the CS1 spring waters collected on this date (figure 7C). This comment applies regardless of the time period considered.

The coupled hydrological and hydrogeochemical approach has been applied for the CS1 spring for 6 dates covering the whole range of the water discharges of the spring (table 1). The modeling results capture the seasonal variations of the water chemical composition of the CS1 spring over the whole range of observed flow rates at CS1 (figure 8). Simulations especially reproduce the 20-30% variation in H_4SiO_4 concentrations (figure 8A), the 10-20% variation in Na^+ concentrations (figure 8C), and the relatively stability of the K^+, Mg^{2+} and pH of the CS1 waters (figure 8E, 8F and 8D). The response of each chemical element to a change in water discharge is related to the initial soil solution concentration, the nature of primary minerals controlling its budget and the degree of its incorporation into clay minerals. Specific concentration-mean transit time relations (C-MTT relations) explain why the response of solute concentrations to hydrological changes (C-Q relations) is different for each element (figure 9). Similar results are obtained for the CS3 spring (figure EA1), showing, as for the CS1 spring, that the model correctly simulates the water chemical composition of the CS3 spring.

Because the lengths of the flow lines vary over time, the patterns of dissolution rates for primary minerals and precipitation rates for clay minerals are mainly controlled by the spatial and temporal variability of the flow lines. During wet conditions, the upper parts of the catchment are the areas of maximal dissolution rates of primary minerals and of maximal precipitation rates of clay minerals in the regolith. During dry conditions, the dissolution and precipitation rates are maximal at mid-slopes, as the upper parts of the catchment are simply dry.

5-2 PZ3 and PZ5 piezometers (southern slope)

The two piezometers PZ3 and PZ5 are located on the southern part of the catchment, and their waters drain a granitic bedrock similar to that drained by the CS sources. As for the CS1 and CS3 springs, the NIHM modeling results show that the flow lines arriving at the PZ3 piezometer are characterized by a relatively simple distribution (figure 4). For the PZ5 piezometer located downstream, the flow lines cover a larger area on the slope, especially during droughts (figure 4). However, for a given date, all the flow lines show similar velocities, with particularly fast flow in the lower portion of the hillslope. These results imply that, as for the CS1 and CS3 springs, the hydrogeochemical simulations of PZ3 and PZ5 piezometer waters can be performed by relying upon a single flow line representative of all the waters collected by the piezometers on a given date. The geochemical integration is able to reproduce the chemical composition of the waters of the two piezometers, as illustrated in figure 10 for the flood of the 05/05/2015 and in figure EA2 for the dry conditions of 10/11/2015. Together, these modeling results show that the flow along linear or slightly convex slopes on the southern part of the catchment allows to correctly capture the water chemistry of each sampling site with a straightforward integration along a single and representative flow line.

5-3 The CS2 and CS4 springs (in the valley axe)

CS2 and CS4 spring waters drain the same granitic bedrock as the CS1 and CS3 waters, but are located in the direction of the small valley of the Strengbach stream and surrounded by slopes of various orientations and inclinations (figure 4). Consequently, the distribution of the flow lines is much more scattered than for the CS1 and CS3 springs. For the CS2 spring, and for all the hydrological conditions, two different groups of flow lines have been determined by the backtracking approach: a northern group characterized by relatively slow velocities and a southern group with higher velocities (figure 4 and figures 11A, 11B). This scattered distribution of the flow lines implies that a single specific flow line cannot be representative of all the waters collected by the spring. The flow lines calculated using the NIHM model allow for constraining the trajectories of the waters within the watershed; however, the simulations performed in this study cannot provide the mass fluxes of water carried by each flow line. Consequently, a straightforward calculation of the chemistry of the CS2 spring, such as depicted above for CS1, is not applicable because the mixing proportions between the different flow lines are unknown.

Alternatively, it is possible to determine the concentrations in the waters carried by the slowest and the fastest flow lines that are feeding the spring and to compare the results with the observed chemistry of the spring water. The results indicate that for all the hydrological conditions, the concentrations calculated from the geochemical integration along the slowest and the fastest flow lines are able to correctly frame the chemical composition in terms of H_4SiO_4, Na^+, K^+, Mg^{2+}, and Ca^{2+} of the CS2 spring waters (results are reported for H_4SiO_4 and Na^+ in figures 11C and 11D). The modeling results for CS2 also suggest that the contributions of the slow and fast flow lines are comparable over most of the hydrological conditions, as the observed concentrations are in general at the midpoint between the min (i.e., fast) and max (i.e., slow) boundaries (figures 11C and 11D). It is only for the important droughts that the spring chemistry seems to be mainly controlled by the southern and faster group of flow lines. Further works to precisely estimate the mass fluxes of water carried by each flow line are necessary to model the chemistry of the CS2 spring water with a weighted mixing calculation. The same conclusions apply to the CS4 spring located close to CS2.

5-4 The RH3 spring (northern slope)

The RH3 spring is located on the northern part of the catchment (figure 4), where steep slopes imply fast water velocities and subparallel flow lines. However, if the distribution of the flow lines on the RH3 hillside is simple (as for the CS1 and CS3 springs) the precise lithological nature of the bedrock drained by the RH3 waters is more difficult to constrain (Ackerer et al., 2018). Unlike the southern slope, the bedrock of the northern part of the catchment reveals a complex lithology, with gneiss outcropping in the upper part of the slope and granite of variable degree of hydrothermal overprinting in the intermediate and lower parts. These lithological variations can explain the differences in chemical composition between the RH3 spring waters and the waters of the southern part of the catchment: the RH3 spring waters are characterized by systematically higher concentrations of K^+ and Mg^{2+} cations but show similar concentrations for the other major elements (Ackerer et al., 2018; Pierret et al., 2018). The vertical extension of the gneiss and the spatial variability of the hydrothermal overprinting along the northern slopes are not well known, with the consequence that a straightforward modeling of water chemistry as done for CS1 is not possible for RH3.

Alternatively, simulations of two extreme cases can be performed by assuming that the flow lines only run, either on gneiss or on hydrothermally altered granite. When only considering the hydrothermally altered granite (VS facies), the simulated concentrations of H_4SiO_4 and Na^+ are close to the measured ones. Nevertheless, the concentrations of K^+ and especially Mg^{2+} are clearly underestimated (figure 12B). In the case of the flow lines only running on gneiss (GN facies), the simulated concentrations of H_4SiO_4 and Na^+ also match the data. However, due to the higher abundance of biotite in the gneiss, the simulated concentrations of K^+ and Mg^{2+} are higher than the measured ones (figure 12A). At this stage, it is therefore reasonable to propose that the chemical composition of the RH3 spring waters reflects mixing of the two lithological influences. By assuming a geochemical conservative mixing, which is likely a too simplistic scenario, the results would indicate that the flow lines portions running on gneiss and on hydrothermally altered granite count for approximately 40-50% and 50-60% of the total water path length, respectively.

Further works to estimate the location of the contact between gneiss and granite are required for more realistic modeling and hence a deeper interpretation of the chemical composition of the RH3 spring waters. In any case, the important point to stress here based on the above simulations is that the complex lithology and bedrock heterogeneity mainly impact the K^+ and the Mg^{2+} budget of the RH3 waters, but not or only slightly the H_4SiO_4 and Na^+ concentrations, which control the main part of global weathering fluxes carried by the Strengbach spring waters. These results readily explain why although the RH3 spring waters exhibits higher Mg^{2+} and K^+ concentrations than the other CS springs, they carry relatively similar global weathering fluxes (Viville et al., 2012; Ackerer et al., 2018).

6- Discussion

The coupling of the NIHM and KIRMAT codes allows for building a better modeling scheme to those commonly used in previous studies regarding the hydrogeochemical modeling of surface waters at the watershed scale. In such previous works, the geochemical simulations were performed mainly along a single 1D flow line, only characterized by homogeneous mean hydrological properties (Goddéris et al., 2006; Maher, 2011; Moore et al., 2012; Lucas et al., 2017; Ackerer et al., 2018). In a previous study on the Strengbach watershed (Ackerer et al., 2018), the soil solutions were also assumed to percolate in the bedrock only at a single starting point of the flow lines. Although these previous approaches were useful for determining the long-term evolution of regolith profiles and/or the mean chemistry of waters at the pluri-annual scale, they cannot be used to discuss the seasonal variations of the water chemical composition. The NIHM-KIRMAT coupling approach makes this possible, as it provides the spatial distribution of the flow lines at the watershed scale and their variations over time. Furthermore, the proposed modeling approach also integrates a soil solution percolation scheme with inlets uniformly distributed along the slope, which is more realistic than a scheme assuming that each sampled site is fed by a single flow line carrying waters with a unique transit time. The good agreement between modeling results and observations over a large panel of hydrological conditions gives strength to the conclusions and implications that can be drawn regarding the hydrogeochemical functioning of this headwater catchment.

6-1 Choices of the reactive surfaces and the kinetic constants

For the geochemical simulations performed in this study, the kinetic constants that were used to describe the dissolution reactions of the primary minerals are standard constants determined through laboratory experiments (supplementary table EA12). The reactive surfaces of the primary minerals were calculated by assuming a simple spherical geometry for all the minerals (supplementary table EA10). Over the last years, several studies have suggested that the kinetic constants determined through laboratory experiments overestimated the rates of the dissolution reactions in natural environments (White and Brantley, 2003; Zhu, 2005; Moore et al., 2012; Fischer et al., 2014). The origin of this laboratory-field discrepancy is still a matter of debate (Fischer et al., 2014). Different processes have been proposed to explain the gap between laboratory and field estimates, such as the crystallographic anisotropy (Pollet-Villard et al., 2016), progressive occlusion of the primary minerals by clays (White and Brantley, 2003), or the formation of passivation layers at the surfaces of the minerals (Wild et al., 2016, Daval et al., 2018). The difficulty to reconcile field and laboratory estimates can also be related to the challenge of defining relevant reactive surfaces at different space scales (Li et al., 2006; Navarre-Sitchler and Brantley, 2007).

The present modeling work regarding the Strengbach catchment shows that the chemical composition variability of the spring and piezometer waters is fully captured via geometric reactive surfaces and standard kinetic constants, while respecting the water-rock interaction times within the catchment. This result suggests that the mean rates of the weathering reactions employed in this modeling work are realistic, which in turn implies that the modeling approach developed in this study does not underline significant mismatches between field and laboratory reaction rates. The calculated rates of the dissolution reactions depend on the product between the kinetic constants of the reactions and the mineral reactive surfaces. In the experimental studies performed for determining the kinetic constants of dissolution reactions, the constants are usually determined by normalizing the experimental weathering rates with the Brunauer-Emmett-Teller surfaces determined from experiments of gas absorption (BET surfaces; Chou and Wollast, 1986; Lundstrom and Ohman, 1990; Acker and Bricker, 1992; Amrhein and Suarez, 1992; Berger et al., 1994; Guidry and Mackenzie, 2003).

In table 3, the BET surfaces are compared with the geometric surfaces of the minerals involved in the dissolution experiments, recalculated from the size ranges of the minerals. For most of the minerals (apatite, quartz, albite, K-feldspar, and anorthite), the geometric surfaces are within the same order of magnitude as the BET surfaces, even if often slightly lower (table 3). However, as the BET surfaces are determined with fairly large uncertainties, especially for low BET surfaces (up to ± 70%), and as they can be very different depending on the gas used (up to 50% of difference between N2 or Kr absorption; Brantley and Mellott, 2000), the above differences between the geometrical and the BET surfaces cannot be considered significant for the majority of minerals used in the Strengbach simulations. A significant difference only appears for biotite, with the geometric surfaces one order of magnitude less than the BET surfaces (table 3). However, for biotite, due to its layered structure, it has been shown that approximately 80 – 90% of the surface area accessible by the gases used to estimate BET surfaces is not accessible for weathering reactions (Nagy, 1995).

The above considerations explain why for a granitic bedrock as found in the Strengbach catchment, the geometric surfaces are relevant to describe the surfaces of water-rock interactions at the space and time scales of this study. An immediate corollary is that the values of the standard kinetic constants (table EA12) are also appropriate to calculate reaction rates with mineral geometric surfaces in our modeling approach. This ability may be related to the fact that all the minerals that have been used in the dissolution experiments and in the kinetic studies were collected in the field (e.g., Acker and Bricker, 1992; Amrhein and Suarez, 1992). These minerals were likely affected by anisotropy, passivation layers, and any types of aging effects related to long-term water-rock interactions. Our results might therefore mean that the standard kinetic constants obtained in such experiments integrate the aging effects that have affected the reactivity of the primary minerals in natural environments. This would explain why it is possible to capture the full variability of the water chemistry in a headwater catchment with simple geometric reactive surfaces and standard kinetic constants.

At this stage, the results of our simulations strengthen the idea that the low surfaces calculated from the geometrical shapes of minerals provide good estimates of the reactive surfaces within this type of environment (Brantley and Mellott, 2000; Gautier et al., 2001; White and Brantley, 2003; Zhu, 2005; Li et al., 2017). They are certainly the values to be used for hydrogeochemical modeling such as that performed in this work, in addition to the use of the experimental kinetic constants for mineral dissolution. These conclusions are certainly not specific to the Strengbach catchment and could be applicable to many other headwater granitic catchments.

6-2 Implications for the acquisition of the water chemistry

The results of the NIHM-KIRMAT hydrogeochemical modeling have strong implications regarding the hydrogeochemical dynamic of the Strengbach watershed. This work reinforces several hypotheses formulated by previous studies conducted in the Strengbach watershed (Viville et al., 2012; Pierret et al., 2014; Pan et al., 2015; Chabaux et al., 2017; Weill et al., 2017; Ackerer et al., 2018), but also brings new insights on the hydrogeochemical functioning of the catchment. Firstly, the modeling results emphasize the importance of water transit times within the watershed as a main feature controlling the chemical composition of subsurface waters. Along all the slopes, the waters coming from the vicinity of the crests and characterized by long transit times systematically render higher concentrations than the waters with shorter pathways and transit times. When the hydrological conditions change from wet to dry periods, the solute concentrations also tend to increase with the increase in the mean transit time of waters. Our results show that for the spring and piezometer waters, the spatial and temporal variations of their geochemical composition are fully explained by the differences in water transit times (figure 13). Transit time variations between high and low discharge periods explain the temporal variations of geochemical signatures within each site. Various mean transit times of waters supplying the different sites explain the various chemical compositions between the sites (figure 13). This key role of the water-rock interaction time is in agreement with previous reactive-transport studies conducted in the Strengbach watershed (Ackerer et al., 2018) and in other sites (e.g. Maher, 2010; Moore et al., 2012; Lebedeva and Brantley; 2013).

This study also brings new constrains on the spatial distribution of the weathering processes. For the modeling strategy employed, the chemical composition of the spring and piezometer waters are calculated by integrating the chemical composition of waters introduced at different starting locations along the active part of the flow lines (figure 5). The modeling results show that through the geochemical integration, the concentrated waters coming from the main crests are naturally counterbalanced by the diluted waters infiltrating close to the sampling sites. The solute chemistry is acquired through reactions and weathering processes that are spatially relatively homogenous along the flow lines of the watersheds. This spatial homogeneity of the weathering processes helps us to understand why the chemical fluxes carried by the Strengbach stream (Viville et al., 2012), the chemical fluxes from the Strengbach spring waters (Ackerer et al., 2018) and the weathering fluxes locally determined along a regolith profile sampled in the catchment (Ackerer et al., 2016), are all very similar.

The modeling also shows that the hydrogeochemical functioning of the watershed is properly simulated by water circulations in the shallow subsurface, i.e., in a saprolitic aquifer. No contribution of waters circulating in the deep fracture network of the granitic bedrock and observed during the drilling campaigns (see Chabaux et al., 2017) is necessary. The deep-water circulations are probably disconnected from the shallow subsurface network, as recently suggested by geochemical studies conducted in the Strengbach watershed (Chabaux et al., 2017; Pierret et al., 2018). This is also in agreement with recent hydrological modeling studies arguing that the catchment behaves like a vertically thin but horizontally wide reservoir (Pan et al., 2015; Weill et al., 2017). The modeling results also show that water in the shallow aquifer flows along streamlines with fairly simple geometries. At the scale of the catchment (figure 4), the geometry of the flow lines validates the hypothesis based on the geochemical and Sr-U isotopic data that the spring waters of these mid-mountain basins are supplied by waters from distinct flow paths without real interconnections (i.e., the Strengbach and Ringelbach watersheds; Schaffhauser et al., 2014; Pierret et al., 2014). Flow paths are therefore distinct along the slopes and occur within the shallow saprolitic aquifer but are not controlled by deep fractures in the bedrock.

6-3 Origins of general chemostatic behavior and of specific C-Q relations

The hydrogeochemical monitoring of the spring, piezometer, and stream waters performed in the Strengbach catchment clearly shows that this catchment has a general chemostatic behavior (e.g., Viville et al., 2012; Ackerer et al., 2018). All the spring and the piezometer waters have chemical concentrations impacted by changes in the hydrological conditions, but the concentration variation ranges are by far narrower than variation ranges of water discharges, which define the chemostatic behavior of a hydrological system. For waters showing the largest concentration variations (spring CS1), there is a modest increase of approximately 10-30% in the concentrations of H_4SiO_4 and Na+ from floods to drought events, while the water discharges may vary by a factor of 15 (figure 8). This modest variability of the solute concentrations over a wide range of water discharges is not specific to the Strengbach catchment; it has been observed in several watersheds spanning different climates and hydrological contexts (Godsey et al., 2009; Clow and Mast, 2010; Kim et al., 2017).

Different origins for the chemostatic behavior have been proposed, such as a modification of the mineral reactive surfaces during changing hydrological conditions (Clow and Mast, 2010), a small concentration difference between slow and fast moving waters (Kim et al., 2017), or the fact of reaching an equilibrium concentration along the water pathway (Maher, 2010). The coupled approach NIHM-KIRMAT renews the opportunity to discuss on the origin of the chemostatic behavior in catchments. It is worth noting that the acquisition and the evolution of the water chemistry can be simulated along flow lines that have been determined via timely and spatially distributed hydrological modeling. The strength of this approach is to constrain water transit times independently and before any geochemical simulation.

The results from the hydrological model show that the characteristics of the flow lines are affected by the changes in the hydrological conditions (section 4.2). This hydrological functioning implies a covariation between flow velocity and flow length over changing hydrological conditions, with faster flows along longer paths during wet conditions and slower flows along shorter paths during dry periods. This hydrological behavior attenuates the variations of the water transit times over changing hydrological conditions. It also explains why the mean transit times span much narrower variation ranges than the water discharges at the collected springs. For example, the calculated mean transit times of waters for the CS1 spring vary from 1.75 to 3.13 months between the strongest flood and the driest period that have been studied, whereas the water discharges vary from 1.523 L/s to 0.098 L/s (figure 8B). Because the time of the water-rock interactions exerts a first-order control on the chemical composition of waters, the weak variability of the mean transit times is directly responsible for the relative stability of the chemical composition of waters within the catchment.

In addition to this general chemostatic behavior, each chemical element has a specific response to a change in water transit time as exemplified in figure 9 where are given the concentration-mean transit time relations (C-MTT relations) for H4SiO4 and the major cations. In the relevant transit time window for the spring and piezometer waters (figure 9b), the C-MTT relations are linear and C-MTT slopes are significant for H_4SiO_4, modest for Na^+ and weak for Mg^{2+} and K^+ concentrations. The modeling results indicate that the C-MTT slopes are controlled by the competition between primary mineral dissolution and element incorporation into clay minerals. When elemental fluxes from primary mineral dissolution to solution are much higher than fluxes from solution to clay minerals (e.g., H_4SiO_4), the element can accumulate in solution, resulting in a significant C-MTT slope. By contrast, when elemental fluxes from primary mineral dissolution to solution are only slightly higher than fluxes from solution to clay minerals (e.g., K^+), the element accumulates only slowly in solution, resulting in a weak C-MTT slope. Interestingly, when fitting power-laws along C-Q relations ($C=aQ^b$, in caption of figure 8), both 'a' coefficient controlling the height of the C-Q laws and 'b' coefficient controlling the curvature of the C-Q laws are sensitive to the C-MTT slopes (figure 9c and 9d). 'a' coefficient is positively corelated with C-MTT slopes while 'b' coefficient is negatively corelated. Solute species with significant C-MTT slopes are more chemodynamic and display higher mean annual concentrations (H_4SiO_4 , $b(H_4SiO_4)=-0.1$, $a(H_4SiO_4)=10^{-4}$), whereas species with weak C-MTT slopes show low mean annual concentrations and are nearly perfectly chemostatic ($a(Mg^{2+})=10^{-5}$, $b(Mg^{2+})=-0.016$, $a(K^+)=10^{-5}$, $b(K^+)=0$, figures 8, 9c and 9d). Our results show that a better knowledge of C-MTT relations is important to explain the contrasted C-Q shapes of chemical elements.

It is important to underline that the hydrological modeling with the NIHM code is performed independently and before any geochemical simulations with the KIRMAT code. The fact that the flow rates are well reproduced for all the hydrological contexts between 2010 and 2015 supports that the water transit times inferred from the NIHM code are realistic. The fact that the chemical composition of waters is well captured indicates that the combination of the geochemical parameters used in KIRMAT code is able to generate realistic reaction rates, as chemistry is well reproduced while respecting realistic water transit times. No modifications of the reactive surfaces and of the dissolution kinetic constants were necessary to reproduce the seasonal variability of the water chemistry. It is also important to emphasize that the simulated chemical compositions of waters remain far from a state of chemical equilibrium with respect to primary minerals. The calculated Gibbs free energy for the primary minerals ranges from -120 to -100 kJ/mol for apatite, -90 to -80 kJ/mol for biotite and anorthite and -30 to -20 kJ/mol for albite and K-feldspar. These far-from-equilibrium values for the Gibbs free energy imply that the reaction rates calculated using hydrogeochemical codes such as KIRMAT, which are based on the transient state theory (TST, Eyring, 1935; Murphy and Helgeson, 1987), are realistic for most of the primary minerals in this type of hydrological context. Regarding the simulations performed in this study, the relatively short residence times of waters and the precipitation of clay minerals prevent reaching a state of chemical equilibrium between waters and primary minerals. Relying upon a clay solid solution is also appropriate to mimic the clay mineral dynamic in this type of watershed, and a clay mineral assemblage precipitating at thermodynamic equilibrium is able to generate reliable water chemistry (this study) and realistic clay precipitation rates (more detail in Ackerer et al., 2018).

Our results indicate that it is not necessary to mix in different proportions soil and deep waters to generate chemostatic behavior, as proposed by Zhi et al. (2019). Chemostatic behavior can be generated within a single regolith layer with a homogeneous mineralogy, if as demonstrated, the transit time variability of shallow subsurface waters is dampened by seasonal fluctuations of flow line properties. A large storage of primary minerals and weathering product in the subsurface, as proposed in Musolff et al. (2015), is required but not sufficient to generate chemostatic behavior. Chemostatic behavior also depends on the covariation between flow velocities and flow lengths over changing hydrological conditions. Chemostatic behavior is not explained by a modification of the reactive-surface of minerals in the subsurface (i.e., Clow and Mast, 2010), or by an absence of chemical contrast between slow and rapid flows (i.e., Kim et al., 2017). The precipitation of clay minerals is essential to correctly capture the water chemistry in our study, but the dissolution or redissolution of clays is not a key process to explain chemostatic behavior (i.e., Li et al., 2017). Our study clearly supports the idea defended by Herndon et al. (2018) that a spatial and temporal variability in flow paths is a key process to explain C-Q relations in this type of headwater catchment. Our conclusions can most likely be extended to the other mountainous and relatively steep watersheds of this type, in which water pathways and short transit times are mainly controlled by gravity driven flow along slopes (Weill et al., 2019).

7- Conclusion

This study exemplifies the potential of coupling of low-dimensional and depth-integrated hydrological modeling with hydrogeochemical modeling as a way to better understand variability over time and space of the composition of surface and subsurface waters. The independent estimation of the water transit times provided by hydrological simulations is a clear added value to constrain the geochemical modeling approaches. Our study demonstrates that the seasonal variability of hydraulic conductivities along the slopes is a key process to understand the dynamic of flow lines and the changes of water transit times in the watershed. The variations in flow lines distributions from drought to flood events result in a modest seasonal variability of mean water transit times, which in turn explains the relative stability of the solute concentrations in waters. Our results also show that a better knowledge of the concentration-mean transit time relations (C-MTT relations) is an interesting new step to understand the diversity of C-Q shapes for different chemical elements. The consistency between measured and modeled concentrations while respecting the water-rock interaction times provided by the hydrological simulations shows that it is possible to capture the chemical composition of waters with simply determined reactive surfaces and standard kinetic constants. The results of our simulations strengthen the idea that the low surfaces calculated from the geometrical shapes of minerals are a good estimate of the reactive surfaces in this type of granitic catchment, and certainly the values to be used for hydrogeochemical modeling such as that performed in this work, in addition to the use of the experimental kinetic constants for mineral dissolution.

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Figure and table captions

Figure 1: sampling locations within the Strengbach catchment. Blue stars represent springs, blue diamonds represent piezometers, and the blue circle represents the stream at the outlet of the watershed. Green circles represent soil solution locations, and black diamonds represent bedrock facies locations.

Figure 2: on the left: calibrated field of thicknesses of the weathered material constituting the shallow unconfined aquifer at the Strengbach catchment used for the simulations by NIHM. The 1D surface draining network used in NIHM is represented by the black lines. The mesh for the groundwater compartment is represented by grey lines. On the right: fitting observed flow rates from the Strengbach stream at the outlet of the catchment with simulations of flow within the watershed (illustrated from 2010 to 2015). The subsurface compartment inherits from the aquifer thicknesses reported in the left panel, and the topography lets the natural outlet of the subsurface compartment being the surface draining network.

Figure 3: principle of the method of backtracking used to determine flow lines that generate flow at the outlet of the Strengbach catchment. Particles are dispatched along the wet fraction of the 1D river network (only one is represented here at a position *a* on 01/01/2010 at 23:59). NIHM generates an output heterogeneous velocity field at that date for the whole watershed, denoted $V_{01/01/2010}$. By using a velocity field of the same magnitude but opposite direction to the particle, the position of the particle is backtracked until 31/12/2009 23:59. Then, to further backtrack the trajectory of the particle, the velocity field is updated accordingly. The frequency of velocity field updates is set to one day.

Figure 4: at the top, flow lines of the subsurface that feed with water the surface draining network on March 1st, 2010 (on the left, high-flow period) and July 1st, 2010 (on the right, low-flow period). The color scale indicates that a water particle reaching the river at a given date started its travel along the streamline or passed at a given location on the streamline x days prior. The density of streamlines is associated with the flowing versus dry fraction of the river network at a prescribed date. Below, flow lines of the subsurface that feed with water the geochemical sampling sites on March 30th, 2010 (on the left, flood event) and November 29th, 2011 (right, drought event) according to NIHM simulations. For each sampling site, 10 particles were dispatched in the direct neighborhood of the site and then backtracked to render 10 stream lines. The color scale for times is similar to that of the top plot.

Figure 5: conceptual scheme used in the modeling of the water chemistry. The soil solutions are used as input solution. Cells represent the grid of the reactive-transport code KIRMAT. The regolith is discretized into a 1D succession of cells along the active parts of the flow lines determined by the NIHM hydrological model. The hydrogeochemical model KIRMAT evaluates transport and geochemical processes within each cell. The integrated chemistry of sampled waters is the arithmetic mean of solute concentrations with regularly distributed inlet points along a stream line.

Figure 6: maps of piezometric gradient and depth-integrated hydraulic conductivity for the Strengbach catchment, as simulated by NIHM, on 29/11/2011 (dry period) and 30/03/2010 (high flows period). The mean hydraulic conductivity is integrated normal to bedrock of the aquifer and thus depends on the water saturation of the vadose zone and the location of the water table.

Figure 7: simulation results for the CS1 spring for an important drought (29/11/2011) and a strong flood event (30/03/2010). At the top, active parts of the flow lines bringing the waters to the CS1 spring for the two sampling dates (7A and7B). Below, simulated chemical compositions of CS1 spring waters after integration along the flow lines and comparison with the initial soil solution and the spring chemistry data (7C and7D). Error bars show analytical uncertainties on measured concentrations and induced uncertainties in model results (the propagation in the KIRMAT simulations of analytical uncertainties from pH and chemical concentrations measured in the soil solutions).

Figure 8: simulation results for the CS1 spring over the whole range of the water discharges from the spring. Results are presented for H_4SiO_4, Na^+, K^+ and Mg^{2+} concentrations (8A, 8C, 8E and 8F), pH (8D) and mean water transit time (8B). Red lines indicate simulated parameters after integration along the flow lines, and blue points show measured values collected between 2005 and 2015. Corresponding dates and data for the modeled samples are given in table 1. The overall geochemical database is available in supplementary table EA1. Error bars show analytical uncertainties on measured concentrations and induced uncertainties in model results (the propagation in the KIRMAT simulations of analytical uncertainties from pH and chemical concentrations measured in the soil solutions). Fitting a power law of type $C=a*Q^b$ along the C-Q relations gives the following parameters: $a(H_4SiO_4)=10^{-4}$, $b(H_4SiO_4)=-0.1$; $a(Na^+)=7\times10^{-5}$, $b(Na^+)=-0.053$; $a(Mg^{2+})=10^{-5}$, $b(Mg^{2+})=-0.016$; $a(K^+)=10^{-5}$, $b(K^+)=0$.

Figure 9: (9A) evolution of solute concentrations for H_4SiO_4, Na^+, K^+, Mg^{2+} and Ca^{2+} as a function of mean water transit time in the Strengbach watershed. Water transit times are between 1.75 and 4 months for all the springs and piezometers in this study. (9B) Focus on the transit time window (1.75-4 months) for the studied waters and equations linking mean water transit

times and concentrations for H_4SiO_4, Na^+, K^+, Mg^{2+} and Ca^{2+}. Relations between transit times and concentrations are linear within this window (9C) relations between 'b' coefficients ($C=a*Q^b$) and the concentration-transit time slopes for the chemical elements. (9D) relations between 'a' coefficients ($C=a*Q^b$) and the concentration-transit time slopes for the chemical elements. Elements with significant concentration-mean transit time slopes are slightly chemodynamic (e.g. H_4SiO_4 and Na^+), while elements with low concentration-mean transit time slopes are almost chemostatic in the watershed (e.g. K^+ and Mg^{2+}). Ca^{2+} is not shown on 9C and 9D figures as this element is affected by a strong multi-annual concentration decrease that prevents a meaningful C-Q power law analysis (Ackerer et al., 2018).

Figure 10: simulation results for the PZ3 and PZ5 piezometers for a flood event (05/05/2015). At the top, active parts of the flow lines that bring waters to the two sampling sites (10A and 10B). Below, simulated chemical compositions of the piezometer waters after integration along the flow lines and comparison with the initial soil solution and the water chemistry data (10C and 10D). Error bars show analytical uncertainties on measured concentrations and induced uncertainties in model results (the propagation in the KIRMAT simulations of analytical uncertainties from pH and chemical concentrations measured in the soil solutions).

Figure 11: simulation results for the CS2 spring. At the top, active parts of the flow lines that bring water to the CS2 spring for drought (29/11/2011) and flood (30/03/2010) events (11A and 11B). The CS2 location results in more scattered flow lines than for CS1 spring. Below, simulation results for the CS2 spring over the whole range of experienced discharges (11C and 11D). Blue lines indicate simulated parameters after integration along the slowest flow line, yellow lines indicate simulated parameters after integration along the fastest flow line, and blue points show measured values collected between 2005 and 2015 (data in table 1 and in

supplementary table EA2). Error bars show analytical uncertainties on measured concentrations and induced uncertainties in model results (the propagation in the KIRMAT simulations of analytical uncertainties from pH and chemical concentrations measured in the soil solutions).

Figure 12: simulation results for the RH3 spring chemistry and for a flood event (30/03/2010). Left, simulated concentrations by assuming flow lines running through gneiss (GN) only (12A). Right, simulated concentrations by assuming flow lines running through hydrothermally altered granite (VS) only (12B). Error bars show analytical uncertainties on measured concentrations and induced uncertainties in model results (the propagation in the KIRMAT simulations of analytical uncertainties from pH and chemical concentrations measured in the soil solutions).

Figure 13: overview of the simulated flow lines in the subsurface that feed with water the geochemical sampling sites CS1, PZ3, and PZ5 on May 5th, 2015. The simulated chemical compositions after geochemical integration along the flow lines are compared with the initial soil solution and the spring chemistry data.

Table 1: measured pH, water discharges and chemical concentrations of H_4SiO_4, Na^+, K^+, Mg^{2+}, and Ca^{2+} in water samples collected at the Strengbach catchment and used for the hydrogeochemical modeling. The sampling sites include springs (CS1, CS2, RH3) and piezometers (PZ3, PZ5).

Table 2: Initial and calibrated values of the hydrodynamic parameters of the aquifer in the hydrological simulation of the Strengbach catchment by NIHM.

Table 3: Comparison between BET surfaces and geometric surfaces for the major primary minerals present in a granitic context. BET surfaces were measured via gas absorption

experiments by [1] Berger et al., 1994; [2] Chou and Wollast, 1985; [3] Lundstrom and Ohman, 1990; [4] Amrhein and Suarez, 1992; [5] Acker and Bricker, 1992; and [6] Guidry and Mackenzie, 2003. Geometric surfaces were recalculated from the granulometric ranges of the minerals and by assuming a spherical geometry.