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

Dear Editor,

The 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 reviewers comments, written in red to distinguish them from the comments, along with a marked-up manuscript version showing the changes made (with changes marked in red).

We would like to thank again the reviewers for the comments and suggestions, which helped us to improve our manuscript.

As you will see below, all comments and remarks have been taken into account.

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

Yours Sincerely

A handwritten signature in black ink, appearing to read 'F. Chabaux', with a long horizontal stroke extending to the left.

François Chabaux, on behalf of the authors.

Answer to Reviewers

Reviewer 1:

Anonymous Referee #1

Received and published: 19 February 2019

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

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

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

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

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

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

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

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

We acknowledge that a few recent works coupling hydrological and geochemical models were omitted. Those relying upon ParCrunchFlow (Beisman et al., 2015) and PHIM simulations (Li et al., 2017) are now quoted, while the introduction was slightly modified to present their content (lines 110-113). This rewriting also better mentions where to find the differences in our contribution compared with these previous works (lines 113-120).

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

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

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

These suggestions have been taken into account in the revised version. Notably, a paragraph has been added to state how the hydrological model is run to match the discharge data at the outlet of

the system (lines 200-222), and which indicator is used to assess the matching between model outputs and data (KGE: Kling Gupta efficiency coefficient, lines 217-219). A new table also gives the parameters used in the NIHM simulations (table 2). Additional information on the KIRMAT model is available. It is specified in the Section on methods (lines 249-252) that KIRMAT is based on the Transient State Theory; clay solid solutions are better depicted (lines 255-262). We also refer to the previous work by Ackerer et al., 2018 where additional information about KIRMAT is available.

Results Line 343: remove “that”

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

“That” in line 343 has been removed.

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

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

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

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

“hydrological methods’ section.

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

These points are now clarified but presented earlier in the manuscript. The fact that a clay solution precipitated at equilibrium can render reasonable precipitation rates for the Strengbach watershed case was previously discussed in Ackerer et al., 2018 (in section 6.2). To avoid useless repetition, the interested reader is referred to this recent work for more details (line 716).

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

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

The conclusions have been slightly trimmed (lines 729-748), but it was found difficult to shorten them more. The figures 7 to 11 have been improved (better organization of axes and titles). The plots are now individually labeled (e.g., 7A, 7B, 7C, 7D) and quoted as such in the main text to improve readability (example lines 669, 676). Error bars are drawn in the figures and their interpretation is given in the captions.

Reviewer 2:

Anonymous Referee #2

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1 **Crossing hydrological and geochemical modeling to understand the spatiotemporal variability**
2 **of water chemistry in an elementary watershed (Strengbach, France)**

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22 **Abstract**

23 Understanding the spatiotemporal variability of the chemical composition of surface waters is a
24 major issue for the scientific community, especially given the prospect of significant
25 environmental changes over the next decades. To date, the study of concentration-discharge
26 relationships has been widely used to assess the spatiotemporal variability of the water
27 chemistry over watersheds. However, the lack of independent estimations of water transit
28 times within catchments limits our ability to model and predict the water chemistry by relying
29 upon geochemical approaches only. This study shows the potential of coupling hydrological and
30 hydrogeochemical modeling to better understand the spatiotemporal variability of the
31 composition of surface waters. In a first step, a dimensionally reduced hydrological model
32 coupling surface flow with subsurface flow (i.e., the Normally Integrated Hydrological Model,
33 NIHM) has been used to constrain the distribution of the flow lines that are feeding the springs.
34 In a second step, hydrogeochemical simulations with the code KIRMAT (Kinetic Reaction and
35 Mass Transport) have been performed to calculate the evolution of the water chemistry along
36 the flow lines. The results indicate that the concentrations of dissolved silica (H_4SiO_4) and basic
37 cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) in the spring waters are correctly reproduced with a simple
38 integration along the flow lines. The water chemistry and clay mass fractions are also correctly
39 captured when clays are handled as solid solutions. The weak variabilities over time in the
40 spatial flow distribution and water velocities render mean transit time of waters that span the

41 narrow range of 1.5 to 3 months in the watershed. These findings indicate that the chemostatic
42 behavior of the spring chemistry is a direct consequence of the strong hydrological control
43 exerted on water transit times within the catchment. The good matching between the
44 measured and modeled concentrations while respecting durations of water-rock interactions
45 provided by hydrological simulations also shows that the chemical composition of waters can be
46 captured by relying upon simply determined reactive surfaces and experimental kinetic
47 constants. These results reinforce the idea that the low surfaces ($< 1 \text{ m}^2/\text{g}$) calculated from the
48 geometrical shapes of primary minerals are valuable estimates of the reactive surfaces within
49 natural environments. The originality of this study is to cross hydrological and geochemical
50 modeling to understand the spatiotemporal variability of hydrogeochemical processes in a
51 mountainous catchment with highly transient hydrological behavior and short water transit
52 times in the subsurface.

53 1- Introduction

54 Understanding the effects of the ongoing climatic changes on the environment is a major issue
55 for the coming years. The global increase of temperature is expected to affect the hydrological
56 cycle at a large scale, and providing a precise estimation of its repercussion on the evolution of
57 soils and on the chemistry of waters remains challenging. This challenge is associated with the
58 diversity of hydrological, geochemical, biological processes, and their coupling, that operate
59 over continental land surfaces (e.g., Gislason et al., 2009; Godd ris et al., 2013; Beaulieu et al.,
60 2012; 2016). Up to now, the study of concentration-discharge relationships has been widely
61 used to assess the coupling between hydrological and geochemical processes at the watershed
62 scale (Kim et al., 2017; Ameli et al., 2017). However, these concentration-discharge relationships
63 are mainly qualitative, and the lack of independent estimates of water transit times limits the
64 ability to model and predict solute mass transfers within catchments. A precise knowledge of
65 the water flow paths and their variability from wet to dry seasons is an important new step to
66 constrain the water transit times within catchments, and then decipher the seasonal
67 fluctuations of the composition of waters. Understanding the variability of water geochemical
68 compositions will require further development of modeling approaches able to combine
69 hydrological and geochemical processes (Kirchner, 2006).

70 Recent efforts in hydrological modeling were conducted to develop spatially distributed
71 approaches that better consider the interplay between surface and subsurface processes (e.g.,
72 Gunduz and Aral, 2005; Kampf and Burges, 2007; Camporese et al., 2010). Due to the
73 complexity of flows in the hydrological processes, several modeling approaches are based on
74 the full resolution of the Richards and Saint-Venant equations to correctly describe the

75 interactions between stream, overland and subsurface waters (Kampf and Burges, 2007). These
76 approaches have shown their ability to capture the hydrological functioning of various
77 watersheds, knowing that the full resolution of **the Richards** and Saint-Venant equations is
78 **computationally demanding** and faces calibration and parameterization difficulties (Ebel and
79 Loague, 2006; Mirus et al., 2011). Questions have been raised regarding the optimal complexity
80 of the equations that are needed to correctly treat the hydrology of catchments in their surface
81 and subsurface compartments with reasonable computation times (Gunduz and Aral, 2005).
82 Low-dimensional and depth-integrated models have attracted growing interest because they
83 represent an interesting compromise **between the system complexity, the calculation efforts,**
84 **and the quality of results** (Pan et al., 2015; Hazenberg et al., 2016; Weill et al., 2013; 2017;
85 Jeannot et al., 2018). These depth-integrated models recently demonstrated their ability to
86 reproduce the results from fully dimensioned approaches in small catchments while reducing
87 computational costs (Pan et al., 2015; Jeannot et al., 2018). Nonetheless, the water transit times
88 calculated from these depth-integrated models are rarely confronted with the water-rock
89 interaction times inferred from hydrogeochemical modeling of water chemistry in watersheds.

90 For its part, the understanding of the hydrogeochemical functioning of the critical zone has
91 been significantly **improved** by the implementation of reactive-transport **processes** in
92 geochemical modeling **tools** (Steeffel et al., 2005; Lucas et al., 2010; 2017; Godd ris et al., 2013;
93 Li et al., 2017). These developments allow for considering a variety of processes, such as flow
94 and transport, ion exchanges, biogeochemical reactions, and the interplay between primary
95 mineral dissolution and secondary mineral precipitation (Moore et al., 2012; Lebedeva and
96 Brantley, 2013; Ackerer et al., 2018). Reactive transport models have been used to explore a

97 wide variety of scientific issues, including the study of global atmospheric CO₂ consumption by
98 weathering reactions (Goddéris et al., 2013; Li et al., 2014), the formation and evolution of soil
99 and regolith profiles (Maher et al., 2009; Navarre-Sitchler et al., 2009; Lebedeva and Brantley,
100 2013), and the variability of water quality and chemistry in the environment (Lucas et al., 2010;
101 2017; Ackerer et al., 2018). However, these approaches usually refer to a simple one-
102 dimensional flow path through a regolith column or along a hill slope to model flow in the
103 system (e.g., Maher et al., 2011; Moore et al., 2012; Lucas et al., 2017; Ackerer et al., 2018). If
104 these approaches are useful to discuss the key processes involved in the regolith formation and
105 the acquisition of the water chemical composition, such one-dimensional transport reactive
106 modeling cannot take into account the diversity or the complexity of the flow trajectories in
107 watersheds; hence, its effects on the water chemistry at the watershed scale.

108 A new step is therefore necessary for the development of hydrogeochemical modeling
109 approaches that are applicable at the watershed scale and are able to integrate the complexity
110 of the water flows and the diversity of the water-rock interaction processes. Recent efforts have
111 been undertaken in this direction by merging hydrological and geochemical codes, as for
112 example the reactive transport code ParCrunchFlow (Beisman et al., 2015), or the coupled
113 hydrogeochemical code RT-Flux-PIHM (Li et al., 2017). An alternative to solving fully
114 dimensioned problems is given in the present study by considering an original dimensionally-
115 reduced approach, with modest computation times even when applied at the scale of a whole
116 watershed. The approach combines for the first time in this manner the results from a
117 hydrological depth-integrated and spatially distributed model (NIHM) with a reactive transport
118 model (KIRMAT). Such coupling allows for modeling the spatial and temporal distribution of the

119 flow trajectories and associated flow rates, the weathering reactions, and the evolution of the
120 water chemistry within an elementary watershed. The Strengbach catchment targeted by this
121 study is one of the reference observatories of the French critical zone network (OZCAR,
122 <http://www.ozcar-ri.org>), where multidisciplinary studies, including hydrological, geochemical
123 and geological investigations, have been performed since 1986 (“Observatoire
124 Hydrog ochimique de l’Environnement”, OHGE; <http://ohge.unistra.fr> ; El Gh’Mari, 1995;
125 Fichter et al., 1998; Viville et al., 2012; Gangloff et al., 2014; 2016; Pierret et al., 2014; Prunier et
126 al., 2015; Pan et al., 2015; Ackerer et al., 2016; 2018; Beaulieu et al., 2016; Chabaux et al., 2017;
127 Schmitt et al., 2017; 2018; Daval et al., 2018). The method proposed in this work will yield
128 precise knowledge of the water flow paths and their variability from wet to dry seasons, which
129 is an important new step to better constrain the water transit times within catchments and to
130 correctly understand the seasonal fluctuations in water chemistry.

131 **2- Site presentation and data acquisition**

132 The Strengbach catchment is a small watershed (0.8 km²) located in the Vosges Mountains of
133 northeastern France at altitudes between 883 and 1147 masl. Its hydroclimatic characteristics
134 can be found in Viville et al. (2012) or in Pierret et al. (2014). It is marked by a mountainous
135 oceanic climate, with an annual mean temperature of 6 °C and an annual mean rainfall of
136 approximately 1400 mm, with 15 to 20% falling as snow during two to four months per year.
137 The snow cover period is quite variable from year to year, and may not be continuous over the
138 entire winter. The annual mean evapotranspiration is of approximately 600 mm, and the annual
139 mean runoff of approximately 800 mm (in Viville et al., 2012). The watershed is currently
140 covered by a beech and spruce forest. The bedrock is a base-poor Hercynian granite covered by

141 a 50 to 100 cm-thick acidic and coarse-in-texture soil. The granitic bedrock was fractured and
142 hydrothermally altered, with a stronger degree of hydrothermal overprinting in the northern
143 than the southern part of the catchment (Fichter et al., 1998). The granite was also affected by
144 surface weathering processes during the Quaternary (Ackerer et al., 2016). The porous and
145 uppermost part of the granitic basement constitutes an aquifer from 2 to approximately 10
146 meters thickness. In the Strengbach watershed, the major floods and high-flow events usually
147 occur during snowmelt periods at the end of the winter season or in the early spring. In
148 contrast, the low-flow periods commonly happen at the end of the summer or during the
149 autumn. Several springs naturally emerge along the slopes (figure 1). The watershed has been
150 equipped with several piezometers and boreholes since 2012, those being located along the
151 slopes on both sides of the watershed (figure 1; Chabaux et al., 2017). **Spring waters are**
152 **regularly collected and analyzed since 2005, with monthly sampling campaigns completed by**
153 **occasional specific samplings to cover the entire range of water discharges in the system.**
154 **Piezometer waters have only been collected during specific sampling campaigns over the period**
155 **2012-2015, and as for the spring waters, these samplings cover different hydrological conditions**
156 **from wet to dry periods. The soil solutions are collected with a monthly frequency on the**
157 **southern slope at a beech plot (named HP) and to the north at a spruce plot (named VP; figure**
158 **1; more details are provided in Prunier et al., 2015).** For all the collected waters, the
159 concentrations of the major dissolved species and the pH were determined by following the
160 analytical techniques used at LHyGeS (Strasbourg, France) and detailed in Gangloff et al. (2014)
161 and Prunier et al. (2015). Discharges of water from the springs were measured during the
162 sampling campaigns, as were the water levels within the piezometers. The mineralogy and the

163 porosity of the bedrock have been studied in detail in previous studies (El Gh’Mari, 1995; Fichter
164 et al., 1998). On the southern part of the catchment, the weakly hydrothermally altered granite
165 (named HPT, figure 1) is mainly composed of quartz (35%), albite (31%), K-feldspar (22%) and
166 biotite (6%). It also contains small amounts of muscovite (3%), anorthite (2%), apatite (0.5%)
167 and clay minerals (0.5%). On the northern part of the catchment, the lithology is more variable,
168 with the presence of gneiss close to the crest lines and the occurrence of hydrothermally
169 altered granite on the rest of the slopes (El Gh’Mari, 1995, figure 1). **The hydrological,
170 geochemical and petrological data obtained from these field investigations are the basis of the
171 modeling work presented in this study.** More precisely, this study is based on hydrogeochemical
172 data from 2005 to 2015 for waters from four springs of the southern part (CS1, CS2, CS3 and
173 CS4) and one spring of the northern part (RH3) of the watershed. Hydrogeochemical data
174 obtained over the period 2012-2015 for two piezometers (PZ3, PZ5) of the southern part of the
175 watershed are also studied. **The complete hydrogeochemical database is available as
176 supplementary material appended to this work (tables EA1 to EA9). The specific chemical data
177 from spring and piezometer waters modeled in this study are reported in table 1.**

178 **3- Modeling methods**

179 **The modeling developments presented herein are a new step in the efforts undertaken at
180 LHyGeS to constrain the mechanisms controlling the geochemical composition of surface waters
181 and to understand their spatial and temporal variability at the scale of elementary mountainous
182 watersheds (Schaffhauser et al., 2014; Lucas et al., 2017; Ackerer et al., 2018).** The main
183 innovation of this work is to couple a spatially distributed hydrological model with a reactive
184 transport model to constrain the spatiotemporal variability of chemical composition of spring

185 and piezometer waters from the Strengbach watershed. To the best of our knowledge, this is
186 the first time that such a coupling between hydrological and hydrogeochemical modeling
187 approaches has been attempted at the watershed scale. The hydrological model determines the
188 distribution of the water flow lines within the watershed and thus constrains the water transit
189 times for any period (summer or fall droughts, winter or spring floods). Then, the
190 hydrogeochemical model is used to simulate the acquisition and the evolution of the water
191 chemistry along the determined flow lines within the catchment.

192 **3-1 Hydrological modeling**

193 To assess the water flows in the watershed, several simulations were performed with the
194 hydrological code NIHM (Normally Integrated Hydrological Model; Pan et al., 2015; Weill et al.,
195 2017; Jeannot et al., 2018). This code is a coupled stream, overland, and depth-integrated
196 subsurface flow model developed at LHyGeS and already tested in the Strengbach watershed
197 (Pan et al., 2015). The stream and overland flows are described by a diffusive-wave equation,
198 and the subsurface flow is handled through an integration (in a direction normal to bedrock) of
199 the unsaturated-saturated flow equation from the bedrock to the soil surface (Weill et al.,
200 2017). Water exchange between the surface and the subsurface compartments are addressed
201 via the hydraulic head differences between the compartments (Jeannot et al., 2018).

202 Regarding the hydrological simulations, the parameters of the aquifer were adjusted in NIHM
203 through a calibration-validation procedure. Several zones of heterogeneity were defined based
204 on field observations (Ackerer et al., 2016; Chabaux et al., 2017). In each zone, the saturated
205 hydraulic conductivity, the depth of the substratum, and the porosity, were set to uniform

206 values, but varying from one zone to the other. Other parameters were set to uniform values
207 over the whole catchment (see table 2). The aquifer thickness that was used for the simulations
208 varied from 2 m near the main crests to up to 8 m in the middle of the watershed (figure 2), in
209 agreement with data collected during the recent geological investigations and drilling
210 campaigns undertaken at the catchment (Ackerer et al., 2016; Chabaux et al., 2017). The
211 uniform precipitations over space applied at the surface of the catchment are drawn from data
212 of the rain gauge station located at the highest elevation of the watershed (site PA, figure 1).
213 The hydrological model NIHM was then run on a first time period (year 1996-1997). The model
214 parameters (table 2) were gradually modified within a simple trial and error process to improve
215 the fit between observed and simulated flow rates of the stream at the outlet of the catchment
216 (these flow rates are the only reliable hydrological data informing on surface and subsurface
217 flow at the catchment scale). The quality of fitting was evaluated via the root mean squared
218 error (RMSE) between observations and simulations, and the Kling-Gupta efficiency coefficient
219 (KGE; Gupta et al., 2009). Once the best fit was obtained, the model was then run over another
220 time period (2010-2015) without changing the parameters anymore, and the quality of the fit
221 was re-assessed on this new time period via the RMSE and KGE indicators. Figure 2 shows the
222 result for the 2010-2015 time period. Once the water discharges were correctly reproduced at
223 the outlet, a backtracking approach was used to constrain the origin of subsurface water exiting
224 the system at prescribed locations, and the spatiotemporal variability of the flow lines within
225 the watershed. To back track the water particles, the velocity fields calculated by the NIHM
226 model were inverted in their direction, and the locations of the backtracked particles were
227 saved at each time-step. A daily time-step was used for the backtracking, as a compromise

228 between computational efforts and a refined description of the transient velocity fields. A
229 schematic representation of the backtracking approach is given in figure 3. This methodology
230 allows for delineating the flow paths that bring water at a given time and a given location within
231 the catchment. This information is of major interest to determine the origin of the spring and
232 piezometer waters. It is shown at the catchment scale, that flow is mainly driven by gravity in
233 association with the steep slopes of the watershed, the latter being almost evenly drained over
234 its whole surface area (figure 4). For each water sampling area, ten flow lines that bring water to
235 the location of interest were determined (figure 4), together with a few features of the flow
236 lines, including: local velocities, mean velocities, and length of the flow paths. It is worth noting
237 that times calculated along the streamlines correspond to a date, x days before arrival, at which
238 a water particle entered the subsurface or passed at a given location along the streamline.
239 Streamlines calculated via backtracking and reaching sampling sites only consider flow in the
240 subsurface compartment (but there is no diffuse surface flow at the Strengbach catchment
241 except routing via the stream network) and are conditional to an arrival date at a prescribed
242 location. As streamlines are not associated with calculations of water flux values, the time
243 distributions drawn from streamline calculations are only an approximation of the actual transit
244 time distributions. An even weight is given to each calculated time, when an exact distribution
245 should weight each time by the mass of water conveyed.

246 **3-2 Hydrogeochemical modeling**

247 The simulations of the water chemical composition along the flow lines were performed with
248 the hydrogeochemical KIRMAT code (Kinetic of Reaction and MAss Transport; Gérard et al.,
249 1998; Lucas et al., 2010; Ngo et al., 2014). KIRMAT is a thermo-kinetic model based on the

250 Transition State Theory (TST, Eyring, 1935; Murphy and Helgeson, 1987) that simultaneously
251 solves equations describing geochemical reactions and transport mass balance in a 1D-porous
252 medium. The mass transport includes the effects of one-dimensional convection, diffusion and
253 kinematic dispersion. Chemical reactions account for the dissolution of primary minerals and
254 oxido-reduction reactions, in addition to the formation of secondary minerals and clay minerals.
255 The clay fraction is defined as a solid solution made up of a combination of pure clay end-
256 members. The clay end-members are defined on the basis of X-ray diffraction analyses of clay
257 minerals present in bedrock samples collected in the field (Fichter et al., 1998; Ackerer et al.,
258 2016; 2018). During the hydrogeochemical simulations, the clay solid solution is precipitated at
259 thermodynamic equilibrium and its composition varies over time, depending on the evolution of
260 the water chemistry and the bedrock mineralogy (Ackerer et al., 2018). This multicomponent
261 solid solution reproduces the non-pure composition of clay phases resulting from low-
262 temperature water-rock interactions (Tardy and Fritz, 1981). The KIRMAT code also accounts for
263 the feedback effects between mineral mass budgets, reactive surfaces, and porosity evolution
264 (Ngo et al., 2014). The reactive surfaces of the primary minerals were calculated by assuming a
265 simple spherical geometry for all the minerals, and the mean size of the minerals was estimated
266 from thin section observations of the bedrock samples. During the simulations, the clay mineral
267 precipitation and the evolution of reactive surfaces of primary minerals are tracked together
268 with chemical processes and water chemical composition. However, in view of the short time
269 scales of transport rendered by the hydrological simulations (weekly to monthly timescale), the
270 change in reactive surfaces of primary minerals became negligible. Precipitation of other
271 secondary minerals such as carbonates, hematite or amorphous silica was tested, but these

272 minerals were not formed given the hydroclimatic context of the Strengbach catchment. The
273 secondary mineral precipitation is therefore controlled by the formation of clay minerals. The
274 KIRMAT code has already been applied in geochemical modeling of alluvial groundwaters (Lucas
275 et al., 2010) and surface waters (Lucas et al., 2017; Ackerer et al., 2018).

276 For this study, the modeling strategy is adapted from Ackerer et al. (2018) to consider the new
277 transit time and water mixing constrains provided by the hydrological code NIHM. To capture
278 the chemical composition of the spring and the piezometer waters, numerical simulations were
279 performed along the flow lines that were determined through the backtracking approach. A
280 sketch of the hydrogeochemical modeling strategy is provided in figure 5. For each flow line,
281 several KIRMAT simulations were performed with different starting positions along the active
282 part of the line. The starting positions represent the locations at which the soil solutions
283 percolate through the subsurface shallow aquifer. These variable starting positions are spaced
284 with a constant distance along the flow line. The deepest soil solutions collected to the south of
285 the catchment at the beech plot (HP) and to the north at the spruce plot (VP) were assumed
286 representative of the soil solutions for the whole southern and northern slopes of the
287 catchment, respectively. The data of the soil solution chemistry used in this study are available
288 in Prunier et al. (2015) and in supplementary tables (tables EA6 and EA7). These soil solutions
289 aggregate the effects of the various surface processes occurring before percolation into the
290 bedrock. As the soil solution evolutions over time are monitored and injected as such into the
291 modeled aquifer, the temporal variability of the soil solution chemistry and its repercussion on
292 the water-rock interactions along the flow paths are taken into account by the modeling
293 approach. Data related to the bedrock properties, such as the mineralogical compositions, the

294 mineral reactive surfaces, and the kinetic constants of dissolution reactions, are given in Ackerer
295 et al. (2018) and in supplementary tables (tables EA10 to EA13). By following this strategy, the
296 simulations that consider soil solutions percolating at the upper part of the catchment reflect
297 the chemical evolution of waters with long path lengths and long transit times within the
298 aquifer. By contrast, shorter path lengths and shorter transit times are associated with the
299 percolation of soil solutions that occurs in the vicinity of the sampling locations (figure 5).
300 Because the springs or the piezometers collect waters from different origins and with
301 contrasted transit times, integration along each water flow line was performed. The aim of the
302 integration is to determine the mean chemical composition resulting from the mixing of the
303 waters characterized by variable transit times (figure 5). The integrated chemical composition of
304 the waters provided by a given flow line is calculated by taking the arithmetic mean of the
305 solute concentrations calculated by the succession of the KIRMAT simulations along the flow
306 line (figure 5). This arithmetic mean reflects a simple full mixing of uniform water fluxes
307 irrespective of their short or long transit times. In other words, the geochemical simulations are
308 based on the hypothesis of spatially homogenous water-rock interactions within the watershed.
309 The soil solutions are assumed to percolate uniformly within the aquifer and are then conveyed
310 along the slopes by uniformly distributed mass of water until reaching the sampling locations.

311 **4- Hydrological modeling results**

312 **4-1 Spatial variability of the flow lines**

313 The results provided by the hydrological code NIHM show that to first order, the Strengbach
314 catchment is well drained and that the topography exerts an important control on the flow line

315 distribution (figure 4). Along the hillsides **with uniform** or slightly convex slopes, the water flow
316 lines **show** simple characteristics. The flow paths are nearly parallel, and the water velocities are
317 similar along the different flow lines on this type of hillside. The water velocities tend to
318 increase when moving downstream (longer traveled distances for a given transit duration, figure
319 4), with slower velocities near the main crests and higher velocities on the steepest parts of the
320 hillsides. The waters collected along this type of hillside are therefore characterized by small
321 variability of transit times. This is the case for the CS1, CS3 and RH3 spring waters located on the
322 southern and northern parts of the catchment (figure 4). This is also the case for the
323 piezometers PZ3 and PZ5 in the southern part of the watershed (figure 4). For the samplings
324 located on **uniform** or slightly convex slopes (CS1, CS3, RH3, PZ3 and PZ5), the characteristics of
325 the different flow lines that feed each site are therefore comparable for a given site and for a
326 given date. By contrast, in the vicinity of the valley and in the topographic depressions, the
327 hydrological modeling indicates that the flow line characteristics are more variable. Because
328 flow lines coming from different **hillsides** can feed a topographic depression, **the** mixing of
329 different flow lines with variable flow paths and contrasting water velocities can occur at these
330 locations. The waters collected in valleys or in topographic depressions are therefore
331 characterized by a higher variability of transit times. This is the case for the CS2 and CS4 springs,
332 which are located in a depression in the axe of the small valley and surrounded by slopes with
333 various orientations and a complex flow line distribution (figure 4). For these two springs, the
334 characteristics of the different flow lines can be different for a given date.

335 **4-2 Temporal variability of the flow lines**

336 Hydrological modeling under general transient conditions can render the evolution over time of
337 water flows in the Strengbach watershed but also of other hydraulic variables or parameters. As
338 an example, after an important rainfall event (30/03/2010, in figure 6), snapshots of the average
339 hydraulic conductivity in the subsurface show increasing values with decreasing elevation in the
340 watershed. The same observation holds for hydraulic conductivity during drought periods (see
341 29/11/2011, in figure 6). Provided that the hydraulic head gradient is largely dominated by the
342 topography and therefore almost constant over time (figure 6), the water velocities are
343 increasing along the flow lines from crests to valleys, irrespective of the wet versus dry
344 hydrological periods. For the CS1 spring, the mean flow velocities along the flow lines vary from
345 approximately 1 m/day to 7 m/day between the severe drought of 29/11/2011 and the strong
346 flood of 30/03/2010 (figures 7A and 7B). These events correspond to the annual maximum and
347 minimum observed flow rates of the stream at the outlet of the Strengbach watershed. For the
348 same dates, the mean velocities vary from 2 – 12 m/day, 1 – 4 m/day and 1 – 9 m/day for the
349 springs CS2, CS3 and CS4, respectively. The variations from drought to flood are very similar for
350 the piezometer waters, with velocities in the ranges 2 – 10 m/day and 2 – 12 m/day for the PZ3
351 and PZ5 piezometers, respectively. The RH3 spring located on a steeper part of the northern
352 slopes exhibits flow velocity variations from 5 to 20 m/day from dry to flood conditions. In
353 addition to the flow velocity variations, the hydrological simulations also reveal variability in the
354 lengths of the active parts of the flow lines. Such variability is triggered by the particular
355 seasonal variations of the hydraulic conductivities within the catchment. During periods of
356 drought, the simulations indicate a strong decrease of hydraulic conductivities close to the main
357 crests and much smaller variations at mid-slopes (figure 6). The crests rapidly dry out, whereas

358 the areas at mid-slopes still supply some water to the stream network. These contrasting
359 hydrological behaviors result from the differences in aquifer thickness and water storage
360 between the crests and the other parts of the catchment (figure 2). A thin aquifer, flow
361 divergence and the absence of feeding areas prevent large water storage on the crests, in
362 opposition to mid-slope parts with much thicker aquifers and the presence of feeding areas
363 upstream. This particular pattern simulated for the hydraulic conductivities implies that the
364 active parts of the flow lines extend up the main crests during important floods, whereas they
365 are limited to mid-slopes after a long dry period. The consequence of this hydrological
366 functioning is to moderate the seasonal variations of the transit times of waters, as the active
367 lengths of flow lines vary simultaneously with water flow rates. Calculations indicate that for the
368 spring and piezometer waters collected in this study, the mean transit times of waters only vary
369 from approximately 1.75 to 4 months between the strongest flood and the driest conditions.
370 These short subsurface water transit times are explained by the small size of the catchment and
371 gravity driven flow along steep slopes.

372 **5- Hydrogeochemical modeling results**

373 Modeling the geochemical composition of waters from the different springs and piezometers
374 selected for this study was performed following the procedure described in paragraph 3-2. The
375 results are presented below by grouping sources and piezometers according to their
376 hydrogeological characteristics.

377 **5-1 CS1 and CS3 springs (southern slope)**

378 The CS1 and CS3 springs emerge on the same slope and drain the same rocks. Their hydrological
379 behavior is also very similar in terms of flow lines and water transit times. The interesting
380 consequence of the simple flow line distribution for these springs is that a single flow line can be
381 considered as representative of all the flow lines that are feeding the spring, irrespective of the
382 hydrological conditions. Hydrogeochemical simulations were performed along a single flow line
383 for different hydrological periods using the methodology illustrated in figure 5. The case of CS1
384 spring is used below to highlight the main results obtained from this approach. For the strong
385 flood of 30/03/2010, the KIRMAT simulations modeling the waters coming from the proximity of
386 the spring and characterized by short transit times produced too much diluted solutions,
387 whereas the waters coming from the main crests are too much concentrated to reproduce the
388 spring water chemical composition. However, after an integration of all the waters arriving at
389 CS1 with the different transit times employed for the simulation, the resulting geochemical
390 composition correctly reproduces the chemical composition of CS1 spring water at this date
391 (H_4SiO_4 , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations, figure 7D). A similar conclusion is obtained for
392 the important drought of 29/11/2011. Again, geochemical integration of all the waters arriving
393 at CS1 along a water line but with different transit times correctly reproduces the chemical
394 composition of the CS1 spring waters collected on this date (figure 7C). This is actually the case
395 regardless of the time period considered. The coupled hydrological and hydrogeochemical
396 approach has been applied for the CS1 spring for 6 dates covering the whole range of the water
397 discharges of the spring (table 1). The modeling results reveal the seasonal variations of the
398 water chemical composition of the CS1 spring over the whole range of observed flow rates at
399 CS1 (figure 8). Simulations especially account for the 20-30% variation in H_4SiO_4 concentrations,

400 the 10-20% variation in Na^+ concentrations, and the relatively stability of the pH of the CS1
401 waters (figures 8A, 8C, 8D). The response in concentration of each chemical element to a
402 change in water discharge is associated with the initial soil solution concentrations, the nature
403 of primary minerals leached by water, and the degree of its incorporation into the clay solid
404 solutions. For example, Na is only provided by a single primary mineral (albite) and is weakly
405 incorporated into clays. Si is provided by several primary minerals (albite, biotite, K-feldspar, ...)
406 and strongly incorporated in clays that are characterized by varying precipitation rates with
407 hydrological conditions. These points explain why the response of solute concentrations to
408 hydrological changes is variable for each element. Similar results are obtained for the CS3 spring
409 (figure EA1), showing, as for the CS1 spring, that the proposed modeling approach is able to
410 correctly capture the water chemical composition of the CS3 spring.

411 **5-2 PZ3 and PZ5 piezometers (southern slope)**

412 The two piezometers PZ3 and PZ5 are located on the southern part of the catchment, and their
413 waters drain granitic bedrock similar to that drained by the CS sources. As for the CS1 and CS3
414 springs, the NIHM modeling results show that the flow lines arriving at the PZ3 piezometer are
415 characterized by a relatively simple distribution. The flow lines are close to each other, and they
416 render similar water velocities on the slopes (figure 4). For the PZ5 piezometer located
417 downstream, the flow lines cover a larger area on the slope, especially during droughts (figure
418 4). However, for a given date, all the flow lines show similar velocities, with particularly fast
419 flows on a lower portion of the hillslope. These results imply that, as for the CS1 and CS3
420 springs, the hydrogeochemical simulations of PZ3 and PZ5 piezometer waters can be performed
421 by relying upon a single flow line representative of all the waters collected by the piezometers

422 on a given date. The geochemical integration along the flow line has been performed in the
423 same manner as detailed above, and this approach is able to reproduce the chemical
424 composition of the waters of the two piezometers, as illustrated in figure 9 for the flood of the
425 05/05/2015 and in figure EA2 for the dry conditions of 10/11/2015. Together, these modeling
426 results show that the linear or slightly convex slopes on the southern part of the catchment
427 allow to correctly capture the water chemistry of each sampling site with a straightforward
428 integration along a single and representative flow line.

429 **5-3 The CS2 and CS4 springs (in the valley axe)**

430 CS2 and CS4 spring waters drain the same granitic bedrock as the CS1 and CS3 waters, but are
431 located in the axe of the small valley of the Strengbach stream and surrounded by slopes of
432 various orientations and inclinations (figure 4). Consequently, the distribution of the flow lines is
433 much more scattered than for the CS1 and CS3 springs. The modeling strategy applied for these
434 two springs and the results are detailed below for the CS2 spring. For this spring, and for all the
435 hydrological conditions, two different groups of flow lines have been determined by the
436 backtracking approach: a northern group characterized by relatively slow velocities and a
437 southern group with higher velocities (figure 4). When the hydrological conditions vary from a
438 strong flood (30/03/2010) to an important drought (29/11/2011), the flow rates tend to
439 decrease along all the flow lines (figures 10A and 10B). For example, the mean flow velocities
440 along the flow lines vary from approximately 12 m/day to 2 m/day between these two dates.
441 However, for a given date, the northern group systematically renders slower velocities than the
442 southern group. This scattered distribution of the flow lines implies that a single specific flow
443 line cannot be representative of all the waters collected by the spring. The flow lines calculated

444 using the NIHM model allow for constraining the trajectories of the waters within the
445 watershed; however, the simulations performed in this study cannot provide the mass fluxes of
446 water carried by each flow line. Consequently, a straightforward calculation of the chemistry of
447 the CS2 spring, such as detailed above for CS1, is not applicable because the mixing proportions
448 between the different flow lines are unknown. Alternatively, it is possible to determine the
449 concentrations in the waters carried by the slowest and the fastest flow lines that are feeding
450 the spring and to compare the results with the observed chemistry of the spring water. The
451 results indicate that for all the hydrological conditions, the concentrations calculated from the
452 geochemical integration along the slowest and the fastest flow lines are able to correctly frame
453 the chemical composition in terms of H_4SiO_4 , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} of the CS2 spring waters
454 (results are presented for H_4SiO_4 and Na^+ in figures 10C and 10D). The observed chemistry of the
455 CS2 spring is bounded by the chemical compositions of the waters carried by the slowest and
456 fastest flow lines. The modeling results also suggest that the contributions of the slow and fast
457 flow lines are comparable over most of the hydrological conditions, as the observed
458 concentrations are in general at the midpoint between the min (i.e., fast) and max (i.e., slow)
459 boundaries (see figures 10C and 10D). It is only for the important droughts that the spring
460 chemistry seems to be mainly controlled by the southern and faster group of flow lines. Further
461 works to precisely estimate the mass fluxes of water carried by each flow line are necessary to
462 calculate the chemistry of the CS2 spring water with a weighted mixing calculation. The same
463 conclusions apply to the CS4 spring located in the proximity of CS2 spring.

464 **5-4 The RH3 spring (northern slope)**

465 The RH3 spring is located on the northern part of the catchment (figure 4), where steep slopes
466 imply fast water velocities and subparallel flow lines. However, if the distribution of the flow
467 lines on the RH3 hillside is simple (as for the CS1 and CS3 springs) the precise lithological nature
468 of the bedrock drained by the RH3 waters is more difficult to constrain (see also Ackerer et al.,
469 2018). Unlike the southern slope, the bedrock of the northern part of the catchment exhibits a
470 complex lithology, with gneiss outcropping in the upper part of the slope and granite of variable
471 degree of hydrothermal overprinting in the intermediate and lower parts. These lithological
472 variations can explain the differences in chemical composition between the RH3 spring waters
473 and the waters of the southern part of the catchment: the RH3 spring waters are characterized
474 by systematically higher concentrations of K^+ and Mg^{2+} cations but show similar concentrations
475 for the other major elements (Ackerer et al., 2018; Pierret et al., 2014). **The vertical extension of
476 the gneiss formation and the spatial variability of the hydrothermal overprinting along the
477 northern slopes of the catchment are not very well known, which renders impossible the
478 straightforward modeling of the RH3 spring water composition, as it was done for the CS1 and
479 CS3 sources.** Alternatively, simulations of two extreme cases can be performed by assuming that
480 the flow lines only run, either on gneiss or on hydrothermally altered granite. When only
481 considering the hydrothermally altered granite (**VS facies**), the simulated concentrations of
482 H_4SiO_4 and Na^+ are close to the measured ones. However, the concentrations of K^+ and
483 especially Mg^{2+} are clearly underestimated (**figure 11B**). In the case of the flow lines only
484 running on gneiss (**GN facies**), the simulated concentrations of H_4SiO_4 and Na^+ also match the
485 data. However, due to the higher abundance of biotite in the gneiss, the simulated
486 concentrations of K^+ and Mg^{2+} are higher than the measured ones (**figure 11A**). At this stage, it is

487 therefore reasonable to propose that the chemical composition of the RH3 spring waters
488 reflects mixing of the two lithological influences. By assuming a geochemical conservative
489 mixing, which is likely a too simplistic scenario, the results would indicate that the flow lines
490 portions running on gneiss and on hydrothermally altered granite count for approximately 40-
491 50% and 50-60% of the total water path length, respectively. Further works to estimate the
492 location of the contact between gneiss and granite are required for more realistic modeling and
493 hence a deeper interpretation of the chemical composition of RH3 spring waters. In any case,
494 the important point to stress here based on the above simulations is that the complex lithology
495 and bedrock heterogeneity mainly impact the K^+ and the Mg^{2+} budget of the RH3 waters, but not
496 or only slightly the H_4SiO_4 and Na^+ concentrations, which control the main part of global
497 weathering fluxes carried by the Strengbach spring waters. These results readily explain why
498 although the RH3 spring waters exhibits higher Mg^{2+} and K^+ concentrations than the other CS
499 springs, they carry relatively similar global weathering fluxes (Viville et al., 2012; Ackerer et al.,
500 2018).

501 **6- Discussion**

502 The modeling approach proposed in this study and based on the coupling of the NIHM and
503 KIRMAT codes, allows for building a better modeling scheme than those commonly used in
504 previous studies regarding the hydrogeochemical modeling of surface waters at the watershed
505 scale. In such previous works, the geochemical simulations were performed mainly along a
506 single 1D flow line, only characterized by homogeneous mean hydrological properties (Goddéris
507 et al., 2006; Maher et al., 2011; Moore et al., 2012; Lucas et al., 2017; Ackerer et al., 2018). In
508 the previous study on the Strengbach watershed (Ackerer et al., 2018), the soil solutions were

509 also assumed to percolate in the bedrock only at a single starting point of the flow lines.
510 Although these previous approaches were useful for determining the long-term evolution of
511 regolith profiles and/or the mean chemistry of waters at the **multiyear** scale, they cannot be
512 used to discuss the seasonal variations of the water chemical composition. The NIHM-KIRMAT
513 coupling approach makes this possible, as it provides the spatial distribution of the flow lines at
514 the watershed scale and their variations over time. Furthermore, the proposed modeling
515 approach also integrates a soil solution percolation scheme with inlets uniformly distributed
516 along the slope, which is more realistic than a scheme assuming that each sampled site is fed by
517 a single flow line carrying waters with a unique transit time. The consistency of the modeling
518 results with the measured concentrations over the whole range of the hydrological conditions
519 certainly gives weight to the application of the proposed modeling approach to the Strengbach
520 catchment. Such consistency also gives weight to the assumptions made regarding the
521 modeling parameters used in this work, i.e., reactive surfaces and kinetic constants. It also gives
522 weight to the conclusions and implications that can be deduced regarding the
523 hydrogeochemical functioning of the watershed, and the origin of the chemostatic character of
524 these waters. These different points are detailed below.

525 **6-1 Choices of the reactive surfaces and the kinetic constants**

526 For the geochemical simulations performed in this study, the kinetic constants that were used
527 to describe the dissolution reactions of the primary minerals are standard constants determined
528 through laboratory experiments (**supplementary table EA12**). The reactive surfaces of the
529 primary minerals were calculated by assuming a simple spherical geometry for all the minerals
530 (**supplementary table EA10**). Such choices **might** appear surprising as over the last years, several

531 studies have suggested that the kinetic constants determined through laboratory experiments
532 overestimate the rates of the dissolution reactions in natural environments (White and
533 Brantley, 2003; Zhu, 2005; Moore et al., 2012; Fischer et al., 2014). The origin of this laboratory-
534 field discrepancy is still a matter of debate (Fischer et al., 2014). Different processes have been
535 proposed to explain the gap between laboratory and field estimates, such as the
536 crystallographic anisotropy (Pollet-Villard et al., 2016), progressive occlusion of the primary
537 minerals by clays (White and Brantley, 2003), or the formation of passivation layers at the
538 surfaces of the minerals (Wild et al., 2016; Daval et al., 2018). The difficulty to reconcile field
539 and laboratory estimates can also be related to the challenge of defining relevant reactive
540 surfaces at different space scales (Li et al., 2006; Navarre-Sitchler and Brantley, 2007). The
541 present modeling work regarding the Strengbach catchment shows that the chemical
542 composition variability of the spring and piezometer waters is fully captured via geometric
543 reactive surfaces and standard kinetic constants, while respecting the water-rock interaction
544 times within the catchment. This result suggests that the mean rates of the weathering
545 reactions employed in this modeling work are realistic, which in turn implies that the modeling
546 approach developed in this study does not underline significant mismatches between field and
547 laboratory reaction rates. More details are given in the following to investigate why geometric
548 reactive surfaces and standard kinetic constants are able to correctly capture the water
549 chemistry. The calculated rates of the dissolution reactions depend on the product between the
550 kinetic constants of the reactions and the mineral reactive surfaces. In the experimental studies
551 performed for determining the kinetic constants of dissolution reactions, the constants are
552 usually determined by normalizing the experimental weathering rates with the Brunauer-

553 Emmett-Teller surfaces determined from experiments of gas absorption (BET surfaces; Chou
554 and Wollast, 1986; Lundstrom and Ohman, 1990; Acker and Bricker, 1992; Amrhein and Suarez,
555 1992; Berger et al., 1994; Guidry and Mackenzie, 2003). In table 3, the BET surfaces are
556 compared with the geometric surfaces of the minerals involved in the dissolution experiments,
557 recalculated from the size ranges of the minerals. For most of the minerals (apatite, quartz,
558 albite, K-feldspar, and anorthite), the geometric surfaces are within the same order of
559 magnitude as the BET surfaces, even if often slightly lower (table 3). However, as the BET
560 surfaces are determined with fairly large uncertainties, especially for low BET surfaces (up to \pm
561 70%), and as they can be very different depending on the gas used (up to 50% of difference
562 between N₂ or Kr absorption; Brantley and Mellott, 2000), the above differences between the
563 geometrical and the BET surfaces cannot be considered significant for the majority of minerals
564 used in the Strengbach simulations. A significant difference only appears for biotite, with the
565 geometric surfaces one order of magnitude less than the BET surfaces (table 3). However, for
566 biotite, due to its layered structure, it has been shown that approximately 80 – 90% of the
567 surface area accessible by the gases used to estimate BET surfaces is not accessible for
568 weathering reactions (Nagy, 1995). In the case of biotite, the effective surface area for the
569 water-rock interactions would thus be, in a rather fortuitous manner, a surface area close to the
570 geometric one. The above considerations and observations thus explain why for a granitic
571 bedrock as found in the Strengbach catchment, the geometric surfaces are relevant to describe
572 the surfaces of water-rock interactions at the space and time scales of this study. An immediate
573 corollary is that the values of the standard kinetic constants (table EA12) are also appropriate to
574 calculate reaction rates with mineral geometric surfaces in our modeling approach. This ability

575 may be related to the fact that all the minerals that have been used in the dissolution
576 experiments and in the kinetic studies were collected in the field (e.g., Acker and Bricker, 1992;
577 Amrhein and Suarez, 1992). These minerals were likely affected by anisotropy, passivation
578 layers, and any types of aging effects related to long-term water-rock interactions. Our results
579 might therefore mean that the standard kinetic constants obtained in such experiments
580 integrate the aging effects that have affected the reactivity of the primary minerals in natural
581 environments. This would explain why it is possible to capture the full variability of the water
582 chemistry in an elemental catchment with simple geometric reactive surfaces and standard
583 kinetic constants. It is important to emphasize at this stage that the results of our simulation
584 strengthen the idea that the low surfaces calculated from the geometrical shapes of minerals
585 provide good estimates of the reactive surfaces within the natural environment (Brantley and
586 Mellott, 2000; Gautier et al., 2001; White and Brantley, 2003; Zhu, 2005; Li et al., 2017). They
587 are certainly the values to be used for hydrogeochemical modeling such as that performed in
588 this work, in addition to the use of the experimental kinetic constants for mineral dissolution.
589 These conclusions are certainly not specific to the Strengbach catchment and could be
590 applicable to many other granitic catchments.

591 **6-2 Implications for the acquisition of the water chemistry**

592 The results of the NIHM-KIRMAT hydrogeochemical modeling have strong implications
593 regarding the hydrogeochemical functioning of the Strengbach watershed. The NIHM modeling
594 shows that the hydrological functioning of the watershed is correctly simulated by water
595 circulations in the shallow subsurface, i.e., in a saprolitic aquifer. No contribution of waters
596 circulating in the deep fracture network of the granitic bedrock and observed during the drilling

597 campaigns is necessary. The deep-water circulation pathways are probably disconnected from
598 the shallow subsurface, or with mean hydraulic heads less than those of the subsurface, at least
599 at the Strengbach catchment scale, and does not significantly impact the water budget of the
600 Strengbach catchment. As detailed in section 4-1, the modeling results show that water in the
601 shallow aquifer flows along streamlines with fairly simple geometries. At the scale of the
602 watershed (figure 4), the geometry of the flow lines validates the hypothesis built on the basis
603 of the geochemical and Sr-U isotopic data that the spring waters of these mid-mountain basins
604 (i.e., the Ringelbach and Strengbach watersheds; Schaffhauser et al., 2014; Pierret et al., 2014)
605 are supplied by waters from distinct flow paths without real interconnections. More
606 importantly, the modeling results emphasize the importance of water transit times within the
607 watershed as a main feature controlling the chemical composition of subsurface waters at the
608 Strengbach catchment. Along all the slopes, the waters coming from the proximity of the crests
609 and characterized by a long transit time systematically render higher concentrations than the
610 waters with shorter pathways and transit times. When the hydrological conditions change from
611 wet to dry periods, the solute concentrations also tend to increase with the increase in the
612 mean transit time of waters. Our results demonstrate in particular that for the CS1 source and
613 for the PZ3 and PZ5 piezometers, all located on the southern slope of the watershed, over a
614 homogeneous granitic bedrock, and all characterized by flow lines of fairly simple geometries
615 (section 4), the spatial and temporal variations of their geochemical composition are fully
616 explained by differences in water residence times (figure 12). Residence time variations
617 between high and low discharge periods explain the temporal variations of geochemical
618 signatures within each site, and the differences in mean residence times of waters supplying the

619 different sources and piezometers explain the various chemical compositions between the
620 different sites (figure 12). Only the CS2 and CS4 springs, located in a depression, are supplied by
621 two different types of water flow lines, the contribution of which could change over time.
622 However, the mixing of different flow lines has probably a relatively modest impact, and at the
623 scale of the watershed, the results show that the duration of water-rock interaction exerts a
624 first-order control on the chemical composition of waters, in addition to the lithological
625 parameter. This study brings also strong constrains on the spatial repartition of the weathering
626 processes. For the modeling strategy developed in this study, the chemical composition of the
627 spring and piezometer waters are calculated by integrating the chemical composition of waters
628 introduced at different starting positions along the active part of the flow lines (figure 5). In
629 each of the simulations, a fixed distance between the initial positions of the KIRMAT simulations
630 along the flow lines was used. The modeling results show that through the geochemical
631 integration, the concentrated waters coming from the main crests are naturally
632 counterbalanced by the diluted waters infiltrating close to the sampling sites. From flood to
633 drought events, the mean transit times are obviously impacted by the variable velocities along
634 the flow lines, but regardless of the hydrological conditions, it is always possible to explain the
635 water chemistry of the sampling sites with the above integration scheme. Such repeatable
636 consistency between data and simulations indicates that this circulation scheme is certainly
637 quite realistic for the Strengbach catchment. This scheme supports the idea suggested in
638 Ackerer et al. (2016) that at the scale of the watershed, the solute chemistry is acquired through
639 reactions and weathering processes that are spatially relatively homogenous within the
640 watershed.

641 **6-3- Origin of the chemostatic behavior in the Strengbach catchment**

642 The hydrogeochemical monitoring of the spring, piezometer, and stream waters performed in
643 the Strengbach catchment clearly shows that this catchment has a chemostatic behavior (e.g.,
644 Viville et al., 2012; Ackerer et al., 2018; this study). All the spring and the piezometer waters
645 have chemical concentrations impacted by changes in the hydrological conditions, but the
646 concentration variation ranges are by far narrower than variation ranges of water discharges,
647 which define the chemostatic behavior of a hydrological system. For the waters exhibiting the
648 largest concentration variations (spring CS1), a moderate increase of approximately 10-30% in
649 the concentrations of H_4SiO_4 and Na^+ is observed from floods to severe drought events, while
650 the water discharges may vary by a factor of 15 (figures 8A and 8C). This weak variability of the
651 solute concentrations over a wide range of water discharges is not specific to the Strengbach
652 catchment; it has rather been observed in several watersheds spanning different climates and
653 hydrological contexts (Godsey et al., 2009; Clow and Mast, 2010; Kim et al., 2017). Different
654 origins for the chemostatic behavior have been proposed, such as a modification of the mineral
655 reactive surfaces during changing hydrological conditions (Clow and Mast, 2010), a small
656 concentration difference between slow and fast moving waters (Kim et al., 2017), or the fact of
657 reaching an equilibrium concentration along the water pathway (Maher, 2010). To date, the
658 study of concentration-discharge relationships has been intensively used to assess the
659 chemostatic behavior of waters (Godsey et al., 2009; Kim et al., 2017; Ameli et al., 2017).
660 However, the lack of precise estimates of water transit times limits the ability to clearly discuss
661 the origin of the chemostatic behavior on the single basis of the concentration-discharge
662 relationships. The coupled approach presented in this study offers a renewed opportunity to

663 discuss the origin of the chemostatic behavior in catchments because the acquisition and the
664 evolution of the water chemistry can be simulated along flow lines determined via timely and
665 spatially distributed hydrological modeling. The strength of this approach is to constrain water
666 transit times independently and before any geochemical simulation.

667 The results from the hydrological model show that the characteristics of the flow lines are
668 affected by the changes in the hydrological conditions. After important precipitations, high
669 water contents and large hydraulic conductivities (as the local mean value integrated over the
670 aquifer thickness including the vadose and saturated zones) are simulated in the vicinity of the
671 crests and all along the small valley of the catchment (figure 6). During drought periods, the
672 crest lines have progressively dried out, and the hydraulic conductivities strongly decrease on
673 the upper parts of the watershed. Only some locations at mid-slopes and along the direction of
674 the principal valley exhibit modest hydraulic conductivities (figure 6). This response of the
675 hydraulic conductivities implies that during floods, the water velocity significantly increases
676 along the flow lines, but the length of the active parts of the flow lines also increase as waters
677 collected downstream may also come from the neighborhood of the main crests. During
678 drought periods, the water velocity is slower, but the length of the active parts of the flow lines
679 also tends to decrease, as the waters are principally supplied by mid-slope areas characterized
680 by a thicker aquifer. For illustration, and for the CS1 spring, the water velocities varied along the
681 flow lines between 7 and 0.5 m/day during the flood of 30/03/2010 and were approximately
682 0.5-1 m/day during the important drought of the 29/11/2011 (figure 6). At the same time, the
683 active parts of the flow lines were reduced from 160 m to 110 m from the flood to the drought
684 events (figures 7A and 7B). This hydrological functioning implies that the water velocities along

685 the flow lines and the active lengths of the flow lines vary in opposite manners from drought to
686 flood events. This hydrological behavior buffers the variations of the water transit times over
687 changing hydrological conditions and explains why the mean transit times span much narrower
688 variation ranges than the discharges of water at the collected springs. For example, the
689 calculated mean transit times of waters for the CS1 spring vary from 1.75 to 3.13 months
690 between the strongest flood and the driest period that have been studied, whereas the water
691 discharges vary from 1.523 L/s to 0.098 L/s (figure 8B). Because the time of the water-rock
692 interactions exerts a first-order control on the chemical composition of waters, the modest
693 variability of the mean transit times is directly responsible for the relative stability of the
694 chemical composition of waters within the catchment.

695 It is worth noting that the hydrological modeling with the NIHM code is performed
696 independently and before any geochemical simulation with the KIRMAT code. The fact that the
697 flow rates are well reproduced for all the hydrological contexts between 2010 and 2015
698 supports the idea that water transit times inferred with NIHM are realistic. With chemical
699 composition of waters well captured by simulations, the combination of the geochemical
700 parameters used in KIRMAT renders realistic reaction rates, as chemistry is well reproduced
701 while respecting water transit times. No modifications of the reactive surfaces and of the
702 dissolution kinetic constants were necessary to reproduce the seasonal variability of the water
703 chemistry. It is also important to emphasize that the simulated chemical compositions of waters
704 remain far from a state of chemical equilibrium with respect to primary minerals. The calculated
705 Gibbs free energy for the primary minerals ranges from -120 to -100 kJ/mol for apatite, -90 to -
706 80 kJ/mol for biotite and anorthite and -30 to -20 kJ/mol for albite and K-feldspar. These far-

707 from-equilibrium values for the Gibbs free energy imply that the reaction rates calculated using
708 hydrogeochemical codes such as KIRMAT, which are based on the transient state theory (TST,
709 Eyring, 1935; Murphy and Helgeson, 1987), are realistic for most of the primary minerals in this
710 type of hydrological context. Regarding the simulations performed in this study, the relatively
711 short residence times of waters and the precipitation of clay minerals prevent reaching a state
712 of chemical equilibrium between waters and primary minerals. The results also indicate that
713 introducing a clay solid solution in the geochemical system is a good way to capture the clay
714 mineral dynamics, with a solid solution precipitated at thermodynamic equilibrium able to
715 generate reliable water chemistry (this study) and realistic clay precipitation rates (more detail
716 in Ackerer et al., 2018). Further development could consider a more precise approach to the
717 formation of the clay phases but would imply to simulate a kinetically-controlled nucleation and
718 growth of clay particles (Fritz et al., 2009, Noguera et al., 2011). Further comparisons facing the
719 results from the hydrological modeling with water isotope variability could also be interesting to
720 discuss the accuracy of the water transit times inferred by simulations. Taken together, the
721 results of this study show that the solute concentrations are not limited by a chemical
722 equilibrium; they simply are weakly variable over time because of the short and moderately
723 variable water residence times in the watershed. The chemostatic behavior of the surface and
724 the shallow subsurface waters is therefore only due to a strong hydrological control of the
725 water transit times within the watershed. This conclusion could probably extend to other
726 mountainous and relatively steep watersheds, in which water pathways and short transit times
727 are mainly controlled by gravity driven flow along slopes.

728 **7- Conclusion**

729 This study emphasizes the potential of coupling low-dimensional and depth-integrated
730 hydrological modeling with hydrogeochemical modeling as a way to better understand
731 variability over time and space of the composition of surface and subsurface waters. The
732 independent estimation of the water transit times provided by hydrological simulations is a
733 clear added value to constrain the geochemical modeling approaches. This study shows that the
734 durations of water-rock interactions exert a first-order control on the chemical composition of
735 waters and that the acquisition of the water chemistry can be explained by weathering
736 processes that are spatially fairly homogeneous over the catchment. The hydrological
737 functioning of the watershed also indicates that the chemostatic behavior of the water
738 chemistry is a direct consequence of the strong control exerted by hydrological processes on
739 water transit times. The variations in flow lines distributions from drought to flood events result
740 in a moderate seasonal variability of mean water transit times, which in turn explains the
741 relative stability of the solute concentrations in waters. The consistency between measured and
742 modeled concentrations while respecting the water-rock interaction times provided by the
743 hydrological simulations shows that it is possible to capture the chemical composition of waters
744 with simply determined reactive surfaces and standard kinetic constants. The results of our
745 simulations strengthen the idea that the low surfaces calculated from the geometrical shapes of
746 minerals are a good estimate of the reactive surfaces within the natural environment and
747 certainly the values to be used for hydrogeochemical modeling such as that performed in this
748 work, in addition to the use of the experimental kinetic constants for mineral dissolution.

749
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952 **Figure captions**

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

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

964 Figure 3: principle of the method of backtracking used to determine flow lines that generate
965 flow at the outlet of the Strengbach catchment. Particles are dispatched along the dry fraction
966 of the 1D river network (only one is represented here at a position α on 01/01/2010 at 23:59).
967 NIHM generates an output heterogeneous velocity field at that date for the whole watershed,
968 denoted $V_{01/01/2010}$. By applying a velocity field of the same magnitude but opposite direction to
969 the particle, the position of the particle can be backtracked until 31/12/2009 23:59. Then, to
970 further backtrack the trajectory of the particle, the velocity field is updated accordingly. The
971 frequency of updating of the velocity field was set to 1 day, as a compromise between the
972 accuracy of results and computational time considerations.

973 Figure 4: at the top, flow lines of the subsurface that feed with water the surface draining
974 network on March 1st, 2010 (on the left, high-flow period) and July 1st, 2010 (on the right, low-
975 flow period). The color scale indicates that a water particle reaching the river at a given date
976 started its travel along the streamline or passed at a given location on the streamline x days
977 before. The density of streamlines is associated with the flowing versus dry fraction of the river
978 network at a prescribed date. Below, flow lines of the subsurface that feed with water the
979 geochemical sampling sites on March 30th, 2010 (on the left, flood event) and November 29th,
980 2011 (right, drought event) according to NIHM simulations. For each sampling site, 10 particles
981 were dispatched in the direct neighborhood of the site and then backtracked. The color scale
982 indicates that a water particle reaching the sampling site at a given date started its travel along
983 the streamline or passed at a given location on the streamline x days before.

984 Figure 5: conceptual scheme used in the modeling of the water chemistry. The soil solutions are
985 used as input solution. The bedrock is discretized into a 1D succession of cells along the active
986 parts of the flow lines previously determined by the hydrological NIHM model. Within each cell,
987 the geochemical and transport equations are numerically solved using the KIRMAT
988 hydrogeochemical code. To calculate the integrated chemical composition of the spring water,
989 several simulations with different entering points of soil solutions along the flow path were
990 performed, and the integrated chemistry was calculated by taking the arithmetic mean of all the
991 simulated solute concentrations.

992 Figure 6: maps of piezometric gradient and mean hydraulic conductivity for the Strengbach
993 catchment, as simulated by NIHM, on 29/11/2011 (dry period) and 30/03/2010 (high flows

994 period). The mean hydraulic conductivity is the mean of all hydraulic conductivities integrated
995 over the depth of the aquifer and thus depends on the water saturation.

996 Figure 7: simulation results for the CS1 spring for an important drought (29/11/2011) and a
997 strong flood event (30/03/2010). At the top, active parts of the flow lines that bring the waters
998 to the CS1 spring for the two sampling dates (7A and 7B). Below, simulated chemical
999 compositions of the CS1 spring waters after integration along the flow lines and comparison
1000 with the initial soil solution and the spring chemistry data (7C and 7D). Error bars show
1001 analytical uncertainties on measured concentrations and subsequent uncertainties in model
1002 results.

1003 Figure 8: simulation results for the CS1 spring over the whole range of the water discharges
1004 from the spring. Results are presented for H_4SiO_4 and Na^+ concentrations (8A and 8C), pH (8D)
1005 and mean water transit time (8B). Red lines indicate simulated parameters after integration
1006 along the flow lines, and blue points show measured values from the field campaigns realized
1007 between 2005 and 2015 (data in table 1 and in supplementary table EA1). Error bars show
1008 analytical uncertainties on measured concentrations and subsequent uncertainties in model
1009 results.

1010 Figure 9: simulation results for the PZ3 and PZ5 piezometers for a strong flood event
1011 (05/05/2015). At the top, active parts of the flow lines that bring the waters to the two sampling
1012 sites are shown (9A and 9B). Below, simulated chemical compositions of the piezometer waters
1013 after integration along the flow lines and comparison with the initial soil solution and the water

1014 chemistry data (9C and 9D). Error bars show analytical uncertainties on measured
1015 concentrations and subsequent uncertainties in model results.

1016
1017 Figure 10: simulation results for the CS2 spring. At the top, active parts of the flow lines that
1018 bring the waters to the CS2 spring for an important drought (29/11/2011) and a strong flood
1019 event (30/03/2010) are shown (10A and 10B). The location of the CS2 spring implies a more
1020 scattered distribution of the flow lines than for the CS1 spring. Below, simulation results for the
1021 CS2 spring over the whole range of the water discharges from the spring are presented (10C and
1022 10D). Blue lines indicate simulated parameters after integration along the slowest flow line,
1023 yellow lines indicate simulated parameters after integration along the fastest flow line, and blue
1024 points show measured values from the field campaigns realized between 2005 and 2015 (data
1025 in table 1 and in supplementary table EA2). Error bars show analytical uncertainties on
1026 measured concentrations and subsequent uncertainties in model results.

1027 Figure 11: simulation results for the RH3 spring chemistry and for a flood event (30/03/2010).
1028 On the left, simulated concentrations for the case assuming that the flow lines only run on
1029 gneiss (GN) are shown (11A). On the right, simulated concentrations for the case assuming that
1030 the flow lines only run on hydrothermally altered granite (VS) are presented (11B). Error bars
1031 show analytical uncertainties on measured concentrations and subsequent uncertainties in
1032 model results.

1033 Figure 12: overview of the flow lines of the subsurface that feed with water the geochemical
1034 sampling sites CS1, PZ3 and PZ5 on May 5th, 2015 according to the NIHM simulations. The

1035 simulated chemical compositions after geochemical integration along the flow lines are also
1036 presented for this transect on the southern part of the watershed (CS1, PZ3 and PZ5) and
1037 compared with the initial soil solution and the spring chemistry data.

1038 Table 1: measured pH, water discharges and chemical concentrations of H_4SiO_4 , Na^+ , K^+ , Mg^{2+} ,
1039 and Ca^{2+} in the waters collected from the sampling sites in the Strengbach catchment. The
1040 sampling sites include springs (CS1, CS2, RH3) and piezometers (PZ3, PZ5).

1041 Table 2: Initial and calibrated values of the hydrodynamic parameters of the aquifer in the
1042 simulation of the Strengbach catchment by NIHM.

1043 Table 3: Comparison between BET surfaces and geometric surfaces for the major primary
1044 minerals present in a granitic context. BET surfaces were measured via gas absorption
1045 experiments by ¹ Berger et al., 1994; ² Chou and Wollast, 1985; ³ Lundstrom and Ohman, 1990; ⁴
1046 Amrhein and Suarez, 1992; ⁵ Acker and Bricker, 1992; and ⁶ Guidry and Mackenzie, 2003.
1047 Geometric surfaces were recalculated from the granulometric ranges of the minerals and by
1048 assuming a spherical geometry.