

François Chabaux
Laboratoire d'Hydrologie et de Géochimie de Strasbourg
Université de Strasbourg-CNRS
1 rue Blessig - 67084 Strasbourg Cedex – France
fchabaux@unistra.fr

2020, May 1st

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

Dear Editor,

The 4th revised version of the manuscript submitted for publication to HESS (Manuscript HESS-2018-609) has been uploaded with this file.

The answers to the reviewer comments along with a marked-up manuscript version showing the changes made are given below.

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.

Reply to Reviewers – 4th round of revisions

Reviewer 1:

The authors addressed previous comments and answered most of my questions. In particular, the authors added an interesting focus on the implications of their work for the Strengbach watershed. I believe the manuscript has improved and can be published after few minor changes.

The modelling approach proposed by the authors is novel and very interesting, and has the great advantage of combining a low-dimension hydrological model with a reactive transport model. The description remains slightly confusing sometimes. Please consider clarifying the following points.

- Kirmat is derived from the Transition State Theory (l. 294) but are all chemical reaction (dissolution of primary minerals, oxido-reduction reactions and clay precipitation l.298) rates calculation based on the kinetic laws derived from the TST? Clays precipitated at the thermodynamic equilibrium (l. 307), therefore I would expect no kinetic laws. Please clarify if TST is only applied for mineral dissolution. Which oxido-reduction reactions are taken into account in this study?

In the hydrogeochemical model KIRMAT, the calculation of the dissolution rates of primary minerals is based on the Transition State Theory (see equation 1 in Ackerer et al., 2018, equation 1 in Ngo et al., 2014 for example). For the secondary minerals presented in Table EA14, and tested in precipitation, the precipitation rates are also derived from TST (equation 2 in Ngo et al., 2014). By contrast, clay minerals are described as a solid solution of clay end members precipitated at thermodynamic equilibrium. Therefore, precipitation of clay minerals is not described by a kinetic law. The precipitation of the clay solid solution depends on the solubility product (K) of the clay end members (Tardy and Fritz, 1981; Fritz, 1985; equations IV-25 and IV-26 in Schaffhauser, 2013): the amount of a given clay mineral precipitated at any step of the simulated reaction is calculated to maintain the chemical equilibrium from the moment it is reached in the geochemical reaction. We clarified these points lines 299-304, 310-323.

KIRMAT includes the oxido-reduction processes of iron (Fe), sulfur (S) and other important species for the corrosion of iron (Fritz, 1981; Marty et al., 2010; Ngo et al., 2014). Oxido-reduction reactions are also involved in the formation of several secondary minerals tested in precipitation in this study (Hematite, Siderite, ...). Oxido-reduction reactions are handled through Nerst equations in KIRMAT (Fritz 1981, Made et al., 1994, Gerard et al., 1998). We clarified these points lines 299-304.

- Clay precipitation rates are said to be realistic (l.768) but I could not find the rates in the paper. Maybe this could be added in the supplementary materials (in a table such as for the dissolution rates).

We provide the clay 'precipitation rate', or the amount of precipitated clays, in the text lines 780-782. Details on the calculation of clay precipitation and comparison with field observations are available in Ackerer et al., 2018 section 6.2. We refer to this study in lines 780-782.

- Simulated chemical compositions are far from a state of chemical equilibrium with respect to primary minerals (l. 756). What would be the order of magnitude of water transit time (or chemical equilibrium length) to reach equilibrium with respect to primary minerals in the watershed?

These points were explored and detailed in Ackerer et al., 2018 section 6.2. A water transit time around 8-12 years and a distance as long as 15-20 km are required to reach a chemical equilibrium between water and primary minerals. This long equilibrium length is explained by the precipitation and the dynamic behavior of clay minerals removing ions from solution and retarding chemical equilibrium with respect to primary minerals. We give additional information on these points in lines 773-777.

- Back tracking was used to constrain the origin of subsurface water exiting the system at certain points, as simulated by the hydrological model (l.243), meaning that water originate from the tipping point of the flow line. However in the geochemical model, the authors consider water percolating all along the flow line. How can the back tracking be used to differentiate between water particle entering the subsurface or just passing at a certain point?

The sentence line 243 was inaccurate. Back tracking was not used to constrain the origin of subsurface water exiting the system at certain points. Back tracking was used to identify which subsurface flow lines reach the sampled sites. This point is rephrased lines 242-243.

With a backtracking technique, the delineated streamlines are conditioned by an "exit" point at a prescribed time. In any case, all locations and times upstream the exit point along a stream line cannot distinguish between the fact that the water parcel (the particle) entered the system (here the subsurface) at a location x at time $T-t$, or simply passed through x at $T-t$. This renders transit time distributions calculated via a backtracking procedure slightly biased in comparison with distributions calculated via a forward tracking (Weill et al. 2019, the paper is quoted in the manuscript). For getting an equiprobable transit time $T-t$ for particles entering the subsurface in x , or simply crossing x at $T-t$, it must be assumed that source terms from the surface to the subsurface are evenly spread over the watershed and continuous over time. This is the case for the Strengbach catchment, thus rendering times $T-t$ calculated via backtracking significant of the time spent by a water parcel entered at a location x and exiting the system (or collected in the system) at T . These transit times are also those relevant to geochemical reactions between water and the solid phase in the subsurface. The caption of figure 4 has been slightly modified in order to make this clearer (lines 1071-1073).

We also corrected that the springs collected in this study are not emerging naturally on the slopes (lines 157-158). These springs are captured for drinkable water supply directly in the subsurface by small collectors (Ackerer et al., 2018). Therefore, spring waters are subsurface waters, not waters exiting the subsurface. For the geochemical modeling, soil solutions percolate into the regolith all along the flow lines, which imply a homogeneous infiltration of soil solutions into the subsurface.

References:

Fritz, B., 1985. Multicomponent Solid Solutions for Clay Minerals and Computer Modeling of Weathering Processes, in: Drever, J. (Ed.), *The Chemistry of Weathering*. Springer Netherlands, pp. 19-34.

Thiébaud Schaffhauser. *Traçage et modélisation des processus d'altération à l'échelle d'un petit bassin versant, le Ringelbach (Vosges, France)*. Sciences de la Terre. Université de Strasbourg, 2013. Français. NNT: 2013STRAH020. tel-00992768

Fritz, B., 1981. *Étude thermodynamique et modélisation des réactions hydrothermales et diagénétiques*. Thèse sci., Strasbourg, Université Louis Pasteur et Sci. Géol., Mém., 65, 197 pages.

Madé, B., Clément, A., Fritz, B., 1994. Modeling mineral/solution interactions: The thermodynamic and kinetic code KINDISP. *Computers & Geosciences* 20, 1347-1363.

Marty, N.C.M., Fritz, B., Clément, A., Michau, N., 2010. Modelling the long term alteration of the engineered bentonite barrier in an underground radioactive waste repository. *Applied Clay Science* Advanced smectitic clay research 47, 82-90.

Tardy, Y., Fritz, B., 1981. An ideal solid solution model for calculating solubility products of clay minerals *16*,361-373.

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

3 Julien Ackerer, Benjamin Jeannot, Frederick Delay, Sylvain Weill, Yann Lucas, Bertrand Fritz,
4 Daniel Viville, François Chabaux

5 Laboratoire d'Hydrologie et de Géochimie de Strasbourg, Université de Strasbourg, CNRS,
6 ENGEES, 1 rue Blessig, 67084 Strasbourg Cedex, France

7
8 *Corresponding authors:

9 Julien Ackerer (julien.ackerer@orange.fr), Benjamin Jeannot (bjeannot.pro@gmail.com),
10 Frederick Delay (fdelay@unistra.fr), François Chabaux (fchabaux@unistra.fr)

22 **Abstract**

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

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

51 **1- Introduction**

52 Understanding the effects of ongoing climatic changes on the environment is a major issue for
53 the coming years. The global increase of temperature is expected to affect the hydrological
54 cycle at a large scale, and providing a precise estimation of its repercussion on the evolution
55 of soils and on the chemistry of waters remains difficult. This challenge results from the wide
56 diversity of hydrological, geochemical, and biological processes, and of their coupling, that
57 operate at the Earth's surface (e.g., Gislason et al., 2009; Godd ris et al., 2013; Beaulieu et al.,
58 2012; 2016). Up today, the study of concentration-discharge relations (C-Q relations) has been
59 intensively used to assess the coupling between hydrological and geochemical processes at
60 the hillslope or watershed scales (Godsey et al., 2009; Kim et al., 2017; Ameli et al., 2017;
61 Diamond and Cohen, 2018).

62 C-Q relations are acknowledged to integrate critical zone structure, the hydrological dynamics
63 and the geochemical processes of watersheds (Chorover et al., 2017). Recent studies debated
64 to which extent the chemical variability of waters is explained by a mixing of different water
65 sources (Zhi et al., 2019), the chemical contrasts between deep and shallow waters (Kim et
66 al., 2017), the variability of transit times (Ackerer et al., 2018) and/or seasonally variable flow
67 paths (Herndon et al., 2018). It is clear that a good knowledge of the water flow paths and of
68 their seasonal variability is an important new step to better constrain the water transit times

69 within catchments, and then, to correctly understand the temporal fluctuations of the
70 composition of waters. Modeling such variability of water flow paths and water geochemical
71 composition would require further development of modeling approaches able to combine
72 hydrological and geochemical processes (e.g. Steefel et al., 2005; Kirchner, 2006).

73 Recent efforts in hydrological modeling were conducted to develop spatially distributed
74 approaches that better consider the interplay between surface and subsurface processes (e.g.,
75 Gunduz and Aral, 2005; Kampf and Burges, 2007; Camporese et al., 2010). Due to the
76 complexity of flows in the hydrological processes, many modeling approaches are based on
77 the full resolution of Richard's and Saint Venant equations to correctly describe the
78 interactions between stream, overland and subsurface waters (Kampf and Burges, 2007).

79 These approaches have shown their ability to capture the hydrological functioning of various
80 watersheds, knowing that the full resolution of Richard's and Saint Venant equations requires
81 long computational times and faces calibration and parameterization difficulties (Ebel and
82 Loague, 2006; Mirus et al., 2011). Questions have been raised regarding the optimal
83 complexity of the equations that are needed to correctly treat the hydrology of catchments in
84 their surface and subsurface compartments with reasonable computation times (Gunduz and
85 Aral, 2005).

86 Low-dimensional models have attracted growing interest because they represent an
87 interesting compromise between equation complexity, computational time, and result
88 accuracy (Pan et al., 2015; Hazenberg et al., 2016; Weill et al., 2013; 2017; Jeannot et al.,
89 2018). The reduction of dimensionality is mainly associated with a subsurface compartment
90 (including both the vadose and the saturated zones) modeled as a two-dimensional layer.
91 Some low-dimensional models, as the one employed in this study, can solve subsurface flow

92 via an integrated Richard's equation, meaning that flow and transport processes are
93 integrated over a vertical direction or a direction normal to bedrock, and manipulate averaged
94 (integrated) hydrodynamic properties. This type of low-dimensional approach recently
95 demonstrated its ability to reproduce the results from fully dimensioned approaches in small
96 catchments while reducing computational costs (Pan et al., 2015; Jeannot et al., 2018).
97 Nonetheless, the water transit times calculated from these depth-integrated models are
98 rarely confronted with the water-rock interaction times inferred from hydrogeochemical
99 modeling of water chemistry in watersheds.

100 For its part, the understanding of the hydrogeochemical functioning of the critical zone has
101 been significantly advanced by the implementation of reactive-transport laws in geochemical
102 modeling codes (Steefel et al., 2005; Lucas et al., 2010; 2017; Godd ris et al., 2013; Li et al.,
103 2017). These developments allow for considering a variety of processes, such as flow and
104 transport processes, ion exchanges, biogeochemical reactions, and the interplay between
105 primary mineral dissolution and secondary mineral precipitation (Moore et al., 2012;
106 Lebedeva and Brantley, 2013; Ackerer et al., 2018). Reactive transport models have been used
107 to explore a wide variety of scientific issues, including the study of global atmospheric CO₂
108 consumption by weathering reactions (Godd ris et al., 2013; Li et al., 2014), the formation
109 and evolution of soil and regolith profiles (Maher et al., 2009; Navarre-Sitchler et al., 2009;
110 Lebedeva and Brantley, 2013), and the variability of water quality and chemistry in the
111 environment (Lucas et al., 2010; 2017; Ackerer et al., 2018). However, these approaches
112 usually rely on a simple 1D flow path through a regolith column or along a hill slope to model
113 flow in the system (e.g. Maher, 2011; Moore et al., 2012; Lucas et al., 2017; Ackerer et al.,
114 2018). 1D reactive-transport models are useful to discuss the key processes involved in the
115 regolith formation and in the acquisition of the water chemical composition, but these models

116 cannot consider the complexity of the flow trajectories in watersheds, and hence, its effects
117 on the water chemistry.

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

131 This catchment is one of the reference observatories of the French critical zone network
132 (OZCAR), where multidisciplinary studies, including hydrological, geochemical and geological
133 investigations, have been performed since 1986 (“Observatoire Hydrogéochimique de
134 l’Environnement”, OHGE; <http://ohge.unistra.fr>; El Gh’Mari, 1995; Fichter et al., 1998; Viville
135 et al., 2012; Gangloff et al., 2014; 2016; Prunier et al., 2015; Pan et al., 2015; Ackerer et al.,
136 2016; 2018; Beaulieu et al., 2016; Chabaux et al., 2017; 2019; Schmitt et al., 2017; 2018; Daval
137 et al., 2018; see also Pierret et al., 2018 for an updated overview of the Strengbach
138 watershed).

139 2- Site presentation and data acquisition

140 The Strengbach catchment is a small watershed (0.8 km²) located in the Vosges Mountains of
141 northeastern France at altitudes between 883 and 1147 m. Its hydroclimatic characteristics
142 can be found in Viville et al. (2012) or in Pierret et al. (2018). It is marked by a mountainous
143 oceanic climate, with an annual mean temperature of 6 °C and an annual mean rainfall of
144 approximately 1400 mm, with 15 to 20% falling as snow during two to four months per year.
145 The snow cover period is quite variable from year to year, and may not be continuous over
146 the entire winter. The annual mean evapotranspiration is of approximately 600 mm, and the
147 annual mean infiltration (no significant surface runoff observed) of approximately 800 mm
148 (Viville et al., 2012). The watershed is currently covered by a beech and spruce forest. The
149 bedrock is a base-poor Hercynian granite covered by a 50 to 100 cm-thick acidic and coarse-
150 in-texture soil. The granitic bedrock was fractured and hydrothermally altered, with a stronger
151 degree of hydrothermal overprinting in the northern than the southern part of the catchment
152 (Fichter et al., 1998). The granite was also affected by surface weathering processes during
153 the Quaternary (Ackerer et al., 2016). The porous and uppermost part of the granitic
154 basement constitutes an aquifer from 2 to approximately 8 m thickness. In the Strengbach
155 watershed, the major floods and high-flow events usually occur during snowmelt periods at
156 the end of the winter season or in the early spring. By contrast, the low-flow periods
157 commonly happen at the end of the summer or during the autumn. Several springs are
158 captured for drinkable water supply directly in the subsurface by small collectors (figure 1). The
159 watershed has been equipped with several piezometers and boreholes since 2012, those
160 being located along the slopes on both sides of the watershed (figure 1 in Chabaux et al.,
161 2017).

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

174 The mineralogy and the porosity of the bedrock have been studied in detail in previous studies
175 (El Gh'Mari, 1995; Fichter et al., 1998). On the southern part of the catchment, the weakly
176 hydrothermally altered granite (named HPT, figure 1) is mainly composed of quartz (35%),
177 albite (31%), K-feldspar (22%) and biotite (6%). It also contains small amounts of muscovite
178 (3%), anorthite (2%), apatite (0.5%) and clay minerals (0.5%). On the northern part of the
179 catchment, the lithology is more variable, with the presence of gneiss close to the crest lines
180 and the occurrence of hydrothermally altered granite on the rest of the slopes (El Gh'Mari,
181 1995, figure 1).

182 The hydrological, geochemical and petrological data obtained from these field investigations
183 are the basis of the modeling exercise presented in this study. More precisely, this study is
184 based on hydrogeochemical data from 2005 to 2015 for waters from four springs of the

185 southern part (CS1, CS2, CS3 and CS4) and one spring of the northern part (RH3) of the
186 watershed (figure 1). Hydrogeochemical data obtained over the period 2012-2015 for two
187 piezometers (PZ3, PZ5) of the southern part of the watershed are also studied (figure 1). The
188 overall hydrogeochemical database is available as supplementary tables (tables EA1 to EA9).
189 The specific chemical data from spring and piezometer waters modeled in this study are
190 reported in table 1.

191 **3- Modeling methods**

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

202 **3-1 Hydrological modeling**

203 To assess the water flows in the watershed, several simulations were performed with the
204 hydrological code NIHM (Normally Integrated Hydrological Model; Pan et al., 2015; Weill et
205 al., 2017; Jeannot et al., 2018). This code is a coupled stream, overland, and low-dimensional
206 (depth-integrated) subsurface flow model developed at LHyGeS and already tested in the
207 Strengbach watershed (Pan et al., 2015). The stream and overland flows are described by a

208 diffusive-wave equation, and the subsurface flow is handled through an integration (in a
209 direction normal to bedrock) of the unsaturated-saturated flow equation from the bedrock to
210 the soil surface (Weill et al., 2017). The exchanges of water between the surface and
211 subsurface flows are addressed via a first-order exchange coefficient involving the thickness
212 and the hydraulic conductivity of an interface layer (e.g., the riverbed, for interactions
213 between surface routing and subsurface compartments), and the hydraulic head differences
214 between the compartments (Jeannot et al., 2018).

215 Regarding the hydrological simulations, NIHM was used with only its stream flow and
216 subsurface flow compartments activated, the Strengbach catchment having never evidenced
217 diffuse two-dimensional surface runoff or subsurface exfiltration over large areas. In addition,
218 and because of the steep slopes, the stream flow process revealed almost insensitive to the
219 roughness and Manning's parameters of the riverbed, which were set to usual values for very
220 small streams of mountainous landscapes. By contrast, the parameters of the subsurface were
221 adjusted in NIHM through a calibration-validation process. Several zones of heterogeneity
222 (figure 2) were defined based on field observations (Ackerer et al., 2016; Chabaux et al., 2017).
223 In each of these zones, the saturated hydraulic conductivity, the depth of substratum, and the
224 porosity, were set to uniform values. Other parameters (the residual water content, the
225 specific storage, the Van Genuchten coefficients n and α , and the saturated hydraulic
226 conductivity of the interface layer between the groundwater compartment and the surface
227 compartment) were set to uniform values over the whole catchment (table 2). The thickness
228 of the aquifer that was used for the simulations varied from 2 m near the main crests to up to
229 8 m in the middle of the watershed (figure 2), in agreement with the data obtained during the
230 recent geological investigations and drilling campaigns undertaken at the catchment (Ackerer
231 et al., 2016; Chabaux et al., 2017). The uniform precipitations over space applied at the surface

232 of the catchment are drawn from data of the pluviometric station located at the highest
233 elevation of the watershed (site PA, figure 1). The hydrological model NIHM was then run over
234 a first time period (years 1996-1997). By a Monte-Carlo approach, the parameters were
235 “randomly” sought to improve the fitting between the observed and simulated flow rates at
236 the outlet of the catchment (table 2). The fit was quantified by the root mean square error
237 (RMSE) and the Kling-Gupta efficiency coefficient (KGE; Gupta et al., 2009), applied to the
238 outlet flow rate of the stream, which is the only reliable and always available hydrological
239 variable monitored in the system.

240 Once the best fit was obtained, the model was then run over another time period (2010-2015),
241 but without changing the parameters anymore, and the quality of the fit was re-assessed for
242 this new time-period with the KGE and RMSE. Figure 2 shows the result for the 2010-2015
243 time period. After the water discharges were correctly reproduced at the outlet, a
244 backtracking approach was used to identify which subsurface flow lines reach the sampled sites. To
245 back track the water particles, the velocity fields calculated by the NIHM model were inverted
246 in their direction, and the locations of the backtracked particles were saved at each time-step.
247 A daily time-step was used for the backtracking, as a compromise between computational
248 efforts and a refined description of the transient velocity fields. A schematic representation
249 of the backtracking approach is given in figure 3. This methodology allows for constraining the
250 flow lines that bring waters for a given time and at a given position on the catchment. This
251 information is of major interest to determine the origin of the spring and piezometer waters.
252 It is shown at the catchment scale, that flows are mainly driven by gravity in association with
253 the steep slopes of the watershed, the latter being almost evenly drained over its whole
254 surface area (figure 4). For each water sampling area, ten flow lines that bring water to the

255 location of interest were determined (figure 4), together with a few features of the flow lines,
256 including: local velocities, mean velocities, and length of the flow paths.

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

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

274 With a conditioning of NIHM limited to the reproduction of the stream flow rates at its outlet,
275 it can be questioned on the reliability of the solution, equifinalities in model outputs being
276 usually all the more present that few data are available to condition the model. The point is
277 that there is no other reliable information on flow patterns, and for example, the few

278 boreholes available (mainly drilled for rock core sampling) are deep enough to intercept a few
279 fractures in the bedrock (under the bottom of the aquifer simulated by NIHM). This renders
280 the water levels monitored in these open boreholes unable to reflect hydraulic pressure heads
281 in the active shallow porous aquifer of the catchment. Nevertheless, the steep slopes of the
282 catchment are the main feature conditioning water velocities, thus rendering transit times
283 (the variable of interest for a geochemical study) very stable over time, irrespective of hydro-
284 meteorological conditions and current head pressure in the system. After the present study
285 was completed, NIHM was employed at the Strengbach to simulate water content
286 distributions with the aim to mimic data from magnetic resonance sounding (Weill et al.,
287 2019). The model was slightly improved in terms of storage and its variability over space, but
288 the modeled distribution of flow paths, their variability, and the associated transit time
289 distributions remained unchanged.

290 **3-2 Hydrogeochemical modeling**

291 The simulations of the water chemical composition along the flow lines were performed with
292 the hydrogeochemical KIRMAT code (Kinetic of Reaction and MAAss Transport; Gérard et al.,
293 1998; Lucas et al., 2010; Ngo et al., 2014; Lucas et al., 2017). KIRMAT is a thermokinetic model
294 derived from the Transition State Theory (TST, Eyring, 1935; Murphy and Helgeson, 1987) that
295 simultaneously solves the equations describing geochemical reactions and transport mass
296 balance in a 1D-porous medium. The mass transport includes the effects of one-dimensional
297 convection, diffusion and kinematic dispersion. Chemical reactions account for the dissolution
298 of primary minerals and oxido-reduction reactions, in addition to the formation of secondary
299 minerals and clay minerals. KIRMAT includes the oxido-reduction processes of iron (Fe), sulfur (S)
300 and other important species for the corrosion of iron (Ngo et al., 2014). Oxido-reduction reactions are

301 handled through Nerst equations (Gerard et al., 1998; Ngo et al., 2014). The calculation of the
302 dissolution rates of primary minerals is based on the TST and on a kinetic law (equation 1 in Ackerer et
303 al., 2018, equation 1 in Ngo et al., 2014). Thermodynamic and kinetic data for the primary minerals
304 are available in supplementary materials (supplementary tables EA10, EA11 and EA12).

305 The clay fraction is defined as a solid solution made up of a combination of pure clay end-
306 members. The clay end-members are defined on the basis of X-ray diffraction analyses of clay
307 minerals present in bedrock samples collected in the field (Fichter et al., 1998; Ackerer et al.,
308 2016; 2018). They consist of K-Illites, Mg-Illites, Ca-Illites, Montmorillonites, Na-
309 Montmorillonites, K-Montmorillonites, Ca-Montmorillonites and Mg-Montmorillonites
310 (supplementary material table EA13). During the hydrogeochemical simulations, the clay solid
311 solution is precipitated at thermodynamic equilibrium and precipitation is not described by a
312 kinetic law. The amount of a given clay mineral precipitated at any step of the simulated reaction is
313 calculated to maintain the chemical equilibrium from the moment it is reached in the geochemical
314 reaction. The amount of clay precipitated depends on the solubility product (K) of the clay end
315 members (Tardy and Fritz, 1981). This multicomponent solid solution reproduces the impurity of
316 the clay minerals formed during low-temperature water-rock interactions (Tardy and Fritz,
317 1981), and its composition varies over time, depending on the evolution of the water
318 chemistry and the bedrock mineralogy (Ackerer et al., 2018). For the secondary minerals other
319 than clay minerals, the precipitation rates are derived from TST and described by a kinetic law
320 (equation 2 in Ngo et al., 2014). Precipitation of typical secondary minerals such as carbonates,
321 hematite or amorphous silica was tested, but these minerals were not formed given the
322 saturation states calculated in the geochemical modeling (supplementary table EA14).
323 Secondary mineral precipitation is therefore controlled by clay mineral formation.

324 The KIRMAT code also includes feedback effects between mineral mass budgets, reactive
325 surfaces, and the evolution of bedrock porosity (Ngo et al., 2014). The reactive surfaces of the
326 primary minerals were calculated by assuming a simple spherical geometry for all the
327 minerals, and the mean size of the minerals was estimated from the observation of thin
328 sections from bedrock samples. During simulations, clay mineral precipitation and the
329 evolution of the reactive surfaces of primary minerals are tracked together with chemical
330 processes and water chemical composition. Given the short time scales reported by the
331 hydrological simulations (monthly timescale), changes in the reactive surfaces of primary
332 minerals over the simulation time were negligible. The KIRMAT code has already been applied
333 in geochemical modeling of alluvial subsurface waters (Lucas et al., 2010) and surface waters
334 (Lucas et al., 2017; Ackerer et al., 2018).

335 For this study, the modeling strategy is adapted from Ackerer et al. (2018) to consider the new
336 transit time constrains provided by the hydrological code NIHM. To capture the chemical
337 composition of the spring and the piezometer waters, numerical simulations were performed
338 along the subsurface streamlines that were determined through the backtracking approach.
339 A sketch of the hydrogeochemical modeling strategy is provided in figure 5. For each
340 streamline, several KIRMAT simulations were performed with different starting positions
341 along the active part of the line. The starting positions represent the locations at which the
342 soil solutions percolate through the subsurface shallow aquifer. These starting positions are
343 spaced with a constant lag distance of 1 m along the subsurface streamlines, which results in
344 a sub-continuous percolation of solutions along the whole length of the lines. The deepest soil
345 solutions collected to the south at the beech site (HP) and to the north at the spruce site (VP)
346 were considered representative of the soil solutions for the southern and northern slopes of
347 the catchment, respectively. The data of soil solution chemistry used in this study are available

348 in Prunier et al. (2015) and in supplementary tables (tables EA6 and EA7). These soil solutions
349 integrate the surface processes occurring before water percolation into the weathered
350 bedrock (regolith). Because the soil solutions can be injected into the aquifer at various times,
351 the temporal variability of the soil solution chemistry and its impact on the water-rock
352 interactions along the flow paths are accounted for in the modeling approach.

353 Data related to the regolith properties, such as the mineralogical compositions, the mineral
354 reactive surfaces and the thermodynamic and kinetic constants are given in Ackerer et al.
355 (2018) and in supplementary tables (tables EA10 to EA14). Mineral phases are assumed
356 homogeneously distributed over the regolith layer. By following this strategy, the simulations
357 that consider soil solutions percolating at the upper part of the catchment reflect the chemical
358 evolution of waters with long path lengths and long transit times within the aquifer. By
359 contrast, shorter path lengths and shorter transit times are associated with the percolation of
360 soil solutions that occurs in the vicinity of the sampling locations (figure 5). Because the springs
361 or the piezometers collect waters from different origins and with various transit times,
362 integration along each water flow line was performed. The aim of the integration is to
363 determine the mean chemical composition resulting from the mixing of the waters
364 characterized by variable transit times (figure 5). The integrated chemical composition of the
365 waters provided by a given flow line is calculated by taking the arithmetic mean of the solute
366 concentrations calculated by the succession of the KIRMAT simulations along the flow line
367 (figure 5). This arithmetic mean reflects a simple full mixing of uniform water fluxes along a
368 stream line irrespective of the short or long transit times. In other words, the geochemical
369 simulations are based on the hypothesis of spatially homogenous water-rock interactions
370 along the flow lines. The soil solutions are assumed to percolate uniformly within the aquifer
371 and are then conveyed along the slopes by uniformly distributed masses of water until

372 reaching the sampling locations. When needed, the eventual calculation of water chemistry
373 exiting several stream lines reaching a sampling location accounts for the spreading associated
374 with various flow paths, spatial variability of water velocities and related travel times.

375 **4- Hydrological modeling results**

376 **4-1 Spatial variability of the flow lines**

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

390 By contrast, in the vicinity of the valley and in the topographic depressions, the hydrological
391 modeling indicates that the flow line characteristics are more variable. Because flow lines
392 coming from different hill-sides can feed a topographic depression, mixing of different flow
393 lines with variable flow paths and contrasted water velocities can occur at these locations.
394 The waters collected in valleys or in topographic depressions are therefore characterized by a

395 higher variability of transit times. This is the case for the CS2 and CS4 springs, which are
396 located in a depression, in the axe of the small valley, and surrounded by slopes with various
397 orientations, and a complex flow line distribution (figure 4). For these two springs, the
398 characteristics of the different flow lines can be different for a given date.

399 **4-2 Temporal variability of the flow lines**

400 Hydrological modeling under general transient conditions can render the evolution over time
401 of water flows in the watershed but also of other hydraulic variables. As an example, after an
402 important rainfall event (30/03/2010 in figure 6), snapshots of the integrated hydraulic
403 conductivity (modeled via the Van Genuchten formulation) in the subsurface and simulated
404 by NIHM at the scale of the mesh size show increasing values with decreasing elevation in the
405 watershed. The same observation holds for conductivities during drought periods (see
406 29/11/2011, in figure 6). Provided that the hydraulic head gradient is largely dominated by
407 the topography and therefore almost constant over time (figure 6), the water velocities are
408 increasing along the flow lines from crests to valleys, irrespective of the wet versus dry
409 hydrological periods. However, it is noticeable that wet periods are favorable to a large
410 extension in the valleys of high values of depth averaged hydraulic conductivity indicating that
411 the aquifer is locally almost completely saturated from bottom to top (e.g., values of 6.5×10^{-5}
412 ms^{-1} in figure 6 for a saturated bound at $8 \cdot 10^{-5} \text{ms}^{-1}$).

413 For the CS1 spring, the mean flow velocities along the flow lines vary from approximately 1
414 m/day to 7 m/day between the severe drought of 29/11/2011 and the strong flood of
415 30/03/2010 (figures 7A and 7B). These events correspond to the annual minimum and
416 maximum flow rates at the outlet of the Strengbach watershed. For the same dates, the mean
417 velocities vary from 2 – 12 m/day, 1 – 4 m/day and 1 – 9 m/day for the springs CS2, CS3 and

418 CS4, respectively. The variations from drought to flood are very similar for the piezometer
419 waters, with velocities in the ranges 2 – 10 m/day and 2 – 12 m/day for the PZ3 and PZ5
420 piezometers, respectively. The RH3 spring located on a steeper part of the northern slopes
421 exhibits flow velocity variations from 5 to 20 m/day from dry to flood conditions.

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

439 The consequence of this hydrological functioning is to moderate the seasonal variations of the
440 transit times of waters, as the active lengths of flow lines vary simultaneously with water flow

441 rates. Calculations indicate that for the spring and piezometer waters collected in this study,
442 the mean transit times of waters only vary from approximately 1.75 to 4 months between the
443 strongest flood and the driest conditions. Notably, these short subsurface water transit times
444 are explained by the small size of the catchment and the steep slopes.

445 **5- Hydrogeochemical modeling results**

446 **5-1 CS1 and CS3 springs (southern slope)**

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

463 transit times correctly reproduces the chemical composition of the CS1 spring waters collected
464 on this date (figure 7C). This comment applies regardless of the time period considered.

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

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

484 **5-2 PZ3 and PZ5 piezometers (southern slope)**

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

500 **5-3 The CS2 and CS4 springs (in the valley axe)**

501 CS2 and CS4 spring waters drain the same granitic bedrock as the CS1 and CS3 waters, but are
502 located in the direction of the small valley of the Strengbach stream and surrounded by slopes
503 of various orientations and inclinations (figure 4). Consequently, the distribution of the flow
504 lines is much more scattered than for the CS1 and CS3 springs. For the CS2 spring, and for all
505 the hydrological conditions, two different groups of flow lines have been determined by the
506 backtracking approach: a northern group characterized by relatively slow velocities and a
507 southern group with higher velocities (figure 4 and figures 11A, 11B). This scattered

508 distribution of the flow lines implies that a single specific flow line cannot be representative
509 of all the waters collected by the spring. The flow lines calculated using the NIHM model allow
510 for constraining the trajectories of the waters within the watershed; however, the simulations
511 performed in this study cannot provide the mass fluxes of water carried by each flow line.
512 Consequently, a straightforward calculation of the chemistry of the CS2 spring, such as
513 depicted above for CS1, is not applicable because the mixing proportions between the
514 different flow lines are unknown.

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

529 **5-4 The RH3 spring (northern slope)**

530 The RH3 spring is located on the northern part of the catchment (figure 4), where steep slopes
531 imply fast water velocities and subparallel flow lines. However, if the distribution of the flow
532 lines on the RH3 hillside is simple (as for the CS1 and CS3 springs) the precise lithological
533 nature of the bedrock drained by the RH3 waters is more difficult to constrain (Ackerer et al.,
534 2018). Unlike the southern slope, the bedrock of the northern part of the catchment reveals
535 a complex lithology, with gneiss outcropping in the upper part of the slope and granite of
536 variable degree of hydrothermal overprinting in the intermediate and lower parts. These
537 lithological variations can explain the differences in chemical composition between the RH3
538 spring waters and the waters of the southern part of the catchment: the RH3 spring waters
539 are characterized by systematically higher concentrations of K^+ and Mg^{2+} cations but show
540 similar concentrations for the other major elements (Ackerer et al., 2018; Pierret et al., 2018).
541 The vertical extension of the gneiss and the spatial variability of the hydrothermal overprinting
542 along the northern slopes are not well known, with the consequence that a straightforward
543 modeling of water chemistry as done for CS1 is not possible for RH3.

544 Alternatively, simulations of two extreme cases can be performed by assuming that the flow
545 lines only run, either on gneiss or on hydrothermally altered granite. When only considering
546 the hydrothermally altered granite (VS facies), the simulated concentrations of H_4SiO_4 and Na^+
547 are close to the measured ones. Nevertheless, the concentrations of K^+ and especially Mg^{2+}
548 are clearly underestimated (figure 12B). In the case of the flow lines only running on gneiss
549 (GN facies), the simulated concentrations of H_4SiO_4 and Na^+ also match the data. However,
550 due to the higher abundance of biotite in the gneiss, the simulated concentrations of K^+ and
551 Mg^{2+} are higher than the measured ones (figure 12A). At this stage, it is therefore reasonable
552 to propose that the chemical composition of the RH3 spring waters reflects mixing of the two
553 lithological influences. By assuming a geochemical conservative mixing, which is likely a too

554 simplistic scenario, the results would indicate that the flow lines portions running on gneiss
555 and on hydrothermally altered granite count for approximately 40-50% and 50-60% of the
556 total water path length, respectively.

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

566 **6- Discussion**

567 The coupling of the NIHM and KIRMAT codes allows for building a better modeling scheme to
568 those commonly used in previous studies regarding the hydrogeochemical modeling of
569 surface waters at the watershed scale. In such previous works, the geochemical simulations
570 were performed mainly along a single 1D flow line, only characterized by homogeneous mean
571 hydrological properties (Goddéris et al., 2006; Maher, 2011; Moore et al., 2012; Lucas et al.,
572 2017; Ackerer et al., 2018). In a previous study on the Strengbach watershed (Ackerer et al.,
573 2018), the soil solutions were also assumed to percolate in the bedrock only at a single starting
574 point of the flow lines. Although these previous approaches were useful for determining the
575 long-term evolution of regolith profiles and/or the mean chemistry of waters at the pluri-
576 annual scale, they cannot be used to discuss the seasonal variations of the water chemical

577 composition. The NIHM-KIRMAT coupling approach makes this possible, as it provides the
578 spatial distribution of the flow lines at the watershed scale and their variations over time.
579 Furthermore, the proposed modeling approach also integrates a soil solution percolation
580 scheme with inlets uniformly distributed along the slope, which is more realistic than a
581 scheme assuming that each sampled site is fed by a single flow line carrying waters with a
582 unique transit time. The good agreement between modeling results and observations over a
583 large panel of hydrological conditions gives strength to the conclusions and implications that
584 can be drawn regarding the hydrogeochemical functioning of this headwater catchment.

585 **6-1 Choices of the reactive surfaces and the kinetic constants**

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

600 relevant reactive surfaces at different space scales (Li et al., 2006; Navarre-Sitchler and
601 Brantley, 2007).

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

615 In table 3, the BET surfaces are compared with the geometric surfaces of the minerals involved
616 in the dissolution experiments, recalculated from the size ranges of the minerals. For most of
617 the minerals (apatite, quartz, albite, K-feldspar, and anorthite), the geometric surfaces are
618 within the same order of magnitude as the BET surfaces, even if often slightly lower (table 3).
619 However, as the BET surfaces are determined with fairly large uncertainties, especially for low
620 BET surfaces (up to $\pm 70\%$), and as they can be very different depending on the gas used (up
621 to 50% of difference between N₂ or Kr absorption; Brantley and Mellott, 2000), the above
622 differences between the geometrical and the BET surfaces cannot be considered significant

623 for the majority of minerals used in the Strengbach simulations. A significant difference only
624 appears for biotite, with the geometric surfaces one order of magnitude less than the BET
625 surfaces (table 3). However, for biotite, due to its layered structure, it has been shown that
626 approximately 80 – 90% of the surface area accessible by the gases used to estimate BET
627 surfaces is not accessible for weathering reactions (Nagy, 1995).

628 The above considerations explain why for a granitic bedrock as found in the Strengbach
629 catchment, the geometric surfaces are relevant to describe the surfaces of water-rock
630 interactions at the space and time scales of this study. An immediate corollary is that the
631 values of the standard kinetic constants (table EA12) are also appropriate to calculate reaction
632 rates with mineral geometric surfaces in our modeling approach. This ability may be related
633 to the fact that all the minerals that have been used in the dissolution experiments and in the
634 kinetic studies were collected in the field (e.g., Acker and Bricker, 1992; Amrhein and Suarez,
635 1992). These minerals were likely affected by anisotropy, passivation layers, and any types of
636 aging effects related to long-term water-rock interactions. Our results might therefore mean
637 that the standard kinetic constants obtained in such experiments integrate the aging effects
638 that have affected the reactivity of the primary minerals in natural environments. This would
639 explain why it is possible to capture the full variability of the water chemistry in a headwater
640 catchment with simple geometric reactive surfaces and standard kinetic constants.

641 At this stage, the results of our simulations strengthen the idea that the low surfaces
642 calculated from the geometrical shapes of minerals provide good estimates of the reactive
643 surfaces within this type of environment (Brantley and Mellott, 2000; Gautier et al., 2001;
644 White and Brantley, 2003; Zhu, 2005; Li et al., 2017). They are certainly the values to be used
645 for hydrogeochemical modeling such as that performed in this work, in addition to the use of

646 the experimental kinetic constants for mineral dissolution. These conclusions are certainly not
647 specific to the Strengbach catchment and could be applicable to many other headwater
648 granitic catchments.

649 **6-2 Implications for the acquisition of the water chemistry**

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

668 watershed (Ackerer et al., 2018) and in other sites (e.g. Maher, 2010; Moore et al., 2012;
669 Lebedeva and Brantley; 2013).

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

682 The modeling also shows that the hydrogeochemical functioning of the watershed is properly
683 simulated by water circulations in the shallow subsurface, i.e., in a saprolitic aquifer. No
684 contribution of waters circulating in the deep fracture network of the granitic bedrock and
685 observed during the drilling campaigns (see Chabaux et al., 2017) is necessary. The deep-water
686 circulations are probably disconnected from the shallow subsurface network, as recently
687 suggested by geochemical studies conducted in the Strengbach watershed (Chabaux et al.,
688 2017; Pierret et al., 2018). This is also in agreement with recent hydrological modeling studies
689 arguing that the catchment behaves like a vertically thin but horizontally wide reservoir (Pan
690 et al., 2015; Weill et al., 2017). The modeling results also show that water in the shallow

691 aquifer flows along streamlines with fairly simple geometries. At the scale of the catchment
692 (figure 4), the geometry of the flow lines validates the hypothesis based on the geochemical
693 and Sr-U isotopic data that the spring waters of these mid-mountain basins are supplied by
694 waters from distinct flow paths without real interconnections (i.e., the Strengbach and
695 Ringelbach watersheds; Schaffhauser et al., 2014; Pierret et al., 2014). Flow paths are
696 therefore distinct along the slopes and occur within the shallow saprolitic aquifer but are not
697 controlled by deep fractures in the bedrock.

698 **6-3 Origins of general chemostatic behavior and of specific C-Q relations**

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

711 Different origins for the chemostatic behavior have been proposed, such as a modification of
712 the mineral reactive surfaces during changing hydrological conditions (Clow and Mast, 2010),
713 a small concentration difference between slow and fast moving waters (Kim et al., 2017), or

714 the fact of reaching an equilibrium concentration along the water pathway (Maher, 2010). The
715 coupled approach NIHM-KIRMAT renews the opportunity to discuss on the origin of the
716 chemostatic behavior in catchments. It is worth noting that the acquisition and the evolution
717 of the water chemistry can be simulated along flow lines that have been determined via timely
718 and spatially distributed hydrological modeling. The strength of this approach is to constrain
719 water transit times independently and before any geochemical simulation.

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

733 In addition to this general chemostatic behavior, each chemical element has a specific
734 response to a change in water transit time as exemplified in figure 9 where are given the
735 concentration-mean transit time relations (C-MTT relations) for H_4SiO_4 and the major cations.
736 In the relevant transit time window for the spring and piezometer waters (figure 9b), the C-

737 MTT relations are linear and C-MTT slopes are significant for H_4SiO_4 , modest for Na^+ and weak
738 for Mg^{2+} and K^+ concentrations. The modeling results indicate that the C-MTT slopes are
739 controlled by the competition between primary mineral dissolution and element
740 incorporation into clay minerals. When elemental fluxes from primary mineral dissolution to
741 solution are much higher than fluxes from solution to clay minerals (e.g., H_4SiO_4), the element
742 can accumulate in solution, resulting in a significant C-MTT slope. By contrast, when elemental
743 fluxes from primary mineral dissolution to solution are only slightly higher than fluxes from
744 solution to clay minerals (e.g., K^+), the element accumulates only slowly in solution, resulting
745 in a weak C-MTT slope. Interestingly, when fitting power-laws along C-Q relations ($C=aQ^b$, in
746 caption of figure 8), both 'a' coefficient controlling the height of the C-Q laws and 'b'
747 coefficient controlling the curvature of the C-Q laws are sensitive to the C-MTT slopes (figure
748 9c and 9d). 'a' coefficient is positively correlated with C-MTT slopes while 'b' coefficient is
749 negatively correlated. Solute species with significant C-MTT slopes are more chemodynamic
750 and display higher mean annual concentrations (H_4SiO_4 , $b(\text{H}_4\text{SiO}_4)=-0.1$, $a(\text{H}_4\text{SiO}_4)=10^{-4}$),
751 whereas species with weak C-MTT slopes show low mean annual concentrations and are
752 nearly perfectly chemostatic ($a(\text{Mg}^{2+})=10^{-5}$, $b(\text{Mg}^{2+})=-0.016$, $a(\text{K}^+)=10^{-5}$, $b(\text{K}^+)=0$, figures 8, 9c
753 and 9d). Our results show that a better knowledge of C-MTT relations is important to explain
754 the contrasted C-Q shapes of chemical elements.

755 It is important to underline that the hydrological modeling with the NIHM code is performed
756 independently and before any geochemical simulations with the KIRMAT code. The fact that
757 the flow rates are well reproduced for all the hydrological contexts between 2010 and 2015
758 supports that the water transit times inferred from the NIHM code are realistic. The fact that
759 the chemical composition of waters is well captured indicates that the combination of the
760 geochemical parameters used in KIRMAT code is able to generate realistic reaction rates, as

761 chemistry is well reproduced while respecting realistic water transit times. No modifications
762 of the reactive surfaces and of the dissolution kinetic constants were necessary to reproduce
763 the seasonal variability of the water chemistry. It is also important to emphasize that the
764 simulated chemical compositions of waters remain far from a state of chemical equilibrium
765 with respect to primary minerals. The calculated Gibbs free energy for the primary minerals
766 ranges from -120 to -100 kJ/mol for apatite, -90 to -80 kJ/mol for biotite and anorthite and -
767 30 to -20 kJ/mol for albite and K-feldspar. These far-from-equilibrium values for the Gibbs free
768 energy imply that the reaction rates calculated using hydrogeochemical codes such as
769 KIRMAT, which are based on the transient state theory (TST, Eyring, 1935; Murphy and
770 Helgeson, 1987), are realistic for most of the primary minerals in this type of hydrological
771 context. Regarding the simulations performed in this study, the relatively short residence
772 times of waters and the precipitation of clay minerals prevent reaching a state of chemical
773 equilibrium between waters and primary minerals **at the watershed scale. A water transit time**
774 **around 8-12 years and a distance as long as 15-20 km would be necessary to reach a chemical**
775 **equilibrium between water and primary minerals (see Ackerer et al., 2018). This long**
776 **equilibrium length is explained by the precipitation and the dynamic behavior of clay minerals**
777 **removing ions from solution and retarding chemical equilibrium with respect to primary**
778 **minerals.** Relying upon a clay solid solution is also appropriate to mimic the clay mineral
779 dynamic in this type of watershed, and a clay mineral assemblage precipitating at
780 thermodynamic equilibrium is able to generate reliable water chemistry (this study) and
781 **realistic amount of clay minerals (mass fraction of clay minerals of 2-3 % in the regolith after**
782 **20 kyr of weathering, more detail in Ackerer et al., 2018).**

783 Our results indicate that it is not necessary to mix in different proportions soil and deep waters
784 to generate chemostatic behavior, as proposed by Zhi et al. (2019). Chemostatic behavior can

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

801 **7- Conclusion**

802 This study exemplifies the potential of coupling of low-dimensional and depth-integrated
803 hydrological modeling with hydrogeochemical modeling as a way to better understand
804 variability over time and space of the composition of surface and subsurface waters. The
805 independent estimation of the water transit times provided by hydrological simulations is a
806 clear added value to constrain the geochemical modeling approaches. Our study
807 demonstrates that the seasonal variability of hydraulic conductivities along the slopes is a key
808 process to understand the dynamic of flow lines and the changes of water transit times in the

809 watershed. The variations in flow lines distributions from drought to flood events result in a
810 modest seasonal variability of mean water transit times, which in turn explains the relative
811 stability of the solute concentrations in waters. Our results also show that a better knowledge
812 of the concentration-mean transit time relations (C-MTT relations) is an interesting new step
813 to understand the diversity of C-Q shapes for different chemical elements. The consistency
814 between measured and modeled concentrations while respecting the water-rock interaction
815 times provided by the hydrological simulations shows that it is possible to capture the
816 chemical composition of waters with simply determined reactive surfaces and standard
817 kinetic constants. The results of our simulations strengthen the idea that the low surfaces
818 calculated from the geometrical shapes of minerals are a good estimate of the reactive
819 surfaces in this type of granitic catchment, and certainly the values to be used for
820 hydrogeochemical modeling such as that performed in this work, in addition to the use of the
821 experimental kinetic constants for mineral dissolution.

822

823 **Acknowledgements:** This work and the Julien Ackerer's salary were financially supported by
824 the French ANR Program (Project CANTARE- Alsace) under grant agreement ANR-15-CE06-
825 0014. This work also benefited from fruitful discussions with D. Daval. The authors thank all
826 the reviewers for their constructive comments that improved the quality of the manuscript.

827

828 **Bibliography**

- 829 Acker, J. G. and Bricker, O. P.: The influence of pH on biotite dissolution and alteration kinetics at low
830 temperature. *Geochim. Cosmochim. Acta*, 56(8), 3073-3092, 1992.
- 831 Ackerer, J., Chabaux, F., Van der Woerd, J., Viville, D., Pelt, E., Kali, E., Lerouge, C., Ackerer, P., Di Chiara
832 Roupert, R. and Négrel, P.: Regolith evolution on the millennial timescale from combined U–
833 Th–Ra isotopes and in situ cosmogenic ¹⁰Be analysis in a weathering profile (Strengbach
834 catchment, France). *Earth Planet. Sci. Lett.*, 453, 33-43, 2016.
- 835 Ackerer, J., Chabaux, F., Lucas, Y., Clément, A., Fritz, B., Beaulieu, E Viville D., Pierret, M.C., Gangloff, S.
836 and Négrel, P.: Monitoring and reactive-transport modeling of the spatial and temporal
837 variations of the Strengbach spring hydrochemistry. *Geochim. Cosmochim. Acta*, 225, 17-35,
838 2018.
- 839 Ameli, A. A., Beven, K., Erlandsson, M., Creed, I. F., McDonnell, J. J. and Bishop, K.: Primary weathering
840 rates, water transit times, and concentration-discharge relations: A theoretical analysis for the
841 critical zone. *Water Resour. Res.*, 53, 942-960, 2017.
- 842 Amrhein, C. and Suarez, D. L.: Some factors affecting the dissolution kinetics of anorthite at 25 C,
843 *Geochim. Cosmochim. Acta*, 56, 1815-1826, 1992.
- 844 Bao, C., Li, L., Shi, Y., & Duffy, C.: Understanding watershed hydrogeochemistry: 1. Development of RT-
845 Flux-PIHM. *Water Resources Research*, 53, 2328-2345, 2017.
- 846 Beaulieu, E., Goddérés, Y., Donnadieu, Y., Labat, D. and Roelandt, C.: High sensitivity of the continental-
847 weathering carbon dioxide sink to future climate change, *Nature Climate Change*, 2, 346, 2012.
- 848 Beaulieu, E., Lucas, Y., Viville, D., Chabaux, F., Ackerer, P., Goddérés, Y. and Pierret, M. C. : Hydrological
849 and vegetation response to climate change in a forested mountainous catchment, *Modeling*
850 *Earth Systems and Environment*, 2, 191, 2016.
- 851 Beisman, J. J., Maxwell, R. M., Navarre-Sitchler, A. K., Steefel, C. I., & Molins, S. ParCrunchFlow: an
852 efficient, parallel reactive transport simulation tool for physically and chemically

853 heterogeneous saturated subsurface environments. *Computational Geosciences*, 19, 403-422,
854 2015.

855 Berger, G., Cadore, E., Schott, J. and Dove, P. M.: Dissolution rate of quartz in lead and sodium
856 electrolyte solutions between 25 and 300 C: Effect of the nature of surface complexes and
857 reaction affinity, *Geochim. Cosmochim. Acta*, 58, 541-551, 1994.

858 Brantley, S. L. and Mellott, N. P.: Surface area and porosity of primary silicate minerals, *Am. Mineral.*,
859 85, 1767-1783, 2000.

860 Camporese, M., Paniconi, C., Putti, M. and Orlandini, S.: Surface-subsurface flow modeling with path-
861 based runoff routing, boundary condition-based coupling, and assimilation of multisource
862 observation data, *Water Resour. Res.* 46, W02512, doi:10.1029/2008WR007536, 2010.

863 Chabaux, F., Viville, D., Lucas, Y., Ackerer, J., Ranchoux, C., Bosia, C, Pierret, M.C., Labasque, T.,
864 Aquilina, L., Wyns, R., Lerouge, C., Dezaye, C. and Négrel, P.: Geochemical tracing and modeling
865 of surface and deep water–rock interactions in first-order granitic watersheds (Strengbach and
866 Ringelbach CZOs, France), *Acta Geochim.*, 36, 363-366, 2017.

867 Chabaux F., Stille P., Prunier J., Gangloff S., Lemarchand D., Morvan G., Négrel J., Pelt E., Pierret M.C.,
868 Rihs S., Schmitt A.D., Trémoilières T., Viville D. Plant-soil-water interactions: Implications from
869 U-Th-Ra isotope analysis in soils, soil solutions and vegetation (Strengbach CZO, France).
870 *Geochimica et Cosmochimica Acta*, 2019.

871 Chorover, J., Derry, L. A., & McDowell, W. H.: Concentration-Discharge Relations in the Critical Zone:
872 Implications for Resolving Critical Zone Structure, Function, and Evolution. *Water Resources*
873 *Research*, 53, 8654-8659, 2017.

874 Chou, L., and Wollast, R.: Steady-state kinetics and dissolution mechanisms of albite. *Am. J. Science*,
875 285, 963-993, 1985.

876 Clow, D. W. and Mast, M. A.: Mechanisms for chemostatic behavior in catchments: implications for
877 CO2 consumption by mineral weathering, *Chem. Geol.*, 269, 40-51, 2010.

878 Diamond, J. S., & Cohen, M. J.: Complex patterns of catchment solute–discharge relationships for
879 coastal plain rivers. *Hydrological processes*, 32, 388-401. 2018.

880 Daval, D., Calvaruso, C., Guyot, F. and Turpault, M. P.: Time-dependent feldspar dissolution rates
881 resulting from surface passivation: Experimental evidence and geochemical implications. *Earth*
882 *Planet. Sci. Lett.*, 498, 226-236, 2018.

883 Ebel, B. A. and Loague, K.: Physics-based hydrologic-response simulation: Seeing through the fog of
884 equifinality. *Hydrological Processes: An International Journal*, 20, 2887-2900, 2006.

885 Eyring, H. The activated complex in chemical reactions. *The Journal of Chemical Physics*, 3, 107-115,
886 1935.

887 Fichter, J., Turpault, M. P., Dambrine, E. and Ranger, J.: Mineral evolution of acid forest soils in the
888 Strengbach catchment (Vosges mountains, NE France), *Geoderma*, 82, 315-340, 1998.

889 Fischer, C., Kurganskaya, I., Schäfer, T. and Lüttge, A.: Variability of crystal surface reactivity: What do
890 we know?, *Applied Geochem.* 43, 132-157, 2014.

891 Gangloff, S., Stille, P., Schmitt, A.D. and Chabaux F.: Factors controlling the chemical composition of
892 colloidal and dissolved fractions in soil solutions and the mobility of trace elements in soils,
893 *Geochim. Cosmochim. Acta*, 189 37–57, 2016.

894 Gangloff, S., Stille, P., Pierret, M. C., Weber, T. and Chabaux, F. : Characterization and evolution of
895 dissolved organic matter in acidic forest soil and its impact on the mobility of major and trace
896 elements (case of the Strengbach watershed), *Geochim. Cosmochim. Acta*, 130, 21-41, 2014.

897 Gautier, J. M., Oelkers, E. H. and Schott, J.: Are quartz dissolution rates proportional to BET surface
898 areas?, *Geochim. Cosmochim. Acta*, 65, 1059-1070, 2001.

899 Gérard, F., Clément, A. and Fritz, B.: Numerical validation of a Eulerian hydrochemical code using a 1D
900 multisolute mass transport system involving heterogeneous kinetically controlled reactions, *J.*
901 *Cont. Hydrol.*, 30, 201-216, 1998.

902 Gh'Mari, E. : *Etude minéralogique, pétrophysique et géochimique de dynamique d'altération d'un*
903 *granite soumis aux dépôts atmosphériques acides (bassin versant du Strengbach, Vosges,*

904 France). *Mécanismes, bilans et modélisation*, PhD Thesis,, Université Louis Pasteur, Strasbourg,
905 pp. 200.

906 Gislason, S. R., Oelkers, E. H., Eiriksdottir, E. S., Kardjilov, M. I., Gísladóttir, G., Sigfusson, B., Snorrason,
907 A., Elefsen, S., Hardardóttir, J., Torssander, P. and Oskarsson, N.: Direct evidence of the
908 feedback between climate and weathering, *Earth Planet. Sci. Lett.*, 277, 213-222, 2009.

909 Goddérís, Y., François, L. M., Probst, A., Schott, J., Moncoulon, D., Labat, D. and Viville, D.: Modelling
910 weathering processes at the catchment scale: the WITCH numerical model, *Geochim.*
911 *Cosmochim. Acta* 70, 1128–1147, 2006.

912 Goddérís, Y., Brantley, S. L., François, L., Schott, J., Pollard, D., Déqué, M. and Dury, M.: Rates of
913 consumption of atmospheric CO₂ through the weathering of loess during the next 100 yr of
914 climate change, *Biogeosciences*, 10, 135-148, 2013.

915 Godsey, S. E., Kirchner, J. W., and Clow, D. W.: Concentration–discharge relationships reflect
916 chemostatic characteristics of US catchments. *Hydrological Processes: An International*
917 *Journal*, 23, 1844-1864, 2009.

918 Guidry, M. W. and Mackenzie, F. T.: Experimental study of igneous and sedimentary apatite
919 dissolution: control of pH, distance from equilibrium, and temperature on dissolution rates,
920 *Geochim. Cosmochim. Acta*, 67, 2949-2963, 2003.

921 Gunduz, O. and Aral, M. M.: River networks and groundwater flow: a simultaneous solution of a
922 coupled system, *J. Hydrol.*, 301, 216-234, 2005.

923 Gupta, H.V., Kling, H., Yilmaz, K.K., Martinez, G.F. Decomposition of the mean squared error and NSE
924 performance criteria: Implications for improving hydrological modelling. *J. Hydrol.* 377, 80–91,
925 2009.

926 Hazenberg, P., Broxton, P., Gochis, D., Niu, G. Y., Pangle, L. A., Pelletier, J. D., ... and Zeng, X. (2016).
927 Testing the hybrid-3-D hillslope hydrological model in a controlled environment, *Wat. Resour.*
928 *Res.*, 52, 1089-1107, 2016.

929 Herndon, E. M., Steinhoefel, G., Dere, A. L., & Sullivan, P. L.: Perennial flow through convergent
930 hillslopes explains chemodynamic solute behavior in a shale headwater catchment. *Chemical*
931 *Geology*, 493, 413-425, 2018.

932 Jeannot, B., Weill, S., Eschbach, D., Schmitt, L. and Delay, F.: A low-dimensional integrated subsurface
933 hydrological model coupled with 2-D overland flow: Application to a restored fluvial
934 hydrosystem (Upper Rhine River–France), *J. Hydrol.*, 563, 495-509, 2018.

935 Kampf, S. K. and Burges, S. J.: A framework for classifying and comparing distributed hillslope and
936 catchment hydrologic models, *Water Resour. Res.*, W05423, doi:10.1029/2006WR005370,
937 2007

938 Kim, H., Dietrich, W. E., Thurnhoffer, B. M., Bishop, J. K. and Fung, I. Y.: Controls on solute
939 concentration-discharge relationships revealed by simultaneous hydrochemistry observations
940 of hillslope runoff and stream flow: The importance of critical zone structure, *Water Resour.*
941 *Res.*, 53, 1424-1443, 2017.

942 Kirchner, J. W.: Getting the right answers for the right reasons: Linking measurements, analyses, and
943 models to advance the science of hydrology, *Water Resour. Res.* 42, W03S04,
944 doi:10.1029/2005WR004362, 2006.

945 Lebedeva, M. I. and Brantley, S. L. : Exploring geochemical controls on weathering and erosion of
946 convex hillslopes: Beyond the empirical regolith production function. *Earth Surface Processes*
947 *and Landforms*, 38, 1793-1807, 2013.

948 Li, D. D., Jacobson, A. D. and McInerney, D. J.: A reactive-transport model for examining tectonic and
949 climatic controls on chemical weathering and atmospheric CO₂ consumption in granitic
950 regolith. *Chem. Geol.*, 365, 30-42 2014.

951 Li, L., Peters, C. A. and Celia, M. A.: Upscaling geochemical reaction rates using pore-scale network
952 modeling. *Advances in water resources*, 29, 1351-1370, 2006.

953 Li, L., Bao, C., Sullivan, P. L., Brantley, S., Shi, Y., & Duffy, C. Understanding watershed
954 hydrogeochemistry: 2. Synchronized hydrological and geochemical processes drive stream
955 chemostatic behavior. *Water Resources Research*, 53, 2346-2367, 2017.

956 Li, L., Maher, K., Navarre-Sitchler, A., Druhan, J., Meile, C., Lawrence, C., ... and Jin, L. : Expanding the
957 role of reactive transport models in critical zone processes. *Earth-Science Reviews*, 165, 280-
958 301, 2017

959 Lucas, Y., Schmitt, A. D., Chabaux, F., Clément, A., Fritz, B., Elsass, P. and Durand, S.: Geochemical
960 tracing and hydrogeochemical modelling of water–rock interactions during salinization of
961 alluvial groundwater (Upper Rhine Valley, France), *Appl. Geochem.*, 25, 1644-1663, 2010.

962 Lucas, Y., Chabaux, F., Schaffhauser, T., Fritz, B., Ambroise, B., Ackerer, J. and Clément, A.:
963 Hydrogeochemical modeling (KIRMAT) of spring and deep borehole water compositions in the
964 small granitic Ringelbach catchment (Vosges Mountains, France), *Applied Geochemistry*, 87, 1-
965 21, 2017.

966 Lundström, U. and Öhman, L. O.: Dissolution of feldspars in the presence of natural, organic solutes,
967 *Journal of Soil Science*, 41, 359-369, 1990.

968 Maher, K., Steefel, C. I., White, A. F., & Stonestrom, D. A.: The role of reaction affinity and secondary
969 minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence,
970 California, *Geochim. Cosmochim. Acta*, 73, 2804-2831, 2009.

971 Maher, K. : The dependence of chemical weathering rates on fluid residence time, *Earth Planet. Sci.*
972 *Lett.*, 294, 101-110, 2010.

973 Maher, K.: The role of fluid residence time and topographic scales in determining chemical fluxes from
974 landscapes, *Earth Planet. Sci. Lett.*, 312, 48-58, 2011.

975 Mirus, B. B., Ebel, B. A., Heppner, C. S. and Loague, K.: Assessing the detail needed to capture rainfall-
976 runoff dynamics with physics-based hydrologic response simulation, *Water Resour. Res.*, 47,
977 W00H10, doi:10.1029/2010WR009906, 2011

978 Moore, J., Lichtner, P. C., White, A. F. and Brantley, S. L.: Using a reactive transport model to elucidate
979 differences between laboratory and field dissolution rates in regolith, *Geochim. Cosmochim.*
980 *Acta*, 93, 235-261, 2012.

981 Murphy, W. M., & Helgeson, H. C. Thermodynamic and kinetic constraints on reaction rates among
982 minerals and aqueous solutions. III. Activated complexes and the pH-dependence of the rates
983 of feldspar, pyroxene, wollastonite, and olivine hydrolysis. *Geochimica et Cosmochimica Acta*,
984 51, 3137-3153, 1987.

985 Nagy, K. L., White, A. F., & Brantley, S. L. Chemical weathering rates of silicate minerals. *Mineralogical*
986 *Society of America. Washington. DC.* 1995.

987 Navarre-Sitchler, A. and Brantley, S.: Basalt weathering across scales, *Earth and Planet. Sci. Let.*, 261,
988 321-334, 2007.

989 Navarre-Sitchler, A., Steefel, C. I., Yang, L., Tomutsa, L. and Brantley, S. L.: Evolution of porosity and
990 diffusivity associated with chemical weathering of a basalt clast, *Journal of Geophysical*
991 *Research: Earth Surface*, 114, F02016, doi:10.1029/2008JF001060, 2009.

992 Ngo, V. V., Delalande, M., Clément, A., Michau, N. and Fritz, B.: Coupled transport-reaction modeling
993 of the long-term interaction between iron, bentonite and Callovo-Oxfordian claystone in
994 radioactive waste confinement systems., *Applied Clay Science*, 101, 430-443, 2014

995 Pan, Y., Weill, S., Ackerer, P. and Delay, F.: A coupled stream flow and depth-integrated subsurface
996 flow model for catchment hydrology, *Journal of Hydrology*, 530, 66-78, 2015

997 Pierret, M. C., Cotel, S., Ackerer, P., Beaulieu, E., Benarioumlil, S., Boucher, M., ... & Friedmann, P.:
998 The Strengbach catchment: A multidisciplinary environmental sentry for 30 years. *Vadose*
999 *Zone Journal*, 17, 2018.

1000 Pierret, M. C., Stille, P., Prunier, J., Viville, D., & Chabaux, F. Chemical and U–Sr isotopic variations in
1001 stream and source waters of the Strengbach watershed (Vosges mountains, France).
1002 *Hydrology and Earth System Sciences*, 18, 2014.

1003 Pollet-Villard, M., Daval, D., Ackerer, P., Saldi, G. D., Wild, B., Knauss, K. G. and Fritz, B.: Does
1004 crystallographic anisotropy prevent the conventional treatment of aqueous mineral reactivity?
1005 A case study based on K-feldspar dissolution kinetics, *Geochim. Cosmochim. Acta*, *190*, 294-
1006 308, 2016.

1007 Prunier, J., Chabaux, F., Stille, P., Gangloff, S., Pierret, M. C., Viville, D. and Aubert, A. : Geochemical
1008 and isotopic (Sr, U) monitoring of soil solutions from the Strengbach catchment (Vosges
1009 mountains, France): Evidence for recent weathering evolution, *Chem. Geol.*, *417*, 289-305,
1010 2015.

1011 Schaffhauser, T., Chabaux, F., Ambroise, B., Lucas, Y., Stille, P., Reuschlé, T., Perrone, T. and Fritz, B. :
1012 Geochemical and isotopic (U, Sr) tracing of water pathways in the granitic Ringelbach
1013 catchment (Vosges Mountains, France), *Chem. Geol.*, *374*, 117-127, 2014.

1014 Schmitt, A.D., Gangloff, S., Labolle, F., Chabaux, F. and Stille, P.: Ca biogeochemical cycle at the beech
1015 tree - soil solution interface from the Strengbach CZO (NE France): insights from stable Ca and
1016 radiogenic Sr isotopes, *Geochim. and Cosmochim. Acta* *213*, 91-109, 2017

1017 Schmitt AD, Borrelli N., Ertlen D., Gangloff S., Chabaux, F. and Osterrieth M.: Stable calcium isotope
1018 speciation and calcium oxalate production within beech tree (*Fagus sylvatica* L.) organs,
1019 *Biogeochemistry*, *137*,197-217, DOI 10.1007/s10533-017-0411-0, 2018.

1020 Steefel, C. I., DePaolo, D. J. and Lichtner, P. C.: Reactive transport modeling: An essential tool and a
1021 new research approach for the Earth sciences, *Earth Planet. Sci. Let.*, *240*, 539-558, 2005

1022 Tardy, Y. and Fritz, B.: An ideal solid solution model for calculating solubility of clay minerals, *Clay*
1023 *minerals*, *16*, 361-373, 1981.

1024 Viville, D., Chabaux, F., Stille, P., Pierret, M. C. and Gangloff, S.: Erosion and weathering fluxes in granitic
1025 basins: the example of the Strengbach catchment (Vosges massif, eastern France), *Catena*, *92*,
1026 122-129, 2012.

1027 Weill, S., Altissimo, M., Cassiani, G., Deiana, R., Marani, M. and Putti, M.: Saturated area dynamics and
1028 streamflow generation from coupled surface–subsurface simulations and field observations,
1029 *Advances in water resources*, 59, 196-208, 2013.

1030 Weill, S., Delay, F., Pan, Y. and Ackerer, P.: A low-dimensional subsurface model for saturated and
1031 unsaturated flow processes: ability to address heterogeneity, *Computational Geosciences*, 21,
1032 301-314, 2017.

1033 Weill, S., Lesparre, N., Jeannot, B., & Delay, F. Variability of Water Transit Time Distributions at the
1034 Strengbach Catchment (Vosges Mountains, France) Inferred Through Integrated Hydrological
1035 Modeling and Particle Tracking Algorithms. *Water*, 2637, 2019.

1036 White, A. F. and Brantley, S. L.: The effect of time on the weathering of silicate minerals: why do
1037 weathering rates differ in the laboratory and field?, *Chem. Geol.*, 202, 479-506, 2003.

1038 Wild, B., Daval, D., Guyot, F., Knauss, K. G., Pollet-Villard, M. and Imfeld, G.: pH-dependent control of
1039 feldspar dissolution rate by altered surface layers, *Chemical Geology*, 442, 148-159, 2016.

1040 Zhi, W., Li, L., Dong, W., Brown, W., Kaye, J., Steefel, C., & Williams, K. H. Distinct Source Water
1041 Chemistry Shapes Contrasting Concentration-Discharge Patterns. *Water Resources Research*.
1042 2019.

1043 Zhu, C.: In situ feldspar dissolution rates in an aquifer, *Geochim. Cosmochim. Acta*, 69, 1435-1453,
1044 2005.

1045

1046

1047 **Figure and table captions**

1048 Figure 1: sampling locations within the Strengbach catchment. Blue stars represent springs,
1049 blue diamonds represent piezometers, and the blue circle represents the stream at the outlet
1050 of the watershed. Green circles represent soil solution locations, and black diamonds
1051 represent bedrock facies locations.

1052 Figure 2: on the left: calibrated field of thicknesses of the weathered material constituting the
1053 shallow unconfined aquifer at the Strengbach catchment used for the simulations by NIHM.
1054 The 1D surface draining network used in NIHM is represented by the black lines. The mesh for
1055 the groundwater compartment is represented by grey lines. On the right: fitting observed flow
1056 rates from the Strengbach stream at the outlet of the catchment with simulations of flow
1057 within the watershed (illustrated from 2010 to 2015). The subsurface compartment inherits
1058 from the aquifer thicknesses reported in the left panel, and the topography lets the natural
1059 outlet of the subsurface compartment being the surface draining network.

1060 Figure 3: principle of the method of backtracking used to determine flow lines that generate
1061 flow at the outlet of the Strengbach catchment. Particles are dispatched along the wet fraction
1062 of the 1D river network (only one is represented here at a position a on 01/01/2010 at 23:59).
1063 NIHM generates an output heterogeneous velocity field at that date for the whole watershed,
1064 denoted $V_{01/01/2010}$. By using a velocity field of the same magnitude but opposite direction to
1065 the particle, the position of the particle is backtracked until 31/12/2009 23:59. Then, to further
1066 backtrack the trajectory of the particle, the velocity field is updated accordingly. The
1067 frequency of velocity field updates is set to one day.

1068

1069 Figure 4: at the top, flow lines of the subsurface that feed with water the surface draining
1070 network on March 1st, 2010 (on the left, high-flow period) and July 1st, 2010 (on the right, low-
1071 flow period). The color scale indicates that a water particle reaching the river at a given date
1072 started its travel along the streamline or passed at a given location on the streamline x days
1073 prior. The density of streamlines is associated with the flowing versus dry fraction of the river
1074 network at a prescribed date. Below, flow lines of the subsurface that feed with water the
1075 geochemical sampling sites on March 30th, 2010 (on the left, flood event) and November 29th,
1076 2011 (right, drought event) according to NIHM simulations. For each sampling site, 10 particles
1077 were dispatched in the direct neighborhood of the site and then backtracked to render 10
1078 stream lines. The color scale for times is similar to that of the top plot.

1079 Figure 5: conceptual scheme used in the modeling of the water chemistry. The soil solutions
1080 are used as input solution. Cells represent the grid of the reactive-transport code KIRMAT. The
1081 regolith is discretized into a 1D succession of cells along the active parts of the flow lines
1082 determined by the NIHM hydrological model. The hydrogeochemical model KIRMAT evaluates
1083 transport and geochemical processes within each cell. The integrated chemistry of sampled
1084 waters is the arithmetic mean of solute concentrations with regularly distributed inlet points
1085 along a stream line.

1086 Figure 6: maps of piezometric gradient and depth-integrated hydraulic conductivity for the
1087 Strengbach catchment, as simulated by NIHM, on 29/11/2011 (dry period) and 30/03/2010
1088 (high flows period). The mean hydraulic conductivity is integrated normal to bedrock of the
1089 aquifer and thus depends on the water saturation of the vadose zone and the location of the
1090 water table.

1091 Figure 7: simulation results for the CS1 spring for an important drought (29/11/2011) and a
1092 strong flood event (30/03/2010). At the top, active parts of the flow lines bringing the waters
1093 to the CS1 spring for the two sampling dates (7A and 7B). Below, simulated chemical
1094 compositions of CS1 spring waters after integration along the flow lines and comparison with
1095 the initial soil solution and the spring chemistry data (7C and 7D). Error bars show analytical
1096 uncertainties on measured concentrations and induced uncertainties in model results (the
1097 propagation in the KIRMAT simulations of analytical uncertainties from pH and chemical
1098 concentrations measured in the soil solutions).

1099 Figure 8: simulation results for the CS1 spring over the whole range of the water discharges
1100 from the spring. Results are presented for H_4SiO_4 , Na^+ , K^+ and Mg^{2+} concentrations (8A, 8C, 8E
1101 and 8F), pH (8D) and mean water transit time (8B). Red lines indicate simulated parameters
1102 after integration along the flow lines, and blue points show measured values collected
1103 between 2005 and 2015. Corresponding dates and data for the modeled samples are given in
1104 table 1. The overall geochemical database is available in supplementary table EA1. Error bars
1105 show analytical uncertainties on measured concentrations and induced uncertainties in model
1106 results (the propagation in the KIRMAT simulations of analytical uncertainties from pH and
1107 chemical concentrations measured in the soil solutions). Fitting a power law of type $C=a*Q^b$
1108 along the C-Q relations gives the following parameters: $a(\text{H}_4\text{SiO}_4)=10^{-4}$, $b(\text{H}_4\text{SiO}_4)=-0.1$;
1109 $a(\text{Na}^+)=7\times 10^{-5}$, $b(\text{Na}^+)=-0.053$; $a(\text{Mg}^{2+})=10^{-5}$, $b(\text{Mg}^{2+})=-0.016$; $a(\text{K}^+)=10^{-5}$, $b(\text{K}^+)=0$.

1110 Figure 9: (9A) evolution of solute concentrations for H_4SiO_4 , Na^+ , K^+ , Mg^{2+} and Ca^{2+} as a function
1111 of mean water transit time in the Strengbach watershed. Water transit times are between
1112 1.75 and 4 months for all the springs and piezometers in this study. (9B) Focus on the transit
1113 time window (1.75-4 months) for the studied waters and equations linking mean water transit

1114 times and concentrations for H_4SiO_4 , Na^+ , K^+ , Mg^{2+} and Ca^{2+} . Relations between transit times
1115 and concentrations are linear within this window (9C) relations between 'b' coefficients
1116 ($C=a*Q^b$) and the concentration-transit time slopes for the chemical elements. (9D) relations
1117 between 'a' coefficients ($C=a*Q^b$) and the concentration-transit time slopes for the chemical
1118 elements. Elements with significant concentration-mean transit time slopes are slightly
1119 chemodynamic (e.g. H_4SiO_4 and Na^+), while elements with low concentration-mean transit
1120 time slopes are almost chemostatic in the watershed (e.g. K^+ and Mg^{2+}). Ca^{2+} is not shown on
1121 9C and 9D figures as this element is affected by a strong multi-annual concentration decrease
1122 that prevents a meaningful C-Q power law analysis (Ackerer et al., 2018).

1123 Figure 10: simulation results for the PZ3 and PZ5 piezometers for a flood event (05/05/2015).
1124 At the top, active parts of the flow lines that bring waters to the two sampling sites (10A and
1125 10B). Below, simulated chemical compositions of the piezometer waters after integration
1126 along the flow lines and comparison with the initial soil solution and the water chemistry data
1127 (10C and 10D). Error bars show analytical uncertainties on measured concentrations and
1128 induced uncertainties in model results (the propagation in the KIRMAT simulations of
1129 analytical uncertainties from pH and chemical concentrations measured in the soil solutions).

1130 Figure 11: simulation results for the CS2 spring. At the top, active parts of the flow lines that
1131 bring water to the CS2 spring for drought (29/11/2011) and flood (30/03/2010) events (11A
1132 and 11B). The CS2 location results in more scattered flow lines than for CS1 spring. Below,
1133 simulation results for the CS2 spring over the whole range of experienced discharges (11C and
1134 11D). Blue lines indicate simulated parameters after integration along the slowest flow line,
1135 yellow lines indicate simulated parameters after integration along the fastest flow line, and
1136 blue points show measured values collected between 2005 and 2015 (data in table 1 and in

1137 supplementary table EA2). Error bars show analytical uncertainties on measured
1138 concentrations and induced uncertainties in model results (the propagation in the KIRMAT
1139 simulations of analytical uncertainties from pH and chemical concentrations measured in the
1140 soil solutions).

1141 Figure 12: simulation results for the RH3 spring chemistry and for a flood event (30/03/2010).
1142 Left, simulated concentrations by assuming flow lines running through gneiss (GN) only (12A).
1143 Right, simulated concentrations by assuming flow lines running through hydrothermally
1144 altered granite (VS) only (12B). Error bars show analytical uncertainties on measured
1145 concentrations and induced uncertainties in model results (the propagation in the KIRMAT
1146 simulations of analytical uncertainties from pH and chemical concentrations measured in the
1147 soil solutions).

1148 Figure 13: overview of the simulated flow lines in the subsurface that feed with water the
1149 geochemical sampling sites CS1, PZ3, and PZ5 on May 5th, 2015. The simulated chemical
1150 compositions after geochemical integration along the flow lines are compared with the initial
1151 soil solution and the spring chemistry data.

1152 Table 1: measured pH, water discharges and chemical concentrations of H_4SiO_4 , Na^+ , K^+ , Mg^{2+} ,
1153 and Ca^{2+} in water samples collected at the Strengbach catchment and used for the
1154 hydrogeochemical modeling. The sampling sites include springs (CS1, CS2, RH3) and
1155 piezometers (PZ3, PZ5).

1156 Table 2: Initial and calibrated values of the hydrodynamic parameters of the aquifer in the
1157 hydrological simulation of the Strengbach catchment by NIHM.

1158 Table 3: Comparison between BET surfaces and geometric surfaces for the major primary
1159 minerals present in a granitic context. BET surfaces were measured via gas absorption

1160 experiments by ¹Berger et al., 1994; ²Chou and Wollast, 1985; ³Lundstrom and Ohman, 1990;
1161 ⁴Amrhein and Suarez, 1992; ⁵Acker and Bricker, 1992; and ⁶Guidry and Mackenzie, 2003.
1162 Geometric surfaces were recalculated from the granulometric ranges of the minerals and by
1163 assuming a spherical geometry.