1 **Crossing hydrological and geochemical modeling to understand the spatiotemporal variability**

2 **of water chemistry in a headwater watershed (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

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9 Corresponding authors : Julien Ackerer, Benjamin Jeannot, Frederick Delay (fdelay@unistra.fr),
10 François Chabaux (fchabaux@unistra.fr).

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Abstract

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

42 chemical elements. The good matching between the measured and modeled concentrations

43 while respecting the water-rock times provided by the hydrological simulations also shows that

44 it is possible to capture the chemical composition of waters using simply determined reactive

45 surfaces and experimental kinetic constants. The results of our simulations also strengthen the

46 idea that the low surfaces calculated from the geometrical shapes of primary minerals are a

47 good estimate of the reactive surfaces within the natural environment.

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1- Introduction

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

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

71 Recent efforts in hydrological modeling were conducted to develop spatially distributed

72 approaches that better consider the interplay between surface and subsurface processes (e.g.,

73 Gunduz and Aral, 2005; Kampf and Burges, 2007; Camporese et al., 2010). Due to the

74 complexity of flows in the hydrological processes, many modeling approaches are based on the

75 full resolution of Richard's and Saint Venant equations to correctly describe the interactions

76 between stream, overland and subsurface waters (Kampf and Burges, 2007). These approaches

77 have shown their ability to capture the hydrological functioning of various watersheds, knowing

78 that the full resolution of Richard's and Saint Venant equations requires long computational

79 times and faces calibration and parameterization difficulties (Ebel and Loague, 2006; Mirus et

80 al., 2011). Questions have been raised regarding the optimal complexity of the equations that

81 are needed to correctly treat the hydrology of catchments in their surface and subsurface

82 compartments with reasonable computation times (Gunduz and Aral, 2005).

83 Low-dimensional models have attracted growing interest because they represent an interesting

84 compromise between equation complexity, computational time, and result accuracy (Pan et al.,

85 2015; Hazenberg et al., 2016; Weill et al., 2013; 2017; Jeannot et al., 2018). The reduction of

86 dimensionality is mainly associated with a subsurface compartment (including both the vadose

87 and the saturated zones) modeled as a two-dimensional layer. Flow and transport processes are

88 integrated over a vertical direction or a direction normal to bedrock and manipulate averaged

89 (integrated) hydrodynamic properties. These low-dimensional models recently demonstrated

90 their ability to reproduce the results from fully dimensioned approaches in small catchments

91 while reducing computational costs (Pan et al., 2015; Jeannot et al., 2018). Nonetheless, the

92 water transit times calculated from these depth-integrated models are rarely confronted with

93   the water-rock interaction times inferred from hydrogeochemical modeling of water chemistry

94   in watersheds.

95   For its part, the understanding of the hydrogeochemical functioning of the critical zone has

96   been significantly advanced by the implementation of reactive-transport laws in geochemical

97   modeling codes (Steefel et al., 2005; Lucas et al., 2010; 2017; Goddéris et al., 2013; Li et al.,

98   2017). These developments allow for considering a variety of processes, such as flow and

99   transport processes, ion exchanges, biogeochemical reactions, and the interplay between

100   primary mineral dissolution and secondary mineral precipitation (Moore et al., 2012; Lebedeva

101   and Brantley, 2013; Ackerer et al., 2018). Reactive transport models have been used to explore

102   a wide variety of scientific issues, including the study of global atmospheric CO_2 consumption by

103   weathering reactions (Goddéris et al., 2013; Li et al., 2014), the formation and evolution of soil

104   and regolith profiles (Maher et al., 2009; Navarre-Sitchler et al., 2009; Lebedeva and Brantley,

105   2013), and the variability of water quality and chemistry in the environment (Lucas et al., 2010;

106   2017; Ackerer et al., 2018). However, these approaches usually rely on a simple 1D flow path

107   through a regolith column or along a hill slope to model flow in the system (e.g. Maher, 2011;

108   Moore et al., 2012; Lucas et al., 2017; Ackerer et al., 2018). 1D reactive-transport models are

109   useful to discuss the key processes involved in the regolith formation and in the acquisition of

110   the water chemical composition, but these models cannot consider the complexity of the flow

111   trajectories in watersheds, and hence, its effects on the water chemistry.

112   A new step is therefore necessary for the development of hydrogeochemical modeling

113   approaches that are applicable at the watershed scale and are able to integrate the complexity

114   of the water flows and the diversity of the water-rock interaction processes. Recent efforts have

115   been undertaken in the direction of merging hydrological and geochemical codes, with for

116   example, the parallel reactive transport code ParCrunchFlow (Beisman et al., 2015), or the

117   coupled hydrogeochemical code RT-Flux-PIHM (Bao et al., 2017; Li et al., 2017).   As an

118   alternative to fully dimensioned codes, this work proposes an original low-dimensional

119   approach, with relatively short computation times and applicable at the watershed scale. This

120   study is combining for the first time in this manner the results from a hydrological low-

121   dimensional (depth-integrated for the subsurface) but spatially distributed model (NIHM) with a

122   reactive-transport model (KIRMAT). The combination allows for simulating over time and space

123   the flow trajectories, the flow rates, the weathering reactions, and the evolution of the water

124   chemistry within a headwater watershed, the Strengbach catchment.

125   This catchment is one of the reference observatories of the French critical zone network

126   (OZCAR), where multidisciplinary studies, including hydrological, geochemical and geological

127   investigations, have been performed since 1986 (“Observatoire Hydrogéochimique de

128   l’Environnement”, OHGE; http://ohge.unistra.fr; El Gh’Mari, 1995; Fichter et al., 1998; Viville et

129   al., 2012; Gangloff et al., 2014; 2016; Prunier et al., 2015; Pan et al., 2015; Ackerer et al., 2016;

130   2018; Beaulieu et al., 2016; Chabaux et al., 2017; 2019; Schmitt et al., 2017; 2018; Daval et al.,

131   2018; see also Pierret et al., 2018 for an updated overview of the Strengbach watershed).

132   **2- Site presentation and data acquisition**

133   The Strengbach catchment is a small watershed (0.8 km²) located in the Vosges Mountains of

134   northeastern France at altitudes between 883 and 1147 m. Its hydroclimatic characteristics can

135   be found in Viville et al. (2012) or in Pierret et al. (2018). It is marked by a mountainous oceanic

136 climate, with an annual mean temperature of 6 $^{\circ}$C and an annual mean rainfall of approximately

137 1400 mm, with 15 to 20% falling as snow during two to four months per year. The snow cover

138 period is quite variable from year to year, and may not be continuous over the entire winter.

139 The annual mean evapotranspiration is of approximately 600 mm, and the annual mean runoff

140 of approximately 800 mm (Viville et al., 2012). The watershed is currently covered by a beech

141 and spruce forest. The bedrock is a base-poor Hercynian granite covered by a 50 to 100 cm-thick

142 acidic and coarse-in-texture soil. The granitic bedrock was fractured and hydrothermally altered,

143 with a stronger degree of hydrothermal overprinting in the northern than the southern part of

144 the catchment (Fichter et al., 1998). The granite was also affected by surface weathering

145 processes during the Quaternary (Ackerer et al., 2016). The porous and uppermost part of the

146 granitic basement constitutes an aquifer from 2 to approximately 8 meters thickness. In the

147 Strengbach watershed, the major floods and high-flow events usually occur during snowmelt

148 periods at the end of the winter season or in the early spring. In contrast, the low-flow periods

149 commonly happen at the end of the summer or during the autumn. Several springs naturally

150 emerge along the slopes (figure 1). The watershed has been equipped with several piezometers

151 and boreholes since 2012, those being located along the slopes on both sides of the watershed

152 (figure 1 in Chabaux et al., 2017).

153 Spring waters have been regularly collected and analyzed since 2005, with monthly sampling

154 supplemented by a few specific campaigns to cover the complete range of water discharges in

155 the watershed. Piezometer waters have been collected only during specific sampling campaigns

156 over the period 2012-2015, and as for the spring waters, these sampling campaigns cover

157 different hydrological conditions from wet to dry periods. The soil solutions were collected with

a monthly frequency on the southern slope at a beech site (named HP) and to the north at a

spruce site (named VP; figure 1; more details in Prunier et al., 2015 or Chabaux et al., 2019). For

all the collected waters, the concentrations of the major dissolved species and the pH were

determined by following the analytical techniques used at LHyGeS (Strasbourg, France) and

detailed in Gangloff et al. (2014) and Prunier et al. (2015). Discharges of water from the springs

were measured during the sampling campaigns, as were the water levels within the

piezometers.

The mineralogy and the porosity of the bedrock have been studied in detail in previous studies

(El Gh'Mari, 1995; Fichter et al., 1998). On the southern part of the catchment, the weakly

hydrothermally altered granite (named HPT, figure 1) is mainly composed of quartz (35%), albite

(31%), K-feldspar (22%) and biotite (6%). It also contains small amounts of muscovite (3%),

anorthite (2%), apatite (0.5%) and clay minerals (0.5%). On the northern part of the catchment,

the lithology is more variable, with the presence of gneiss close to the crest lines and the

occurrence of hydrothermally altered granite on the rest of the slopes (El Gh'Mari, 1995, figure

1).

The hydrological, geochemical and petrological data obtained from these field investigations are

the basis of the modeling exercise presented in this study. More precisely, this study is based on

hydrogeochemical data from 2005 to 2015 for waters from four springs of the southern part

(CS1, CS2, CS3 and CS4) and one spring of the northern part (RH3) of the watershed.

Hydrogeochemical data obtained over the period 2012-2015 for two piezometers (PZ3, PZ5) of

the southern part of the watershed are also studied. The overall hydrogeochemical database is

179   available as supplementary tables (tables EA1 to EA9). The specific chemical data from spring

180   and piezometer waters modeled in this study are reported in table 1.

181   **3- Modeling methods**

182   The modeling developments presented in this study represent a new step in the efforts

183   undertaken to constrain the mechanisms controlling the geochemical composition of surface

184   waters and to understand their spatial and temporal variations at the scale of headwater

185   mountainous watersheds (Schaffhauser et al., 2014; Lucas et al., 2017; Ackerer et al., 2018). The

186   main innovation of this present work is to couple a spatially distributed and low-dimensional

187   hydrological model with a reactive transport code to constrain the spatiotemporal variability of

188   chemical composition of waters from a headwater watershed. To the best of our knowledge,

189   this is the first time that such a coupling between low-dimensional hydrological and

190   hydrogeochemical modeling approaches has been attempted in this way at the watershed scale.

191   **3-1 Hydrological modeling**

192   To assess the water flows in the watershed, several simulations were performed with the

193   hydrological code NIHM (Normally Integrated Hydrological Model; Pan et al., 2015; Weill et al.,

194   2017; Jeannot et al., 2018). This code is a coupled stream, overland, and low-dimensional

195   (depth-integrated) subsurface flow model developed at LHyGeS and already tested in the

196   Strengbach watershed (Pan et al., 2015). The stream and overland flows are described by a

197   diffusive-wave equation, and the subsurface flow is handled through an integration (in a

198   direction normal to bedrock) of the unsaturated-saturated flow equation from the bedrock to

199   the soil surface (Weill et al., 2017). The exchanges of water between the surface and subsurface

200 flows are addressed via the hydraulic head differences between the compartments (Jeannot et

201 al., 2018).

202 Regarding the hydrological simulations, the parameters of the aquifer have been adjusted in

203 NIHM through a calibration-validation process. Several zones of heterogeneity were defined

204 based on field observations (Ackerer et al., 2016; Chabaux et al., 2017). In each of these zones,

205 the saturated hydraulic conductivity, the depth of substratum, and the porosity, were set to

206 uniform values. Other parameters were set to uniform values over the whole catchment (see

207 table 2). The thickness of the aquifer that was used for the simulations varied from 2 meters

208 near the main crests to up to 8 meters in the middle of the watershed (figure 2), in agreement

209 with the data obtained during the recent geological investigations and drilling campaigns

210 undertaken at the catchment (Ackerer et al., 2016; Chabaux et al., 2017). The uniform

211 precipitations over space applied at the surface of the catchment are drawn from data of the

212 pluviometric station located at the highest elevation of the watershed (site PA, figure 1). The

213 hydrological model NIHM was then run over a first time period (years 1996-1997). By a process

214 of trial and error, the parameters were gradually modified to improve the fitting between the

215 observed and simulated flow rates at the outlet of the catchment (table 2). The fit was

216 quantified by the root mean square error (RMSE) and the Kling-Gupta efficiency coefficient

217 (KGE; Gupta et al., 2009).

218 Once the best fit was obtained, the model was then run over another time period (2010-2015),

219 but without changing the parameters anymore, and the quality of the fit was re-assessed for

220 this new time-period with the KGE and RMSE. Figure 2 shows the result for the 2010-2015 time

221 period. Once the water discharges were correctly reproduced at the outlet, a backtracking

222 approach was used to constrain the origin of subsurface water exiting the system at prescribed

223 locations, and the spatiotemporal variability of the flow lines within the watershed. To back

224 track the water particles, the velocity fields calculated by the NIHM model were inverted in their

225 direction, and the locations of the backtracked particles were saved at each time-step. A daily

226 time-step was used for the backtracking, as a compromise between computational efforts and a

227 refined description of the transient velocity fields. A schematic representation of the

228 backtracking approach is given in figure 3. This methodology allows for constraining the flow

229 lines that bring waters for a given time and at a given position on the catchment. This

230 information is of major interest to determine the origin of the spring and piezometer waters. It

231 is shown at the catchment scale, that flows are mainly driven by gravity in association with the

232 steep slopes of the watershed, the latter being almost evenly drained over its whole surface

233 area (figure 4). For each water sampling area, ten flow lines that bring water to the location of

234 interest were determined (figure 4), together with a few features of the flow lines, including:

235 local velocities, mean velocities, and length of the flow paths.

236 It is worth noting that NIHM is a depth-integrated model for its subsurface compartment where

237 flow is simulated over a 2D-mesh and under the assumption of an instantaneous hydrostatic

238 equilibrium in the direction perpendicular to the substratum. Therefore, times calculated along

239 the backtracked streamlines correspond to a date, x days before arrival, at which a water

240 particle entered the subsurface or passed at a given location along the streamline. Streamlines

241 calculated via backtracking and reaching sampling sites only consider flow in the subsurface

242 compartment and are conditional to an arrival date at a prescribed location. As backtracked

243   streamlines are not associated with mean water flux values, the transit time distributions drawn

244   from streamline calculations are only an approximation of the actual transit time distributions.

245   **3-2 Hydrogeochemical modeling**

246   The simulations of the water chemical composition along the flow lines were performed with

247   the hydrogeochemical KIRMAT code (KInectic of Reaction and MAss Transport; Gérard et al.,

248   1998; Lucas et al., 2010; Ngo et al., 2014). KIRMAT is a thermokinetic model derived from the

249   Transition State Theory (TST, Eyring, 1935; Murphy and Helgeson, 1987) that simultaneously

250   solves the equations describing geochemical reactions and transport mass balance in a 1D-

251   porous medium. The mass transport includes the effects of one-dimensional convection,

252   diffusion and kinematic dispersion. Chemical reactions account for the dissolution of primary

253   minerals and oxido-reduction reactions, in addition to the formation of secondary minerals and

254   clay minerals. Thermodynamic and kinetic data for the primary minerals are available in

255   supplementary materials (tables EA10, EA11 and EA12).

256   The clay fraction is defined as a solid solution made up of a combination of pure clay end-

257   members. The clay end-members are defined on the basis of X-ray diffraction analyses of clay

258   minerals present in bedrock samples collected in the field (Fichter et al., 1998; Ackerer et al.,

259   2016; 2018). They consist of K-Illites, Mg-Illites, Ca-Illites, Montmorillonites, Na-

260   Montmorillonites, K-Montmorillonites, Ca-Montmorillonites and Mg-Montmorillonites

261   (supplementary material table EA13). During the hydrogeochemical simulations, the clay solid

262   solution is precipitated at thermodynamic equilibrium and its composition varies over time,

263   depending on the evolution of the water chemistry and the bedrock mineralogy (Ackerer et al.,

264   2018). This multicomponent solid solution reproduces the diversity of the clay minerals formed

265   during low-temperature water-rock interactions (Tardy and Fritz, 1981).

266   The KIRMAT code also includes feedback effects between mineral mass budgets, reactive

267   surfaces, and the evolution of bedrock porosity (Ngo et al., 2014). The reactive surfaces of the

268   primary minerals were calculated by assuming a simple spherical geometry for all the minerals,

269   and the mean size of the minerals was estimated from the observation of thin sections from

270   bedrock samples. During simulations, clay mineral precipitation and the evolution of the

271   reactive surfaces of primary minerals are tracked together with chemical processes and water

272   chemical composition. Given the short time scales reported by the hydrological simulations

273   (monthly timescale), changes in the reactive surfaces of primary minerals over the simulation

274   time were negligible. Precipitation of other secondary minerals such as carbonates, hematite or

275   amorphous silica was also tested, but these minerals were not formed given the saturation

276   states calculated in the geochemical modeling (supplementary table EA14). Secondary mineral

277   precipitation is therefore controlled by clay mineral formation. The KIRMAT code has already

278   been applied in geochemical modeling of alluvial groundwaters (Lucas et al., 2010) and surface

279   waters (Lucas et al., 2017; Ackerer et al., 2018).

280   For this study, the modeling strategy is adapted from Ackerer et al. (2018) to consider the new

281   transit time constrains provided by the hydrological code NIHM. To capture the chemical

282   composition of the spring and the piezometer waters, numerical simulations were performed

283   along the flow lines that were determined through the backtracking approach. A sketch of the

284   hydrogeochemical modeling strategy is provided in figure 5. For each flow line, several KIRMAT

285   simulations were performed with different starting positions along the active part of the line.

286 The starting positions represent the locations at which the soil solutions percolate through the

287 subsurface shallow aquifer. These variable starting positions are spaced with a constant

288 distance along the flow line. The deepest soil solutions collected to the south at the beech site

289 (HP) and to the north at the spruce site (VP) were considered representative of the soil solutions

290 for the southern and northern slopes of the catchment, respectively. The data of soil solution

291 chemistry used in this study are available in Prunier et al. (2015) and in supplementary tables

292 (tables EA6 and EA7). These soil solutions integrate the surface processes occurring before

293 water percolation into the bedrock. Because the soil solutions are injected into the aquifer, the

294 temporal variability of the soil solution chemistry and its impact on the water-rock interactions

295 along the flow paths are accounted for in the modeling approach.

296 Data related to the bedrock properties, such as the mineralogical compositions, the mineral

297 reactive surfaces and the thermodynamic and kinetic constants, are given in Ackerer et al.

298 (2018) and in supplementary tables (tables EA10 to EA14). Mineral phases are assumed

299 homogeneously distributed over the regolith layer. By following this strategy, the simulations

300 that consider soil solutions percolating at the upper part of the catchment reflect the chemical

301 evolution of waters with long path lengths and long transit times within the aquifer. By contrast,

302 shorter path lengths and shorter transit times are associated with the percolation of soil

303 solutions that occurs in the vicinity of the sampling locations (figure 5). Because the springs or

304 the piezometers collect waters from different origins and with contrasted transit times,

305 integration along each water flow line was performed. The aim of the integration is to

306 determine the mean chemical composition resulting from the mixing of the waters

307 characterized by variable transit times (figure 5). The integrated chemical composition of the

308   waters provided by a given flow line is calculated by taking the arithmetic mean of the solute

309   concentrations calculated by the succession of the KIRMAT simulations along the flow line

310   (figure 5). This arithmetic mean reflects a simple full mixing of uniform water fluxes irrespective

311   of their short or long transit times. In other words, the geochemical simulations are based on

312   the hypothesis of spatially homogenous water-rock interactions along the flow lines. The soil

313   solutions are assumed to percolate uniformly within the aquifer and are then conveyed along

314   the slopes by uniformly distributed mass of water until reaching the sampling locations.

315   **4- Hydrological modeling results**

316   **4-1 Spatial variability of the flow lines**

317   The results provided by the hydrological code NIHM show that to the first order, the Strengbach

318   catchment is well drained and that the topography exerts an important control on the flow line

319   distribution (figure 4). Along the hillsides presenting linear or slightly convex slopes, the water

320   flow lines show simple characteristics. The flow paths are nearly parallel, and the water

321   velocities are similar along the different flow lines on this type of hillside. The water velocities

322   tend to increase when moving downstream, with slower velocities near the main crests and

323   higher velocities on the steepest parts of the hillsides. The waters collected along this type of

324   hillside are therefore characterized by small variability of transit times. This is the case for the

325   CS1, CS3 and RH3 spring waters located on the southern and northern parts of the catchment

326   (figure 4). This is also the case for the piezometers PZ3 and PZ5 in the southern part of the

327   watershed (figure 4). For the samplings located on linear or slightly convex slopes (CS1, CS3,

328   RH3, PZ3 and PZ5), the characteristics of the different flow lines that feed each site are

329   therefore comparable for a given site and for a given date.

330   By contrast, in the vicinity of the valley and in the topographic depressions, the hydrological

331   modeling indicates that the flow line characteristics are more variable. Because flow lines

332   coming from different hill-sides can feed a topographic depression, mixing of different flow lines

333   with variable flow paths and contrasted water velocities can occur at these locations. The

334   waters collected in valleys or in topographic depressions are therefore characterized by a higher

335   variability of transit times. This is the case for the CS2 and CS4 springs, which are located in a

336   depression in the axe of the small valley and surrounded by slopes with various orientations and

337   a complex flow line distribution (figure 4). For these two springs, the characteristics of the

338   different flow lines can be different for a given date.

339   **4-2 Temporal variability of the flow lines**

340   Hydrological modeling under general transient conditions can render the evolution over time of

341   water flows in the watershed but also of other hydraulic variables or parameters. As an

342   example, after an important rainfall event (30/03/2010 in figure 6), snapshots of the average

343   hydraulic conductivity in the subsurface show increasing values with decreasing elevation in the

344   watershed. The same observation holds for hydraulic conductivity during drought periods (see

345   29/11/2011, in figure 6). Provided that the hydraulic head gradient is largely dominated by the

346   topography and therefore almost constant over time (figure 6), the water velocities are

347   increasing along the flow lines from crests to valleys, irrespective of the wet versus dry

348   hydrological periods.

349   For the CS1 spring, the mean flow velocities along the flow lines vary from approximately 1

350   m/day to 7 m/day between the severe drought of 29/11/2011 and the strong flood of

351   30/03/2010 (figures 7A and 7B). These events correspond to the annual minimum and

352   maximum flow rates at the outlet of the Strengbach watershed. For the same dates, the mean

353   velocities vary from 2 – 12 m/day, 1 – 4 m/day and 1 – 9 m/day for the springs CS2, CS3 and

354   CS4, respectively. The variations from drought to flood are very similar for the piezometer

355   waters, with velocities in the ranges 2 – 10 m/day and 2 – 12 m/day for the PZ3 and PZ5

356   piezometers, respectively. The RH3 spring located on a steeper part of the northern slopes

357   exhibits flow velocity variations from 5 to 20 m/day from dry to flood conditions.

358   In addition to the flow velocity variations, the hydrological simulations also reveal variability in

359   the lengths of the active parts of the flow lines. Such variability is triggered by the particular

360   seasonal variations of the hydraulic conductivities within the catchment. During periods of

361   drought, the simulations indicate a strong decrease of hydraulic conductivities close to the main

362   crests and much smaller variations at mid-slopes (figure 6). The crests rapidly dry out, whereas

363   the areas at mid-slopes still supply some water to the stream network. These contrasting

364   hydrological behaviors result from the differences in aquifer thickness and water storage

365   between the crests and the other parts of the catchment (figure 2). Thin aquifer, flow

366   divergence and absence of feeding areas prevent large water storage on the crests, in

367   opposition to mid-slope parts with much thicker aquifers and the presence of feeding areas

368   upstream. This particular pattern simulated for the hydraulic conductivities implies that the

369   active parts of the flow lines extend up the main crests during important floods, whereas they

370   are limited to mid-slopes after a long dry period.

371 The consequence of this hydrological functioning is to moderate the seasonal variations of the

372 transit times of waters, as the active lengths of flow lines vary simultaneously with water flow

373 rates. Calculations indicate that for the spring and piezometer waters collected in this study, the

374 mean transit times of waters only vary from approximately 1.75 to 4 months between the

375 strongest flood and the driest conditions. These short subsurface water transit times are

376 explained by the small size of the catchment and the relatively steep slopes.

377 **5- Hydrogeochemical modeling results**

378 **5-1 CS1 and CS3 springs (southern slope)**

379 The CS1 and CS3 springs emerge on the same slope and drain the same rocks. Their hydrological

380 behavior is also very similar in terms of flow lines and water transit times. The interesting

381 consequence of the simple flow line distribution for these springs is that a single flow line can be

382 considered as representative of all the flow lines that are feeding the spring, irrespective of the

383 hydrological conditions. Hydrogeochemical simulations were performed along a single flow line

384 for different hydrological periods using the methodology illustrated in figure 5. The case of CS1

385 spring is used below to highlight the main results obtained from this approach. For the strong

386 flood of 30/03/2010, the KIRMAT simulations modeling the waters coming from the proximity of

387 the spring and characterized by short transit times produced too much diluted solutions,

388 whereas the waters coming from the main crests are too much concentrated to reproduce the

389 spring water chemical composition. However, after an integration of all the waters arriving at

390 CS1 with the different transit times employed for the simulation, the resulting geochemical

391 composition correctly reproduces the chemical composition of CS1 spring water at this date

392   (H_4SiO_4, Na^+, K^+, Mg^{2+}, and Ca^{2+} concentrations, figure 7D). A similar conclusion is obtained for

393   the important drought of 29/11/2011. Again, geochemical integration of all the waters arriving

394   at CS1 along a water line but with different transit times correctly reproduces the chemical

395   composition of the CS1 spring waters collected on this date (figure 7C). This comment applies

396   regardless of the time period considered.

397   The coupled hydrological and hydrogeochemical approach has been applied for the CS1 spring

398   for 6 dates covering the whole range of the water discharges of the spring (table 1). The

399   modeling results capture the seasonal variations of the water chemical composition of the CS1

400   spring over the whole range of observed flow rates at CS1 (figure 8). Simulations especially

401   account for the 20-30% variation in H_4SiO_4 concentrations (figure 8A), the 10-20% variation in

402   Na^+ concentrations (figure 8C), and the relatively stability of the K^+, Mg^{2+} and pH of the CS1

403   waters (figure 8E, 8F and 8D). The response of each chemical element to a change in water

404   discharge is related to the initial soil solution concentration, the nature of primary minerals

405   controlling its budget and the degree of its incorporation into clay minerals. Specific

406   concentration-mean transit time relations (C-MTT relations) explain why the response of solute

407   concentrations to hydrological changes is different for each element (figure 9). Similar results

408   are obtained for the CS3 spring (figure EA1), showing, as for the CS1 spring, that the model

409   correctly simulates the water chemical composition of the CS3 spring.

410   **5-2 PZ3 and PZ5 piezometers (southern slope)**

411   The two piezometers PZ3 and PZ5 are located on the southern part of the catchment, and their

412   waters drain a granitic bedrock similar to that drained by the CS sources. As for the CS1 and CS3

413 springs, the NIHM modeling results show that the flow lines arriving at the PZ3 piezometer are

414 characterized by a relatively simple distribution. The flow lines are close to each other, and they

415 render similar water velocities on the slopes (figure 4). For the PZ5 piezometer located

416 downstream, the flow lines cover a larger area on the slope, especially during droughts (figure

417 4). However, for a given date, all the flow lines show similar velocities, with particularly fast

418 flows on the lower portion of the hillslope. These results imply that, as for the CS1 and CS3

419 springs, the hydrogeochemical simulations of PZ3 and PZ5 piezometer waters can be performed

420 by relying upon a single flow line representative of all the waters collected by the piezometers

421 on a given date.

422   The geochemical integration along the flow line has been performed in the same manner as

423 detailed above, and this approach is able to reproduce the chemical composition of the waters

424 of the two piezometers, as illustrated in figure 10 for the flood of the 05/05/2015 and in figure

425 EA2 for the dry conditions of 10/11/2015. Together, these modeling results show that the flow

426 along linear or slightly convex slopes on the southern part of the catchment allows to correctly

427 capture the water chemistry of each sampling site with a straightforward integration along a

428 single and representative flow line.

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

430 CS2 and CS4 spring waters drain the same granitic bedrock as the CS1 and CS3 waters, but are

431 located in the direction of the small valley of the Strengbach stream and surrounded by slopes

432 of various orientations and inclinations (figure 4). Consequently, the distribution of the flow

433 lines is much more scattered than for the CS1 and CS3 springs. For the CS2 spring, and for all the

434   hydrological conditions, two different groups of flow lines have been determined by the

435   backtracking approach: a northern group characterized by relatively slow velocities and a

436   southern group with higher velocities (figure 4). When the hydrological conditions vary from a

437   strong flood (30/03/2010) to an important drought (29/11/2011), the flow rates tend to

438   decrease along all the flow lines (figures 11A and 11B). For example, the mean flow velocities

439   along the flow lines vary from approximately 12 m/day to 2 m/day between these two dates.

440   For a given date, the northern group systematically renders slower velocities than the southern

441   group. This scattered distribution of the flow lines implies that a single specific flow line cannot

442   be representative of all the waters collected by the spring. The flow lines calculated using the

443   NIHM model allow for constraining the trajectories of the waters within the watershed;

444   however, the simulations performed in this study cannot provide the mass fluxes of water

445   carried by each flow line. Consequently, a straightforward calculation of the chemistry of the

446   CS2 spring, such as detailed above for CS1, is not applicable because the mixing proportions

447   between the different flow lines are unknown.

448   Alternatively, it is possible to determine the concentrations in the waters carried by the slowest

449   and the fastest flow lines that are feeding the spring and to compare the results with the

450   observed chemistry of the spring water. The results indicate that for all the hydrological

451   conditions, the concentrations calculated from the geochemical integration along the slowest

452   and the fastest flow lines are able to correctly frame the chemical composition in terms of

453   H_4SiO_4, Na^+, K^+, Mg^{2+}, and Ca^{2+} of the CS2 spring waters (results are reported for H_4SiO_4 and Na^+

454   in figures 11C and 11D). The observed chemistry of the CS2 spring is bounded by the chemical

455   compositions of the waters carried by the slowest and fastest flow lines. The modeling results

456 also suggest that the contributions of the slow and fast flow lines are comparable over most of

457 the hydrological conditions, as the observed concentrations are in general at the midpoint

458 between the min (i.e., fast) and max (i.e., slow) boundaries (figures 11C and 11D). It is only for

459 the important droughts that the spring chemistry seems to be mainly controlled by the southern

460 and faster group of flow lines. Further works to precisely estimate the mass fluxes of water

461 carried by each flow line are necessary to model the chemistry of the CS2 spring water with a

462 weighted mixing calculation. The same conclusions apply to the CS4 spring located close to CS2.

463 **5-4 The RH3 spring (northern slope)**

464 The RH3 spring is located on the northern part of the catchment (figure 4), where steep slopes

465 imply fast water velocities and subparallel flow lines. However, if the distribution of the flow

466 lines on the RH3 hillside is simple (as for the CS1 and CS3 springs) the precise lithological nature

467 of the bedrock drained by the RH3 waters is more difficult to constrain (Ackerer et al., 2018).

468 Unlike the southern slope, the bedrock of the northern part of the catchment reveals a complex

469 lithology, with gneiss outcropping in the upper part of the slope and granite of variable degree

470 of hydrothermal overprinting in the intermediate and lower parts. These lithological variations

471 can explain the differences in chemical composition between the RH3 spring waters and the

472 waters of the southern part of the catchment: the RH3 spring waters are characterized by

473 systematically higher concentrations of K^+ and Mg^{2+} cations but show similar concentrations for

474 the other major elements (Ackerer et al., 2018; Pierret et al., 2018). The vertical extension of

475 the gneiss and the spatial variability of the hydrothermal overprinting along the northern slopes

476 are not well known, with the consequence that a straightforward modeling of water chemistry

477 as done for CS1 is not possible for RH3.

478   Alternatively, simulations of two extreme cases can be performed by assuming that the flow

479   lines only run, either on gneiss or on hydrothermally altered granite. When only considering the

480   hydrothermally altered granite (VS facies), the simulated concentrations of H_4SiO_4 and Na^+ are

481   close to the measured ones. Nevertheless, the concentrations of K^+ and especially Mg^{2+} are

482   clearly underestimated (figure 12B). In the case of the flow lines only running on gneiss (GN

483   facies), the simulated concentrations of H_4SiO_4 and Na^+ also match the data. However, due to

484   the higher abundance of biotite in the gneiss, the simulated concentrations of K^+ and Mg^{2+} are

485   higher than the measured ones (figure 12A). At this stage, it is therefore reasonable to propose

486   that the chemical composition of the RH3 spring waters reflects mixing of the two lithological

487   influences. By assuming a geochemical conservative mixing, which is likely a too simplistic

488   scenario, the results would indicate that the flow lines portions running on gneiss and on

489   hydrothermally altered granite count for approximately 40-50% and 50-60% of the total water

490   path length, respectively.

491   Further works to estimate the location of the contact between gneiss and granite are required

492   for more realistic modeling and hence a deeper interpretation of the chemical composition of

493   the RH3 spring waters. In any case, the important point to stress here based on the above

494   simulations is that the complex lithology and bedrock heterogeneity mainly impact the K^+ and

495   the Mg^{2+} budget of the RH3 waters, but not or only slightly the H_4SiO_4 and Na^+ concentrations,

496   which control the main part of global weathering fluxes carried by the Strengbach spring waters.

497   These results readily explain why although the RH3 spring waters exhibits higher Mg^{2+} and K^+

498   concentrations than the other CS springs, they carry relatively similar global weathering fluxes

499   (Viville et al., 2012; Ackerer et al., 2018).

6- Discussion

500

501 The coupling of the NIHM and KIRMAT codes allows for building a better modeling scheme to

502 those commonly used in previous studies regarding the hydrogeochemical modeling of surface

503 waters at the watershed scale. In such previous works, the geochemical simulations were

504 performed mainly along a single 1D flow line, only characterized by homogeneous mean

505 hydrological properties (Goddéris et al., 2006; Maher, 2011; Moore et al., 2012; Lucas et al.,

506 2017; Ackerer et al., 2018). In the previous study on the Strengbach watershed (Ackerer et al.,

507 2018), the soil solutions were also assumed to percolate in the bedrock only at a single starting

508 point of the flow lines. Although these previous approaches were useful for determining the

509 long-term evolution of regolith profiles and/or the mean chemistry of waters at the pluri-annual

510 scale, they cannot be used to discuss the seasonal variations of the water chemical composition.

511 The NIHM-KIRMAT coupling approach makes this possible, as it provides the spatial distribution

512 of the flow lines at the watershed scale and their variations over time. Furthermore, the

513 proposed modeling approach also integrates a soil solution percolation scheme with inlets

514 uniformly distributed along the slope, which is more realistic than a scheme assuming that each

515 sampled site is fed by a single flow line carrying waters with a unique transit time. The good

516 agreement between modeling results and observations over a large panel of hydrological

517 conditions gives weight to the conclusions and implications that can be drawn regarding the

518 hydrogeochemical functioning of this headwater catchment.

519 **6-1 Choices of the reactive surfaces and the kinetic constants**

520   For the geochemical simulations performed in this study, the kinetic constants that were used

521   to describe the dissolution reactions of the primary minerals are standard constants determined

522   through laboratory experiments (supplementary table EA12). The reactive surfaces of the

523   primary minerals were calculated by assuming a simple spherical geometry for all the minerals

524   (supplementary table EA10). Over the last years, several studies have suggested that the kinetic

525   constants determined through laboratory experiments overestimate the rates of the dissolution

526   reactions in natural environments (White and Brantley, 2003; Zhu, 2005; Moore et al., 2012;

527   Fischer et al., 2014). The origin of this laboratory-field discrepancy is still a matter of debate

528   (Fischer et al., 2014). Different processes have been proposed to explain the gap between

529   laboratory and field estimates, such as the crystallographic anisotropy (Pollet-Villard et al.,

530   2016), progressive occlusion of the primary minerals by clays (White and Brantley, 2003), or the

531   formation of passivation layers at the surfaces of the minerals (Wild et al., 2016, Daval et al.,

532   2018). The difficulty to reconcile field and laboratory estimates can also be related to the

533   challenge of defining relevant reactive surfaces at different space scales (Li et al., 2006; Navarre-

534   Sitchler and Brantley, 2007).

535   The present modeling work regarding the Strengbach catchment shows that the chemical

536   composition variability of the spring and piezometer waters is fully captured via geometric

537   reactive surfaces and standard kinetic constants, while respecting the water-rock interaction

538   times within the catchment. This result suggests that the mean rates of the weathering

539   reactions employed in this modeling work are realistic, which in turn implies that the modeling

540   approach developed in this study does not underline significant mismatches between field and

541   laboratory reaction rates. The calculated rates of the dissolution reactions depend on the

542   product between the kinetic constants of the reactions and the mineral reactive surfaces. In the

543   experimental studies performed for determining the kinetic constants of dissolution reactions,

544   the constants are usually determined by normalizing the experimental weathering rates with

545   the Brunauer-Emmett-Teller surfaces determined from experiments of gas absorption (BET

546   surfaces; Chou and Wollast, 1986; Lundstrom and Ohman, 1990; Acker and Bricker, 1992;

547   Amrhein and Suarez, 1992; Berger et al., 1994; Guidry and Mackenzie, 2003).

548   In table 3, the BET surfaces are compared with the geometric surfaces of the minerals involved

549   in the dissolution experiments, recalculated from the size ranges of the minerals. For most of

550   the minerals (apatite, quartz, albite, K-feldspar, and anorthite), the geometric surfaces are

551   within the same order of magnitude as the BET surfaces, even if often slightly lower (table 3).

552   However, as the BET surfaces are determined with fairly large uncertainties, especially for low

553   BET surfaces (up to ± 70%), and as they can be very different depending on the gas used (up to

554   50% of difference between N2 or Kr absorption; Brantley and Mellott, 2000), the above

555   differences between the geometrical and the BET surfaces cannot be considered significant for

556   the majority of minerals used in the Strengbach simulations. A significant difference only

557   appears for biotite, with the geometric surfaces one order of magnitude less than the BET

558   surfaces (table 3). However, for biotite, due to its layered structure, it has been shown that

559   approximately 80 – 90% of the surface area accessible by the gases used to estimate BET

560   surfaces is not accessible for weathering reactions (Nagy, 1995).

561   The above considerations explain why for a granitic bedrock as found in the Strengbach

562   catchment, the geometric surfaces are relevant to describe the surfaces of water-rock

563   interactions at the space and time scales of this study. An immediate corollary is that the values

564 of the standard kinetic constants (table EA12) are also appropriate to calculate reaction rates

565 with mineral geometric surfaces in our modeling approach. This ability may be related to the

566 fact that all the minerals that have been used in the dissolution experiments and in the kinetic

567 studies were collected in the field (e.g., Acker and Bricker, 1992; Amrhein and Suarez, 1992).

568 These minerals were likely affected by anisotropy, passivation layers, and any types of aging

569 effects related to long-term water-rock interactions. Our results might therefore mean that the

570 standard kinetic constants obtained in such experiments integrate the aging effects that have

571 affected the reactivity of the primary minerals in natural environments. This would explain why

572 it is possible to capture the full variability of the water chemistry in a headwater catchment with

573 simple geometric reactive surfaces and standard kinetic constants.

574 At this stage, the results of our simulations strengthen the idea that the low surfaces calculated

575 from the geometrical shapes of minerals provide good estimates of the reactive surfaces within

576 the natural environment (Brantley and Mellott, 2000; Gautier et al., 2001; White and Brantley,

577 2003; Zhu, 2005; Li et al., 2017). They are certainly the values to be used for hydrogeochemical

578 modeling such as that performed in this work, in addition to the use of the experimental kinetic

579 constants for mineral dissolution. These conclusions are certainly not specific to the Strengbach

580 catchment and could be applicable to many other granitic catchments.

581 **6-2 Implications for the acquisition of the water chemistry**

582 The results of the NIHM-KIRMAT hydrogeochemical modeling have strong implications

583 regarding the hydrogeochemical functioning of the Strengbach watershed. Firstly, the modeling

584 results emphasize the importance of water transit times within the watershed as a main feature

585   controlling the chemical composition of subsurface waters. Along all the slopes, the waters

586   coming from the vicinity of the crests and characterized by long transit times systematically

587   render higher concentrations than the waters with shorter pathways and transit times. When

588   the hydrological conditions change from wet to dry periods, the solute concentrations also tend

589   to increase with the increase in the mean transit time of waters. Our results show that for the

590   spring and piezometer waters, the spatial and temporal variations of their geochemical

591   composition are fully explained by the differences in water transit times (figure 13). Transit time

592   variations between high and low discharge periods explain the temporal variations of

593   geochemical signatures within each site. Various mean transit times of waters supplying the

594   different sites explain the various chemical compositions between the sites (figure 13). This key

595   role of the water-rock interaction time is in agreement with previous reactive-transport studies

596   (e.g. Maher, 2010; Moore et al., 2012; Lebedeva and Brantley; 2013).

597   This study also brings strong constrains on the spatial distribution of the weathering

598   processes. For the modeling strategy employed, the chemical composition of the spring and

599   piezometer waters are calculated by integrating the chemical composition of waters introduced

600   at different starting locations along the active part of the flow lines (figure 5). The modeling

601   results show that through the geochemical integration, the concentrated waters coming from

602   the main crests are naturally counterbalanced by the diluted waters infiltrating close to the

603   sampling sites. This scheme supports the ideas suggested in Ackerer et al. (2016) and in Viville et

604   al. (2012) that the solute chemistry is acquired through reactions and weathering processes that

605   are spatially relatively homogenous along the flow lines of the watersheds. Because the lengths

606   of the flow lines vary with time, the patterns of dissolution rates for primary minerals are mainly

607 controlled by the spatial and temporal variability of the flow lines. During wet conditions, the

608 upper parts of the catchment are the areas of maximal dissolution rates of primary minerals in

609 the regolith. During dry conditions, the dissolution rates are maximal at mid-slopes, as the

610 upper parts of the catchment are simply dry.

611 The NIHM modeling also shows that the hydrological functioning of the watershed is properly

612 simulated by water circulations in the shallow subsurface, i.e., in a saprolitic aquifer. No

613 contribution of waters circulating in the deep fracture network of the granitic bedrock and

614 observed during the drilling campaigns is necessary. The deep-water circulations are probably

615 disconnected from the shallow subsurface network, as recently suggested by geochemical

616 studies conducted in the Strengbach watershed (Chabaux et al., 2017). The modeling results

617 also show that water in the shallow aquifer flows along streamlines with fairly simple

618 geometries. At the scale of the catchment (figure 4), the geometry of the flow lines validates the

619 hypothesis based on the geochemical and Sr-U isotopic data that the spring waters of these

620 mid-mountain basins are supplied by waters from distinct flow paths without real

621 interconnections (i.e., the Strengbach and Ringelbach watersheds; Schaffhauser et al., 2014;

622 Pierret et al., 2018).

623 **6-3- Origins of general chemostatic behavior and of specific C-Q relations**

624 The hydrogeochemical monitoring of the spring, piezometer, and stream waters performed in

625 the Strengbach catchment clearly shows that this catchment has a general chemostatic behavior

626 (e.g., Viville et al., 2012; Ackerer et al., 2018). All the spring and the piezometer waters have

627 chemical concentrations impacted by changes in the hydrological conditions, but the

628 concentration variation ranges are by far narrower than variation ranges of water discharges,

629 which define the chemostatic behavior of a hydrological system. For waters showing the largest

630 concentration variations (spring CS1), there is a modest increase of approximately 10-30% in the

631 concentrations of H_4SiO_4 and Na^+ from floods to drought events, while the water discharges

632 may vary by a factor of 15 (figure 8). This modest variability of the solute concentrations over a

633 wide range of water discharges is not specific to the Strengbach catchment; it has been

634 observed in several watersheds spanning different climates and hydrological contexts (Godsey

635 et al., 2009; Clow and Mast, 2010; Kim et al., 2017).

636 Different origins for the chemostatic behavior have been proposed, such as a

637 modification of the mineral reactive surfaces during changing hydrological conditions (Clow and

638 Mast, 2010), a small concentration difference between slow and fast moving waters (Kim et al.,

639 2017), or the fact of reaching an equilibrium concentration along the water pathway (Maher,

640 2010). The coupled approach NIHM-KIRMAT renews the opportunity to discuss on the origin of

641 the chemostatic behavior in catchments. It is worth noting that the acquisition and the

642 evolution of the water chemistry can be simulated along flow lines that have been determined

643 via timely and spatially distributed hydrological modeling. The strength of this approach is to

644 constrain water transit times independently and before any geochemical simulation.

645 The results from the hydrological model show that the characteristics of the flow lines are

646 affected by the changes in the hydrological conditions. After important precipitations, high

647 water contents and large hydraulic conductivities are simulated in the vicinity of the crests and

648 all along the small valley of the catchment (figure 6). During drought periods, the crest lines

649 have progressively dried out, and the hydraulic conductivities decrease on the upper parts of

650 the watershed. Only some locations at mid-slopes and along the direction of the principal valley

651 exhibit larger hydraulic conductivities (figure 6). This response of the hydraulic conductivities

652 implies that during floods, the water velocity significantly increases along the flow lines, but the

653 length of the active parts of the flow lines also increase as waters collected downstream may

654 also come from the neighborhood of the main crests. During drought periods, the water velocity

655 is slower, but the length of the active parts of the flow lines also tends to decrease, as the

656 waters are principally supplied by mid-slope areas characterized by a thicker aquifer.

657 For illustration, velocities of water supplying the CS1 spring varied along the flow lines between

658 7 and 0.5 m/day during the flood of 30/03/2010 and were approximately 0.5-1 m/day during

659 the important drought of the 29/11/2011 (figure 6). At the same time, the active parts of the

660 flow lines were reduced from 160 m to 110 m from the flood to the drought events (figures 7A

661 and 7B). This hydrological functioning implies a covariation between flow velocity and flow

662 length over changing hydrological conditions, with faster flows along longer paths during wet

663 conditions and slower flows along shorter paths during dry periods. This hydrological behavior

664 attenuates the variations of the water transit times over changing hydrological conditions. It

665 also explains why the mean transit times span much narrower variation ranges than the water

666 discharges at the collected springs. For example, the calculated mean transit times of waters for

667 the CS1 spring vary from 1.75 to 3.13 months between the strongest flood and the driest period

668 that have been studied, whereas the water discharges vary from 1.523 L/s to 0.098 L/s (figure

669 8B). Because the time of the water-rock interactions exerts a first-order control on the chemical

670 composition of waters, the weak variability of the mean transit times is directly responsible for

671 the relative stability of the chemical composition of waters within the catchment.

672　In addition to the general chemostatic behavior, each chemical element has a specific response

673　to a change in water transit time as apparent in figure 9 where are given the concentration-

674　mean transit time relations (C-MTT relations) for H4SiO4 and the major cations. In the relevant

675　transit time window for the spring and piezometer waters (figure 9b), the C-MTT relations are

676　linear and C-MTT slopes are significant for H_4SiO_4, modest for Na^+ and weak for Mg^{2+} and K^+

677　concentrations. Modeling results indicate that the C-MTT slopes are controlled by the

678　competition between primary mineral dissolution and element incorporation into clay minerals.

679　When elemental fluxes from primary mineral dissolution to solution are much higher than fluxes

680　from solution to clay minerals (e.g. H_4SiO_4), the element can accumulate in solution, resulting in

681　a significant C-MTT slope. By contrast, when elemental fluxes from primary mineral dissolution

682　to solution are only slightly higher than fluxes from solution to clay minerals (e.g. K^+), the

683　element accumulates only slowly in solution, resulting in a weak C-MTT slope. Interestingly,

684　when fitting power-laws along C-Q relations ($C=aQ^b$, figure 8 caption), both 'a' coefficient

685　controlling the height of the C-Q laws and 'b' coefficient controlling the curvature of the C-Q

686　laws are sensitive to the C-MTT slopes (figure 9c and 9d). 'a' coefficient is positively corelated

687　with C-MTT slopes while 'b' coefficient is negatively corelated. Solute species with significant C-

688　MTT slopes are more chemodynamic and display higher mean annual concentrations (H_4SiO_4 ,

689　b(H_4SiO_4)=-0.1, a(H_4SiO_4)=10^{-4}), whereas species with weak C-MTT slopes show low mean

690　annual concentrations and are nearly perfectly chemostatic (a(Mg^{2+})=10^{-5}, b(Mg^{2+})=-0.016,

691　a(K^+)=10^{-5}, b(K^+)=0, figures 8, 9c and 9d). Our results show that a better knowledge of C-MTT

692　relations is important to explain the contrasted C-Q shapes of chemical elements.

693   It is important to underline that the hydrological modeling with the NIHM code is

694   performed independently and before any geochemical simulations with the KIRMAT code. The

695   fact that the flow rates are well reproduced for all the hydrological contexts between 2010 and

696   2015 supports that the water transit times inferred from the NIHM code are realistic. The fact

697   that the chemical composition of waters is well captured indicates that the combination of the

698   geochemical parameters used in KIRMAT code is able to generate realistic reaction rates, as

699   chemistry is well reproduced while respecting realistic water transit times. No modifications of

700   the reactive surfaces and of the dissolution kinetic constants were necessary to reproduce the

701   seasonal variability of the water chemistry. It is also important to emphasize that the simulated

702   chemical compositions of waters remain far from a state of chemical equilibrium with respect to

703   primary minerals. The calculated Gibbs free energy for the primary minerals ranges from -120 to

704   -100 kJ/mol for apatite, -90 to -80 kJ/mol for biotite and anorthite and -30 to -20 kJ/mol for

705   albite and K-feldspar. These far-from-equilibrium values for the Gibbs free energy imply that the

706   reaction rates calculated using hydrogeochemical codes such as KIRMAT, which are based on

707   the transient state theory (TST, Eyring, 1935; Murphy and Helgeson, 1987), are realistic for most

708   of the primary minerals in this type of hydrological context. Regarding the simulations

709   performed in this study, the relatively short residence times of waters and the precipitation of

710   clay minerals prevent reaching a state of chemical equilibrium between waters and primary

711   minerals. The results also indicate that relying upon a model of clay solid solution is appropriate

712   to mimic the clay mineral dynamics in this type of watershed and that a clay solid solution

713   precipitated at the thermodynamic equilibrium is able to generate reliable water chemistry (this

714   study) and realistic clay precipitation rates (more details in Ackerer et al., 2018).

715   Our results indicate that it is not necessary to mix in different proportions soil and deep waters

716   to generate chemostatic behavior, as proposed by Zhi et al. (2019). Chemostatic behavior can

717   be generated within a single regolith layer with a homogeneous mineralogy, if as demonstrated,

718   the transit time variability of shallow subsurface waters is dampened by seasonal fluctuations of

719   flow line properties. A large storage of primary minerals and weathering product in the

720   subsurface, as proposed in Musolff et al. (2015), is required but not sufficient to generate

721   chemostatic behavior. Chemostatic behavior also depends on the covariation between flow

722   velocities and flow lengths over changing hydrological conditions. Chemostatic behavior is not

723   explained by a modification of the reactive-surface of minerals in the subsurface (i.e. Clow and

724   Mast, 2010), or by an absence of chemical contrast between slow and rapid flows (i.e. Kim et al.,

725   2017). The precipitation of clay minerals is essential to correctly capture the water chemistry in

726   our study, but the dissolution or redissolution of clays is not a key process to explain

727   chemostatic behavior (i.e. Li et al., 2017). Our study clearly supports the idea defended by

728   Herndon et al. (2018) that a spatial and temporal variability in flow paths is a key process to

729   explain C-Q relations. This conclusion can most likely be extended to the other mountainous and

730   relatively steep watersheds of this type, in which water pathways and short transit times are

731   mainly controlled by gravity driven flow along slopes.

732   **7- Conclusion**

733   This study exemplifies the potential of coupling of low-dimensional and depth-integrated

734   hydrological modeling with hydrogeochemical modeling as a way to better understand

735   variability over time and space of the composition of surface and subsurface waters. The

736   independent estimation of the water transit times provided by hydrological simulations is a

737 clear added value to constrain the geochemical modeling approaches. Our study demonstrates

738 that the seasonal variability of hydraulic conductivities along the slopes is a key process to

739 understand the dynamic of flow lines and the changes of water transit times in the watershed.

740 The variations in flow lines distributions from drought to flood events result in a modest

741 seasonal variability of mean water transit times, which in turn explains the relative stability of

742 the solute concentrations in waters. Our results also show that a better knowledge of the

743 concentration-mean transit time relations (C-MTT relations) is an interesting new step to

744 understand the diversity of C-Q shapes for different chemical elements. The consistency

745 between measured and modeled concentrations while respecting the water-rock interaction

746 times provided by the hydrological simulations shows that it is possible to capture the chemical

747 composition of waters with simply determined reactive surfaces and standard kinetic constants.

748 The results of our simulations strengthen the idea that the low surfaces calculated from the

749 geometrical shapes of minerals are a good estimate of the reactive surfaces within the natural

750 environment and certainly the values to be used for hydrogeochemical modeling such as that

751 performed in this work, in addition to the use of the experimental kinetic constants for mineral

752 dissolution.

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Figure captions

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

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

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

989   Figure 4: at the top, flow lines of the subsurface that feed with water the surface draining

990   network on March 1st, 2010 (on the left, high-flow period) and July 1st, 2010 (on the right, low-

991   flow period). The color scale indicates that a water particle reaching the river at a given date

992   started its travel along the streamline or passed at a given location on the streamline x days

993   prior. The density of streamlines is associated with the flowing versus dry fraction of the river

994   network at a prescribed date. Below, flow lines of the subsurface that feed with water the

995   geochemical sampling sites on March 30th, 2010 (on the left, flood event) and November 29th,

996   2011 (right, drought event) according to NIHM simulations. For each sampling site, 10 particles

997   were dispatched in the direct neighborhood of the site and then backtracked. The color scale for

998   times is similar to that of the top plot.

999   Figure 5: conceptual scheme used in the modeling of the water chemistry. The soil solutions are

1000   used as input solution. The bedrock is discretized into a 1D succession of cells along the active

1001   parts of the flow lines determined the NIHM hydrological model. The hydrogeochemical model

1002   KIRMAT evaluates reactive transport within each cell. The integrated chemistry of sampled

1003   waters is the arithmetic mean of solute concentrations with regularly distributed inlet points

1004   along a stream line.

1005   Figure 6: maps of piezometric gradient and mean hydraulic conductivity for the Strengbach

1006   catchment, as simulated by NIHM, on 29/11/2011 (dry period) and 30/03/2010 (high flows

1007   period). The mean hydraulic conductivity is integrated normal to bedrock of the aquifer and

1008   thus depends on the water saturation of the vadose zone and the location of the water table.

1009

1010   Figure 7: simulation results for the CS1 spring for an important drought (29/11/2011) and a

1011   strong flood event (30/03/2010). At the top, active parts of the flow lines bringing the waters to

1012   the CS1 spring for the two sampling dates (7A and7B). Below, simulated chemical compositions

1013   of CS1 spring waters after integration along the flow lines and comparison with the initial soil

1014   solution and the spring chemistry data (7C and7D). Error bars show analytical uncertainties on

1015   measured concentrations and induced uncertainties in model results.

1016   Figure 8: simulation results for the CS1 spring over the whole range of the water discharges

1017   from the spring. Results are presented for H_4SiO_4, Na^+, K^+ and Mg^{2+} concentrations (8A, 8C, 8E

1018   and 8F), pH (8D) and mean water transit time (8B). Red lines indicate simulated parameters

1019   after integration along the flow lines, and blue points show measured values collected between

1020   2005 and 2015 (data in table 1 and in supplementary table EA1). Error bars show analytical

1021   uncertainties on measured concentrations and induced uncertainties in model results. Fitting a

1022   power law of type $C=a*Q^b$ along the C-Q relations gives the following parameters: $a(H_4SiO_4)=10^{-4}$,

1023 $b(H_4SiO_4)=-0.1$; $a(Na^+)=7\times10^{-5}$, $b(Na^+)=-0.053$; $a(Mg^{2+})=10^{-5}$, $b(Mg^{2+})=-0.016$; $a(K^+)=10^{-5}$,

1024 $b(K^+)=0$.

1025   Figure 9: (9A) evolution of solute concentrations for H_4SiO_4, Na^+, K^+, Mg^{2+} and Ca^{2+} as a function

1026   of mean water transit time in the Strengbach watershed. Water transit times are between 1.75

1027   and 4 months for all the springs and piezometers in this study. (9B) Focus on the transit time

1028   window (1.75-4 months) for the studied waters and equations linking mean water transit times

1029   and concentrations for H_4SiO_4, Na^+, K^+, Mg^{2+} and Ca^{2+}. Relations between transit times and

1030   concentrations are linear within this window (9C) relations between 'b' coefficients ($C=a*Q^b$)

1031   and the concentration-transit time slopes for the chemical elements. (9D) relations between 'a'

1032 coefficients ($C=a*Q^b$) and the concentration-transit time slopes for the chemical elements.

1033 Elements with significant concentration-mean transit time slopes are slightly chemodynamic

1034 (e.g. H_4SiO_4 and Na^+), while elements with low concentration-mean transit time slopes are

1035 almost chemostatic in the watershed (e.g. K^+ and Mg^{2+}). Ca^{2+} is not shown on 9C and 9D figures

1036 as this element is affected by a strong multi-annual concentration decrease that prevents a

1037 meaningful C-Q power law analysis.

1038 Figure 10: simulation results for the PZ3 and PZ5 piezometers for a flood event (05/05/2015). At

1039 the top, active parts of the flow lines that bring waters to the two sampling sites (10A and 10B).

1040 Below, simulated chemical compositions of the piezometer waters after integration along the

1041 flow lines and comparison with the initial soil solution and the water chemistry data (10C and

1042 10D). Error bars show analytical uncertainties on measured concentrations and induced

1043 uncertainties in model results.

1044 Figure 11: simulation results for the CS2 spring. At the top, active parts of the flow lines that

1045 bring water to the CS2 spring for drought (29/11/2011) and flood (30/03/2010) events (11A and

1046 11B). The CS2 location results in more scattered flow lines than for CS1 spring. Below,

1047 simulation results for the CS2 spring over the whole range of experienced discharges (11C and

1048 11D). Blue lines indicate simulated parameters after integration along the slowest flow line,

1049 yellow lines indicate simulated parameters after integration along the fastest flow line, and blue

1050 points show measured values collected between 2005 and 2015 (data in table 1 and in

1051 supplementary table EA2). Error bars show analytical uncertainties on measured concentrations

1052 and induced uncertainties in model results.

1053   Figure 12: simulation results for the RH3 spring chemistry and for a flood event (30/03/2010).

1054   Left, simulated concentrations by assuming flow lines running through gneiss (GN) only (12A).

1055   Right, simulated concentrations by assuming flow lines running through hydrothermally altered

1056   granite (VS) only (12B). Error bars show analytical uncertainties on measured concentrations

1057   and induced uncertainties in model results.

1058   Figure 13: overview of the simulated flow lines in the subsurface that feed with water the

1059   geochemical sampling sites CS1, PZ3, and PZ5 on May 5th, 2015. The simulated chemical

1060   compositions after geochemical integration along the flow lines are compared with the initial

1061   soil solution and the spring chemistry data.

1062   Table 1: measured pH, water discharges and chemical concentrations of H_4SiO_4, Na^+, K^+, Mg^{2+},

1063   and Ca^{2+} in waters collected at the Strengbach catchment. The sampling sites include springs

1064   (CS1, CS2, RH3) and piezometers (PZ3, PZ5).

1065   Table 2: Initial and calibrated values of the hydrodynamic parameters of the aquifer in the

1066   hydrological simulation of the Strengbach catchment by NIHM.

1067   Table 3: Comparison between BET surfaces and geometric surfaces for the major primary

1068   minerals present in a granitic context. BET surfaces were measured via gas absorption

1069   experiments by [1] Berger et al., 1994; [2] Chou and Wollast, 1985; [3] Lundstrom and Ohman, 1990; [4]

1070   Amrhein and Suarez, 1992; [5] Acker and Bricker, 1992; and [6] Guidry and Mackenzie, 2003.

1071   Geometric surfaces were recalculated from the granulometric ranges of the minerals and by

1072   assuming a spherical geometry.

	Na$^+$ (mmol/L)	K$^+$ (mmol/L)	Mg^{2+} (mmol/L)	Ca^{2+} (mmol/L)	H$_4$SiO$_4$ (mmol/L)	pH	Water Discharge (L/s)
Spring CS1							
16/09/2008	0.071	0.013	0.017	0.044	0.129	6.28	0.954
30/03/2010	0.074	0.014	0.015	0.043	0.120	5.61	1.523
29/03/2011	0.074	0.013	0.015	0.038	0.145	6.23	0.345
04/10/2011	0.080	0.012	0.016	0.042	0.176	6.57	0.122
29/11/2011	0.088	0.015	0.019	0.034	0.177	6.30	0.098
05/05/2015	0.065	0.012	0.012	0.054	0.121	5.33	1.410
Spring CS2							
30/03/2010	0.090	0.020	0.020	0.080	0.122	6.15	6.274
29/03/2011	0.090	0.020	0.020	0.070	0.144	6.18	0.956
02/08/2011	0.090	0.020	0.020	0.060	0.170	6.50	2.171
04/10/2011	0.100	0.020	0.020	0.070	0.177	6.76	0.413
29/11/2011	0.100	0.020	0.020	0.060	0.180	6.22	0.285
05/05/2015	0.077	0.016	0.018	0.074	0.123	6.14	7.500
Spring RH3							
30/03/2010	0.083	0.028	0.032	0.081	0.127	6.28	-
Piezometer PZ3							
05/05/2015	0.074	0.013	0.011	0.053	0.153	6.29	-
Piezometer PZ5							
05/05/2015	0.072	0.013	0.017	0.058	0.132	6.16	-

Table 1

Parameter	Unit	Initial Value	Calibrated value
Depth of substratum	m	4	See figure 2
Saturated hydraulic conductivity (all zones except the low depth zone at the catchment peak (see figure 2))	m.s^{-1}	1.10^{-4}	8.10^{-5}
Saturated hydraulic conductivity (catchment peak)	m.s^{-1}	1.10^{-4}	1.10^{-4}
porosity (all zones except the low depth zone at the catchment peak)	-	0.1	0.08
Porosity (catchment peak)	-	0.1	0.2
Residual water content (all zones)	-	0.01	0.01
Specific storage (all zones)	m^{-1}	1.10^{-8}	1.10^{-8}
n (Van genuchten coefficient, all zones)	-	2	2
α (Van genuchten coefficient, all zones)	m^{-1}	1	1.5

Table 2

Mineral	Mineral density (g/cm³)	Granulometric range (µm)	Particle radius (µm)	Spherical geometric surface (m²/g)	BET surface (m²/g)
Quartz[1]	2.62	< 50	1 - 25	1.150 - 0.046	0.310
Albite[2]	2.60	50 - 100	25 - 50	0.046 - 0.023	0.075
K-feldspar[3]	2.56	< 50	1 - 25	1.170 - 0.047	1.420
Anorthite[4]	2.73	20 - 50	10 - 25	0.044 - 0.111	0.500
Biotite[5]	3.09	150 - 400	75 - 200	0.013 - 0.005	0.240
Apatite[6]	3.19	100 - 200	50 - 100	0.018 – 0.009	0.026

Table 3
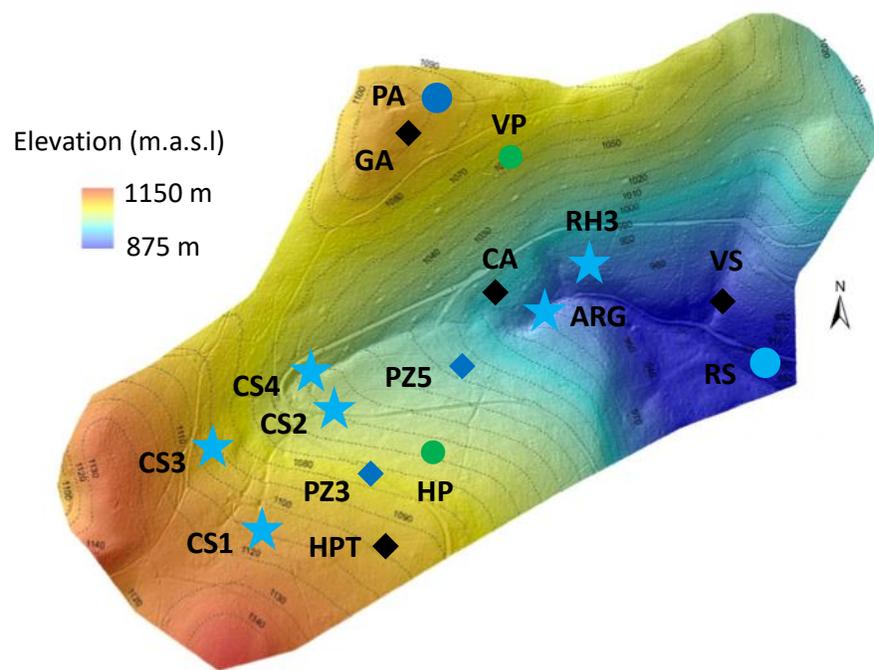
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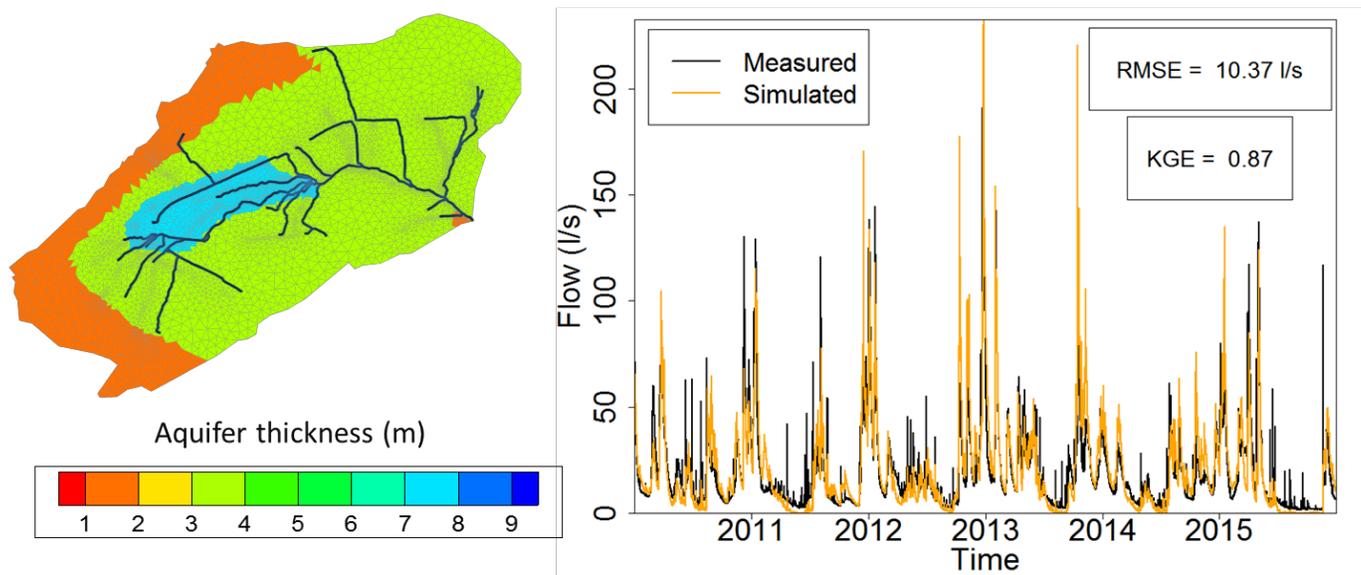
Figure 2

Figure 3

Figure 4

Soil solution   Soil solution

Δx   Bedrock   0

Long transit time   Short transit time

Mean water chemistry

Figure 5

29/11/2011

30/03/2010

Piezometric gradient (m/m)   Mean hydraulic conductivity (m/s)
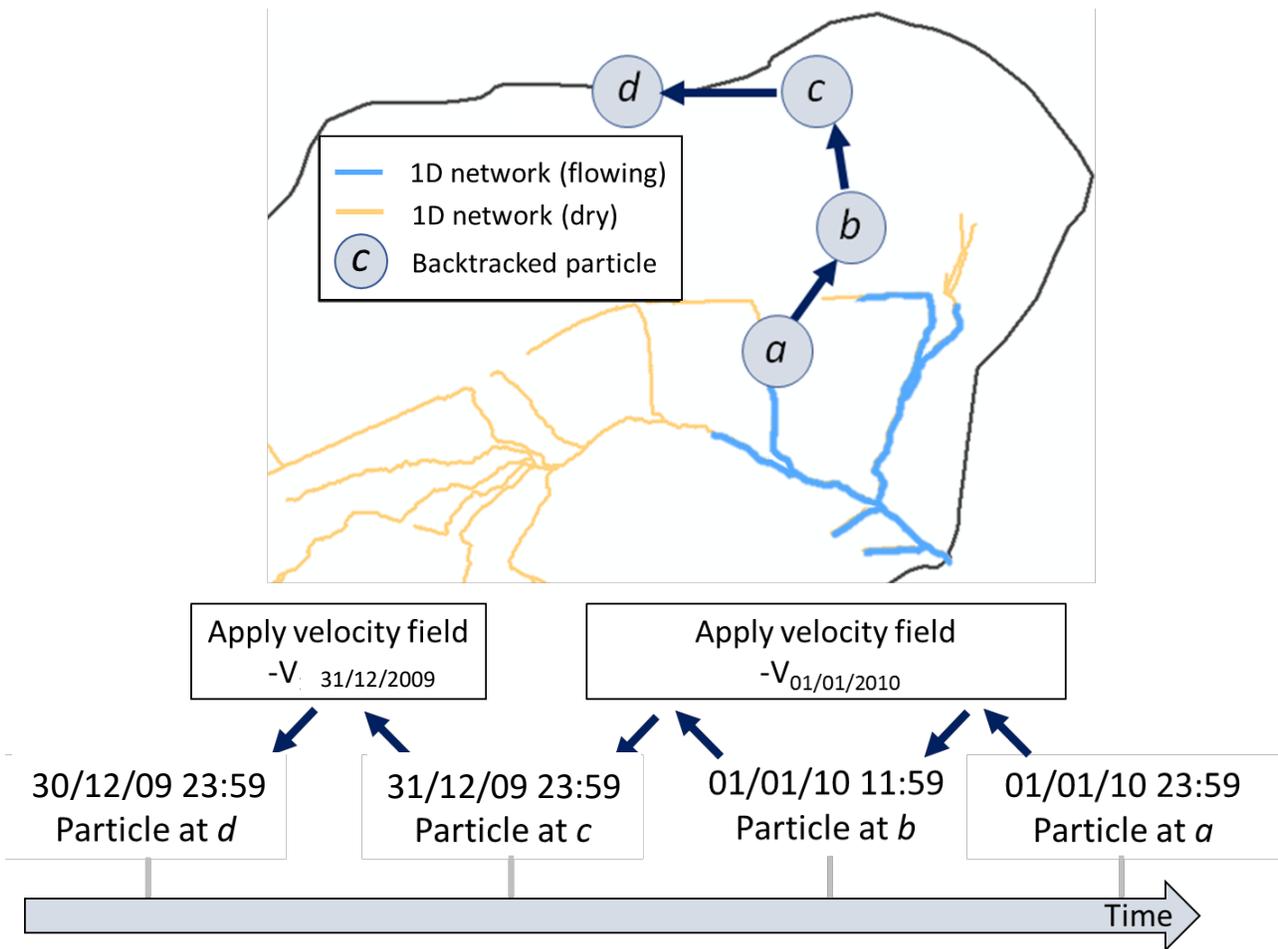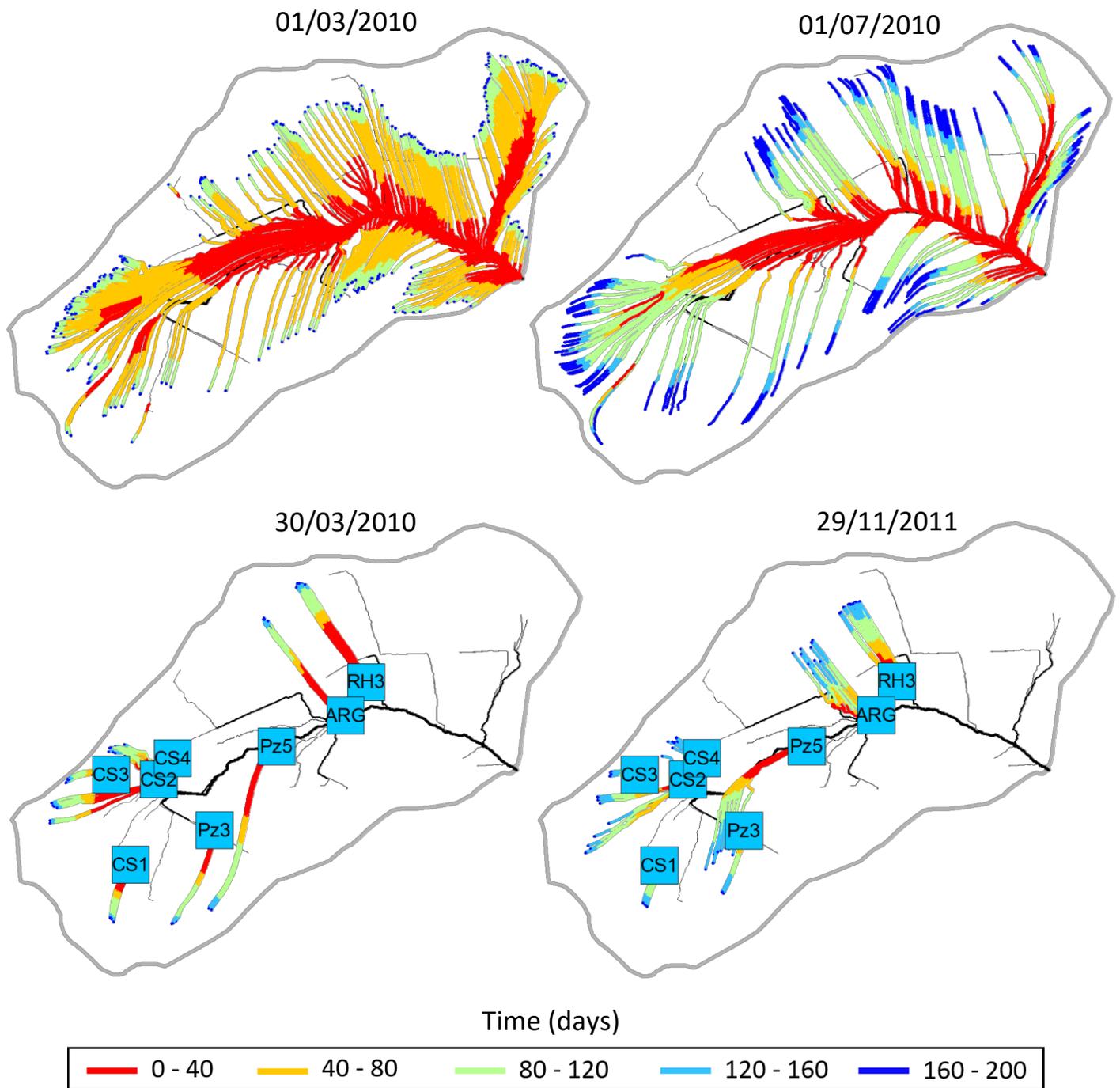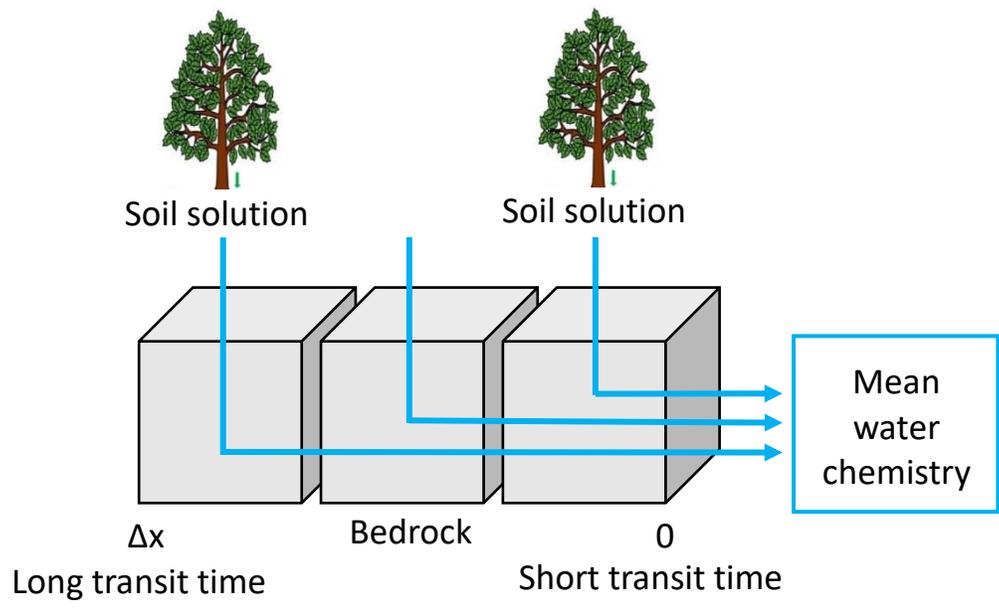
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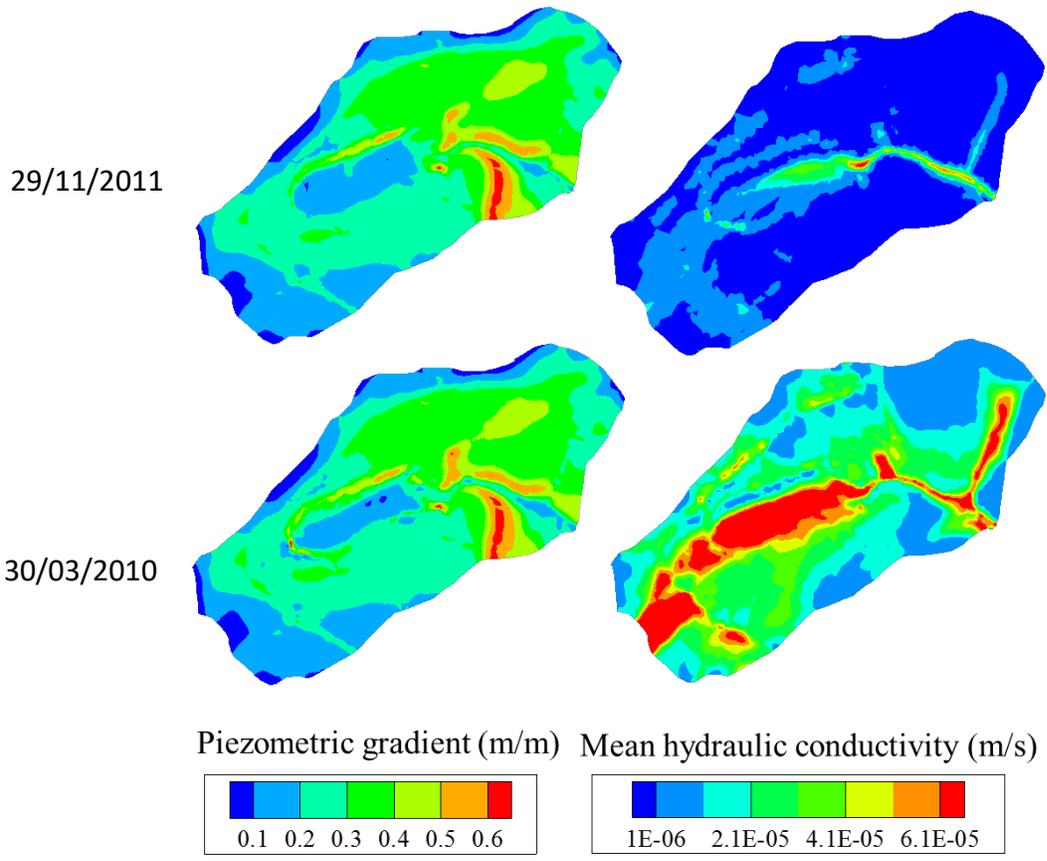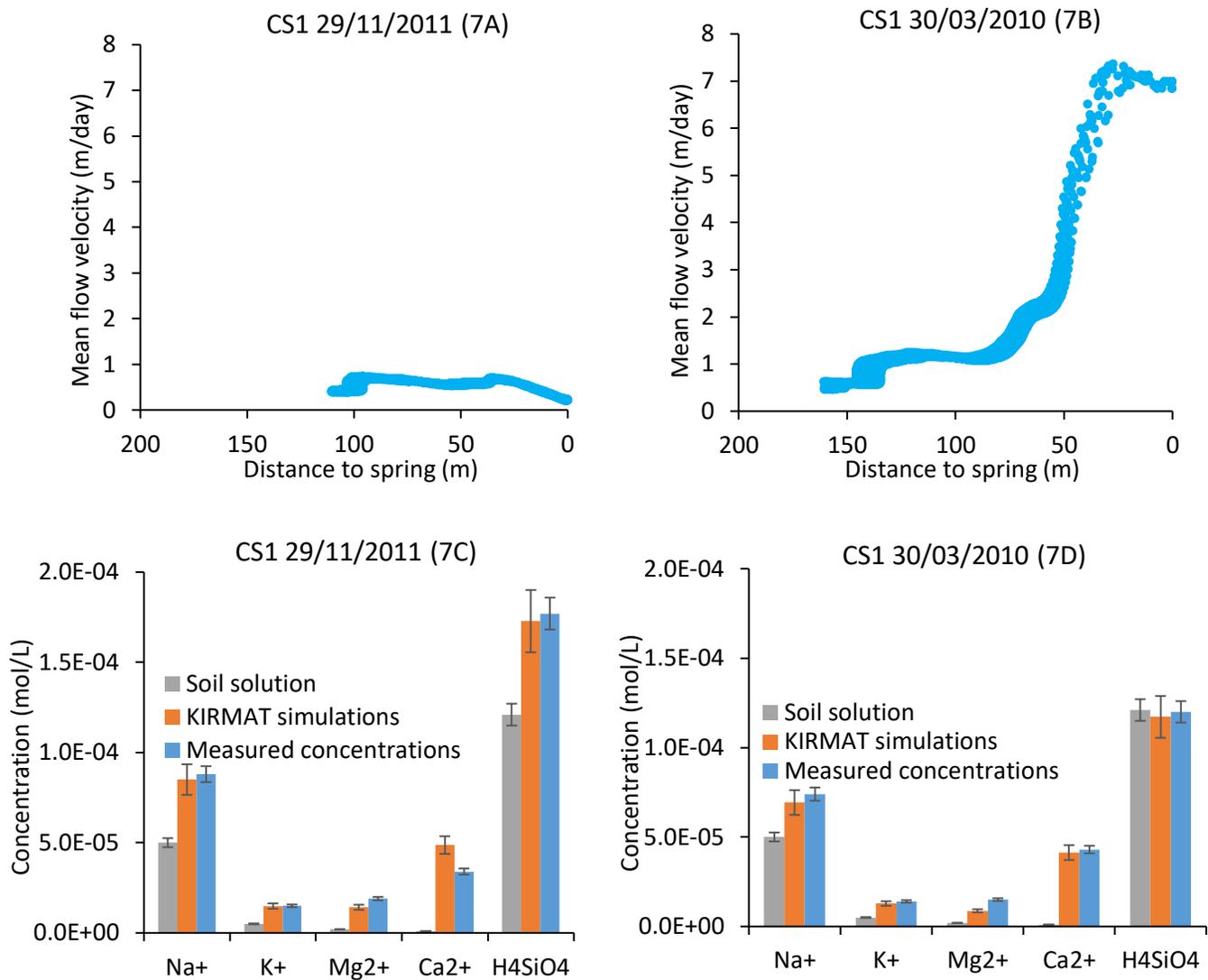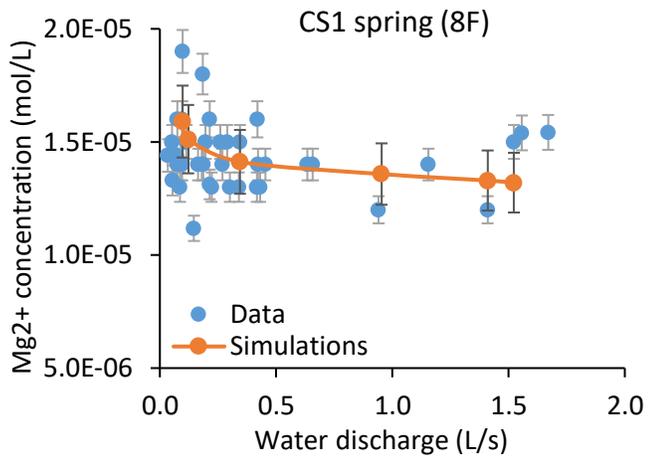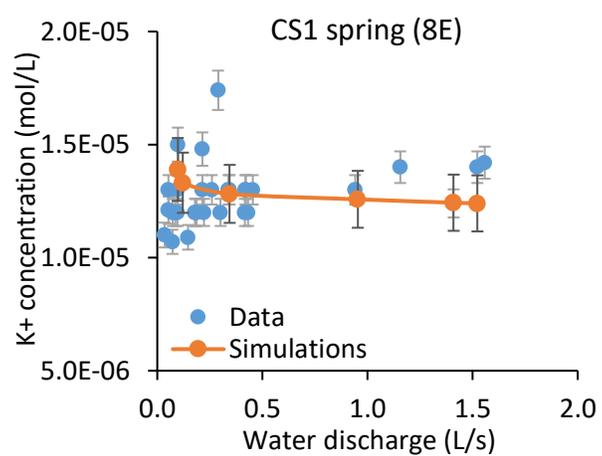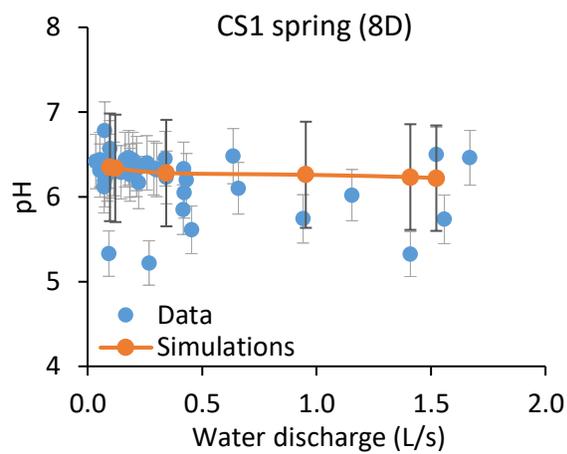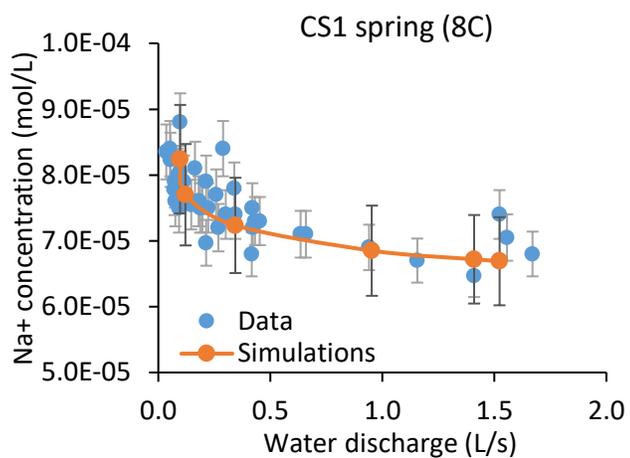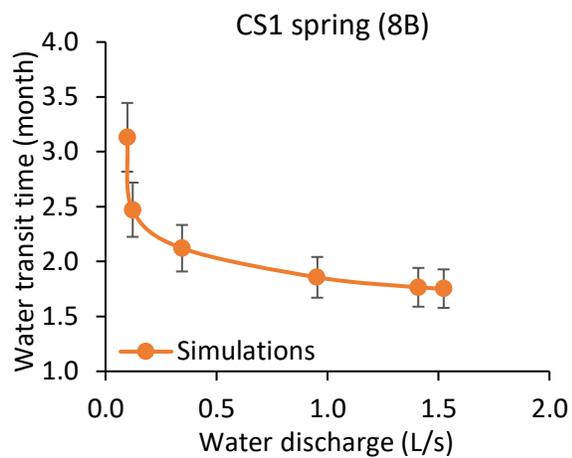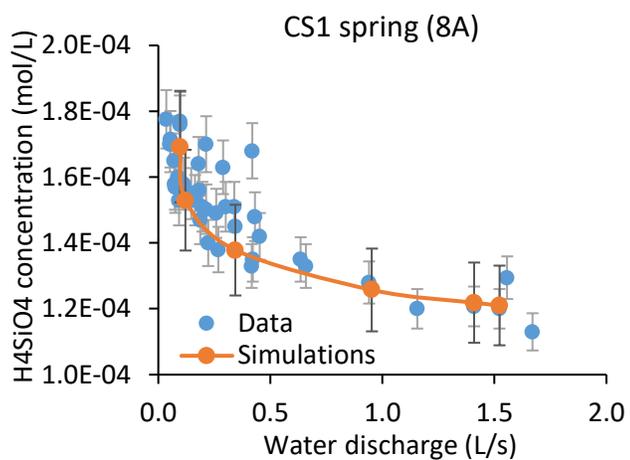
Figure 6

Figure 7

Figure 8
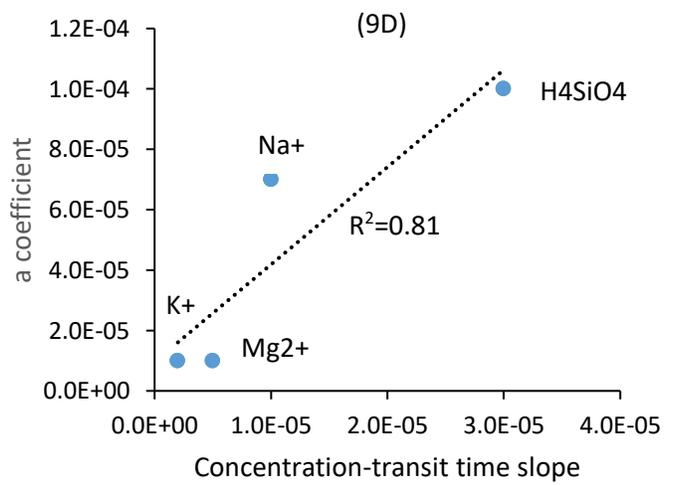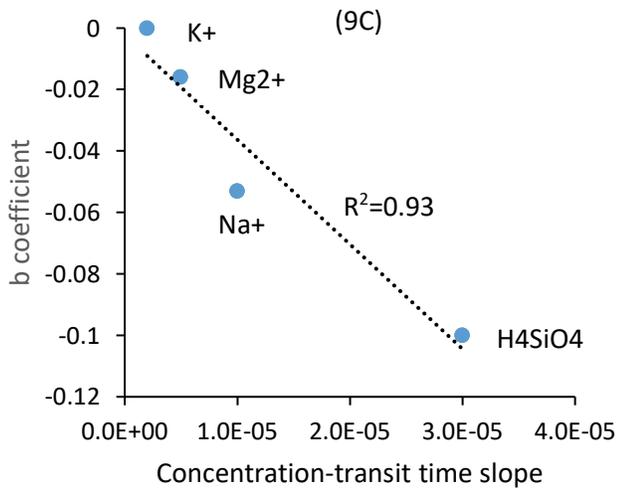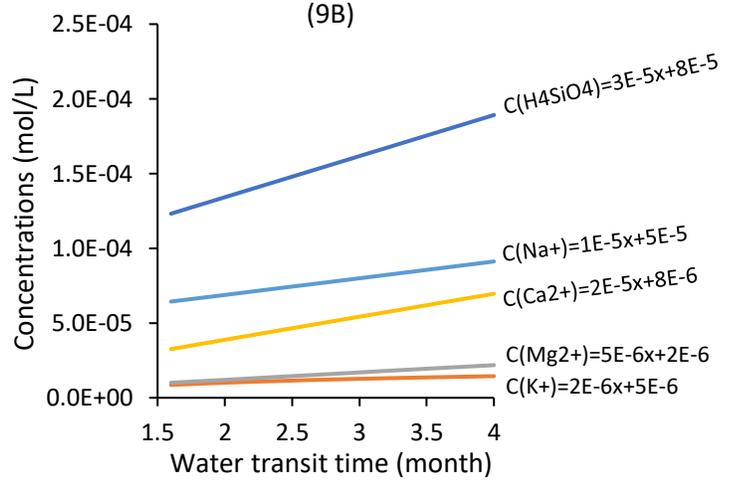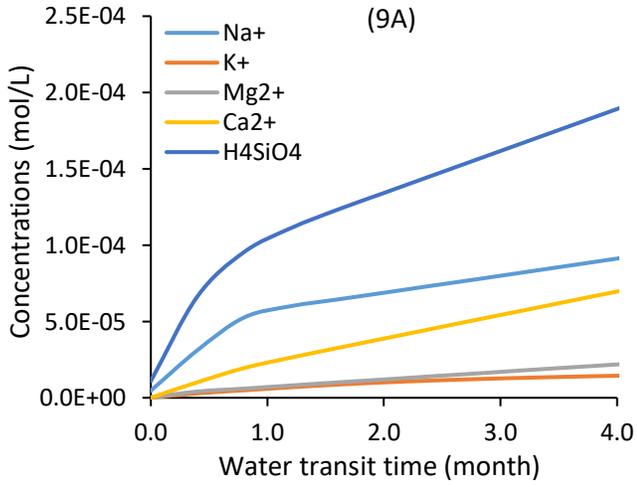
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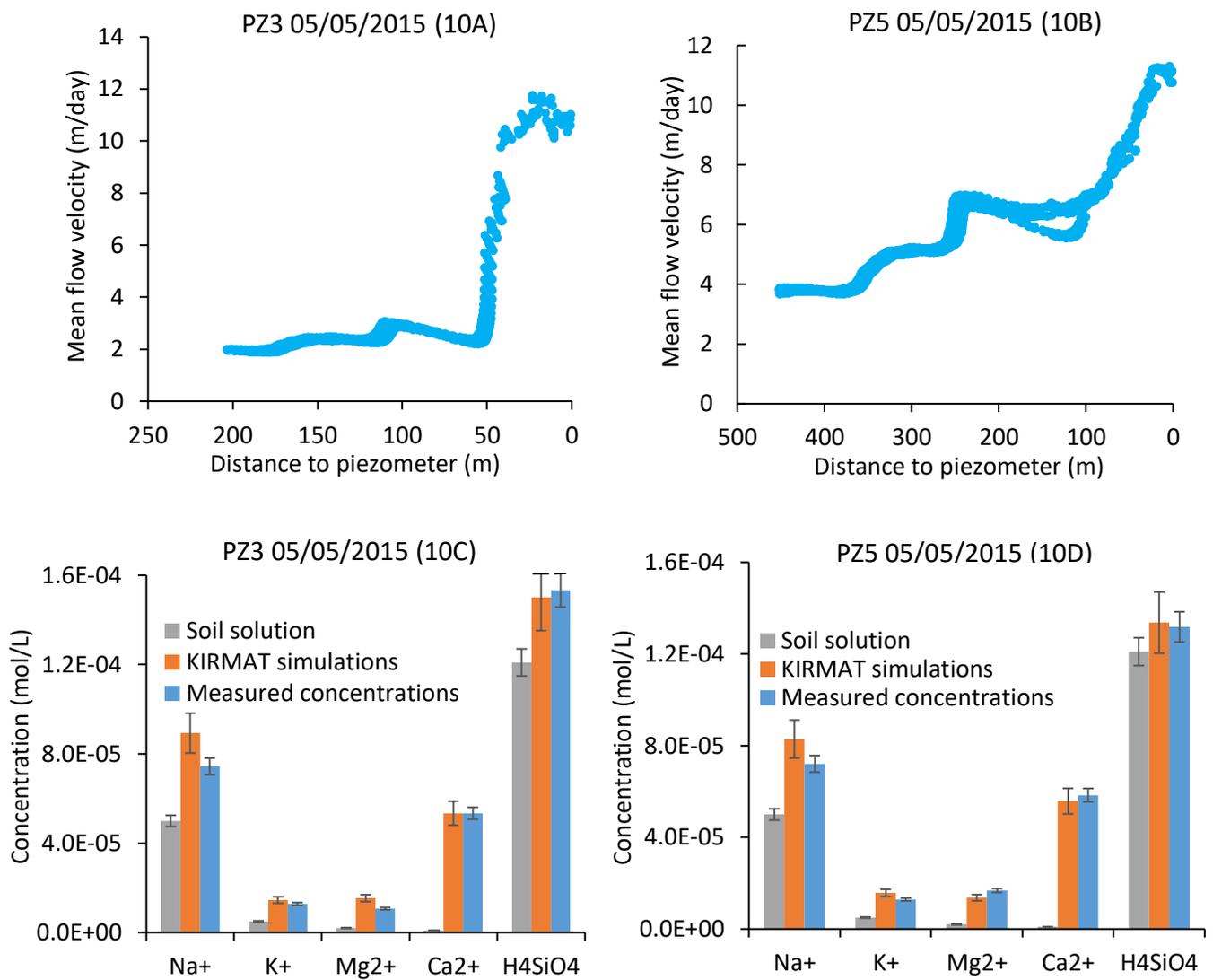
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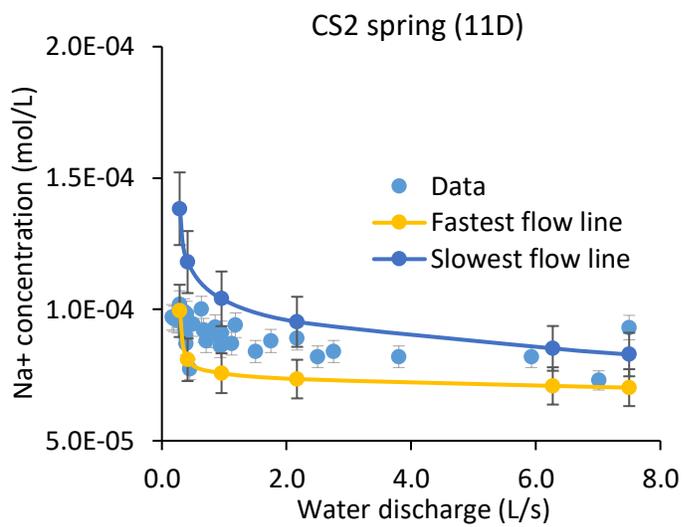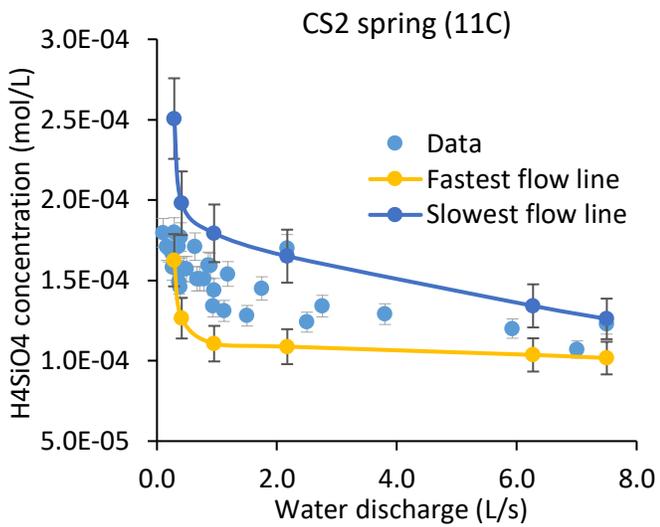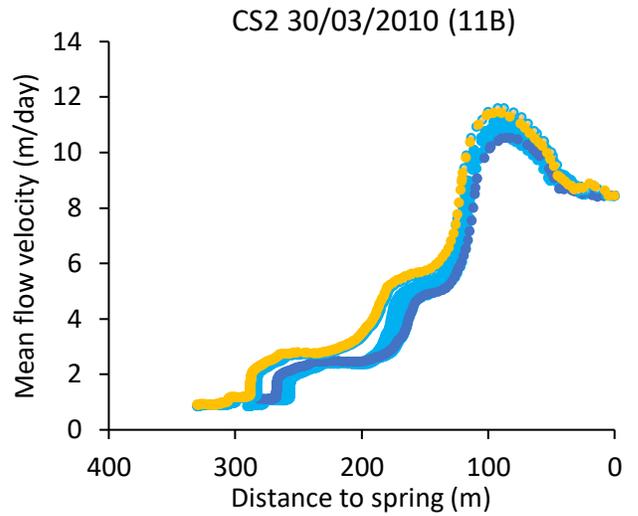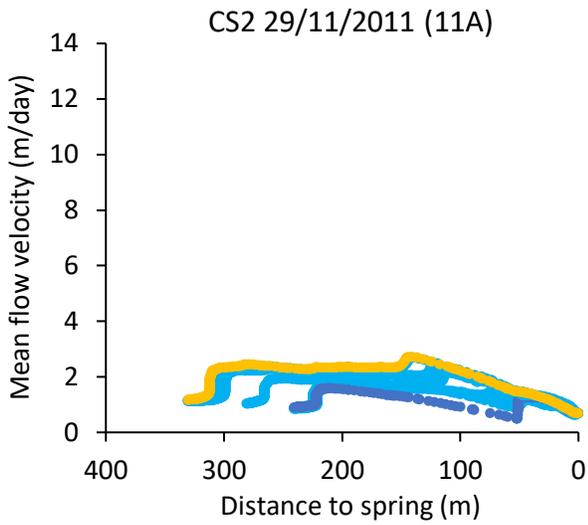
Figure 11

Figure 12

Figure 13