Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

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

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Manuscript under review for journal Hydrol. Earth Syst. Sci.
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Abstract

Understanding the spatiotemporal variability of the chemical composition of surface waters is a major issue for the scientific community, especially given the prospect of significant environmental changes for the next decades. To date, the study of concentration-discharge relationships 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 our ability to model and predict the water chemistry with only geochemical approaches. This study demonstrates the potential of coupling hydrological and hydrogeochemical modeling to better understand the spatiotemporal variability of the composition of surface waters. In a first step, 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 that are feeding the springs. In a second step, hydrogeochemical simulations with the code KIRMAT (KInectic Reaction and MAss Transport) have been performed to calculate the evolution of the water chemistry along the flow lines. The results indicate that the concentrations of dissolved silica (H_4SiO_4) and in basic cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) in the spring waters are correctly reproduced with a simple integration along the flow lines. The results also show that the modest variabilities of the flow line distribution and of the flow velocity imply that the water transit times only vary from approximately 1.5 to 3 months from floods to drought events. These findings demonstrate that the chemostatic behavior of the spring chemistry is a direct consequence of the strong hydrological control of the water transit times within the catchment. The good matching between the measured and modeled concentrations while respecting the water-rock interaction

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Discussion started: 8 January 2019

times provided by the hydrological simulations also shows that it is possible to capture the chemical composition of waters using simply determined reactive surfaces and experimental kinetic constants. The results of our simulation strengthen the idea that the low surfaces calculated from the geometrical shapes of minerals are a good estimate of the reactive surfaces within the natural environment and certainly the one to be used for hydrogeochemical modeling such as that performed in this work. Overall, this work shows that the hydrogeochemical functioning of an elementary watershed, such as the Strengbach catchment, is relatively simple. The acquisition and variability of the water chemistry can be explained through process-based modeling approaches and by only formulating few hypotheses on the functioning of the watershed.

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. That 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). Forecasting the evolution of the Earth's surface relies on our ability to develop process-based models integrating a large number of processes over different spatial and temporal scales. This is especially the case for modeling the variability of the water geochemical composition at a watershed scale, which requires the development of modeling codes able to combine, as closely as possible, hydrological and geochemical processes (Kirchner, 2006).

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

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Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
Discussions

are needed to correctly treat the hydrology of catchments in their surface and subsurface compartments with reasonable computation times (Gunduz and Aral, 2005). Low-dimensional and depth-integrated models have attracted growing interest because they represent an interesting compromise between equation complexity, computational time, and result accuracy (Pan et al., 2015; Hazenberg et al., 2016; Weill et al., 2013; 2017; Jeannot et al., 2018). These depth-integrated models recently demonstrated their ability to reproduce the results from fully dimensioned approaches in small catchments while reducing computational costs (Pan et al., 2015; Jeannot et al., 2018). Nonetheless, the water transit times calculated from these depth-integrated models are rarely confronted with the water-rock interaction times inferred from hydrogeochemical modeling of water chemistry in watersheds.

For its part, the understanding of the hydrogeochemical functioning of the critical zone has been significantly advanced by the implementation of reactive-transport laws in geochemical modeling codes (Steefel et al., 2005; Lucas et al., 2010; 2017; Goddéris et al., 2013; Li et al., 2017). These developments allow for considering a variety of processes, such as flow and transport processes, ion exchanges, biogeochemical reactions, and the interplay between primary mineral dissolution and secondary mineral precipitation (Moore et al., 2012; Lebedeva and Brantley, 2013; Ackerer et al., 2018). Reactive transport models have been used to explore a wide variety of scientific issues, including the study of global atmospheric CO_2 consumption by weathering reactions (Goddéris et al., 2013; Li et al., 2014), the formation and evolution of soil and regolith profiles (Maher et al., 2009; Navarre-Sitchler et al., 2009; Lebedeva and Brantley, 2013), and the variability of water chemistry in the environment (Lucas et al., 2010; 2017; Ackerer et al., 2018). However, these approaches usually rely on a simple 1D flow path through

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
EGU
Discussions

a regolith column or along a hill slope to model flow in the system (e.g., Maher et al., 2011; Moore et al., 2012; Lucas et al., 2017; Ackerer et al., 2018). If these approaches are useful to discuss the key processes involved in regolith formation and in the acquisition of the water chemical composition, such 1D transport reactive modeling cannot take into account the diversity or the complexity of the flow trajectories in watersheds; hence, its effects on the water chemistry at the watershed scale.

A new step is therefore necessary for the development of hydrogeochemical modeling approaches that are applicable at the watershed scale and are able to integrate the complexity of the water flows and the diversity of the water-rock interaction processes. This is the aim of this work, which combines for the first time in this manner the results from a hydrological depth-integrated and spatially distributed model (NIHM) with a reactive-transport model (KIRMAT). This coupling allows for modeling the spatial and temporal simulation of the flow trajectories, the flow rates, the weathering reactions, and the evolution of the water chemistry within an elementary watershed, the Strengbach catchment. This catchment is one of the reference observatories of the French critical zone network (OZCAR), where multidisciplinary studies, including hydrological, geochemical and geological investigations, have been performed since 1986 ("Observatoire Hydrogéochimique de l'Environnement", OHGE; http://ohge.unistra.fr; El Gh'Mari, 1995; Fichter et al., 1998; Viville et al., 2012; Gangloff et al., 2014; 2016; Pierret et al., 2014; Prunier et al., 2015; Pan et al., 2015; Ackerer et al., 2016; 2018; Beaulieu et al., 2016; Chabaux et al., 2017; Schmitt et al., 2017; 2018; Daval et al., 2018). The method proposed in this work will yield precise knowledge of the water flow paths and their variability from wet to dry seasons, which is an important new step to better constrain the

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
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Discussion started: 8 January 2019

water transit times within catchments and to correctly understand the seasonal fluctuations in water chemistry.

2- Site presentation and data acquisition

The Strengbach catchment is a small watershed (0.8 km^2) located in the Vosges Mountains of northeastern France at altitudes between 883 and 1147 omsl. Its hydroclimatic characteristics can be found in Viville et al. (2012) or in Pierret et al. (2014). It is marked by a mountainous oceanic climate, with an annual mean temperature of 6 $^{\circ}$C and an annual mean rainfall of approximately 1400 mm, with 15 to 20% falling as snow during two to four months per year. The snow cover period is quite variable from year to year, and may not be continuous over the entire winter. The annual mean evapotranspiration is of approximately 600 mm, and the annual mean runoff of approximately 800 mm (in Viville et al., 2012). The watershed is currently covered by a beech and spruce forest. The bedrock is a base-poor Hercynian granite covered by a 50 to 100 cm-thick acidic and coarse-in-texture soil. The granitic bedrock was fractured and hydrothermally altered, with a stronger degree of hydrothermal overprinting in the northern than the southern part of the catchment (Fichter et al., 1998). The granite was also affected by surface weathering processes during the Quaternary (Ackerer et al., 2016). The porous and uppermost part of the granitic basement constitutes an aquifer from 2 to approximately 10 meters thickness. In the Strengbach watershed, the major floods and high-flow events usually occur during snowmelt periods at the end of the winter season or in the early spring. In contrast, the low-flow periods commonly happen at the end of the summer or during the autumn. Several springs naturally emerge along the slopes (figure 1). The watershed has ~~also~~ been equipped with several piezometers and boreholes since 2012, those being located along

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Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
Discussions

the slopes on both sides of the watershed (figure 1; Chabaux et al., 2017). Spring waters are regularly collected and analyzed since 2005, with a sampling frequency allowing for covering the entire range of water discharges from important droughts to strong flood events. Piezometer waters have been collected during sampling campaigns since 2012, and as for the spring waters, these sampling campaigns cover all the types of hydrological conditions encountered at the Strengbach catchment. The soil solutions are also regularly collected on the southern slope at a beech site (named HP) and to the north at a spruce site (named VP; figure 1; more details are provided in Prunier et al., 2015). For all the collected waters, the concentrations of the major dissolved species and the pH were determined by following the analytical techniques used at LHyGeS (Strasbourg, France) and detailed in Gangloff et al. (2014) and Prunier et al. (2015). Discharges of water from the springs were measured during the sampling campaigns, as were the water levels within the piezometers. The mineralogy and the porosity of the bedrock have been studied in detail in previous studies (El Gh'Mari, 1995; Fichter et al., 1998). On the southern part of the catchment, the weakly hydrothermally altered granite (named HPT, figure 1) is mainly composed of quartz (35%), albite (31%), K-feldspar (22%) and biotite (6%). It also contains small amounts of muscovite (3%), anorthite (2%), apatite (0.5%) and clay minerals (0.5%). On the northern part of the catchment, the lithology is more variable, with the presence of gneiss close to the crest lines and the occurrence of hydrothermally altered granite on the rest of the slopes (El Gh'Mari, 1995, figure 1). The hydrological, geochemical and petrological data obtained from these field investigations are the basis of the modeling work presented in the following. 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 chemical data from spring and piezometer waters modeled this study are reported in Table 1.

3- Modeling methods

The modeling developments presented in this study constitute a new step in the efforts undertaken at LHyGeS to constrain the mechanisms controlling the acquisition of geochemical composition of surface waters and to understand their spatial and temporal variations at the scale of elementary mountainous watersheds (Schaffhauser et al., 2014; Lucas et al., 2017; Ackerer et al., 2018). The main innovation of this work is to couple a spatially distributed hydrological model with a reactive transport model to constrain the spatiotemporal variability of chemical composition of spring and piezometer waters from the Strengbach watershed. To the best of our knowledge, this is the first time that such a coupling between hydrological and hydrogeochemical modeling approaches has been attempted at the watershed scale. In the present study, the hydrological model determines the distribution of the water flow lines within the watershed and thus constrains the water transit times for any period (summer or fall droughts, winter or spring floods). Then, the hydrogeochemical model is used to simulate the acquisition and the evolution of the water chemistry along the determined flow lines within the catchment.

3-1 Hydrological modeling

To assess the water flows in the watershed, several simulations were performed with the hydrological code NIHM (Normally Integrated Hydrological Model; Pan et al., 2015; Weill et al.,

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

2017; Jeannot et al., 2018). This code is a coupled stream, overland, and depth-integrated subsurface flow model developed at LHyGeS and already tested in the Strengbach watershed (Pan et al., 2015). The stream and overland flows are described by a diffusive-wave equation, and the subsurface flow is handled through an integration (in a direction normal to bedrock) of the unsaturated-saturated flow equation from the bedrock to the soil surface (Weill et al., 2017). The water exchanges between the surface and subsurface flows are addressed via the hydraulic head differences between the two compartments (Jeannot et al., 2018). First, numerical simulations were performed to correctly reproduce the water discharges from the Strengbach stream at the outlet of the watershed between 2010 and 2015 (figure 2). The thickness of the aquifer that was used for the simulations varied from 2 meters near the main crests to up to 8 meters in the middle of the watershed (figure 2), in agreement with the data obtained during the recent geological investigations and drilling campaigns undertaken at the catchment (Ackerer et al., 2016; Chabaux et al., 2017). The uniform precipitations over space applied at the surface of the catchment are drawn from data of the pluviometric station located at the highest elevation of the watershed (site PA, figure 1). Once the water discharges were correctly reproduced at the outlet, a backtracking approach was used to constrain the origin of subsurface water exiting the system at prescribed locations, and the spatiotemporal variability of the flow lines within the watershed. To back track the water particles, the velocity fields calculated by the NIHM model were inverted in their direction, and the locations of the backtracked particles were saved at each time-step. A daily time-step was used for the backtracking, as a compromise between computational efforts and a refined description of the transient velocity fields. A schematic representation of the backtracking approach is given in

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Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
Discussions

figure 3. This methodology allows for constraining the flow lines that bring the waters for a given time and at a given position on the catchment. This information is of major interest to determine the origin of the spring and piezometer waters. It is shown at the catchment scale, that flows are mainly driven by gravity in association with the steep slopes of the watershed, the latter being almost evenly drained over its whole surface area (figure 4). For each water sampling area, ten flow lines that bring water to the location of interest were determined (figure 4), together with a few features of the flow lines, including: local velocities, mean velocities, and length of the flow paths. It is worth noting that streamlines calculated via backtracking only consider flow in the subsurface compartment and are conditional to an arrival date at a prescribed location. Therefore, times calculated along the streamlines correspond to a date, x days before arrival, at which a water particle entered the subsurface or passed at a given location along the streamline. As streamlines are not associated with mean water flux values, the time distributions drawn from streamline calculations are only an approximation of the actual transit time distributions.

3-2 Hydrogeochemical modeling

The simulations of the water chemical composition along the flow lines were performed with the hydrogeochemical KIRMAT code (KInectic of Reaction and MAss Transport; Gérard et al., 1998; Lucas et al., 2010; Ngo et al., 2014). KIRMAT is a thermokinetic model that simultaneously solves equations describing geochemical reactions and transport mass balances in a 1D-porous medium. The mass transport includes the effects of one-dimensional convection, diffusion and kinematic dispersion. Chemical reactions account for the dissolution of primary minerals and oxido-reduction reactions, in addition to the formation of secondary minerals and clay minerals.

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
Discussions

The clay fraction is defined as a solid solution made up of a combination of pure clay end-members. The clay solid solution has a composition that changes over time, reflecting the impurity of the precipitating clays during low-temperature water-rock interactions (Tardy and Fritz, 1981). The KIRMAT code has already been applied in geochemical modeling of alluvial groundwaters (Lucas et al., 2010) and surface waters (Lucas et al., 2017; Ackerer et al., 2018). For this study, the modeling strategy is adapted from Ackerer et al. (2018) to consider the new transit time and water mixing constrains provided by the hydrological code NIHM. To capture the chemical composition of the spring and the piezometer waters, numerical simulations were performed along the flow lines that were determined through the backtracking approach. A sketch of the hydrogeochemical modeling strategy is provided in figure 5. For each flow line, several KIRMAT simulations were performed with different starting positions along the active part of the line. The starting positions represent the locations at which the soil solutions percolate through the subsurface shallow aquifer. These variable starting positions are spaced with a constant distance along the flow line. The soil solutions collected in the south at the beech site (HP) and in the north at the spruce site (VP) were considered representative of the soil solutions for the southern and northern parts of the catchment, respectively. The data of soil solution chemistry used in this study are available in Prunier et al. (2015). Data related to the bedrock properties, such as the mineralogical compositions, the mineral reactive surfaces and the kinetic constants of the dissolution reactions, are given in Ackerer et al. (2018). By following this modeling strategy, the simulations that consider soil solutions percolating at the upper part of the catchment reflect the chemical evolution of waters with long path lengths and long transit times within the aquifer. By contrast, shorter path lengths and shorter transit times

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
Discussions

are associated with the percolation of soil solutions that occurs in the vicinity of the sampling locations (figure 5). Because the springs or the piezometers collect waters from different origins and with contrasted transit times, integration along each water flow line was performed. The aim of the integration is to determine the mean chemical composition resulting from the mixing of the waters characterized by variable transit times (figure 5). The integrated chemical composition of the waters provided by a given flow line is calculated by taking the arithmetic mean of the solute concentrations calculated by the succession of the KIRMAT simulations along the flow line (figure 5). This arithmetic mean reflects a simple full mixing of uniform water fluxes irrespective of their short or long transit times. In other words, the soil solutions are assumed to percolate uniformly within the aquifer and are then conveyed along the slopes by uniformly distributed mass of water until reaching the sampling locations.

4- Hydrological modeling results

4-1 Spatial variability of the flow lines

The results provided by the hydrological code NIHM show that to first order, the Strengbach catchment is well drained and that the topography exerts an important control on the flow line distribution (figure 4). Along the hillsides presenting linear or slightly convex slopes, the water flow lines present simple characteristics. The flow paths are nearly parallel, and the water velocities are similar along the different flow lines on this type of hillside. The water velocities tend to increase when moving downstream (longer traveled distances for a given transit duration, see Fig. 4), with slower velocities near the main crests and higher velocities on the steepest parts of the hillsides. The waters collected along this type of hillside are therefore characterized by small variability of transit times. This is the case for the CS1, CS3 and RH3 spring waters located on the southern and northern parts of the catchment (figure 4). This is also the case for the piezometers PZ3 and PZ5 in the southern part of the watershed (figure 4). For the samplings located on linear or slightly convex slopes (CS1, CS3, RH3, PZ3 and PZ5), the characteristics of the different flow lines that feed each site are therefore comparable for a given site and for a given date. By contrast, in the vicinity of the valley and in the topographic depressions, the hydrological modeling indicates that the flow line characteristics are more variable. Because flow lines coming from different hill-sides can feed a topographic depression, mixing of different flow lines with variable flow paths and contrasting water velocities can occur at these locations. The waters collected in valleys or in topographic depressions are therefore characterized by a higher variability of transit times. This is the case for the CS2 and CS4 springs, which are located in a depression in the axe of the small valley and surrounded by slopes with various orientations and a complex flow line distribution (figure 4). For these two springs, the characteristics of the different flow lines can be different for a given date.

4-2 Temporal variability of the flow lines

Hydrological modeling under general transient conditions can render the evolution over time of water flows in the Strengbach watershed but also of other hydraulic variables or parameters. As an example, after an important rainfall event (30/03/2010 in Fig. 6), snapshots of the average hydraulic conductivity in the subsurface show increasing values with decreasing elevation in the watershed. The same observation holds for hydraulic conductivity during drought periods (see 29/11/2011, in Fig. 6). Provided that the hydraulic head gradient is largely dominated by the topography and therefore almost constant over time (Fig. 6), the water velocities are increasing along the flow lines from crests to valleys, irrespective of the wet versus dry hydrological periods. For the CS1 spring, the mean flow velocities along the flow lines vary from approximately 1 m/day to 7 m/day between the severe drought of 29/11/2011 and the strong flood of 30/03/2010 (figure 7). For the same dates, the mean velocities vary from 2 – 12 m/day, 1 – 4 m/day and 1 – 9 m/day for the springs CS2, CS3 and CS4, respectively. The variations from drought to flood are very similar for the piezometer waters, with velocities in the ranges 2 – 10 m/day and 2 – 12 m/day for the PZ3 and PZ5 piezometers, respectively. The RH3 spring located on a steeper part of the northern slopes exhibits flow velocity variations from 5 to 20 m/day from dry to flood conditions. In addition to the flow velocity variations, the hydrological simulations also reveal variability in the lengths of the active parts of the flow lines. Such variability is triggered by the particular seasonal variations of the hydraulic conductivities within the catchment. During periods of drought, the simulations indicate a strong decrease of hydraulic conductivities close to the main crests and much smaller variations at mid-slopes (figure 6). The crests rapidly dry out, whereas the areas at mid-slopes still supply some water to the stream network. These contrasting hydrological behaviors result from the differences in aquifer thickness and water storage between the crests and the other parts of the catchment (figure 2). Thin aquifer, flow divergence and absence of feeding areas prevent large water storage on the crests, in opposition to mid-slope parts with much thicker aquifers and the presence of feeding areas upstream. This particular pattern simulated for the hydraulic conductivities implies that the active parts of the flow lines extend up the main crests during important floods, whereas they are limited to mid-slopes after a long dry period. The consequence of this hydrological functioning is to moderate the seasonal variations of the transit times of waters, as the active lengths of flow lines vary simultaneously with water flow rates. Calculations indicate that for the spring and piezometer waters collected in this study, the mean transit times of waters only vary from approximately 1.75 to 4 months between the strongest flood and the driest conditions.

5- Hydrogeochemical modeling results

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

5-1 CS1 and CS3 springs (southern slope)

The CS1 and CS3 springs emerge on the same slope and drain the same rocks. Their hydrological behavior is also very similar in terms of flow lines and water transit times. The interesting consequence of the simple flow line distribution for these springs is that a single flow line can be considered as representative of all the flow lines that are feeding the spring, irrespective of the hydrological conditions. Hydrogeochemical simulations were performed along a single flow line for different hydrological periods using the methodology illustrated in figure 5. The case of CS1 spring is used below to highlight the main results obtained from this approach. For the strong flood of 30/03/2010, the KIRMAT simulations modeling the waters coming from the proximity of the spring and characterized by short transit times produced too much diluted solutions, whereas the waters coming from the main crests are too much concentrated to reproduce the spring water chemical composition. However, after an integration of all the waters arriving at

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

CS1 with the different transit times employed for the simulation, the resulting geochemical composition correctly reproduces the chemical composition of CS1 spring water at this date (H_4SiO_4, Na^+, K^+, Mg^{2+}, and Ca^{2+} concentrations, figure 7). A similar conclusion is obtained for the important drought of 29/11/2011. Again, geochemical integration of all the waters arriving at CS1 along a water line but with different transit times correctly reproduces the chemical composition of the CS1 spring waters collected on this date (figure 7). This is actually the case regardless of the time period considered. The coupled hydrological and hydrogeochemical approach has been applied for the CS1 spring for 6 dates covering the whole range of the water discharges of the spring (tables 1). The modeling results show that the seasonal variations of the water chemical composition of the CS1 spring over the whole range of observed flow rates at CS1 (figure 8). Simulations especially account for the 20-30% variation in H_4SiO_4 concentrations, the 10-20% variation in Na^+ concentrations, and the relatively stability of the pH of the CS1 waters (figure 8). Similar results are obtained for the CS3 spring (EA1), showing, as for the CS1 spring, that the proposed modeling approach is able to correctly capture the water chemical composition of the CS3 spring.

5-2 PZ3 and PZ5 piezometers (southern slope)

The two piezometers PZ3 and PZ5 are located on the southern part of the catchment, and their waters drain granitic bedrock similar to that drained by the CS sources. As for the CS1 and CS3 springs, the NIHM modeling results show that the flow lines arriving at the PZ3 piezometer are characterized by a relatively simple distribution. The flow lines are close to each other, and they render similar water velocities on the slopes (figure 4). For the PZ5 piezometer located downstream, the flow lines cover a larger area on the slope, especially during droughts (figure

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

4). However, for a given date, all the flow lines show similar velocities, with particularly fast flows on a lower portion of the hillslope. These results imply that, as for the CS1 and CS3 springs, the hydrogeochemical simulations of PZ3 and PZ5 piezometer waters can be performed by relying upon a single flow line representative of all the waters collected by the piezometers on a given date. The geochemical integration along the flow line has been performed in the same manner as detailed above, and this approach is able to reproduce the chemical composition of the waters of the two piezometers, as illustrated in figure 9 for the flood of the 05/05/2015 and in EA2 for the dry conditions of 10/11/2015. For the CS1 and CS3 springs, the results also point to a modest variability of the solute concentrations over changing hydrological conditions (not shown). Together, these modeling results show that the linear or slightly convex slopes on the southern part of the catchment allow to correctly capture the water chemistry of each sampling site with a straightforward integration along a single and representative flow line.

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

CS2 and CS4 spring waters drain the same granitic bedrock as the CS1 and CS3 waters, but are located in the axe/along the direction of the small valley of the Strengbach stream and surrounded by slopes of various orientations and inclinations (figure 4). Consequently, the distribution of the flow lines is much more scattered than for the CS1 and CS3 springs. The modeling strategy applied for these two springs and the results are detailed below for the CS2 spring. For this spring, and for all the hydrological conditions, two different groups of flow lines have been determined by the backtracking approach: a northern group characterized by relatively slow velocities and a southern group with higher velocities (figure 4). When the hydrological conditions vary from a strong flood (30/03/2010) to an important drought

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

(29/11/2011), the flow rates tend to decrease along all the flow lines (figure 10). For example, the mean flow velocities along the flow lines vary from approximately 12 m/day to 2 m/day between these two dates. However, for a given date, the northern group systematically renders slower velocities than the southern group. This scattered distribution of the flow lines implies that a single specific flow line cannot be representative of all the waters collected by the spring. The flow lines calculated using the NIHM model allow for constraining the trajectories of the waters within the watershed; however, the simulations performed in this study cannot provide the mass fluxes of water carried by each flow line. Consequently, a straightforward calculation of the chemistry of the CS2 spring, such as detailed above for CS1, is not applicable because the mixing proportions between the different flow lines are unknown. Alternatively, it is possible to determine the concentrations in the waters carried by the slowest and the fastest flow lines that are feeding the spring and to compare the results with the observed chemistry of the spring water. The results indicate that for all the hydrological conditions, the concentrations calculated from the geochemical integration along the slowest and the fastest flow lines are able to correctly frame the chemical composition in terms of H_4SiO_4, Na^+, K^+, Mg^{2+}, and Ca^{2+} of the CS2 spring waters (figure 10). The observed chemistry of the CS2 spring is bounded by the chemical compositions of the waters carried by the slowest and fastest flow lines. The modeling results also suggest that the contributions of the slow and fast flow lines are comparable over most of the hydrological conditions, as the observed concentrations are in general at the midpoint between the min (i.e., fast) and max (i.e., slow) boundaries (see Fig. 10). It is only for the important droughts that the spring chemistry seems to be mainly controlled by the southern and faster group of flow lines. Further works to precisely estimate the mass fluxes of water

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

carried by each flow line are necessary to calculate the chemistry of the CS2 spring water with a weighted mixing calculation. The same conclusions apply to the CS4 spring located in the proximity of CS2 spring.

5-4 The RH3 spring (northern slope)

The RH3 spring is located on the northern part of the catchment (figure 4), where steep slopes imply fast water velocities and subparallel flow lines. However, if the distribution of the flow lines on the RH3 hillside is simple (as for the CS1 and CS3 springs) the precise lithological nature of the bedrock drained by the RH3 waters is more difficult to constrain (see also Ackerer et al., 2018). Unlike the southern slope, the bedrock of the northern part of the catchment exhibits a complex lithology, with gneiss outcropping in the upper part of the slope and granite of variable degree of hydrothermal overprinting in the intermediate and lower parts. These lithological variations can explain the differences in chemical composition between the RH3 spring waters and the waters of the southern part of the catchment: the RH3 spring waters are characterized by systematically higher concentrations of K^+ and Mg^{2+} cations but show similar concentrations for the other major elements (Ackerer et al., 2018; Pierret et al., 2014). The vertical extension of the gneiss and the spatial variability of the hydrothermal overprinting on the northern slopes are not very well known. It is therefore difficult to determine the exact lithology that is percolated by the flow lines feeding the RH3 spring. A straightforward modeling of the RH3 spring waters, such as that performed for the CS1 and CS3 sources, is thus not possible. Alternatively, simulations of two extreme cases can be performed by assuming that the flow lines only run, either on gneiss or on hydrothermally altered granite. When only considering the hydrothermally altered granite, the simulated concentrations of H_4SiO_4 and Na^+ are close to the measured ones. However, the concentrations of K^+ and especially Mg^{2+} are clearly underestimated (figure 11). In the case of the flow lines only running on gneiss, the simulated concentrations of H_4SiO_4 and Na^+ also match the data. However, due to the higher abundance of biotite in the gneiss, the simulated concentrations of K^+ and Mg^{2+} are much higher than the measured ones (figure 11). At this stage, it is therefore reasonable to propose that the chemical composition of the RH3 spring waters reflects mixing of the two lithological influences. By assuming a geochemical conservative mixing, which is likely a too simplistic scenario, the results would indicate that the flow lines portions running on gneiss and on hydrothermally altered granite count for approximately 40-50% and 50-60% of the total water path length, respectively. Further works to estimate the location of the contact between gneiss and granite are required for more realistic modeling and hence a deeper interpretation of the chemical composition of RH3 spring waters. In any case, the important point to stress here based on the above simulations is that the complex lithology and bedrock heterogeneity mainly impact the K^+ and the Mg^{2+} budget of the RH3 waters, but not or only slightly the H_4SiO_4 and Na^+ concentrations, which control the main part of global weathering fluxes carried by the Strengbach spring waters. These results readily explain why although the RH3 spring waters exhibits higher Mg^{2+} and K^+ concentrations than the other CS springs, they carry relatively similar global weathering fluxes (Viville et al., 2012; Ackerer et al., 2018).

6- Discussion

The modeling approach proposed in this study and based on the coupling of the NIHM and KIRMAT codes, allows for building a better modeling scheme than those commonly used in previous studies regarding the hydrogeochemical modeling of surface waters at the watershed scale. In such previous works, the geochemical simulations were performed mainly along a single 1D flow line, only characterized by homogeneous mean hydrological properties (Goddéris et al., 2006; Maher et al., 2011; Moore et al., 2012; Lucas et al., 2017; Ackerer et al., 2018). In the previous study on the Strengbach watershed (Ackerer et al., 2018), the soil solutions were also assumed to percolate in the bedrock only at a single starting point of the flow lines. Although these previous approaches were useful for determining the long-term evolution of regolith profiles and/or the mean chemistry of waters at the pluri-annual scale, they cannot be used to discuss the seasonal variations of the water chemical composition. The NIHM-KIRMAT coupling approach makes this possible, as it provides the spatial distribution of the flow lines at the watershed scale and their variations over time. Furthermore, the proposed modeling approach also integrates a soil solution percolation scheme with inlets uniformly distributed along the slope, which is more realistic than a scheme assuming that each sampled site is fed by a single flow line carrying waters with a unique transit time. The consistency of the modeling results with the measured concentrations over the whole range of the hydrological conditions certainly gives weight to the application of the proposed modeling approach to the Strengbach catchment. Such consistency also gives weight to the assumptions made regarding the modeling parameters used in this work, i.e., reactive surfaces and kinetic constants. It also gives weight to the conclusions and implications that can be deduced regarding the hydrogeochemical functioning of the watershed, and the origin of the chemostatic character of these waters. These different points are detailed below.

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

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

For the geochemical simulations performed in this study, the kinetic constants that were used to describe the dissolution reactions of the primary minerals are standard constants determined through laboratory experiments. The reactive surfaces of the primary minerals were calculated by assuming a simple spherical geometry for all the minerals, and the mean size of the minerals was estimated from thin section observations of the bedrock samples. Such choices can appear surprising as over the last years, several studies have suggested that the kinetic constants determined through laboratory experiments overestimate the rates of the dissolution reactions in natural environments (White and Brantley, 2003; Zhu, 2005; Moore et al., 2012; Fischer et al., 2014). The origin of this laboratory-field discrepancy is still a matter of debate (Fischer et al., 2014). Different processes have been proposed to explain the gap between laboratory and field estimates, such as the crystallographic anisotropy (Pollet-Villard et al., 2016), progressive occlusion of the primary minerals by clays (White and Brantley, 2003), or the formation of passivation layers at the surfaces of the minerals (Wild et al., 2016, Daval et al., 2018). The difficulty to reconcile field and laboratory estimates can also be related to the challenge of defining relevant reactive surfaces at different space scales (Li et al., 2006; Navarre-Sitchler and Brantley, 2007). The present modeling work regarding the Strengbach catchment shows that the chemical composition variability of the spring and piezometer waters is fully captured via geometric reactive surfaces and standard kinetic constants, while respecting the water-rock interaction times within the catchment. This result suggests that the mean rates of the weathering reactions employed in this modeling work are realistic, which in turn implies that the modeling approach developed in this study does not underline significant mismatches between field and laboratory reaction rates. More details are given in the following to

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

investigate why geometric reactive surfaces and standard kinetic constants are able to correctly capture the water chemistry. The calculated rates of the dissolution reactions depend on the product between the kinetic constants of the reactions and the mineral reactive surfaces. In the experimental studies performed for determining the kinetic constants of dissolution reactions, the constants are usually determined by normalizing the experimental weathering rates with the Brunauer-Emmett-Teller surfaces determined from experiments of gas absorption (BET surfaces; Chou and Wollast, 1986; Lundstrom and Ohman, 1990; Acker and Bricker, 1992; Amrhein and Suarez, 1992; Berger et al., 1994; Guidry and Mackenzie, 2003). In table 2, the BET surfaces are compared with the geometric surfaces of the minerals involved in the dissolution experiments, recalculated from the size ranges of the minerals. For most of the minerals (apatite, quartz, albite, K-feldspar, and anorthite), the geometric surfaces are within the same order of magnitude as the BET surfaces, even if often slightly lower (table 2). However, as the BET surfaces are determined with fairly large uncertainties, especially for low BET surfaces (up to ± 70%), and as they can be very different depending on the gas used (up to 50% of difference between N2 or Kr absorption; Brantley and Mellott, 2000), the above differences between the geometrical and the BET surfaces cannot be considered significant for the majority of minerals used in the Strengbach simulations. A significant difference only appears for biotite, with the geometric surfaces one order of magnitude less than the BET surfaces (table 2). However, for biotite, due to its layered structure, it has been shown that approximately 80 – 90% of the surface area accessible by the gases used to estimate BET surfaces is not accessible for weathering reactions (Nagy, 1995). In the case of biotite, the effective surface area for the water-rock interactions would thus be, in a rather fortuitous manner, a surface area close to the geometric one. The above considerations and observations thus explain why for a granitic bedrock as found in the Strengbach catchment, the geometric surfaces are relevant to describe the surfaces of water-rock interactions at the space and time scales of this study. An immediate corollary is that the values of the standard kinetic constants are also appropriate to calculate reaction rates with mineral geometric surfaces in our modeling approach. This ability may be related to the fact that all the minerals that have been used in the dissolution experiments and in the kinetic studies were collected in the field (e.g., Acker and Bricker, 1992; Amrhein and Suarez, 1992). These minerals were likely affected by anisotropy, passivation layers, and any types of aging effects related to long-term water-rock interactions. Our results might therefore mean that the standard kinetic constants obtained in such experiments integrate the aging effects that have affected the reactivity of the primary minerals in natural environments. This would explain why it is possible to capture the full variability of the water chemistry in an elemental catchment with simple geometric reactive surfaces and standard kinetic constants. It is important to emphasize at this stage that the results of our simulation strengthen the idea that the low surfaces calculated from the geometrical shapes of minerals provide good estimates of the reactive surfaces within the natural environment (Brantley and Mellott, 2000; Gautier et al., 2001; White and Brantley, 2003; Zhu, 2005; Li et al., 2017). They are certainly the values to be used for hydrogeochemical modeling such as that performed in this work, in addition to the use of the experimental kinetic constants for mineral dissolution. These conclusions are certainly not specific to the Strengbach catchment and could be applicable to many other granitic catchments.

6-2 Implications for the acquisition of the water chemistry

The results of the NIHM-KIRMAT hydrogeochemical modeling have strong implications regarding the hydrogeochemical functioning of the Strengbach watershed. The NIHM modeling shows that the hydrological functioning of the watershed is correctly simulated by water circulations in the shallow subsurface, i.e., in a saprolitic aquifer. No contribution of waters circulating in the deep fracture network of the granitic bedrock and observed during the drilling campaigns is necessary. The deep-water circulation pathways are probably disconnected from the shallow subsurface, or with mean hydraulic heads less than those of the subsurface, at least at the Strengbach catchment scale, and does not significantly impact the water budget of the Strengbach catchment. As detailed in section 4-1, the modeling results show that water in the shallow aquifer flows along streamlines with fairly simple geometries. At the scale of the watershed (figure 4), the geometry of the flow lines validates the hypothesis built on the basis of the geochemical and Sr-U isotopic data that the spring waters of these mid-mountain basins (i.e., the Strengbach and Ringelbach watersheds; Schaffhauser et al., 2014; Pierret et al., 2014) are supplied by waters from distinct flow paths without real interconnections. More importantly, the modeling results emphasize the importance of water transit times within the watershed as a main feature controlling the chemical composition of subsurface waters at the Strengbach catchment. Along all the slopes, the waters coming from the proximity of the crests and characterized by a long transit time systematically render higher concentrations than the waters with shorter pathways and transit times. When the hydrological conditions change from wet to dry periods, the solute concentrations also tend to increase with the increase in the mean transit time of waters. Our results demonstrate in particular that for the CS1 and CS3 sources and for the PZ3 and PZ5 piezometers, all located on the southern slope of the

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
Discussions

watershed, over a homogeneous granitic bedrock, and all characterized by flow lines of fairly simple geometries (section 4), the spatial and temporal variations of their geochemical composition are fully explained by differences in water residence times. Residence time variations between high and low discharge periods explain the temporal variations of geochemical signatures within each site, and the differences in mean residence times of waters supplying the different sources and piezometers explain the various chemical compositions between the different sites. Only the CS2 and CS4 springs, located in a depression, are supplied by two different types of water flow lines, the contribution of which could change over time. However, the mixing of different flow lines has probably a relatively modest impact, and at the scale of the watershed, the results show that the duration of water-rock interaction exerts a first-order control on the chemical composition of waters, in addition to the lithological parameter. This study brings also strong constrains on the spatial repartition of the weathering processes. For the modeling strategy developed in this study, the chemical composition of the spring and piezometer waters are calculated by integrating the chemical composition of waters introduced at different starting positions along the active part of the flow lines (figure 5). In each of the simulations, a fixed distance between the initial positions of the KIRMAT simulations along the flow lines was used. The modeling results show that through the geochemical integration, the concentrated waters coming from the main crests are naturally counterbalanced by the diluted waters infiltrating close to the sampling sites. From flood to drought events, the mean transit times are obviously impacted by the variable velocities along the flow lines, but regardless of the hydrological conditions, it is always possible to explain the water chemistry of the sampling sites with the above integration scheme. Such repeatable consistency between data and simulations indicates that this circulation scheme is certainly quite realistic for the Strengbach catchment. In other words, this scheme supports the idea suggested in Ackerer et al. (2016) that at the scale of the watershed, the solute chemistry is acquired through reactions and weathering processes that are spatially relatively homogenous within the watershed.

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

The hydrogeochemical monitoring of the spring, piezometer, and stream waters performed in the Strengbach catchment clearly shows that this catchment has a chemostatic behavior (e.g., Viville et al., 2012; Ackerer et al., 2018; this study). All the spring and the piezometer waters have chemical concentrations impacted by changes in the hydrological conditions, but the concentration variation ranges are by far narrower than variation ranges of water discharges, which define the chemostatic behavior of a hydrological system. For the waters exhibiting the largest concentration variations (spring CS1), there is a modest increase of approximately 10-30% in the concentrations of H4SiO4 and Na+ from floods to severe drought events, while ~~at the same time,~~ the water discharges may vary by a factor of 15 (figure 7). This modest variability of the solute concentrations over a wide range of water discharges is not specific to the Strengbach catchment; it has rather been observed in several watersheds spanning different climates and hydrological contexts (Godsey et al., 2009; Clow and Mast, 2010; Kim et al., 2017). Different origins for the chemostatic behavior have been proposed, such as a modification of the mineral reactive surfaces during changing hydrological conditions (Clow and Mast, 2010), a small concentration difference between slow and fast moving waters (Kim et al., 2017), or the fact of reaching an equilibrium concentration along the water pathway (Maher, 2010). To date,

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
Discussions

the study of concentration-discharge relationships has been intensively used to assess the chemostatic behavior of waters (Godsey et al., 2009; Kim et al., 2017; Ameli et al., 2017). However, the lack of precise knowledge regarding the water transit times limits our ability to clearly discuss the origin of the chemostatic behavior on the single basis of the concentration-discharge relationships. The coupled approach presented in this study offers a renewed opportunity to discuss the origin of the chemostatic behavior in catchments because the acquisition and the evolution of the water chemistry can be simulated along flow lines that have been independently determined via timely and spatially distributed hydrological modeling.

The results from the hydrological model show that the characteristics of the flow lines are affected by the changes in the hydrological conditions. After important precipitations, high water contents and large hydraulic conductivities (as the local mean value integrated over the aquifer thickness including the vadose and saturated zones) are simulated in the vicinity of the crests and all along the small valley of the catchment (figure 6). During drought periods, the crest lines have progressively dried out, and the hydraulic conductivities strongly decrease on the upper parts of the watershed. Only some locations at mid-slopes and along the direction of the principal valley exhibit modest hydraulic conductivities (figure 6). This response of the hydraulic conductivities implies that during floods, the water velocity significantly increases along the flow lines, but the length of the active parts of the flow lines also increase as waters collected downstream may also come from the neighborhood of the main crests. During drought periods, the water velocity is slower, but the length of the active parts of the flow lines also tends to decrease, as the waters are principally supplied by mid-slope areas characterized by a thicker aquifer. For illustration, and for the CS1 spring, the water velocities varied along the

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

flow lines between 7 and 0.5 m/day during the flood of 30/03/2010 and were approximately 0.5-1 m/day during the important drought of the 29/11/2011 (figure 6). At the same time, the active parts of the flow lines were reduced from 160 m to 110 m from the flood to the drought events (figure 7). This hydrological functioning implies that the water velocities along the flow lines and the active lengths of the flow lines vary in opposite manners from drought to flood events. This hydrological behavior buffers the variations of the water transit times over changing hydrological conditions and explains why the mean transit times span much narrower variation ranges than the discharges of water at the collected springs. For example, the calculated mean transit times of waters for the CS1 spring vary from 1.75 to 3.13 months between the strongest flood and the driest period that have been studied, whereas the water discharges vary from 1.523 L/s to 0.098 L/s (figure 7). Because the time of the water-rock interactions exerts a first-order control on the chemical composition of waters, the modest variability of the mean transit times is directly responsible for the relative stability of the chemical composition of waters within the catchment.

It is important to be reminded that no modifications of the reactive surfaces and of the dissolution kinetic constants were necessary to reproduce the seasonal variability of the water chemistry. It is also important to emphasize that the simulated chemical compositions of waters remain far from a state of chemical equilibrium with respect to primary minerals. The calculated Gibbs free energy for the primary minerals ranges from -120 to -100 kJ/mol for apatite, -90 to -80 kJ/mol for biotite and anorthite and -30 to -20 kJ/mol for albite and K-feldspar. These far-from-equilibrium values for the Gibbs free energy imply that the reaction rates calculated using hydrogeochemical codes such as KIRMAT, which are based on the transient state theory (TST;

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Eyring, 1935), are realistic for most of the primary minerals in this type of hydrological context. Regarding the simulations performed in this study, the relatively short residence times of waters and the precipitation of clay minerals prevent reaching a state of chemical equilibrium between waters and primary minerals. The results also indicate that a clay solid solution is a relevant method to capture the clay dynamic in this type of watershed and that a clay solid solution precipitated in thermodynamic equilibrium is able to generate realistic clay precipitation rates and reliable water chemistry (Ackerer et al., 2018; this study). A more precise approach of the formation of clay phases would request to simulate a kinetically-controlled nucleation and growth of clay particles: it is clear that such complex phases are probably produced in oversaturation state as can be described using the numerical code NANOKIN (Fritz et al., 2009, Noguera et al. , 2011). However, the results obtained here show that equilibrium condition for clay formation is a reasonable first approximation for predicting clay production. Taken together, these results show that the solute concentrations are not limited by a chemical equilibrium; they simply are weakly variable over time because of the short and moderately variable water residence times in the watershed. The chemostatic behavior of the surface and the shallow subsurface waters is therefore only due to a strong hydrological control of the water transit times within the watershed. This conclusion can most likely be extended to the other mountainous watersheds of this type, in which water pathways and transit times are mainly controlled by gravity driven flow along steep slopes.

7- Conclusion

This study demonstrates the potential of coupling physically based and distributed hydrological modeling with hydrogeochemical modeling as a way to better understand variability over time

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

and space of the composition of surface and subsurface waters. The independent estimation of the water transit times provided by hydrological simulations is a clear added value to constrain the geochemical modeling approaches. This study shows that the durations of water-rock interactions exert a first-order control on the chemical composition of waters and that the acquisition of the water chemistry can be explained by weathering processes that are spatially fairly homogeneous over the catchment. The hydrological functioning of the watershed also indicates that the chemostatic behavior of the water chemistry is a direct consequence of the strong control exerted by hydrological processes on water transit times. In the present case, The variations in flow lines distributions from drought to flood events result in a modest seasonal variability of mean water transit times, which in turn explains the relative stability of the solute concentrations in waters. The consistency between measured and modeled concentrations while respecting the water-rock interaction times provided by the hydrological simulations shows that it is possible to capture the chemical composition of waters with simply determined reactive surfaces and standard kinetic constants. The results of our simulations strengthen the idea that the low surfaces calculated from the geometrical shapes of minerals are a good estimate of the reactive surfaces within the natural environment and certainly the values to be used for hydrogeochemical modeling such as that performed in this work, in addition to the use of the experimental kinetic constants for mineral dissolution. Overall, this work shows that the hydrogeochemical functioning of an elementary watershed such as the Strengbach catchment is relatively simple. It is possible to correctly assess the variability of the chemical composition of waters through process-based modeling approaches and by only formulating few simple hypotheses regarding the functioning of the watershed.

Acknowledgements: This work and the Julien Ackerer's salary were financially supported by the French ANR Program (Project CANTARE- Alsace) under grant agreement ANR-15-CE06-0014. This work also benefited from fruitful discussions with D. Daval.

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
Discussions

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Discussion started: 8 January 2019

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Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Open Access
Discussions

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 of 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 dry 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 applying a velocity field of the same magnitude but opposite direction to the particle, the position of the particle can be 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 updating of the velocity field was set to 1 day, as a compromise between the accuracy of results and computational time considerations.

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

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

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

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

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

Figure 7: simulation results for the CS1 spring for an important drought (29/11/2011) and a strong flood event (30/03/2010). At the top, active parts of the flow lines that bring the waters to the CS1 spring for the two sampling dates. Below, simulated chemical compositions of the CS1 spring waters after integration along the flow lines and a comparison with the initial soil solution and the spring chemistry data are presented.

Figure 8: simulation results for the CS1 spring over the whole range of the water discharges from the spring. Red lines indicate simulated parameters after integration along the flow lines, and blue points show measured values from the field campaigns realized between 2005 and 2015.

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

Figure 10: simulation results for the CS2 spring. At the top, active parts of the flow lines that bring the waters to the CS2 spring for an important drought (29/11/2011) and a strong flood event (30/03/2010) are shown. The location of the CS2 spring implies a more scatted distribution of the flow lines than for the CS1 spring. Below, simulation results for the CS2 spring over the whole range of the water discharges from the spring are presented. Blue lines indicate

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

Hydrology and Earth System Sciences
Discussions

simulated parameters after integration along the slowest flow line, yellow lines indicate simulated parameters after integration along the fastest flow line, and blue points show measured values from the field campaigns realized between 2005 and 2015.

Figure 11: simulation results for the RH3 spring chemistry and for a flood event (30/03/2010). On the left, simulated concentrations for the case assuming that the flow lines only run on gneiss (GN) are shown. On the right, simulated concentrations for the case assuming that the flow lines only run on hydrothermally altered granite (VS) are presented.

Figure 12: overview of the flow lines of the subsurface that feed with water the geochemical sampling sites CS1, PZ3 and PZ5 on May 5th, 2015 according to the NIHM simulations. The simulated chemical compositions after geochemical integration along the flow lines are also presented for this transect on the southern part of the watershed (CS1, PZ3 and PZ5) and compared with the initial soil solution and the spring chemistry data.

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

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

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

	Na^+ (mmol/L)	**K^+** (mmol/L)	**Mg^{2+}** (mmol/L)	**Ca^{2+}** (mmol/L)	**H_4SiO_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

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

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 2

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

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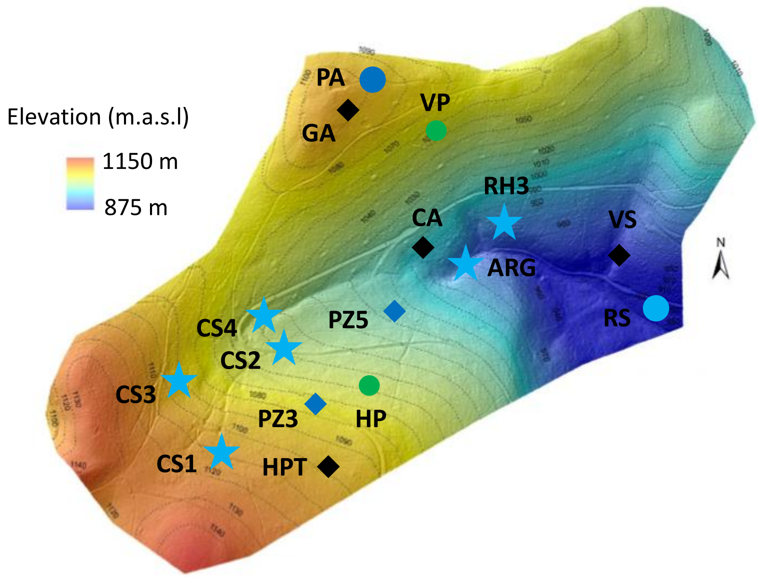

Figure 1

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-609
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Discussion started: 8 January 2019

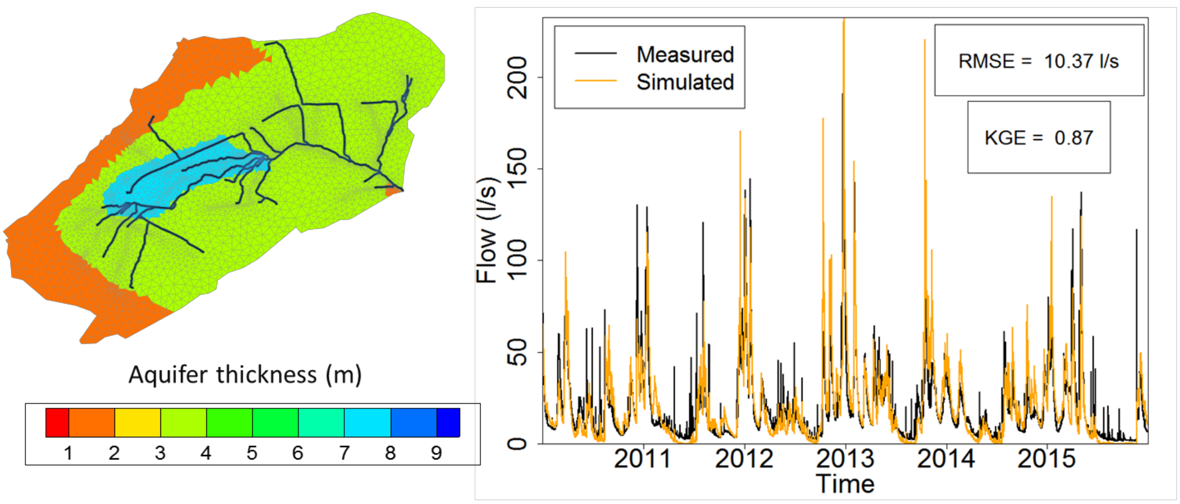

Figure 2

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Discussion started: 8 January 2019

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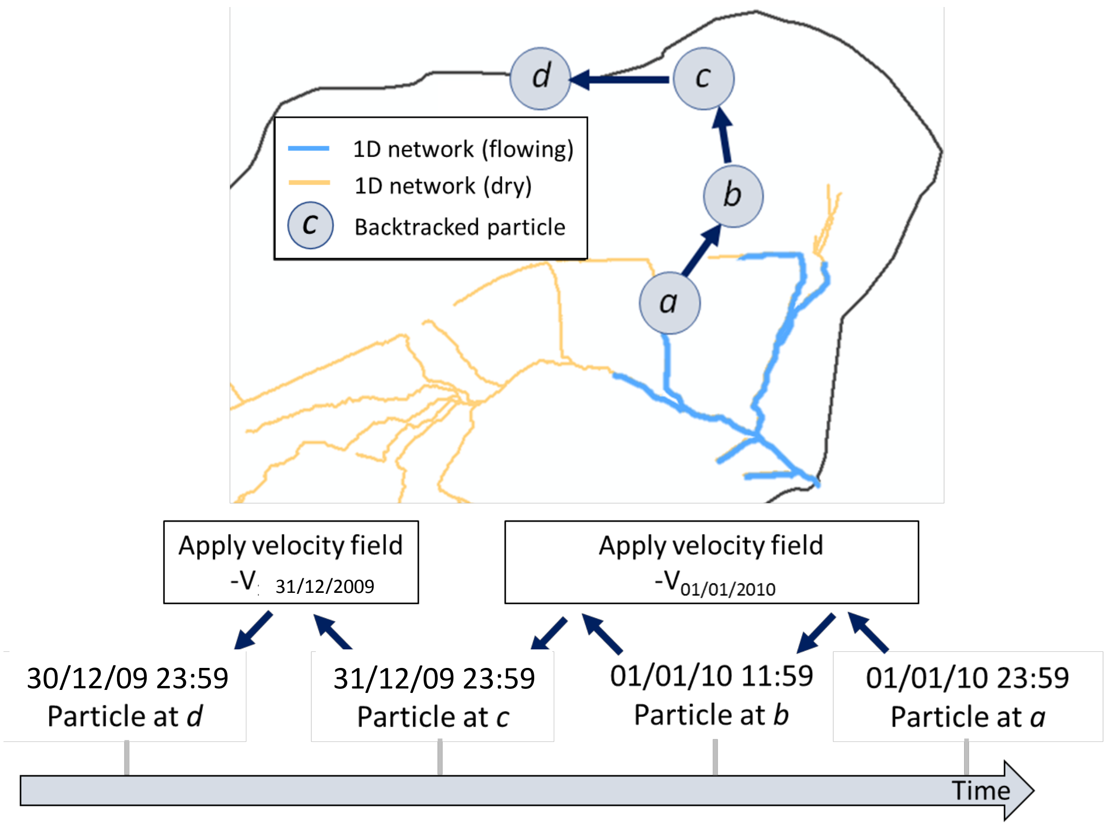

Figure 3

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Discussion started: 8 January 2019

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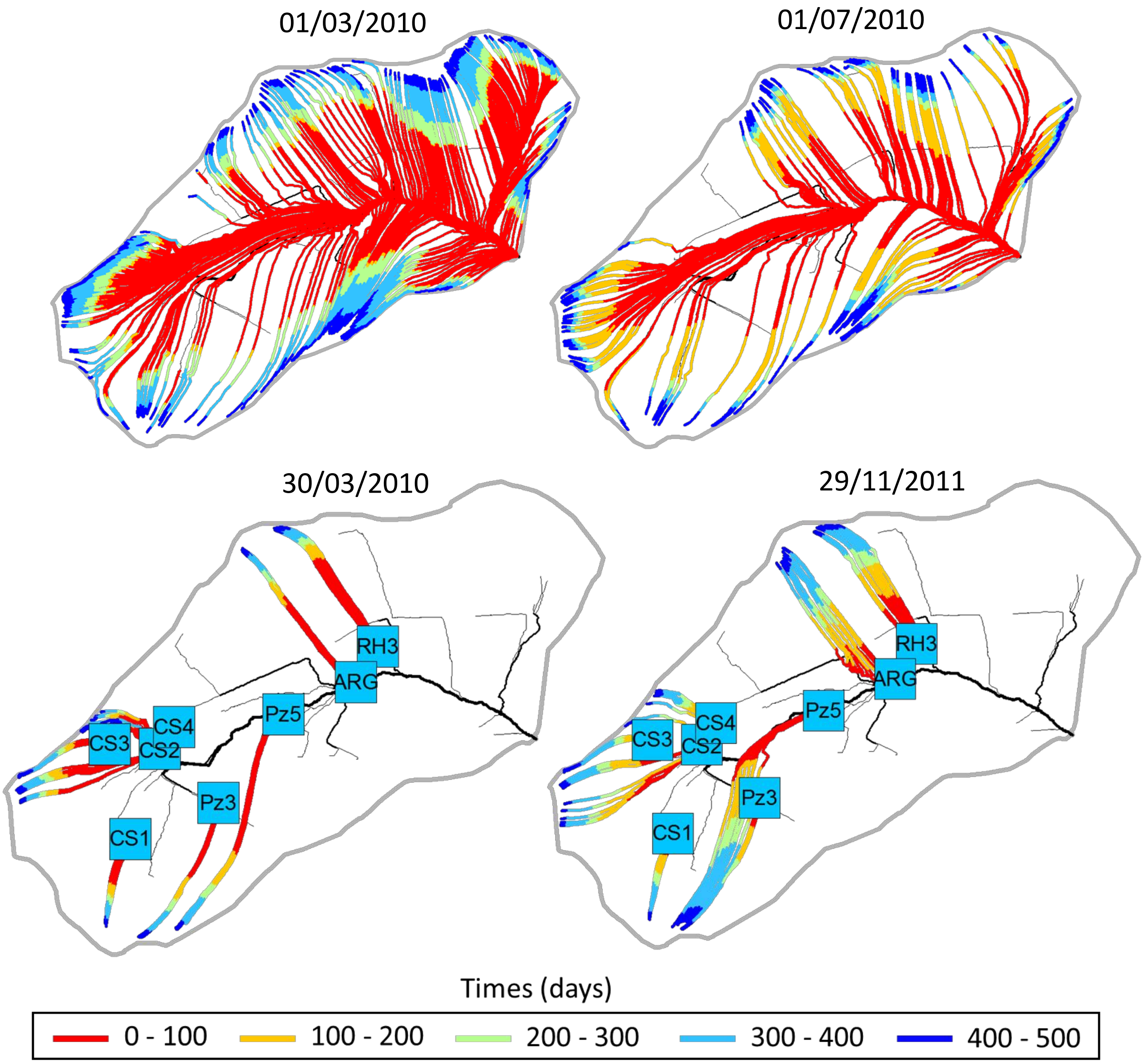

Figure 4

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Discussion started: 8 January 2019

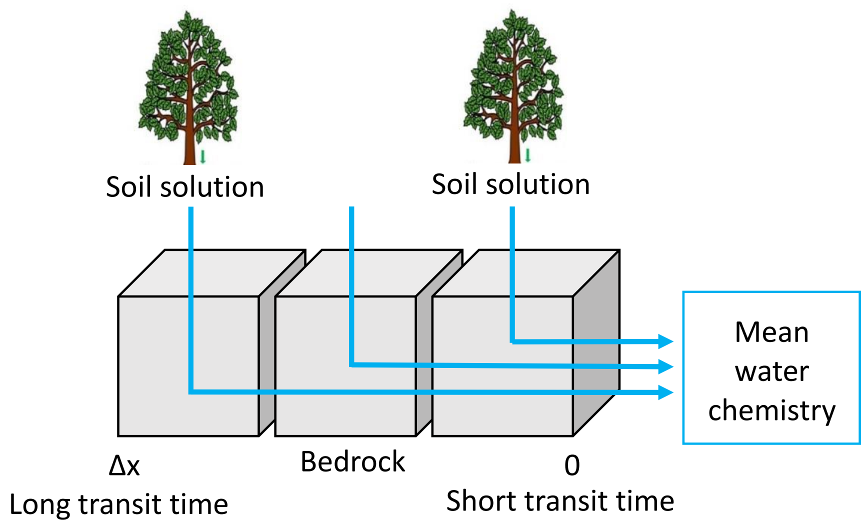

Figure 5

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Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

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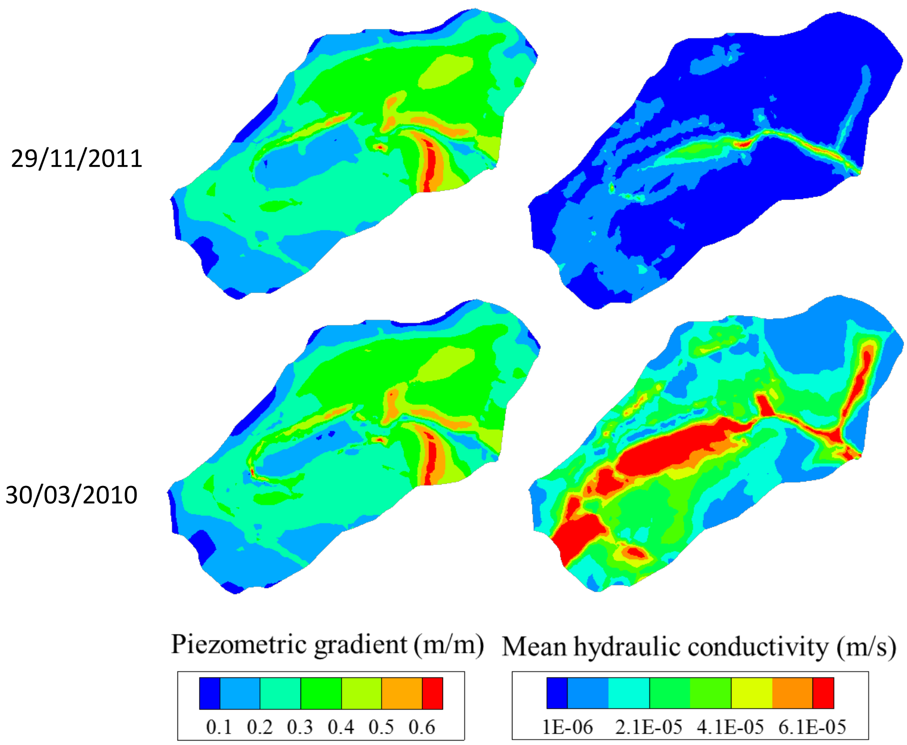

Figure 6

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Discussion started: 8 January 2019

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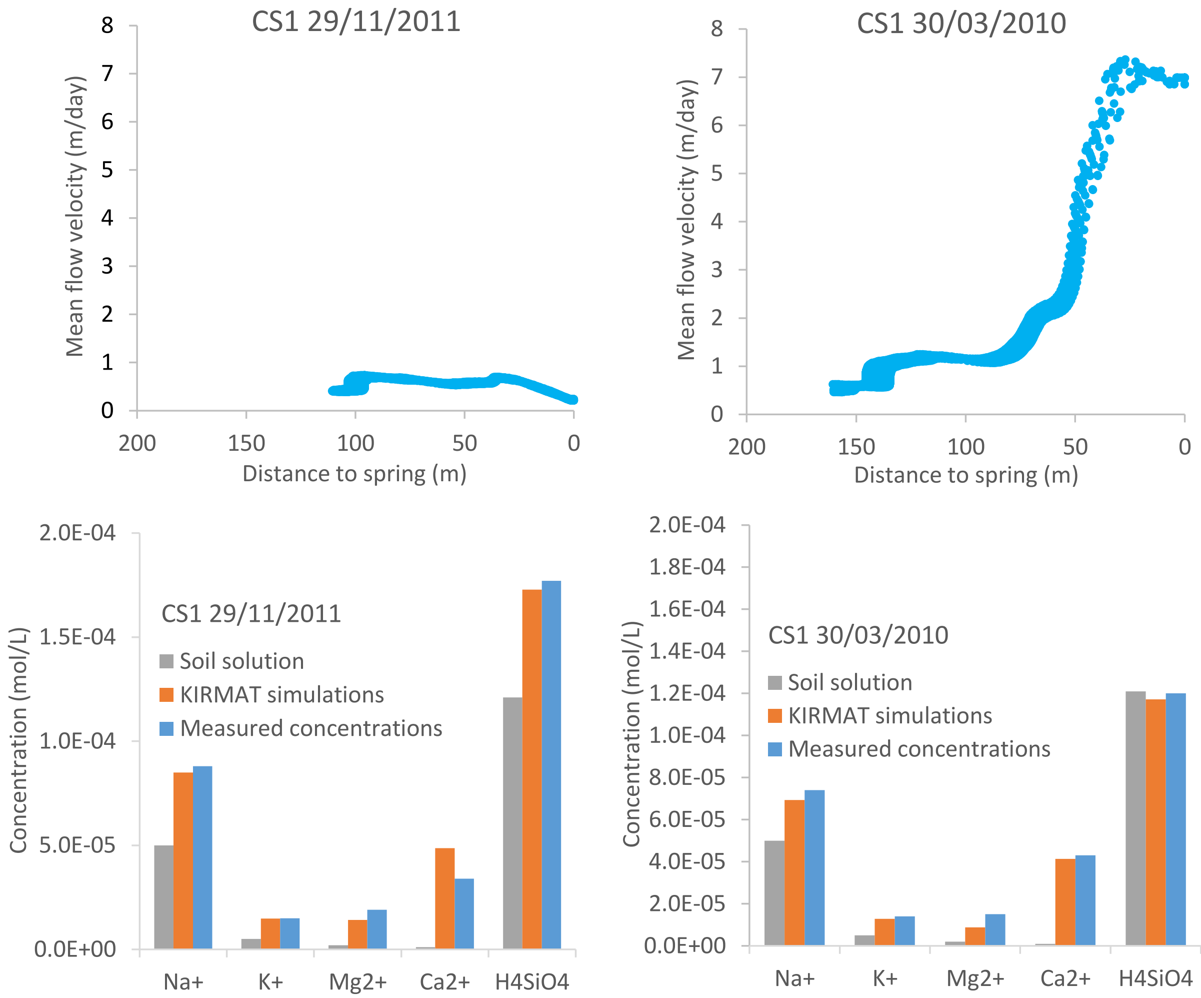

Figure 7

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Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

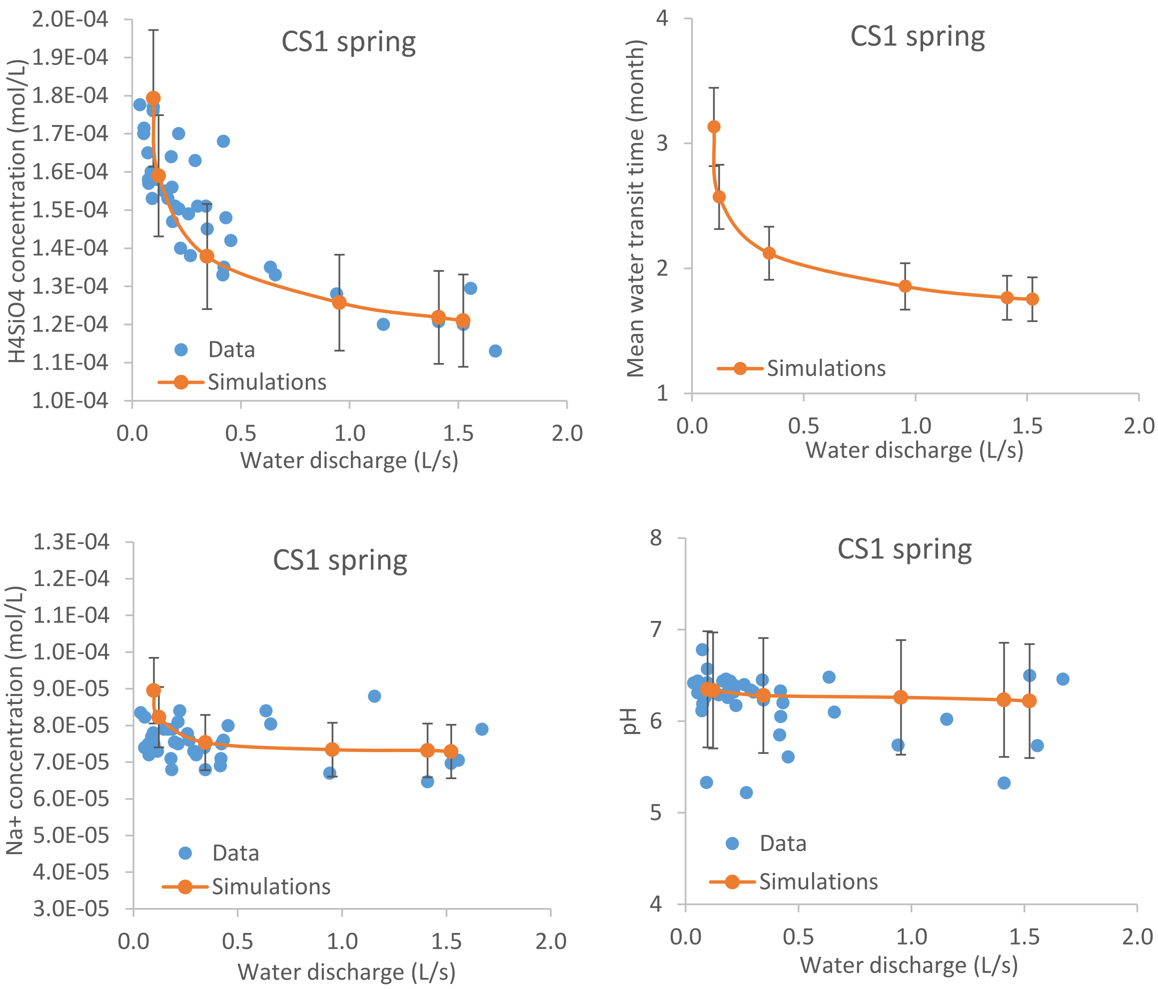

Figure 8

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Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

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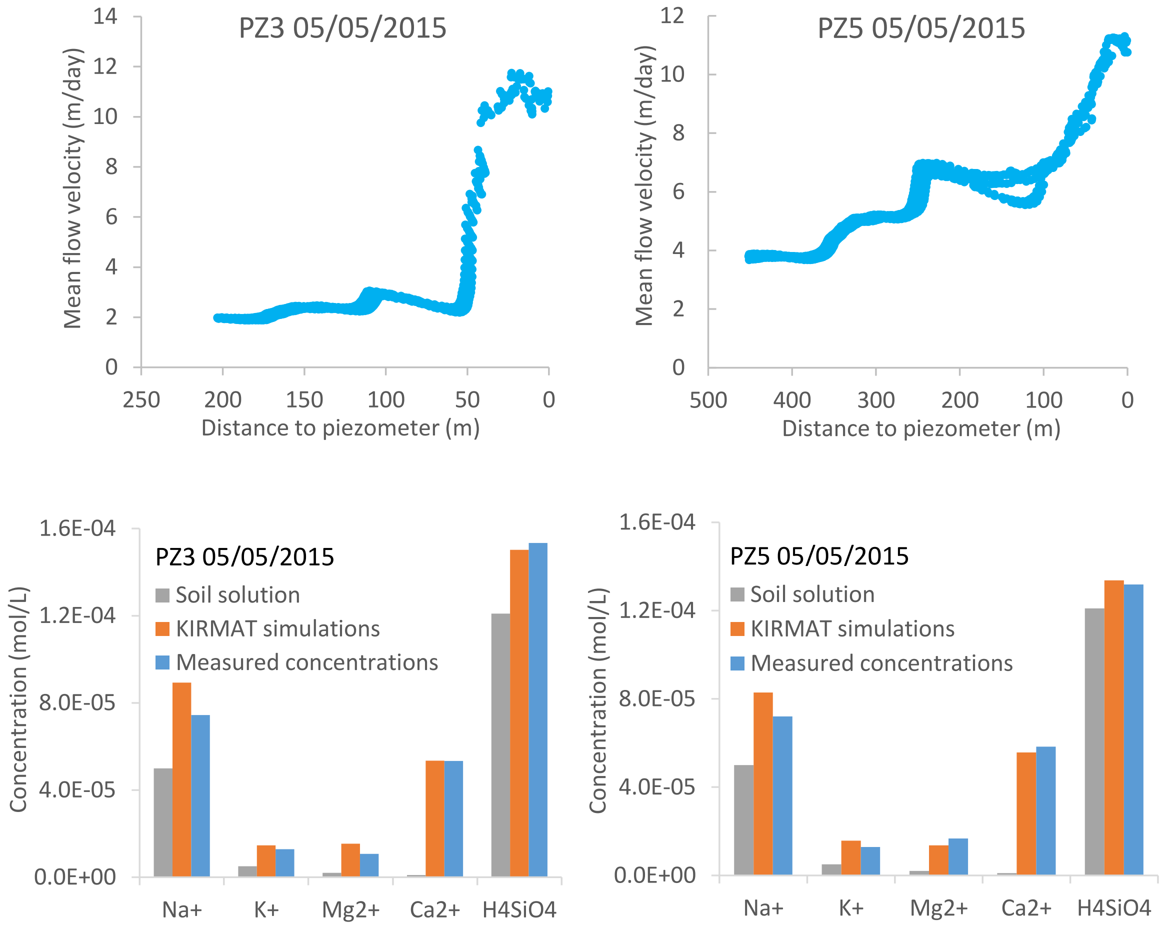

Figure 9

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Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

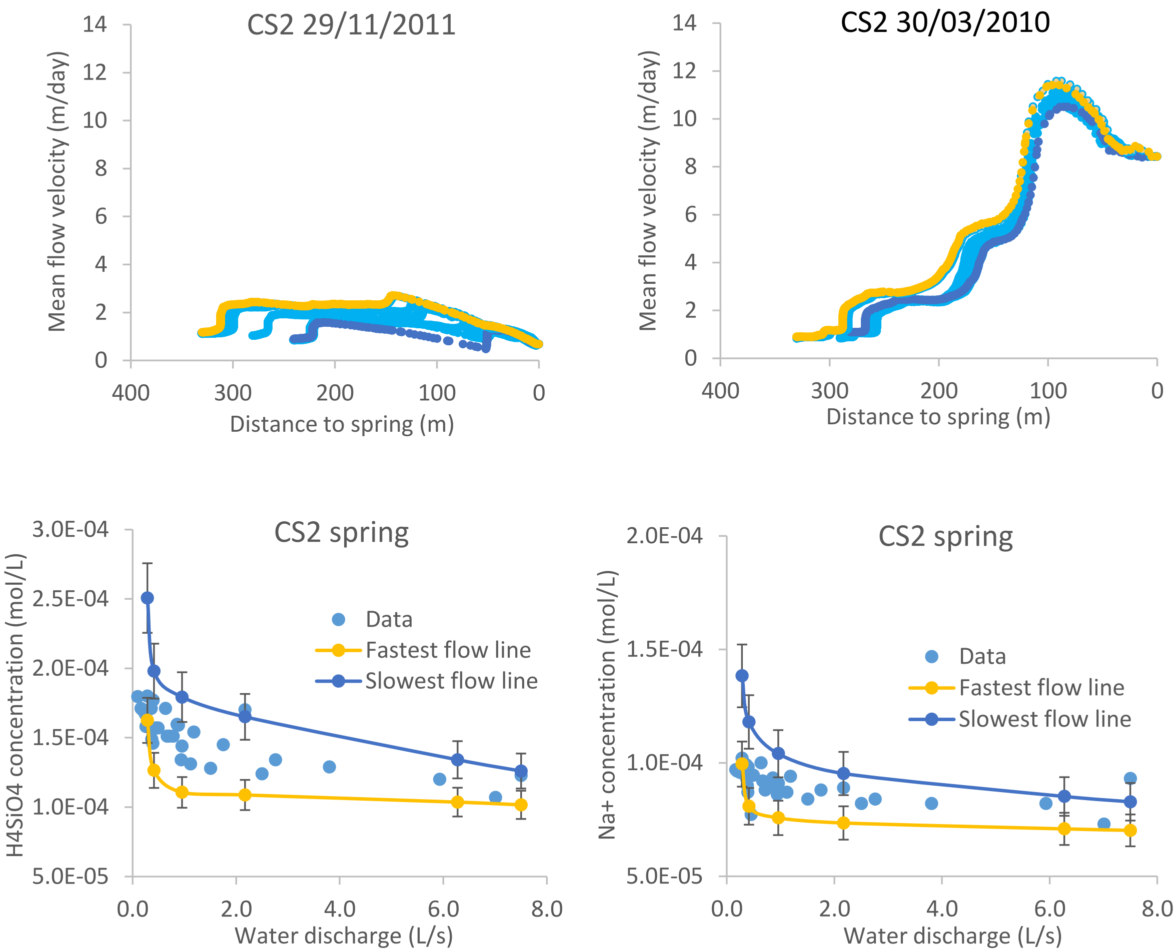

Figure 10

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Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 8 January 2019

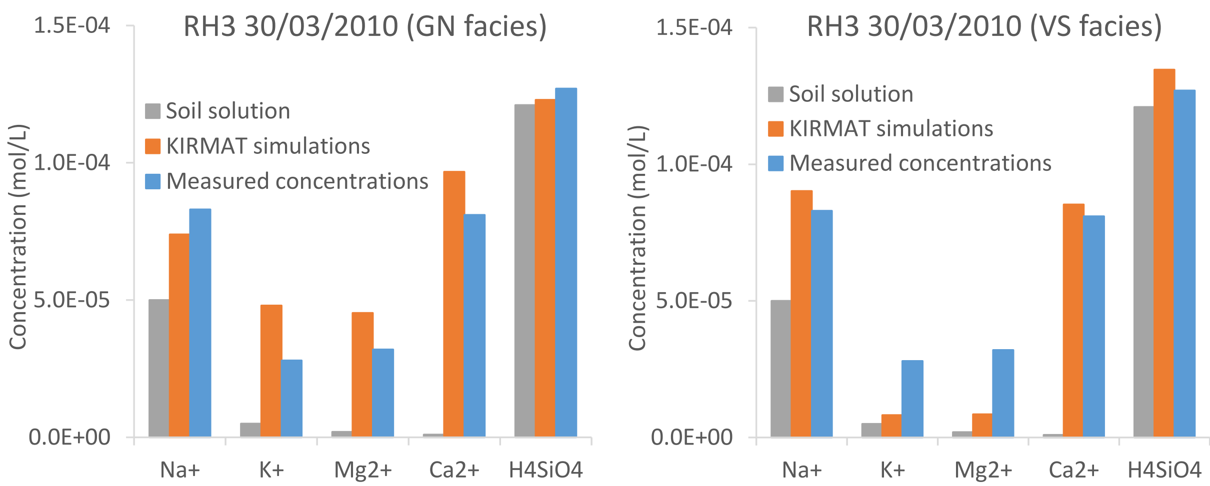

Figure 11

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Discussion started: 8 January 2019

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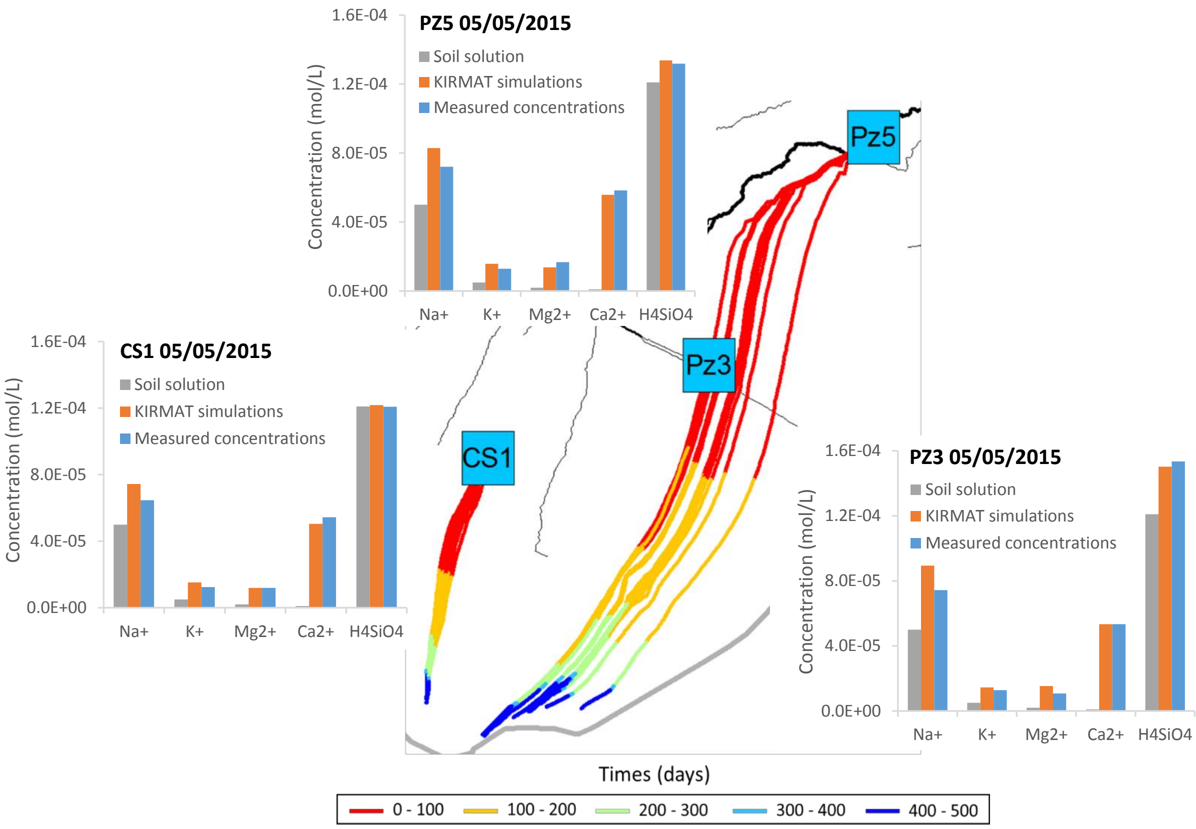

Figure 12