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Key Points:

- Multi-year calibration to discharge and chemical exports enables reasonable prediction of watershed hydro-geochemical response
- The role of vertical mineral heterogeneity is captured by differences in the C-Q response in the wet and dry years
- A heterogeneous landscape response is also observable but is diluted in terms of aggregate C-Q response

Supporting Information:

Supporting Information may be found in the online version of this article.

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Understanding the Hydrogeochemical Response of a Mountainous Watershed Using Integrated Surface-Subsurface Flow and Reactive Transport Modeling

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Abstract Climate change and other disturbances significantly impact hydrogeochemical exports from mountainous headwater catchments such as the Upper Colorado River Basin. Developing a mechanistic understanding of how the physical and chemical processes interact in time and space in an integrated manner is key to quantifying the future impacts of such disturbances. The hydrogeochemical response of a mountainous catchment in the 2010–2019 period is evaluated quantitatively using a high-resolution model that simulates integrated hydrology, and transport and reactions for selected solutes and minerals. The model assumes that pyrite is present only at depth while calcite is distributed uniformly, and captures the observed C-Q reasonably well. Distinct C-Q dynamics are observed in an average (WY16), a wet (WY17), and a dry (WY18) water year. The model also quantifies the water fraction from surface, shallow and deep groundwater compartments using tracers, and suggests greater groundwater contributions to peak stream discharge in the dry WY18. Results demonstrate that calcium concentrations do not change significantly from year to year, while sulfate shows significant temporal variability. Pyrite dissolution is affected by the changing hydrological drivers where it is enhanced in the dry WY18; calcite dissolution supplements calcium dilution under high flow conditions. The model simulates the reaction hotspots controlled by hydrological conditions, and the spatially-resolved results show that higher soil saturation and less snowpack occur earlier on the south-facing side than on the north-facing side. This is a first-of-its-kind demonstration of a model that integrates hydrologic processes, including evapotranspiration, and reactive transport to enable a predictive understanding of hydrogeochemical exports.

Plain Language Summary Climate change significantly impacts water resources, including water quantity and quality, particularly in mountainous headwater catchments such as the Upper Colorado River Basin that are key for water supply in downstream regions of the western U.S. In this work, we used a mathematical model to quantify the movement of water and chemical species under changing weather and climate conditions. Changing rainfall and early snowmelt affects both the volume of water and the amount of minerals that dissolve, impacting water quality observed at the gauged stations downstream. Consistent with the available measurements, the three-dimensional model makes it possible to understand how the watershed's topography and the flow of water in the streams and the groundwater interact in time and in space. In particular, we found that the mineral composition with depth explains in part the changes in observed concentrations between dry and wet periods and that the north- and south-facing slopes of the river valley contribute differently to these concentrations. These effects are relatively small in this study but larger climate variability could enhance them.

1. Introduction

Mountainous watersheds supply a significant portion of the water resources used in regions downstream of these headwater catchments, particularly in arid and semi-arid regions. These watersheds are especially sensitive to the climate changes that are likely to impact the management of water resources. An example is the upper Colorado River watershed, which serves as the primary water source in the western United States (U.S.). However, the western U.S. has been experiencing water scarcity (Garrick et al., 2008), for example, low volumes at Lake Mead, Nevada have triggered for the first time a water shortage declaration (Fountain, 2021). Snow-dominated mountainous watersheds store water in the form of snowpack in the winter and release it by snowmelt in the summer. As a result, global warming could fundamentally alter the rain-snowfall ratio, shift early snowmelt, and

lead to changes in groundwater levels, vegetation cover, and mineral weathering. Changes in weather extremes and land cover may lead to both short-term flooding and/or long-term drought events and alter the hydrological response. Hydrological changes can in turn affect the solute transport and biogeochemical processes that take place both in above- and below-ground environments, impacting chemical exports from mountainous watersheds. Solute fluxes in the riverine system are important components in the global carbon and nitrogen cycle and affect downstream water quality. Understanding how perturbations to the hydrological cycle affect solute exports in mountainous watersheds is essential to improve the predictability of watershed systems, particularly for the future impacts of climate change.

Data analysis and modeling approaches such as end-member mixing analysis (EMMA) and C-Q analyses have been applied to investigate how watersheds function as integrated hydrogeochemical systems. EMMA can also be used to quantitatively compute non-reactive solute concentrations under different hydrological scenarios (Christophersen & Hooper, 1992) and to estimate groundwater transit times; for example, how solute concentrations are diluted in response to a precipitation event (Carroll et al., 2018). The relationship between solute concentrations and discharge (C-Q) in the stream is widely used as a metric for interpreting the interaction of hydrological processes, chemical transport, and mineral reactions in watersheds (Knapp et al., 2020; Olshansky et al., 2018). The C-Q relationship has been widely used as an important method to inform key geochemical processes (e.g., Dehaspe et al. [2021]), and evaluate the chemical dynamics (e.g., Winter et al., 2021) at various temporal scales. Distinct C-Q responses, including dilution, chemostasis, and mobilization processes, when concentration is decreasing, stable, or increasing with discharge, reflect different watershed behaviors (Ackerer et al., 2020; Arora et al., 2020; Godsey et al., 2009; Knapp et al., 2020; Musolff et al., 2015). In addition, C-Q relationships may be used to interpret the impacts of snow dynamics and its contribution to the stream water behavior across different temporal scales in mountainous watersheds, as a spike of discharge due to snowmelt is usually associated with specific behaviors of solute concentrations (Knapp et al., 2020). C-Q relationships also reflect the distribution of transit times of water in the subsurface (Torres & Baronas, 2021), allowing also for its quantitative evaluation (Ameli et al., 2017). Hysteresis in the C-Q relationship, that is, the different trajectory of the C-Q relationships during rising and falling limbs of the hydrograph, indicate differences in the timing of the hydrological responses from the surface and subsurface compartments (Knapp et al., 2020), and in the contributions from surface water, shallow and deep groundwater (Arora et al., 2020). Therefore, analyses based on C-Q, with data collected at a sampling location, are generally a useful approach to understanding watershed dynamics, and quantifying how the catchment store and release water and solutes at different times. However, they are limited to the aggregated responses over the catchment and do not capture explicitly the spatial heterogeneity of hydrological and geochemical processes inside the watershed (Chen et al., 2020).

Physically-based modeling can be used to develop a mechanistic understanding of hydro-biogeochemical processes in watersheds. In combination with the aforementioned analytical tools, they can provide a quantitative validation of conceptual models and provide spatially-resolved insights into the response of mountainous watersheds. Integrated hydrology (e.g. (Kollet et al., 2017; Maxwell et al., 2014)) and solute transport models have been developed and applied at various scales (Paniconi & Putti, 2015). However, they have rarely considered complex multicomponent reaction networks. In contrast, reactive transport codes are widely used to understand the subsurface flow and chemical interaction, however, they rarely included surface-subsurface water interactions, often incorporating surface water scenarios with a simplified boundary condition and sink/source terms (Dwivedi et al., 2018; Li et al., 2017). Recently, applications of a newly developed watershed reactive transport model (Bao et al., 2017) have demonstrated that the combination of integrated hydrology and multicomponent reactive transport is a powerful tool to understand the hydro-geochemical response of watersheds.

Modeling has been used to understand chemostasis and dilution in different watersheds. Both behaviors were observed for geogenic and biogenic species undergoing chemical transformations in Zhi et al. (2019). The model of Li et al. (2017) explained magnesium chemostasis due to the balance of dissolving clay and flowing water under various hydrological conditions by comparison to the non-reactive chloride, which was staying in the vadose zone before rainfall events reconnected the watershed and flushed it out. Models have also been widely used for quantifying the contribution of water sources to the water budget and their effect on observed solute patterns. The analysis of transit and residence time distribution was used to quantify surface-subsurface mixing (Yang et al., 2018). Transit times controlled the spatial patterns of aerobic respiration and denitrification in the riparian zone, finely resolved in a small watershed model (Nogueira et al., 2021). The work of Liggett et al. (2015) highlighted the

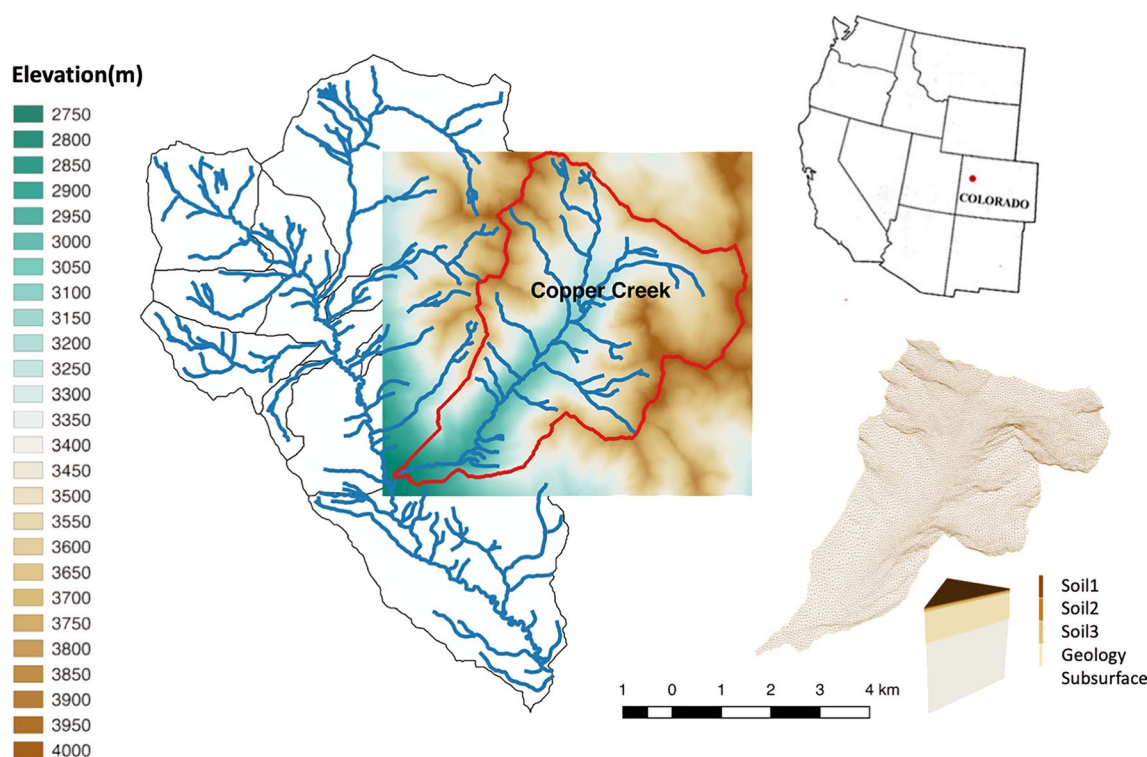


Figure 1. Copper Creek at the East River watershed in Colorado, and the five-layer (shown in the 1-D column) 50-m resolution triangle mesh used in the simulation.

importance of considering surface–subsurface solute transport in evaluating internal model processes and the need for solute field data for constraining the solute transport model. The model by (Zhi et al., 2019) found that in most dilution-dominated scenarios, the C-Q relationship can be explained by the mixing of multiple sources and attributed to processes such as chemical reactions with the solid phase along the pathway of water flow.

Applications of integrated hydrology and reactive transport however have been limited to simulating relatively small catchments, using relatively coarse resolution with explicit consideration of the drainage network, or to addressing relatively short simulated times of a year or less. Understanding responses to changing conditions, where water inputs vary significantly from year to year, requires the ability to simulate and contrast multiple water years, as well as to minimize assumptions relating to the existence of stream networks. Here, we use the Advanced Terrestrial Simulator (ATS) (Coon et al., 2019; Molins et al., 2022) to simulate integrated hydrology and geochemistry processes together in a novel method, in the Upper Colorado river basin. Integrated hydrology processes, including surface–subsurface flow, snow dynamics, and evapotranspiration (ET), are coupled with reactive transport processes over a multi-year period in a high-elevation mountainous watershed. The objectives are to apply integrated hydrology and reactive transport model to reproduce the C-Q relationship observed at the outlet of the watershed. With the model, we quantitatively evaluate the water and solute fluxes within the watershed to understand their contributions to the aggregate watershed response. We conduct this study at the Copper Creek catchment — taking advantage of the availability of data over multiple years at the site — to elucidate mechanisms behind the evolution of the watershed response under the seasonal and year-to-year changing conditions. We quantify the interactions between mineral reactions and hydrological processes, including infiltration and groundwater table fluctuations.

2. Background

2.1. Site Description

This study focuses on the simulation of integrated hydrology and reactive transport processes in the Copper Creek catchment, the largest sub-catchment of the East River watershed (Figure 1). The East River watershed is a representative mountainous headwater catchment of the Upper Colorado River basin near Gothic, Colorado (Dwivedi

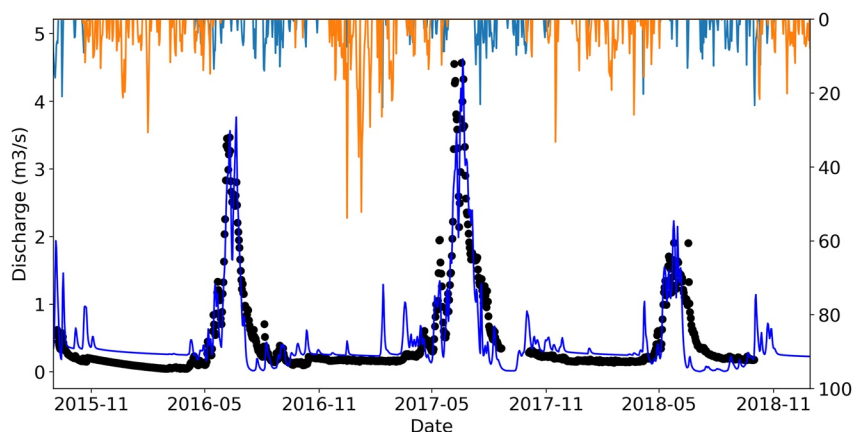


Figure 2. Simulated and observed discharge at the Copper Creek outlet.

et al., 2022; Hubbard et al., 2018; Matheus et al., 2020; Newcomer et al., 2021; Wan et al., 2021). The annual average temperature is 0°C, and the area-weighted average precipitation across the basin is 700 mm/yr, with the majority occurring as snowfall in the winters and a few late-summer storm rainfall events (Daly et al., 1997). Streamflow is strongly influenced by the effects of snowmelt in early summer and late-summer monsoon rainfall. During winter, snow accumulates on the surface and the baseflow magnitude is small, while in late spring and summer the snowpack melts and dominates the discharge peak, accounting for 53% of the total discharge. The East River geology is dominated by the Cretaceous Mancos Shale Formation, with carbonate and pyrite contents of roughly 20% and 1%, respectively, and shallow sediment overlying the fractured Mancos shales (Morrison et al., 2012). Mancos Shale releases elevated concentrations of major ions, trace elements, and potential contaminants during weathering (Morrison et al., 2012).

Field investigations indicate that Copper Creek is underlain by a combination of Mancos shale, Paleozoic sedimentary rocks (Morrison, Maroon, and Gothic Formations), and Tertiary granodiorite (Winnick et al., 2017). However, a detailed geophysical survey is not available in Copper Creek to confirm the subsurface structure. Compared to other sub-basins in the East River watershed, higher SO₄ concentrations are observed at the outlet of Copper Creek, and these exhibit seasonal patterns during baseflow and snowmelt regimes. As is often the case in many other mountainous watersheds, Copper Creek lacks monitoring wells for groundwater data, and riverine gauges inside the catchment for discharge and chemical data. The only discharge and concentration data available are from the station located at the outlet of Copper Creek, which represents the aggregate response of Copper Creek.

2.2. Discharge and Geochemical Data at the Outlet of Copper Creek

Discharge measurements are available at a daily frequency (Rose et al., 2018). Here we focus on 3 water years (WY16, WY17, WY18). WY16 was an average year, WY17 a relatively wet year, and WY18 a relatively dry year. The total precipitation volumes were 700 mm (107% of the 6-year average between WY14 and WY19), 760 mm (116%), and 410 mm (63%), respectively, as measured by the nearest SNOTEL station (Crested Butte). In Copper Creek, discharge increases rapidly in May and usually reaches a peak of discharge in late May or mid-June depending on the timing of snowmelt and snowpack accumulation conditions, and remains in baseflow condition during winter (Figure 2). Discharge falls back to baseflow condition very early in July, but can occasionally spike in August and September before the snow season due to the late summer storm events. The peak discharge is in June in the average WY16 and wet WY17, while it is reached a few weeks earlier in the dry WY18.

Stream chemistry data are collected intermittently at weekly or bi-weekly frequency (W. Dong et al., 2020; B. C. Dong et al., 2020; Williams et al., 2020; Varadharajan et al., 2019). The major solutes in the effluent are Ca, Mg, SO₄, and DIC (Figure 3). Among them, Ca, DIC, and SO₄ are products of calcite and pyrite reactions, which are included in the simulations described below. Overall, the concentrations are greater in the baseflow period during winter when discharge is low, and lower in the snowmelt period during summer when discharge increases (Figure 3). Solute concentrations decrease with increasing discharge starting in early summer due to snowmelt,

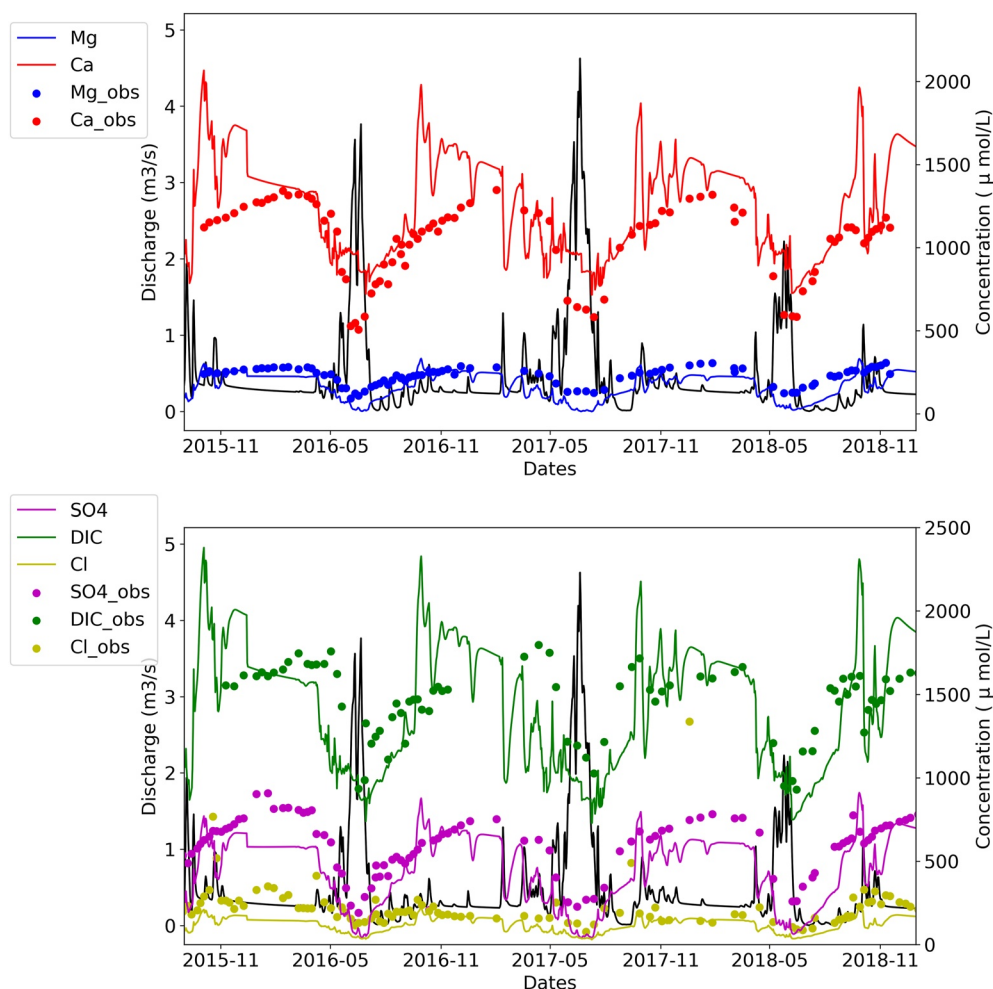


Figure 3. Time series of discharge and concentrations (observed and simulated) at the Copper Creek outlet in WY16 (average), WY17 (wet), and WY18 (dry).

and increase when stream discharge decreases to a baseflow condition in early fall. The highest concentrations are always observed in the periods of late summer or early fall of the water year when a few discharge spikes are associated with late summer monsoon precipitation events. The magnitudes of most species' concentrations are similar in WY18 (dry) compared to the previous 2 years, except higher SO_4 concentration are found in WY18 than in WY16 (average) and WY17 (wet).

3. Methods

3.1. Advanced Terrestrial Simulator (ATS)

The model resolves spatiotemporally hydrologic and multicomponent reactive transport processes in the surface and subsurface compartments. The ATS (Coon et al., 2019; Molins et al., 2022) is used to perform the simulations. ATS is an open-source code for solving distributed ecosystem-based, integrated, distributed hydrology, as well as thermal process, energy balances, snow dynamics, plant dynamics, and reactive transport. This work uses a subset of these general capabilities. Surface and subsurface flow are considered via the diffusive wave and Richards equations, respectively, which are solved as strongly coupled processes (Coon et al., 2019). Multicomponent transport is simulated with the advection-diffusion equation, which is solved explicitly using the approach described in Molins et al. (2022). Geochemical calculations are coupled to transport using the operator splitting approach. The coupling is accomplished with the use of a generic software interface (Andre et al., 2013), with the calculations performed by PFLOTRAN (Hammond et al., 2014).

3.2. Model Description

The domain is delineated using the ridges as indicators of the water divide in both the surface and the subsurface. The 10-m resolution USGS Digital Elevation Maps (DEM) (Survey, 2019) are used for this purpose and processed with the QGIS watershed spatial analysis tool (QGIS Development Team, 2021). The horizontal grid resolution of the model is 50 m, distributed uniformly spatially using an unstructured triangular mesh. This mesh is extruded vertically to obtain a 3D representation of the subsurface domain using a terrain-following approach. The triangular mesh was generated with TInterator-LaGrIT (LANL, 2018). The depth of the subsurface domain is set to 30 m distributed in five layers with thicknesses of 0.1, 0.3, 0.6, 8.0, and 21.0 m, respectively, from top to bottom. The top one-m layer represents the soil layer, the layers between the depths of 1.0 and 9.0 m comprise the alluvial sediment, and the bottom layer below 9.0 m is the bedrock. This vertical discretization is the same as used in a previous study of the East River watershed (Pribulick et al., 2016).

Precipitation is the only external water flux that drives the hydrological process in the catchment. Surface water infiltrates and supplies higher $O_2(aq)$ concentration and lower pH that drives the reactive transport processes. Hence the aggregated response of the catchment in the form of concentration and discharge at the outlet can be compared to observed data. Precipitation is distributed spatially according to data from the Daymet forcing datasets (Thornton et al., 2014). Daymet provides daily, 1-km resolution gridded weather parameters of precipitation and daily minimum and maximum surface temperature, which are remapped by bilinear interpolation onto the surface mesh. Since Daymet does not differentiate between snowfall and rain in precipitation, the model assumes that precipitation is in the form of snowfall when the surface temperature is below freezing point and rainfall when the surface temperature is above freezing temperature. Snow dynamics are simulated on the surface domain. Snow melts according to an empirical coefficient of snowmelt rate of $2.74 \text{ mm day}^{-1} \text{ } ^\circ\text{C}^{-1}$ at 2.0° above the freezing point (273.15 K), and can either infiltrates into the subsurface domain or become overland flow on the surface. The Daymet dataset also includes shortwave radiation and wind speed data as meteorological forcing, which are used for calculating ET fluxes. ET is computed via the simplified Priestley-Taylor equation (Priestley & Taylor, 1972) considering vegetation transpiration only but not canopy and bare soil evaporation. Transpiration is turned off in winter when deciduous trees are not transpiring, using the parameterization and adjustment factors from the estimation in a study by Carroll et al. (2018).

3.3. Initial and Boundary Conditions

No-flow boundary conditions are imposed on all sides of the catchment except at the river outlet, where a critical depth boundary condition allows for water to flow out of the domain freely. The pressure field is initialized from a hydrostatic condition in a one-dimensional column and then extended to the three-dimensional domain assuming the same depth to the water table everywhere.

The conceptual geochemical model proposed by Winnick et al. (2017) is tested quantitatively in this work. That implies that we consider two key minerals in the simulation, pyrite, and calcite, and their distribution in the subsurface is simply based on depth. Two subsurface regions are considered, a shallow one (between the ground surface and 9 m of depth) and a deep one (between 9 and 30 m below the surface). Pyrite is absent in the shallow layer and present in the deep layer with a volume fraction of 0.0135%. In contrast, calcite is distributed uniformly and present in both regions. The composition of the groundwater is initialized by assuming equilibrium with the minerals present in each region (Table 2). The surface water is initialized with the composition of the rainwater. The geochemical system consists of 15 primary species and 35 aqueous secondary complexes that are in equilibrium with the primary species (Table 2). The reaction parameters for calcite and pyrite dissolution-precipitation have been taken from previous work (Table 3). While the geochemical model only considers two reactive phases, it is supported by EMMA results, which found that carbonate weathering dominates over silicate weathering in East River (Morrison et al., 2012; Winnick et al., 2017). This approach proved to be sufficient to capture the major solute exports and their dynamics (see Section 5.4).

Rainwater and snowmelt sources are assumed to have the same composition and to be in equilibrium with atmospheric conditions (NADP [2016], Table 2), with the relevant reactive gases being O_2 and CO_2 . When these sources infiltrate into the subsurface, they are in disequilibrium with both minerals and drive dissolution reactions. Dissolution reactions are described with a transition-state-theory-type rate law, and their reaction rates are based on Arora et al. (2016). Solute transport takes place by advection and diffusion in both the surface and

Table 1
Hydrological Model Parameters by Subsurface Layer

Parameter	Soil	Sediment	Bedrock
Calibrated permeability (m^2)	2.26×10^{-12}	2.26×10^{-13}	5.67×10^{-14}
van Genuchten alpha (Pa^{-1})	2.69×10^{-4}	1.59×10^{-4}	3.50×10^{-4}
van Genuchten m [-]	0.591	0.586	0.500
Residual saturation [-]	0.1	0.1	0.1
Porosity	0.375	0.3	0.2

subsurface compartments, determined by the approach described in (Molins et al., 2022). In this approach, solutes in the rainwater and the snowmelt contribute to the subsurface mass balance when water is not present on the surface.

3.4. Simulation Design and Calibration

A two-step process is used to initialize the simulation. Spin-up simulations are run for 20,000 days (more than 50 years) with a constant average precipitation rate until steady-state conditions are obtained for groundwater table and soil saturation. The simulations are then run for 10 years covering the time period between 2010 and 2019 using the Daymet datasets as forcing and

the subsurface pressure from the steady-state spin-up simulation as the initial condition for flow. The first 5 years of the simulations (2010–2014) are discarded as spin-up for the reactive transport problem to eliminate the effect of the initial conditions.

Calibration of the model is performed manually to discharge and solute concentrations time series spanning 2015–2019. The results are shown in Figure S1 in Supporting Information S1 and a description of the selected case is presented in Section 4.1. The calibration process seeks to provide a reasonable agreement between the simulation results at the outlet of Copper Creek and discharge and concentration data measured at the Copper Creek outlet in the period from WY16 to WY18 when both discharge and concentration measurements are available. The only parameter varied in the calibration process is the permeability of the subsurface materials. The calibration uses as a starting point the permeability values from an earlier hydrological model of the larger East River watershed Pribulick et al. (2016). Permeability is the most important parameter in integrated hydrology simulations, while other parameters such as the Manning coefficient or the van Genuchten parameters have no or relatively small impact on the results (Lauren & Reed, 2019). The hydrological parameters used in the simulations are given in Table 1.

The Nash–Sutcliffe efficiency (NSE) coefficient and Mean-Absolute-Error (MAE) are used as the performance metrics for permeability calibration with discharge data and solute concentrations, respectively. NSE is widely used for discharge but is not considered appropriate for concentrations (McCuen et al., 2006). The MAE is used here as a better performance metric for concentrations (Gupta & Kling, 2011).

The simulations were performed on Cori, a Cray XC40 computer of the National Energy Research Scientific Computing Center (NERSC), using 64 processors for the integrated hydrology spin-up and 192 processors for the transient reactive transport simulations.

4. Results

4.1. Calibration of Concentration-Discharge Time Series

4.1.1. Calibration With Discharge Only

Six cases are considered that vary the permeabilities of soil, sediment, and bedrock (Table 4). Case 1 is the reference case and follows the previous study of Pribulick et al. (2016) in the East River watershed. Case 2 to Case 6 are obtained by adjusting permeability values in each layer separately. Case 3 is identified as the best case for discharge simulation with the highest NSE, while the simulation with permeability values used in Pribulick et al. (2016) yields the lowest NSE value (Table 4, and Figure S1 in Supporting Information S1). By comparing Case 1–4 with Case 5–6, it is apparent that permeability in the shallow layers has a greater impact on discharge than in the deep layers. Cases with lower permeability simulate lower baseflow discharge, indicating that the hydrological response is more sensitive to rainfall and snowmelt with longer residence time and lower baseflow discharge from the geological layers. Neither the total discharge over the water year nor the timing of summer spikes is found to be sensitive to permeability. Total discharge is only determined by accumulated precipitation and ET in the catchment without inflow. The timing of peak discharge is controlled by snowmelt hence the temperature and radiation in the forcing meteorological datasets. In almost all cases, the simulated discharge decreases more rapidly than the observation in the falling limb of the hydrograph and consistently overestimates the baseflow discharge.

Table 2
Geochemical and Mineral Initial Conditions ($\mu\text{mol/L}$) in the Shallow and Deep Layers of the Model, and the Atmospheric Deposition Concentrations

Parameter	Rainwater		
	(Atmos. Deposition)	Shallow	Bedrock
Ph	5.31	7.57 ^(a)	7.57 ^(a)
DIC	1.00×10^{-20}	1.92×10^{-03}	1.92×10^{-03}
Ca	2.80×10^{-6}	1.55×10^{-03}	1.55×10^{-03}
Fe	1.00×10^{-20}	4.66×10^{-07}	4.66×10^{-07}
O ₂ (aq)	3.23×10^{-4}	2.41×10^{-06}	5.35×10^{-71} . ^(b)
SO4	2.48×10^{-6}	8.00×10^{-04}	8.00×10^{-04}
K	3.59×10^{-7}	2.66×10^{-05}	2.66×10^{-05}
Mg	5.36×10^{-7}	3.58×10^{-04}	3.58×10^{-04}
Cl	1.19×10^{-6}	8.00×10^{-06}	8.00×10^{-06}
Na	1.40×10^{-6}	8.44×10^{-05}	8.44×10^{-05}
Al	1.00×10^{-20}	9.40×10^{-07}	9.40×10^{-07}
SiO ₂ (aq)	1.00×10^{-20}	8.73×10^{-05}	8.73×10^{-05}
Calcite vol. frac.	-	1.0×10^{-3}	1.0×10^{-3}
Calcite spec. surf. area (<i>m</i> ⁻¹)	-	60,000	60,000
Pyrite vol. frac.	-	-	1.35×10^{-4}
Pyrite spec. surf. area (<i>m</i> ⁻¹)	-	-	60,000

Note. Shallow layer includes soil and sediment layers. (a). Fixed by equilibrium with calcite; (b). Fixed by equilibrium with pyrite.

4.1.2. Calibration With Solute Concentrations

Numerous studies have suggested that calibration against hydraulic heads and surface water discharge may not be sufficient and other data may be needed, including concentrations (e.g. Partington et al., 2020; Schilling et al., 2019). The calibration here reached a similar result in that both discharge and concentration data are needed. While Case 3 outperforms all other cases for discharge, it also has the highest MAE for almost all species across all six cases, meaning the worst goodness-of-fit for concentration simulation against observation. This indicates that the calibration to discharge over time does not necessarily lead to the best calibration of geochemical concentrations. Rather, a compromise must be made between the overall goodness-of-fit and the goodness-of-fit of each component. In this work, equal weight is given to each component, and by ranking the cases according to the goodness-of-fit in each component, Case 4 is selected as it has overall the second best NSE value for

Table 3
Kinetic Parameters for Mineral Dissolution/Precipitation Reactions

Mineral	Neutral mechanism		Acid mechanism		Additional mechanism	
	k_{nu} ($\text{mol kg}_{\text{H}_2\text{O}}^{-1} \text{m}^{-2} \text{s}^{-1}$)	E_{nu} (kJ mol^{-1})	k_a ($\text{mol kg}_{\text{H}_2\text{O}}^{-1} \text{m}^{-2} \text{s}^{-1}$)	E_a (kJ mol^{-1})	k_{ex} ($\text{mol kg}_{\text{H}_2\text{O}}^{-1} \text{m}^{-2} \text{s}^{-1}$)	E_{ex} (kJ mol^{-1})
Calcite ^a	1.55×10^{-6}	23.5	5.01×10^{-1}	14.4	3.31×10^{-4}	35.4
Pyrite ^b	0.0	56.9			2.63×10^{-8} ^c	56.9
					7.94×10^{-8} ^d	56.9

Note. Values are from Arora et al. (2016) and Dwivedi et al. (2018).

^a $\text{CaCO}_3(\text{s}) + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$ (Palandri & Kharaka, 2004). ^b $\text{FeS}_2(\text{s}) + 3.5\text{O}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{SO}_4^{2-} + 2\text{H}^+$ and $\text{FeS}_2(\text{s}) + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \leftrightarrow 15\text{Fe}^{2+}(\text{aq}) + 2\text{SO}_4^{2-} + 16\text{H}^+$ (Williamson & Rimstidt, 1994). ^cSpecies involved $\alpha_{ij}^y: [\text{Fe}^{3+}]^{0.3}, [\text{Fe}^{2+}]^{-0.47}, [\text{H}^+]^{-0.32}$ (Williamson & Rimstidt, 1994). ^dSpecies involved $\alpha_{ij}^y: [\text{O}_2]^{0.5}, [\text{H}^+]^{-0.11}$ (Williamson & Rimstidt, 1994).

Table 4
Permeabilities Used in the Different Calibration Cases and the Corresponding Error Metrics for Discharge and Concentration Simulations

Cases	Permeabilities (m^2)			Error metrics	
	Soil	Sediment	Bedrock	NSE for Discharge	MAE ($\mu\text{mol/L}$) for Concentrations
Case 1	5.67×10^{-13}	5.67×10^{-13}	5.67×10^{-14}	0.56	154.02
Case 2	1.13×10^{-12}	5.67×10^{-13}	5.67×10^{-14}	0.61	150.52
Case 3	1.13×10^{-12}	1.13×10^{-13}	5.67×10^{-14}	0.80	186.84
Case 4	2.26×10^{-12}	2.26×10^{-13}	5.67×10^{-14}	0.79	150.35
Case 5	5.67×10^{-13}	5.67×10^{-14}	2.84×10^{-14}	0.71	166.19
Case 6	2.26×10^{-12}	2.26×10^{-13}	1.13×10^{-13}	0.75	143.65

Note. NSE is used for discharge, averaged MAE ($\mu\text{mol/L}$) is used for the concentrations of four species (Ca, Mg, DIC, and SO_4) and provided here as an average (individual values are presented in Table S1 in Supporting Information S1).

discharge and second best for concentration simulations, particularly for Ca and HCO_3 species. The comparison of goodness-of-fit for both discharge and concentration highlights that calibration to concentration has provided values for improving the model performance and understanding the physical processes in the catchment. Therefore, C-Q time series plots in Case 4 are shown in Figure 3 and discussed in the rest of the paper.

Generally, simulated concentrations oscillate more than measured concentrations at relatively coarser resolution. In particular, significant fluctuation of concentrations is observed in simulation results before and after the peak of discharge due to quick response to precipitation or snowmelt, but are not noticeable in the baseflow period. Thus, these fluctuations are likely due to the immediate response of the model to snowmelt or late-summer rainfall events that affect the mixing between groundwater and surface water. To elucidate the linkages between chemical exports and discharge, particularly under the rising and falling limbs of the hydrograph, the C-Q relationship dynamics are explored in what follows.

4.2. C-Q Dynamics

In this section, we present the results of the model in the form of C-Q relationships. We do so by water year for 3 water years (WY16, WY17, and WY18). The WY16 is referred to as an average water year with similar precipitation and discharge to the 10-year climatological average, while the WY17 is a relatively wet year with 20% more discharge than the average, and WY18 is a relatively dry year with 20% less discharge than the average. While the C-Q responses are different in the 3 water years, especially during the wet season (April to September), the significant negative correlation between geochemical concentrations and discharge (Figures 4 and 5) indicates that the watershed behavior is mostly controlled by dilution. The response in WY16 (average) and WY17 (wet) are relatively similar and are presented together below, while the response in WY18 (dry) is presented separately. Overall, concentrations are lower in WY17 (wet) and higher in WY18 (dry) years, indicating inter-annual variability in the C-Q relationship. The daily frequency of the simulation output captures year-to-year variations in the hysteretic behavior possible, particularly when observations are not available at coarse temporal resolution.

4.2.1. Average WY16 and Wet WY17

Figure 4 (left and middle columns) shows that the timing and magnitude of peak discharge are generally captured well in the simulations. In general, simulated Ca-Q exhibits L-shape clockwise hysteresis with higher concentrations on the rising limb in May than on the falling limb in July. Model results for Ca compare reasonably well to observations in May, July, and August in the middle of both rising and falling limbs, with higher concentrations, are observed at the peak discharge period in June and significantly higher in September. Simulated Mg-Q exhibits similar L-shape clockwise hysteresis C-Q relationship with a higher concentration in the rising limbs than in the falling limbs. The greatest simulated Mg concentration is found in September, which is higher than the observation, and the lowest Mg concentration is lower than observations in June, concurrent with the spike in discharge. The convex, clockwise simulated hysteresis for Mg-Q is closer to the observed C-Q hysteresis than that obtained for the L-shape hysteresis for Ca-Q (Figure 4).

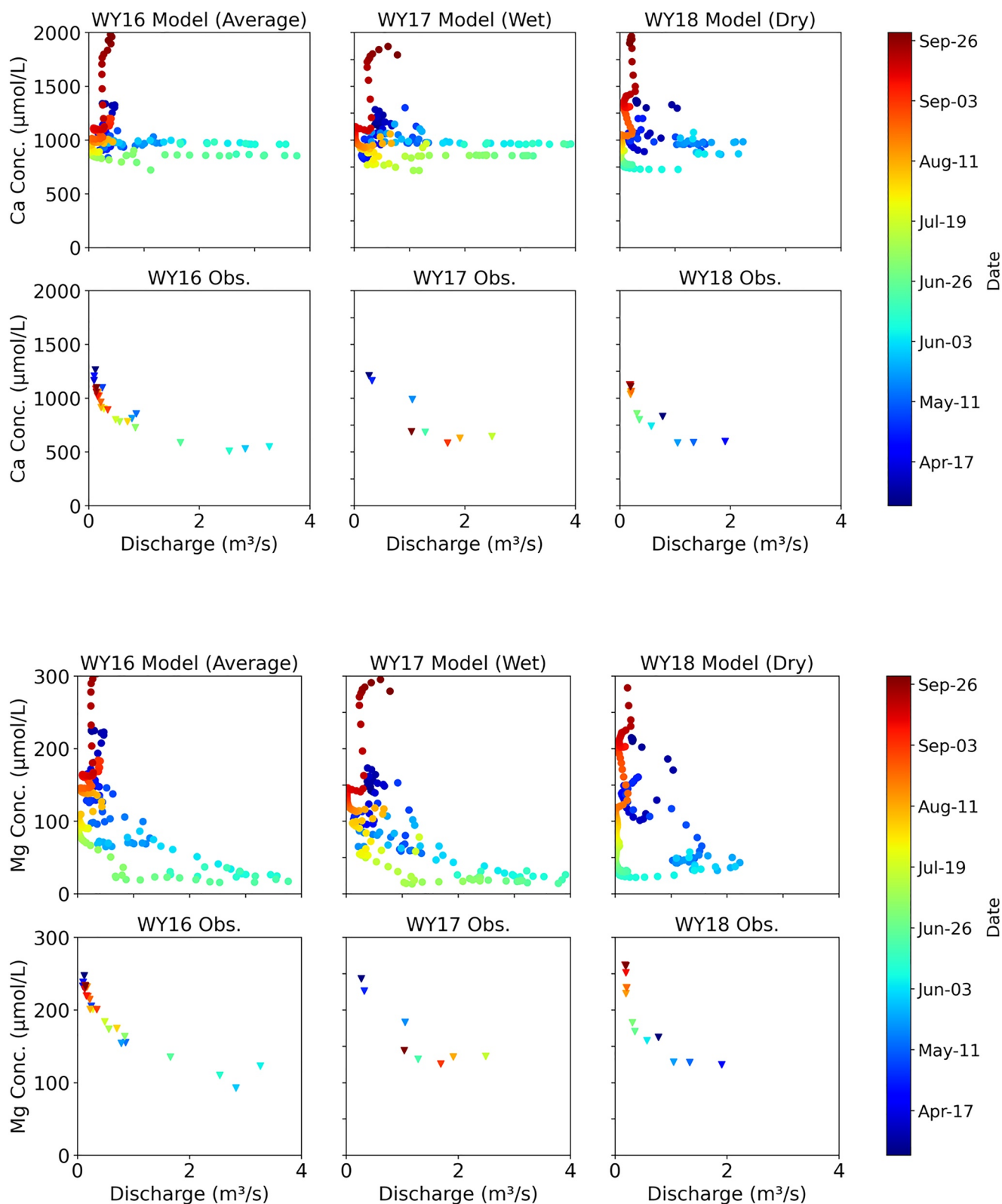


Figure 4. The discharge versus concentrations of cations (Ca and Mg) at the river outlet for April to September (WY16-18). Simulated results are plotted at daily frequency. For observations, each point represents one sample. Data are color-coded by date.

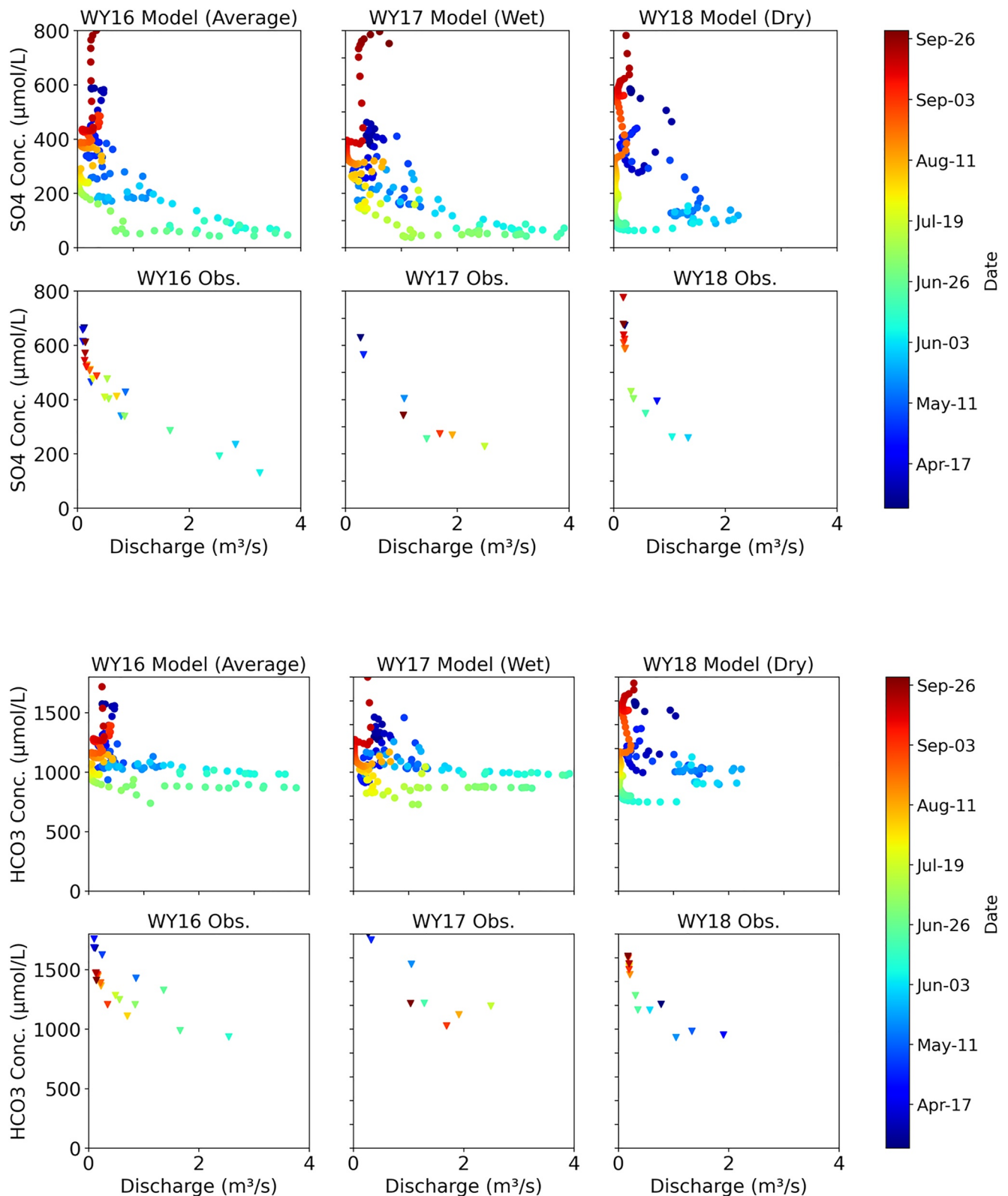


Figure 5. The discharge versus concentrations of anions (SO_4 and HCO_3) at the river outlet from April to September (WY16-18). Simulated results are plotted at daily frequency. For observations, and each point represents one sample. Data are color-coded by date.

Figure 5 (left and middle columns) shows that simulated and observed SO_4 exhibit similar C-Q hysteresis dynamics with a convex pattern. SO_4 concentrations match well observations in the rising limb but are lower than observations in the falling limb. The difference between rising limb and falling limbs are more pronounced in the simulation than in the observations. The simulated DIC C-Q hysteresis is similar to the Ca pattern and shows an L-shape clockwise hysteresis. Simulated DIC concentration capture observed concentrations well during the peak discharge period in June and baseflow period in September, but are lower in both rising and falling limbs.

4.2.2. Dry WY18

C-Q dynamics are quite different in both timing and hysteresis patterns (Figure 4, right column) in the dryer, WY18 compared to the wetter years. Peak discharge happens nearly 1-month earlier (i.e., at the end of May) due to early snowmelt and at peak value is less than $2.0 \text{ m}^3/\text{s}$ due to lower winter snowpack accumulation. In contrast to the L-shape clockwise hysteresis C-Q shown in WY16 (average), the C-Q relationship in WY18 shows a circular pattern of clockwise hysteresis C-Q, with a significantly higher concentration in rising limbs as compared to the falling limb. Due to the sparsity of measurements, the circle pattern of C-Q hysteresis cannot be confirmed in the observations. However, the difference in measured Ca concentrations between the rising limb in May and the falling limb in June are greater than their differences in the previous WY16 and WY17 and are consistent with the distinct pattern of C-Q hysteresis in the simulation. Similarly, the simulated Mg shows a pattern similar to observations, namely, that Mg concentrations in May are greater than the concentrations in June of WY18.

In WY18, simulated SO_4 and DIC concentrations remain high until a spike of discharge in early April, gradually decrease during peak discharge through May and June, and increase from July to September (Figure 5, right column). In comparison to the L-shape or convex-shaped C-Q hysteresis in the WY16 (average) and WY17 (wet) for DIC and SO_4 (Figure 5, left and middle columns), the simulated C-Q hysteresis in WY18 (dry) shows a circular clockwise pattern with greater differences between the rising and falling limbs. The measured C-Q hysteresis does not exhibit a circular pattern due to the coarseness of the sampling frequency, however, the higher concentrations in May than in June are in agreement with simulations.

4.3. Spatial Dynamics

The concentration-discharge data presented in Section 4.2 are aggregate measures of the processes in the catchment and reflect how the different watershed compartments interact temporally and spatially. Simulations are used here to understand how these interactions affect the aggregate response. For this purpose, we use the results from the wet WY17 as a reference.

The solution to the integrated hydrology problem, in which our approach does not prescribe any river routing, produces a well-defined stream network (Figure 6). The simulated water depth in Copper Creek is generally less than 1 m, except near the outlet and at Copper Lake, a high-elevation lake. Soil saturation results in the top layer of the subsurface indicate that soil is almost fully saturated near the river valley of Copper Creek but relatively drier in the mountain ridges where the groundwater table is deeper (Figure 6). In the high-elevation ridges, the soil is dry in the winter but relatively wet during the snowmelt periods. Snow accumulation is greater in the higher elevation mountains, but less in the river valleys (shown as snow water equivalent, or SWE, in Figure 6). Before and after the discharge peaks in May and July, respectively, more than 300 mm SWE remains on top of the surrounding mountains, while the snowpack melts completely in the late summer.

Water saturation on the north-facing side is higher in the late spring, before and during the peak of discharge (Figure 6), while on the south facing side it is higher in early and middle summer, during and after the peak of discharge. The snowpack remains longer on the north-facing side due to later snowmelt. This difference in the timing of the snowmelt results in heterogeneous water distribution in the north-versus south-facing sides of the catchment (Figure 6).

Concentrations on the surface are relatively uniform in the areas where water is present over the domain (Figure 7). In general, concentrations of both Ca and SO_4 are high in the winter, lowest in May, and rebound slightly in July. In July, concentration gradients are greater in the steeper upstream regions and in certain streams to the north of Copper Creek. These concentration differences mirror the north-south differences seen in the snow distribution in May WY17 and the subsurface water distribution in July WY17 (Figure 6).

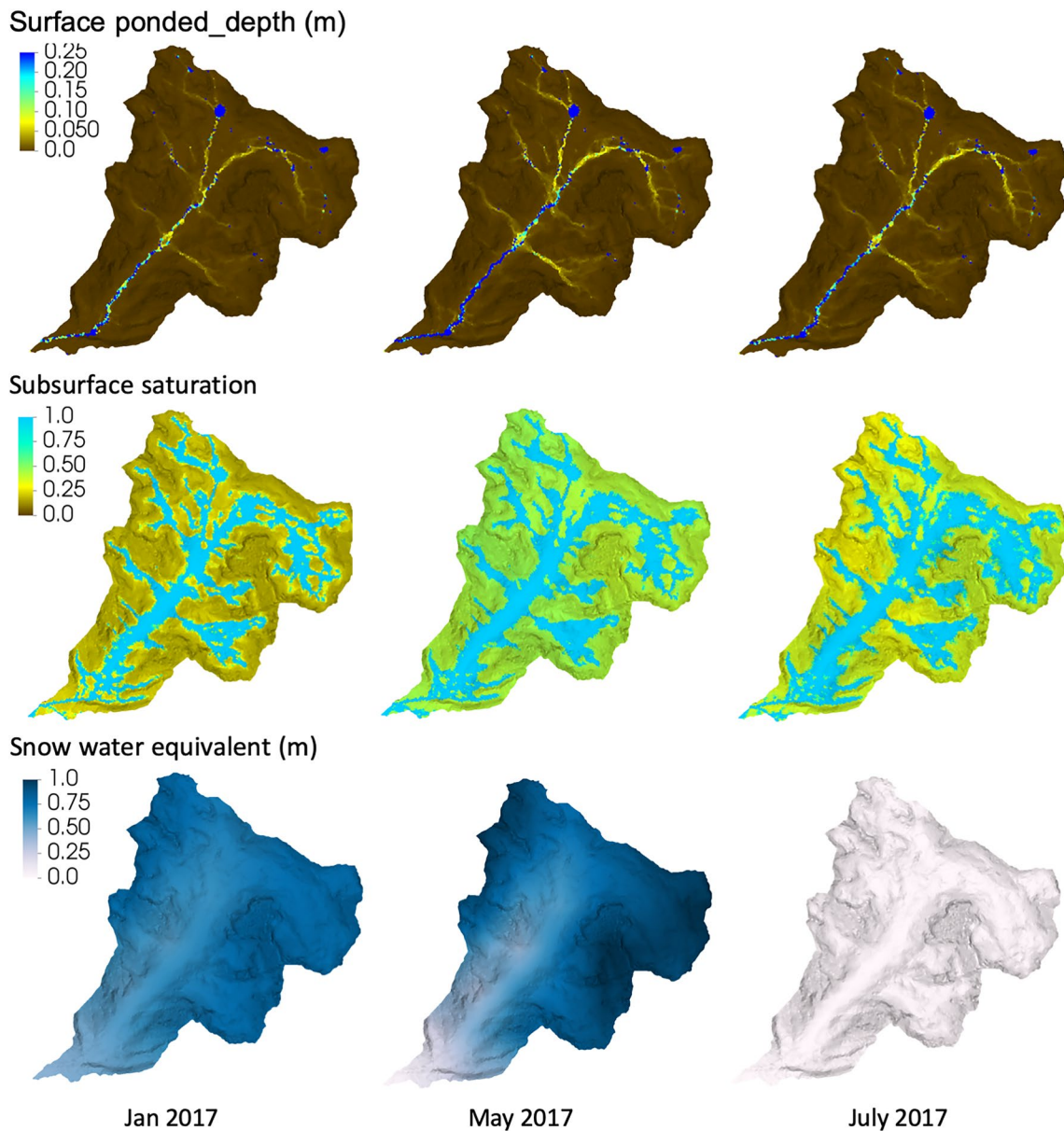


Figure 6. Simulated spatial distribution of select hydrological variables in the wet WY17 in the baseflow period (Jan), wet period before rising limbs (May), and dry period after falling limb (July). Top row: ponded depth on the surface; Middle row: saturation_liquid on the top layer of subsurface domain; Bottom row: snow water equivalent on the surface domain.

In the subsurface, concentrations are not as uniform as on the surface, with gradients present throughout the year (Figure 8). Because the source of the solutes is in the subsurface, concentrations in the subsurface are greater than on the surface (compare Figures 7 to Figure 8). A key feature of the model used here is that exchange fluxes between the surface and the subsurface are part of the solution (Molins et al., 2022). In other words, the model resolves spatially where and how much water (and with it the solutes) infiltrates into the subsurface, discharges back to the surface, and potentially re-infiltrates locally into the subsurface. Thus, as described in the following paragraph, concentration results (Figures 7 and 8) reflect the spatial and temporal distribution of the computed exchange fluxes (Figure 14).

During baseflow, concentrations on the surface are closer to values in the top subsurface, consistent with larger groundwater discharge (Figure 14). Concentrations gradients are also steeper, especially for SO₄, with higher concentrations computed below the streams, where exchange fluxes are larger. In May during the rising limb

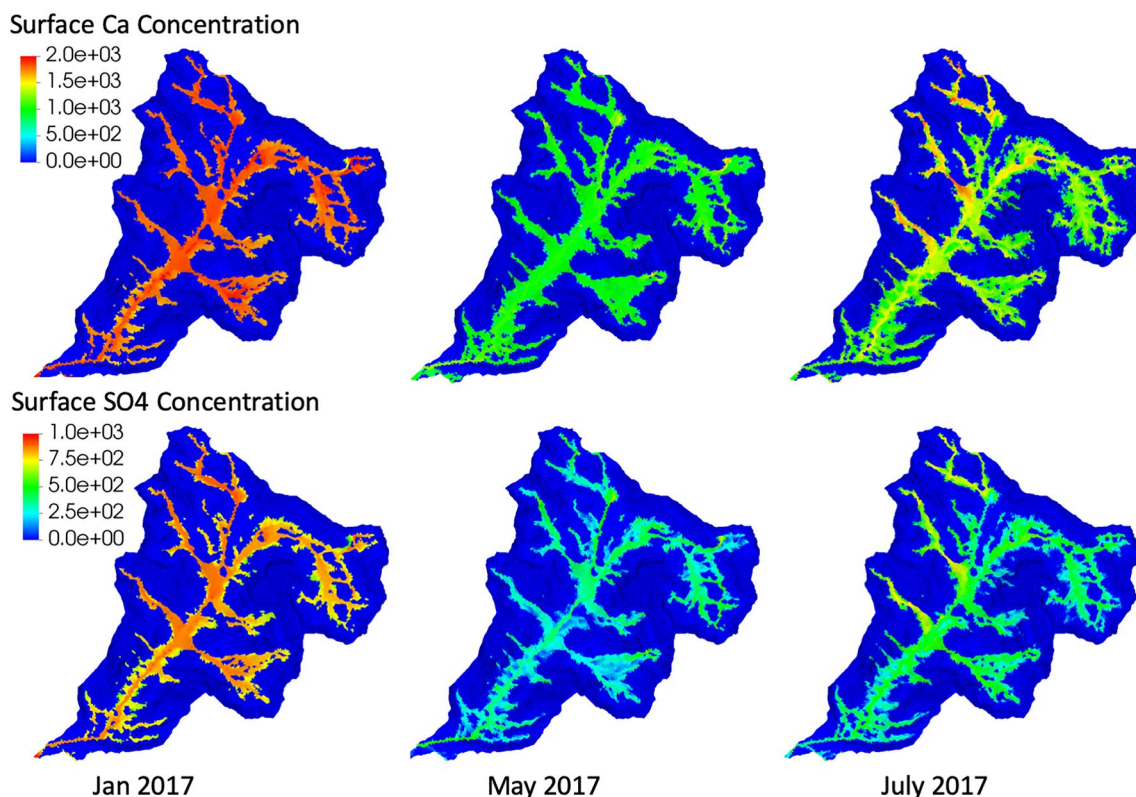


Figure 7. Simulated Ca and SO_4 concentrations ($\mu\text{mol/L}$) on the surface domain in the wet WY17 in January, May, and July. Concentrations are undefined in the dry areas of the surface (Figure 6), where values are arbitrarily set to 0, appearing in dark blue (i.e., ponded depth $<10^{-14}\text{m}$).

of the hydrograph, subsurface contributions to the surface and concentrations in the streams decrease significantly. Concentrations in the subsurface remain high near the streams but decrease quickly away from the streams indicating a dilution effect from the surface water infiltration (Figure 8). The regions that become saturated in the subsurface are also affected by the dilution effect. In July during the falling limb of the hydrograph, Ca concentrations in the groundwater increase, as calcite dissolves and groundwater flow transitions from infiltration to discharge. SO_4 concentrations are only significant in the portion of the subsurface around the surface streams (Figure 8). This is because SO_4 is the product of pyrite dissolution only at depth, but is transported downgradient, wells up, and discharges into the surface streams.

In comparison to the average year (WY17), the snow accumulation in May is much less than in WY18 (Figure 9). As a result, the surface hotspots of Ca concentrations in the high-elevation regions show in May 2018, two months earlier than in 2017 where they happen in July. Calcium surface concentrations in July 2018 are also significantly greater than in July 2017 in narrower streams.

5. Discussion

5.1. Contributions to Discharge and Exports

The fact that L-shaped C-Q hysteresis is observed in the average and wet years (WY16 and WY17) and a figure-eight-patterned C-Q hysteresis in the dry year (WY18) indicates that the groundwater contribution is greater in the dry WY18. Figure-8-type hysteresis behavior has been noted when groundwater contribution is greater than the total of surface water and soil water (Arora et al., 2020). We use conservative tracers to quantify the surface water and groundwater contributions (Figure 10). In WY16 (average) and WY17 (wet), the surface water contribution starts to increase 1 month before peak discharge, mostly due to early snowmelt. Surface water makes up over 90% of the total discharge and peaks at the same time, and then remains at nearly 60% of the total discharge in the falling limb. In contrast to the wet WY17, the dry WY18 has a smaller fraction of

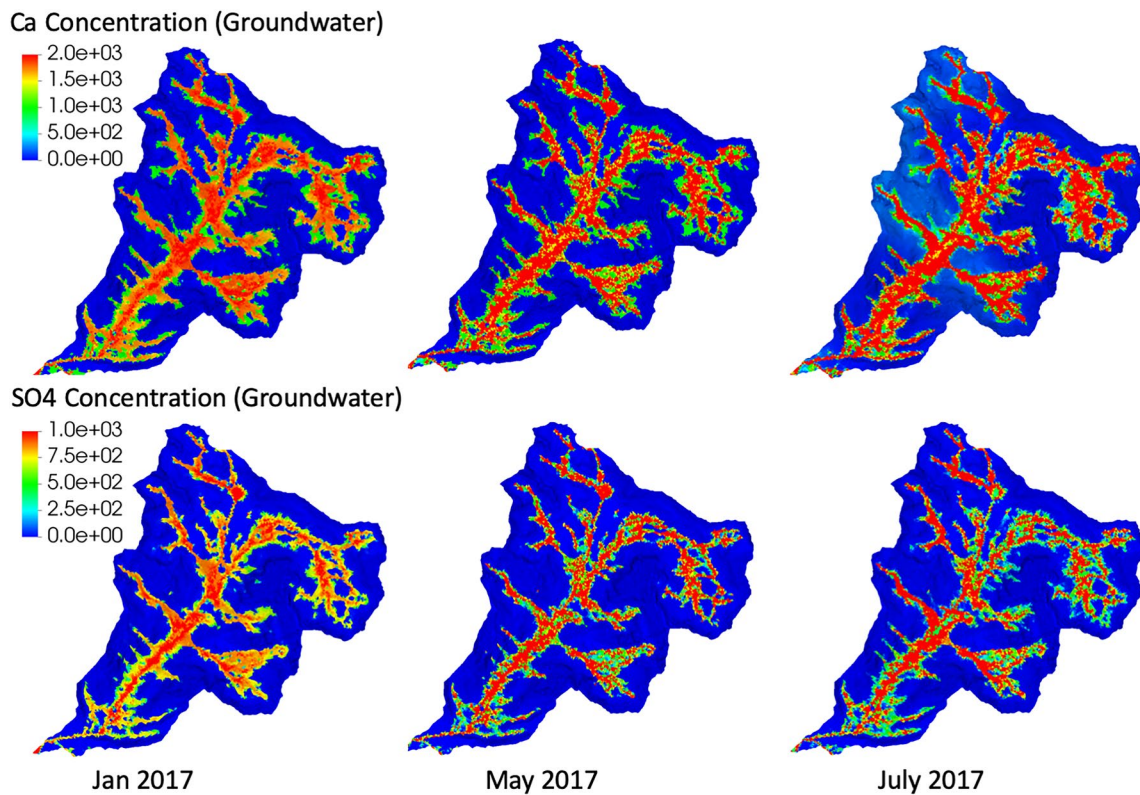


Figure 8. Simulated Ca and SO₄ concentrations ($\mu\text{mol/L}$) in the top layer of the subsurface domain in January, May and July of wet WY17. Concentrations are very small in most regions shown in dark blue but not zero as subsurface concentrations are defined everywhere.

new surface water in the discharge so the groundwater contribution is higher (Figure 10). The distribution of surface-subsurface exchange fluxes also shows that infiltration remains relatively high in July of WY17 (wet) but becomes minimal in July of WY18 (dry) (Figure 14). This is consistent with the conclusions in Arora et al. (2020)

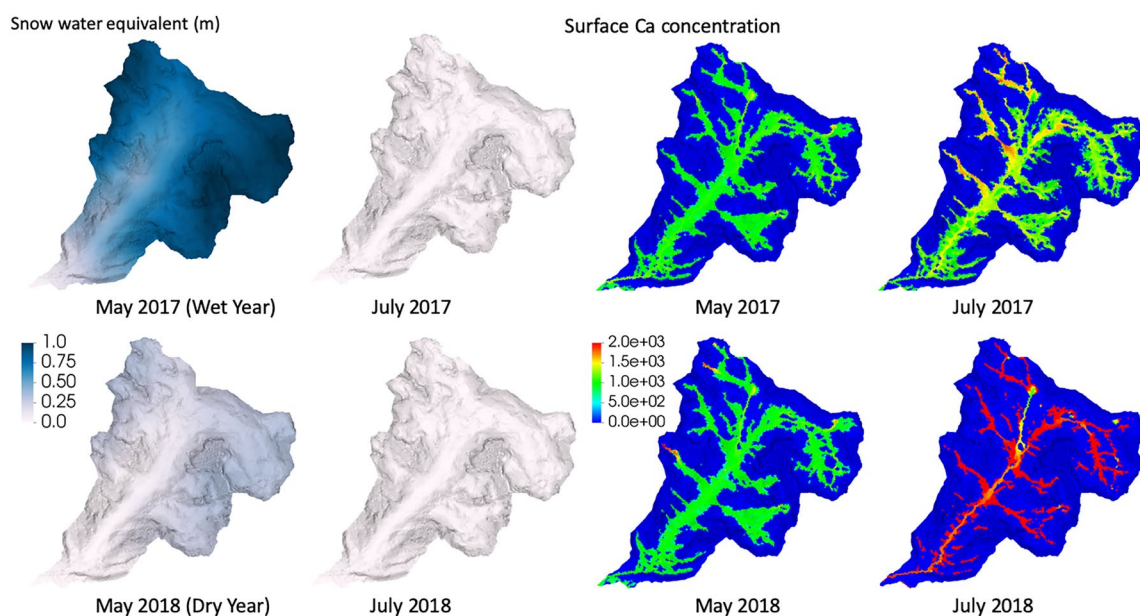


Figure 9. Simulated snow water equivalent and Ca surface concentration in May and July of 2017 and 2018. Top: wet year 2017; Bottom: dry year 2018. Concentration units are $\mu\text{mol/L}$.

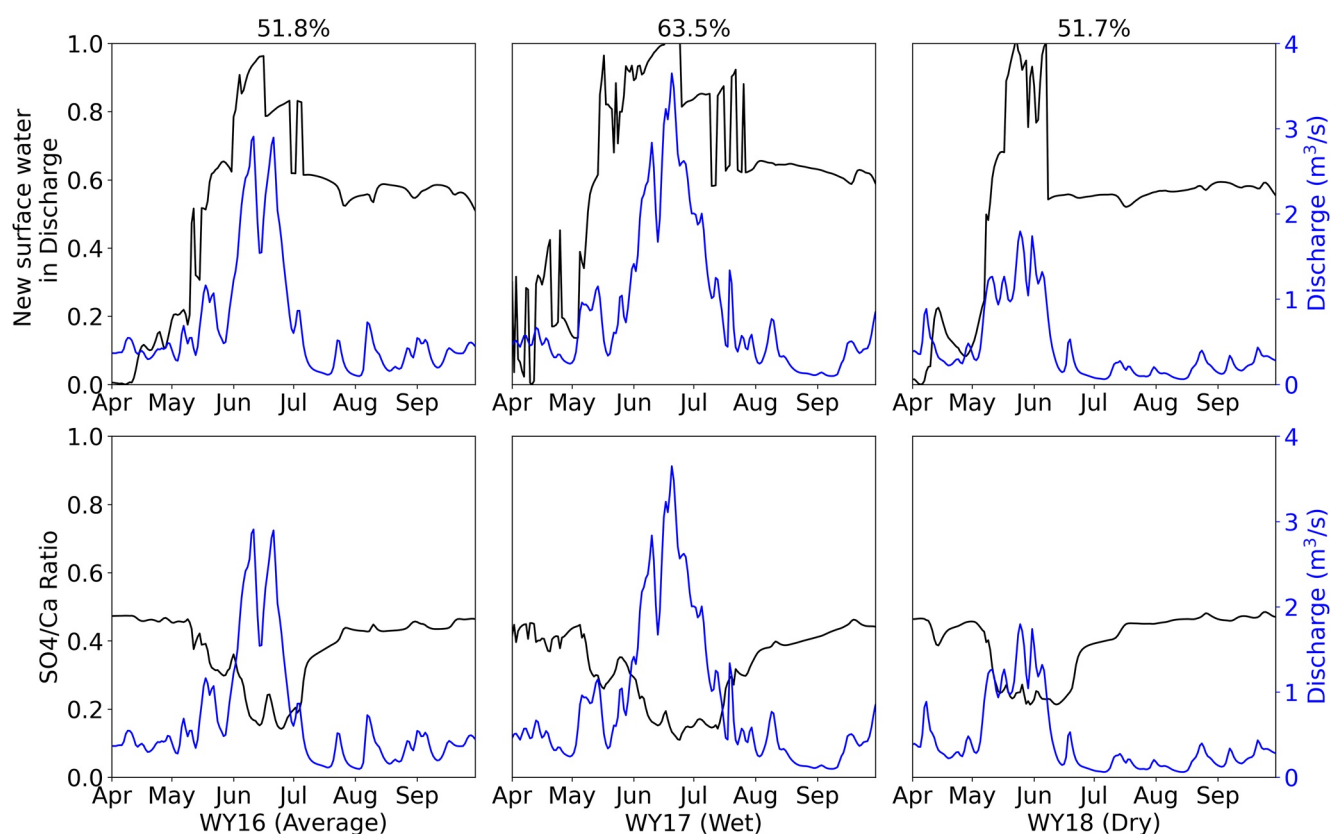


Figure 10. Top: Fraction of new surface water (rainwater and snowmelt) in the discharge at the river outlet from April to September in the three water years, calculated using EMMA of an auxiliary tracer with a very high concentration ($10,000 \mu\text{mol/L}$) in the rain snow and a low initial concentration ($10^{-14} \mu\text{mol/L}$) in the groundwater. The auxiliary tracer concentrations are $\leq 10^{-9} \mu\text{mol/L}$ in most of the subsurface domain and do not contribute to EMMA calculations. Bottom: The ratio of SO_4 to Ca concentrations in the discharge.

for the greater East River watershed. Overall, the evolution of ratios in Figure 10 (top) is in agreement with the observation that stream water is dominated by shallow water under high flow conditions and by deep water under low flow conditions (Zhi & Li, 2020).

The ratio of SO_4 to Ca concentrations (Figure 10, bottom) is used to evaluate the contribution of deep groundwater and the extent of groundwater mixing under different hydrological conditions. Larger SO_4/Ca ratios are associated with baseflow and low-discharge periods (Figure 10), where the deep groundwater contribution is larger. This is because Ca is sourced from calcite in the entire subsurface domain, while SO_4 comes from deep groundwater where pyrite is present (Figure 10, bottom). Further, the deep groundwater contribution is relatively small in the wet WY17 compared to the dry WY18, where shallow groundwater and streamflow make up a larger portion of the contribution to discharge. In contrast, a greater contribution of deep groundwater is observed during the dry WY18, with the SO_4/Ca ratio starting to increase as early as late June.

Two non-reactive tracers, Tracer1 and Tracer2, with the same initial and rainwater concentrations as those of Ca and SO_4 , respectively, are used to evaluate the effect of the dissolution reactions and the transport processes (Figure 11). Non-reactive tracer concentrations are high during baseflow conditions and become diluted in high discharge conditions, hence following a trend similar to that of Ca and SO_4 . However, Ca concentrations are less affected by changing hydrological conditions than those of Tracer1. That is, Tracer1 concentrations are greater than Ca concentration during baseflow and smaller during high discharge (Figure 12). This implies that calcite dissolution increases during wet seasons, and Ca is retained during dry seasons. This is also observed in the different water years, with differences being more significant in the average and wet years than in the dry year. Concentrations of SO_4 and Tracer2 show an opposite behavior, although differences are smaller (Figure 12). This is consistent with increased pyrite dissolution during the falling of the limb of the hydrograph when oxygen is available at depth (see Section 5.2).

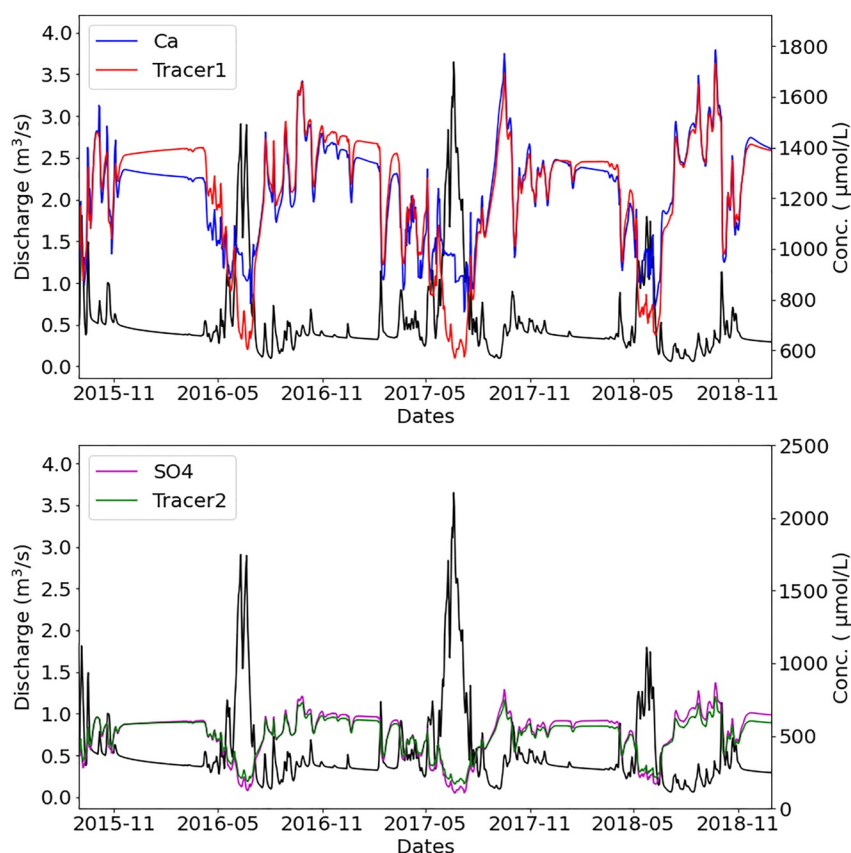


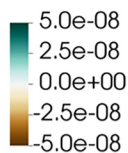
Figure 11. Time series of simulated solute concentrations and associated tracers at the river outlet (Top: Ca and Tracer1; Bottom: SO₄ and Tracer2). The initial concentrations of Tracer1 and Tracer2 are set to be the same as the initial Ca and SO₄, respectively. The first five years of the simulations are discarded as spin-up and only results from WY16–18 are shown. To facilitate the visualization, Tracer1 and Tracer2 concentrations on 1 Oct 2015 in this figure are reset to Ca and SO₄ values, respectively. Simulated discharge is shown as a black line for reference.

5.2. Effect of Vertical Heterogeneity

The differences between water years in the contributions to discharge suggest that the vertical heterogeneity assumed in the model in mineral composition, where pyrite is only present at depth, may also result in distinct responses in the chemical export. Reaction rates (Figure 12) show that the model captures the timing of pyrite dissolution as proposed by Winnick et al. (2017). Pyrite rates are relatively high in the period of the rising limb hydrograph when rainwater infiltrates into the deep surface with dissolved oxygen that contributes to pyrite dissolution (Figure 12). The reaction rates are the greatest, however, in the period of falling limb hydrograph when groundwater table decreases while infiltration continues supplying low pH, high oxygen water. In winter, pyrite reaction rates decrease when little water infiltrates into the deep subsurface layers and increases in the period of rising limb hydrograph when rainwater infiltrates into the deep surface with dissolved oxygen that contributes to pyrite dissolution. Calcite reaction rates are negligible during the base flow condition when the groundwater table is low and infiltration is low. In the May and July wet periods, calcite reaction rates are only significant in the fully-saturated subsurface layers but remain very low in other regions because calcite reactions require the presence of water.

To quantify the contribution of the solutes, we compute the fluxed-averaged concentrations in each period of the hydrograph (Figure 13). The difference between Ca and SO₄ concentrations between wet and dry years during the phases of baseflow, rising limb, and falling limb may be attributed to the impacts of the evolving hydrological regime on the mineral reactions, since Ca is sourced from calcite dissolution, and SO₄ is sourced from pyrite dissolution. Compared to SO₄, Ca concentration is not diluted significantly in the wet WY17 because calcite exists in the shallow layers, and the contribution of groundwater with higher Ca concentration from shallow

Calcite Reaction Rate



Pyrite Reaction Rate

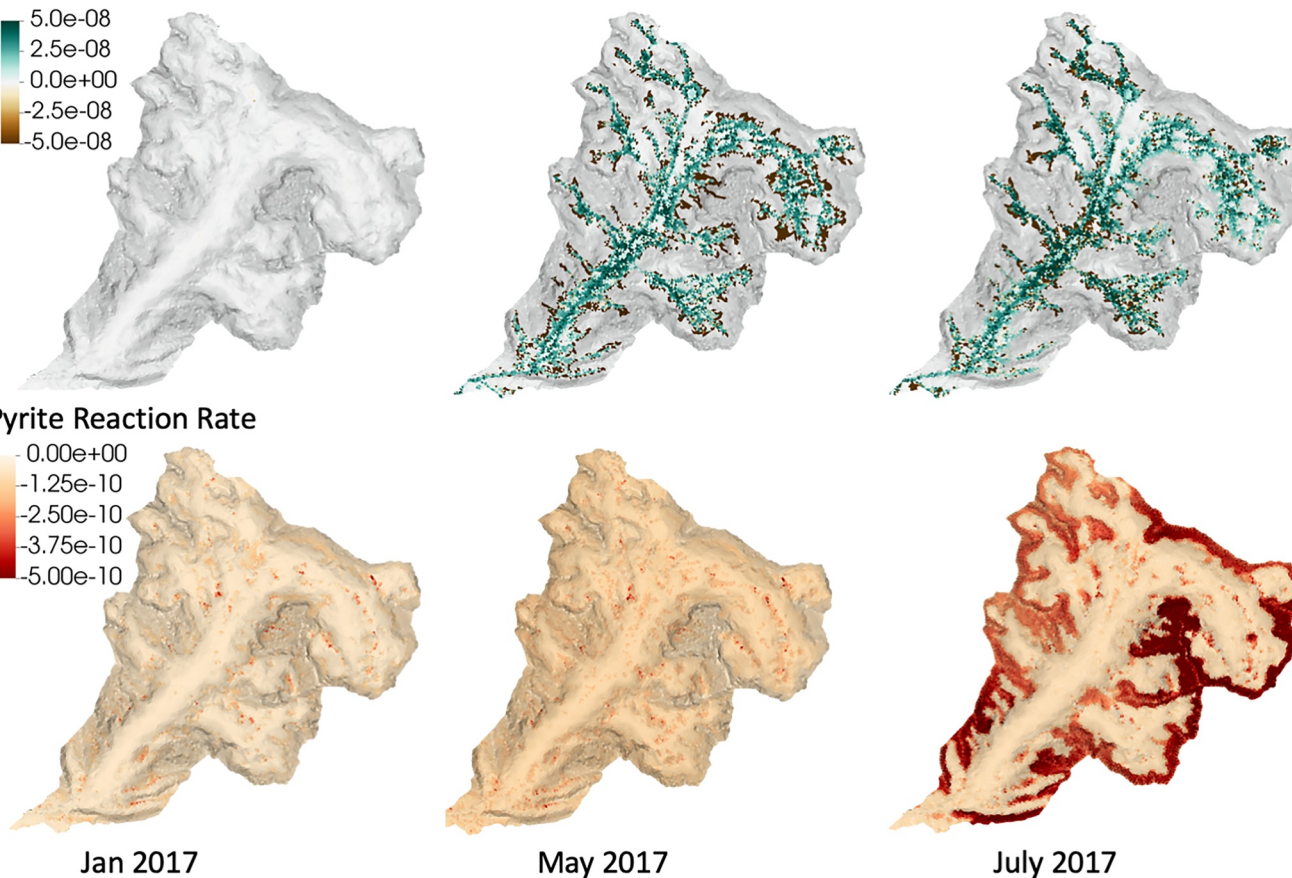
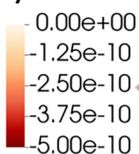


Figure 12. Top: calcite reaction rate in the top layer of the subsurface domain. Bottom: pyrite reaction rate on the bottom layer of the subsurface domain in the wet WY17. The reaction rate unit is $\text{mol kg}_{\text{H}_2\text{O}}^{-1} \text{m}^{-2} \text{s}^{-1}$.

layers is more than the dry WY18. More rapid calcite dissolution supplements Ca concentration dilution under high flow conditions, and the shallow water dominates stream discharge and concentration in the C-Q dynamics. SO_4 concentrations increase from pyrite dissolution and are higher in the deeper groundwater where pyrite is present. Since WY18 is a dry year, the dilution effect driven by rainfall and infiltration is less significant than in the normal WY16 and the wet WY17, hence the contribution from the SO_4 -rich, deeper groundwater is greater. Compared to dry WY18, the SO_4 concentration in the stream is relatively low in the wet WY17 due to the stronger dilution associated with higher infiltration. The SO_4 concentrations vary significantly between dry and wet years, particularly in the rising limb when infiltration water with high $\text{O}_2(\text{aq})$ is abundant, indicating that pyrite reactions are enhanced in the dry year. This simulated behavior is in agreement with recent observations in two monitored sites that indicate that stream chemistry mirrors subsurface waters, especially where there are distinct shallow and deep end members (Stewart et al., 2021). The aggregate C-Q behaviors described by (Arora et al., 2020) are captured by the model by resolving the spatially and temporally heterogeneous response.

5.3. Effect of Landscape Heterogeneity

Despite that permeabilities and mineral composition are horizontally homogeneous in the model, results show a heterogeneous response for hydrology and geochemical concentrations (Figure 7), due to topographic effects and spatially-resolved heterogeneous meteorological forcing data. Water transit times vary seasonally, that is, flow velocity is higher in summer than winter, with flow velocity being generally greater in the wet WY17 than the dry WY18 (Figure S2 in Supporting Information S1). As noted in Section 4.3, there are differences between north- and south-facing sides of the catchment, and there are concentrations of hotspots during certain periods. The

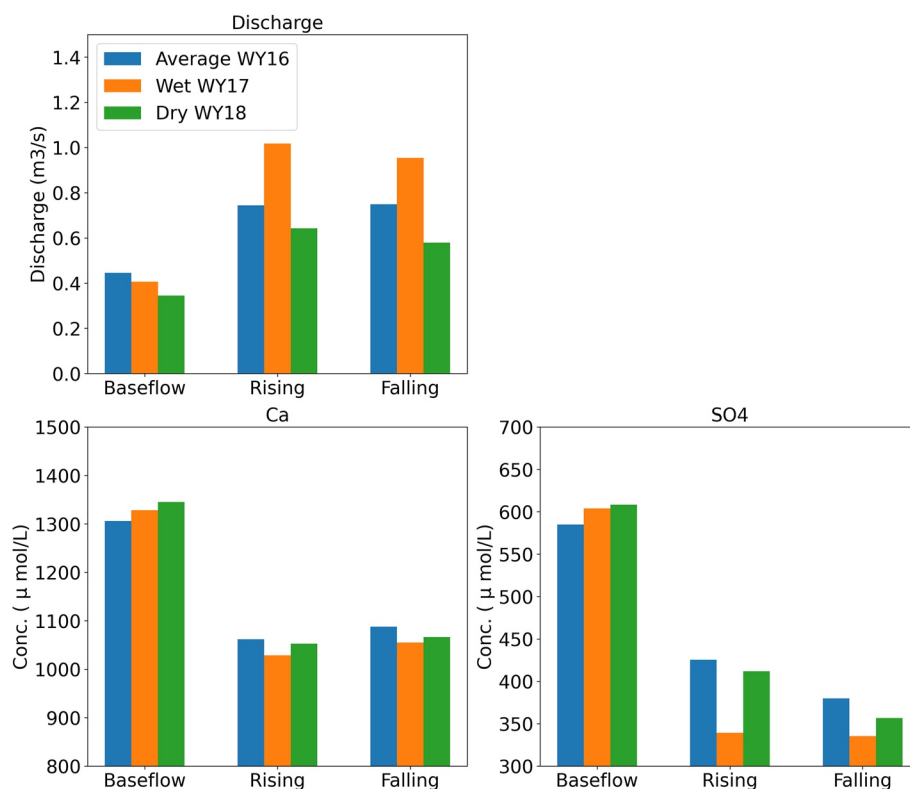


Figure 13. Discharge and major chemical species average concentrations in the three phases (baseflow, rising limb and falling limb) in the three water years at the river outlet. The rising limb is defined from April 1st to the day with maximum discharge of the water year, the falling limb is defined as the same length as rising limb after the peak discharge for consistent comparison purposes. The baseflow period is computed from Oct 1st of the previous year to March 31st, and the rest of the water year from the end of falling limb. The number of days for rising and falling limbs varies in each water year. There are 73 days in WY16 (average), 82 days in WY17 (wet), and 56 days in WY18 (dry) for the rising or falling limb period.

difference of temperature in the meteorological forcing is likely the largest driver of the difference between north- and south-facing slopes due to the radiations received on the two sides. The difference can be explained as the hydrological response is dominated by the snow dynamics, and the snow dynamics are sensitive to temperature. However, the differences are also attributable to the topographic gradients in the catchment with concentration hotspots appearing near streams in narrow canyons (Section 4.3).

C-Q analysis shows that Ca and SO₄ concentrations start to increase in July WY17 from high (Figures 4 and 5), consistent with the early increase in surface concentrations on the south-facing side of the catchment (Figures 8 and 7). In contrast, concentrations in July WY18 increase somewhat earlier due to the earlier discharge peak (Figure 4), and thus elevated concentrations appear earlier in the streams in May and become significantly higher than in WY17 (Figure 9). Figure 14 also shows that infiltration in the south facing side decreases earlier than on the north facing side, particularly in the dry WY18. The hotspots of Ca concentrations appear earlier on the south facing side, indicating that variable infiltration affects calcite reaction that contributes to Ca concentration. However, the differences caused by landscape heterogeneity in the aggregate C-Q response are relatively small and in fact hard to quantify, given other uncertainties in the model.

5.4. Limitations

Although simulated C-Q agrees reasonably well with observations (Figures 3–5), discrepancies exist both in the baseflow and in peak discharge periods. This indicates that the 30-m depth of the subsurface domain may be insufficient to capture all groundwater baseflow. Our model consistently overestimates the baseflow, which is likely due to the limit of spatial homogenization for hydrological dynamics discussed in Wen et al. (2021). Further, the model assumes that groundwater in the subsurface does not freeze, which leads to an overestimation

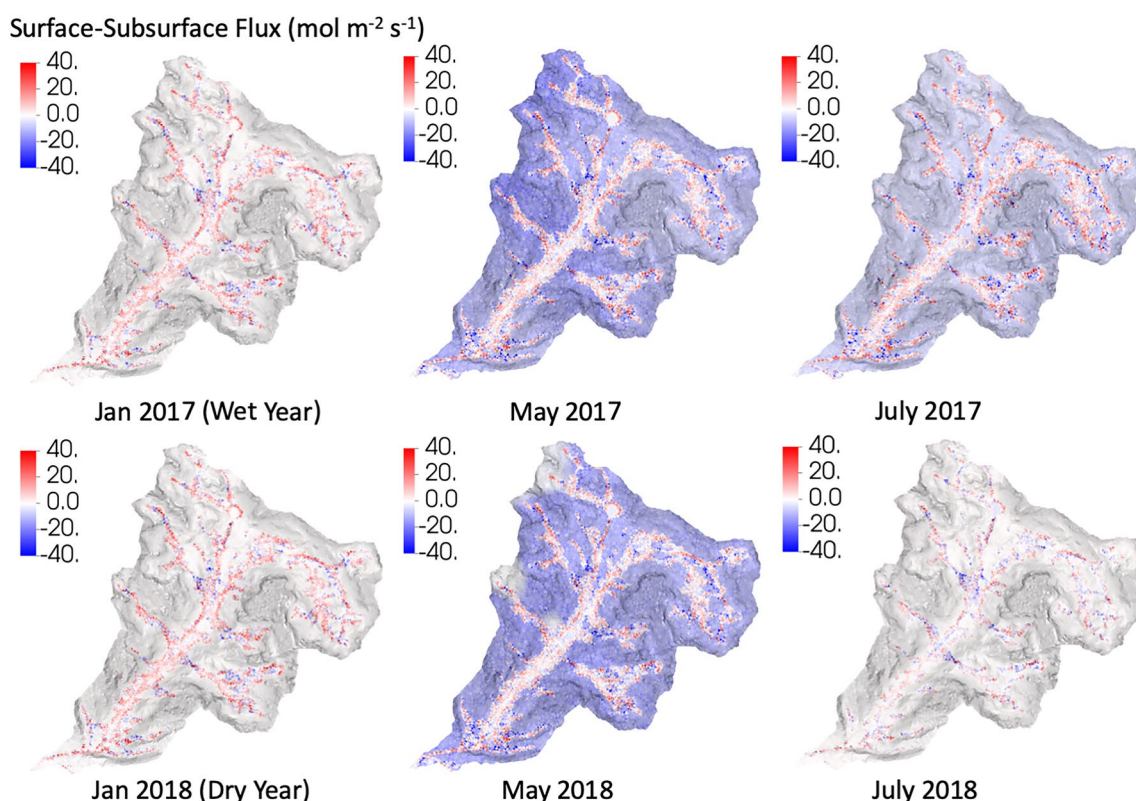


Figure 14. Surface-subsurface exchange flux in January, May, and July of WY17 (wet) and WY18 (dry). Blue indicates infiltration or surface water recharging the subsurface domain, and red indicates exfiltration of subsurface groundwater and discharge into surface water, including streams.

of groundwater discharge in winter. Field investigation suggested only the top 10 cm may freeze in winter so the impacts of this limitation would be negligible. In late summer and early fall periods, simulated discharge decreases earlier than in the observations and exhibits a few spikes due to monsoon-related rainfall events, indicating the permeabilities of top layers need to be fine-tuned. Groundwater level measurements are not available, which hinders the ability to contrast the results of the simulation in the subsurface against data. However, this is often the case in mostly undisturbed, hard-to-access mountainous catchments such as Copper Creek. The 5-layer vertical discretization may also be insufficient to best characterize groundwater level in the simulations, as well as how the water table affects mineral reactions, particularly the pyrite reaction in the deep layers.

The geochemical model considered two reactive phases and a simplified spatial distribution based on depth (Winnick et al., 2017). This approach was conditioned by two facts: the lack of subsurface aqueous geochemistry data and information about the distribution of reactive phases in the subsurface, as well as the results from preliminary simulation, which showed that the sensitivity of model results to more complex reaction networks did not result in differences large enough (compared to available C-Q data) that would have affected significantly the discussion presented. In particular, we explored the effect of smectite as representative of clay minerals in the domain. This approach, thus, has proven to be parsimonious and sufficient to capture the major solute exports and their dynamics. We acknowledge however that this does not mean that additional reactive phases should be neglected, rather than more complex geochemical models require additional aqueous and mineralogical data, especially to capture minor and trace solutes. The largest discrepancy seen here has been for SO_4 . While Ca and Mg concentrations behave similarly at Copper Creek and in the larger East River watershed (Dong et al., 2020), SO_4 concentrations at Copper Creek are generally higher in winter, potentially due to the presence of gypsum. The MAE for individual solutes (Table S1 in Supporting Information S1) shows that SO_4 has the largest error in all cases, indicating uncertainties in the mineral composition, including the distribution of pyrite and possibly neglecting the presence of gypsum, had the most impact on capturing geochemical exports.

Concentration results oscillate significantly with discharge, indicating a quick response of the model to hydrological inputs. This indicates that the model does not include additional processes, for example, the detailed land surface processes such as canopy interception, which may retard water on the surface and smooth the hydrogeochemical response. Improvement of process representation and fidelity in the model is very necessary to capture the full dynamics of this watershed response; these include land-cover-based ET estimation and consideration of seasonal and long-term vegetation dynamics as typically considered in land surface models.

Computational costs still limit certain aspects of the work, such as the use of automating ensemble simulations or inverse modeling for parameter calibration, that would have supported increasing model complexity in this work.

6. Summary and Conclusions

An integrated hydrologic and reactive transport model was applied to evaluate the response C-Q and understand the underlying spatial dynamics in a mountainous watershed. In the model calibration, NSE and MAE are the metrics for evaluating discharge and concentration simulations against observations. We used both discharge and concentration data to calibrate permeabilities in the subsurface. This highlights that performing reactive transport simulations are essential in addition to flow simulations where water quality data are available.

Multi-year simulations enable contrasting the response in years with distinct precipitation input patterns and totals. We observe significantly different C-Q hysteresis in relatively wet years compared to relatively dry years. The model is able to capture this year-to-year variability, and it highlights its potential as a tool to not only understand but also predict the impacts of climate variability on the hydrogeochemical response of mountainous watersheds in future scenarios. Our model also quantifies the partitioning of groundwater and surface water contributions to aggregated discharge and evaluates how changing hydrology conditions affect mineral reaction across years. Although it does not result in a noticeable signal in the aggregated response, spatially-resolved results show that higher soil saturation and less snowpack occurred earlier on the south-facing side than on the north-facing side. This result of concentration hotspots earlier in the south-facing side during the falling limb from discharging groundwater contribution.

This work demonstrates how mechanistic simulations with spatially-resolved outputs can provide quantitative estimates of hydrological and geochemical exports in a watershed over time and space, especially C-Q dynamics. The simulations also can help to understand heterogeneous watershed responses, particularly in ungauged watersheds. While recent C-Q studies indicate the importance of vertical heterogeneity over landscape heterogeneity (Stewart et al., 2021), spatial data analyses suggest that watershed function is heterogeneously distributed over the landscape (Wainwright et al., 2021). Simulation of future climate scenarios is beyond the scope of this work but it is a critical direction of research in watershed science. Simulations will provide a valuable tool for understanding the impact of climate disturbances and providing quantitative-based solutions for watershed management.

Data Availability Statement

All authors contributed to the article and approved the submitted version. Input data and output files for these simulations are available at Xu et al. (2022) ATS (Advanced Terrestrial Simulator) integrated hydrology and reactive transport model output in Copper Creek, Colorado. Watershed Function SFA, ESS-DIVE repository. Dataset. doi:[10.15485/1877377](https://doi.org/10.15485/1877377). The Advanced Terrestrial Simulator (Coon et al., 2019) is released under a 3-clause BSD license. Release version 1.2.0 was used to run the simulations and is archived at doi.org/10.5281/zenodo.6679807.

References

- Ackerer, J., Steefel, C., Liu, F., Bart, R., Safeeq, M., O'geen, A., et al. (2020). Determining how critical zone structure constrains hydrogeochemical behavior of watersheds: Learning from an elevation gradient in California's sierra Nevada. *Frontiers in Water*, 2, 23. <https://doi.org/10.3389/frwa.2020.00023>
- Ameli, A. A., Beven, K., Erlandsson, M., Creed, I. F., McDonnell, J. J., & Bishop, K. (2017). Primary weathering rates, water transit times, and concentration-discharge relations: A theoretical analysis for the critical zone. *Water Resources Research*, 53(1), 942–960. <https://doi.org/10.1002/2016wr019448>
- Andre, B., Molins, S., Johnson, J., & Steefel, C. (2013). Alquimia. [Computer Software]. Alquimia. <https://doi.org/10.1157/dc.20210416.49>

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- Arora, B., Burrus, M., Newcomer, M., Steefel, C. I., Carroll, R. W., Dwivedi, D., et al. (2020). Differential cq analysis: A new approach to inferring lateral transport and hydrologic transients within multiple reaches of a mountainous headwater catchment. *Frontiers in Water*, 2, 24. <https://doi.org/10.3389/frwa.2020.00024>
- Arora, B., Spycher, N. F., Steefel, C. I., Molins, S., Bill, M., Conrad, M. E., et al. (2016). Influence of hydrological, biogeochemical and temperature transients on subsurface carbon fluxes in a flood plain environment. *Biogeochemistry*, 127(2–3), 367–396. <https://doi.org/10.1007/s10533-016-0186-8>
- Bao, C., Li, L., Shi, Y., & Duffy, C. (2017). Understanding watershed hydrogeochemistry: 1. Development of rt-flux-pihm. *Water Resources Research*, 53(3), 2328–2345. <https://doi.org/10.1002/2016wr018934>
- Carroll, R. W. H., Bearup, L. A., Brown, W., Dong, W., Bill, M., & Williams, K. H. (2018). Factors controlling seasonal groundwater and solute flux from snow-dominated basins. *Hydrological Processes*, 32(14), 2187–2202. <https://doi.org/10.1002/hyp.13151>
- Chen, X., Lee, R. M., Dwivedi, D., Son, K., Fang, Y., Zhang, X., et al. (2020). Integrating field observations and process-based modeling to predict watershed water quality under environmental perturbations. *Journal of Hydrology*, 125762.
- Christophersen, N., & Hooper, R. P. (1992). Multivariate analysis of stream water chemical data: The use of principal components analysis for the end-member mixing problem. *Water Resources Research*, 28(1), 99–107. <https://doi.org/10.1029/91wr02518>
- Coon, E., Svyatsky, D., Jan, A., Kikinzon, E., Berndt, M., Atchley, A., et al. (2019). *Advanced Terrestrial simulator*. Los Alamos National Laboratory (LANL). Retrieved 2021-11-11, fromLanguage: en). <https://doi.org/10.11578/DC.20190911.1>
- Daly, C., Taylor, G., & Gibson, W. (1997). The prism approach to mapping precipitation and temperature. In *Proceedings of the 10th AMS Conference on Applied Climatology* (pp. 20–23).
- Dehaspe, J., Sarrazin, F., Kumar, R., Fleckenstein, J. H., & Musolff, A. (2021). Bending of the concentration discharge relationship can inform about in-stream nitrate removal. *Hydrology and Earth System Sciences*, 25(12), 6437–6463. <https://doi.org/10.5194/hess-25-6437-2021>
- Dong, B. C., Brown, W., Newman, A., Versteeg, R., & Williams, K. H. (2020). Cation data for the East River watershed, Colorado (Tech. Rep.). Watershed Functionality scientific focus area. <https://doi.org/10.15485/1668055>
- Dong, W., Bhattacharyya, A., Fox, P. M., Bill, M., Dwivedi, D., Carrero, S., et al. (2020). Geochemical controls on release and speciation of Fe (II) and Mn (II) from hyporheic sediments of east river, Colorado. *Frontiers in Water*, 2, 49–52. <https://doi.org/10.3389/frwa.2020.562298>
- Dwivedi, D., Steefel, C. I., Arora, B., Banfield, J., Bargar, J., Boyanov, M. I., et al. (2022). From legacy contamination to watershed systems science: A review of scientific insights and technologies developed through doe-supported research in water and energy security. *Environmental Research Letters*, 17(4), 043004. <https://doi.org/10.1088/1748-9326/ac59a9>
- Dwivedi, D., Steefel, C. I., Arora, B., Newcomer, M., Moulton, J. D., Dafflon, B., et al. (2018). Geochemical exports to river from the intramember hyporheic zone under transient hydrologic conditions: East river mountainous watershed, Colorado. *Water Resources Research*, 54(10), 8456–8477. <https://doi.org/10.1029/2018wr023377>
- Fountain, H. (2021). In *A first, U.S. declares shortage on Colorado river, forcing water cuts*. The New York Times. Retrieved 2021-09-07, from Retrieved from <https://www.nytimes.com/2021/08/16/climate/colorado-river-water-cuts.html>
- Garrick, D., Jacobs, K., & Garfin, G. (2008). Models, assumptions, and stakeholders: Planning for water supply variability in the Colorado River basin 1. *JAWRA Journal of the American Water Resources Association*, 44(2), 381–398. <https://doi.org/10.1111/j.1752-1688.2007.00154.x>
- Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration–discharge relationships reflect chemostatic characteristics of us catchments. *Hydrological Processes: International Journal*, 23(13), 1844–1864. <https://doi.org/10.1002/hyp.7315>
- Gupta, H. V., & Kling, H. (2011). On typical range, sensitivity, and normalization of Mean Squared Error and Nash-Sutcliffe Efficiency type metrics. *Water Resources Research*, 47(10). Retrieved 2021-07-07, from <https://doi.org/10.1029/2011WR010962>
- Hammond, G. E., Lichtner, P. C., & Mills, R. T. (2014). Evaluating the performance of parallel subsurface simulators: An illustrative example with pflotran. *Water Resources Research*, 50, 208–228. <https://doi.org/10.1002/2012WR013483>
- Hubbard, S. S., Williams, K. H., Agarwal, D., Banfield, J., Beller, H., Bouskill, N., et al. (2018). The East river, Colorado, watershed: A mountainous community testbed for improving predictive understanding of multiscale hydrological–biogeochemical dynamics. *Vadose Zone Journal*, 17(1), 1–25. <https://doi.org/10.2136/vzj2018.03.0061>
- Knapp, J. L., Freyberg, J. v., Studer, B., Kiewiet, L., & Kirchner, J. W. (2020). Concentration–discharge relationships vary among hydrological events, reflecting differences in event characteristics. *Hydrology and Earth System Sciences*, 24(5), 2561–2576. <https://doi.org/10.5194/hess-24-2561-2020>
- Kollet, S., Sulis, M., Maxwell, R. M., Paniconi, C., Putti, M., Bertoldi, G., et al. (2017). The integrated hydrologic model intercomparison project, IH-MIP2: A second set of benchmark results to diagnose integrated hydrology and feedbacks. *Water Resources Research*, 53, 867–890. <https://doi.org/10.1002/2016WR019191>
- LANL. (2018). Los alamos grid toolbox (Tech. Rep.). Retrieved from <https://lagrit.lanl.gov/>
- Lauren, F., & Reed, M. (2019). Sensitivity analysis of hydraulic conductivity and Manning's n parameters lead to new method to scale effective hydraulic conductivity across model resolutions. *Hydrological Processes*, 33(3), 332–349.
- LiBao, C., Sullivan, P. L., Brantley, S., Shi, Y., Duffy, C., & Duffy, C. (2017). Understanding watershed hydrogeochemistry: 2. Synchronized hydrological and geochemical processes drive stream chemostatic behavior. *Water Resources Research*, 53(3), 2346–2367. <https://doi.org/10.1002/2016wr018935>
- Liggett, J. E., Partington, D., Frei, S., Werner, A. D., Simmons, C. T., & Fleckenstein, J. H. (2015). An exploration of coupled surface–subsurface solute transport in a fully integrated catchment model. *Journal of Hydrology*, 529, 969–979. <https://doi.org/10.1016/j.jhydrol.2015.09.006>
- Matheus, C., Lavy, A., Thomas, A., Crits-Christoph, A., Diamond, S., Meeheust, R., et al. (2020). Meanders as a scaling motif for understanding of floodplain soil microbiome and biogeochemical potential at the watershed scale.
- Maxwell, R., Putti, M., Meyerhoff, S., Delfs, J.-O., Ferguson, I., Ivanov, V., et al. (2014). Surface-subsurface model intercomparison: A first set of benchmark results to diagnose integrated hydrology and feedbacks. *Water Resources Research*, 50(2), 1531–1549. <https://doi.org/10.1002/2013WR013725>
- McCuen, R. H., Knight, Z., & Cutter, A. G. (2006). Evaluation of the nash–sutcliffe efficiency index. *Journal of Hydrologic Engineering*, 11(6), 597–602. [https://doi.org/10.1061/\(asce\)1084-0699\(2006\)11:6\(597\)](https://doi.org/10.1061/(asce)1084-0699(2006)11:6(597))
- Molins, S., Svyatski, D., Xu, Z., Coon, E. T., & Moulton, J. D. (2022). A new modeling approach for the simulation of integrated hydrology and multicomponent reactive transport problems. *Water Resource Research*, 120–121, 27–44. <https://doi.org/10.1029/2022WR032074>
- Morrison, S. J., Goodknight, C. S., Tigar, A. D., Bush, R. P., & Gil, A. (2012). Naturally occurring contamination in the mancos shale. *Environmental Science & Technology*, 46(3), 1379–1387. <https://doi.org/10.1021/es203211z>
- Musolff, A., Schmidt, C., Selle, B., & Fleckenstein, J. H. (2015). Catchment controls on solute export. *Advances in Water Resources*, 86, 133–146. <https://doi.org/10.1016/j.advwatres.2015.09.026>
- National Atmospheric Deposition Program (NRSP-3). (2016). NADP Program Office, Illinois State Water Survey, Univ. of Illinois, Champaign, Ill.

- Newcomer, M. E., Bouskill, N. J., Wainwright, H., Maavara, T., Arora, B., Siirila-Woodburn, E. R., et al. (2021). Hysteresis patterns of watershed nitrogen retention and loss over the past 50 years in United States hydrological basins. *Global Biogeochemical Cycles*, 35(4), e2020GB006777. <https://doi.org/10.1029/2020gb006777>
- Nogueira, G., Schmidt, C., Brunner, P., Graeber, D., & Fleckenstein, J. (2021). Transit-time and temperature control the spatial patterns of aerobic respiration and denitrification in the riparian zone. *Water Resources Research*, 57(12), e2021WR030117. <https://doi.org/10.1029/2021wr030117>
- Olshansky, Y., White, A. M., Moravec, B. G., McIntosh, J., & Chorover, J. (2018). Subsurface pore water contributions to stream concentration-discharge relations across a snowmelt hydrograph. *Frontiers of Earth Science*, 6, 181. <https://doi.org/10.3389/feart.2018.00181>
- Palandri, J. L., & Kharaka, Y. K. (2004). A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. Geological Survey Menlo Park CA. <https://doi.org/10.3133/ofr20041068>
- Paniconi, C., & Putti, M. (2015). Physically based modeling in catchment hydrology at 50: Survey and outlook. *Water Resources Research*, 51(9), 7090–7129. <https://doi.org/10.1002/2015wr017780>
- Partington, D., Knowling, M. J., Simmons, C. T., Cook, P. G., Xie, Y., Iwanaga, T., & Bouchez, C. (2020). Worth of hydraulic and water chemistry observation data in terms of the reliability of surface water-groundwater exchange flux predictions under varied flow conditions. *Journal of Hydrology*, 590, 125441. <https://doi.org/10.1016/j.jhydrol.2020.125441>
- Pribulick, C. E., Foster, L. M., Bearup, L. A., Navarre-Sitchler, A. K., Williams, K. H., Carroll, R. W., & Maxwell, R. M. (2016). Contrasting the hydrologic response due to land cover and climate change in a mountain headwaters system. *Ecohydrology*, 9(8), 1431–1438. <https://doi.org/10.1002/eco.1779>
- Priestley, C., & Taylor, R. (1972). On the assessment of surface heat flux and evaporation using large-scale parameters. *Monthly Weather Review*, 100(2), 81–92. [https://doi.org/10.1175/1520-0493\(1972\)100<0081:otaosh>2.3.co;2](https://doi.org/10.1175/1520-0493(1972)100<0081:otaosh>2.3.co;2)
- QGIS development Team. (2021). Qgis geographic information system. [Computer software manual]. QGIS. Retrieved from <https://www.qgis.org>
- Rose, L. A., Karwan, D. L., & Godsey, S. E. (2018). Concentration–discharge relationships describe solute and sediment mobilization, reaction, and transport at event and longer timescales. *Hydrological Processes*, 32(18), 2829–2844. <https://doi.org/10.1002/hyp.13235>
- Schilling, O. S., Cook, P. G., & Brunner, P. (2019). Beyond classical observations in hydrogeology: The advantages of including exchange flux, temperature, tracer concentration, residence time, and soil moisture observations in groundwater model calibration. *Reviews of Geophysics*, 57(1), 146–182. <https://doi.org/10.1029/2018rg000619>
- Stewart, B., Shanley, J. B., Kirchner, J. W., Norris, D., Adler, T., Bristol, C., et al. (2021). Streams as mirrors: Reading subsurface water chemistry from stream chemistry. *Water Resources Research*, e2021WR029931.
- Survey, U. G. (2019). National hydrography dataset (ver. usgs national hydrography dataset best resolution (nhd) for hydrologic unit (hu) 4-2001.
- Thornton, P. E., Thornton, M. M., Mayer, B. W., Wilhelmi, N., Wei, Y., Devarakonda, R., & Cook, R. B. (2014). *Daymet: Daily surface weather data on a 1-km grid for north America, version 2. (Tech. Rep.)*. Oak Ridge National Lab.(ORNL).
- Torres, M. A., & Baronas, J. J. (2021). Modulation of riverine concentration-discharge relationships by changes in the shape of the water transit time distribution. *Global Biogeochemical Cycles*, 35(1), e2020GB006694. <https://doi.org/10.1029/2020gb006694>
- Varadharajan, C., Agarwal, D. A., Brown, W., Burrus, M., Carroll, R. W., Christianson, D. S., et al. (2019). Challenges in building an end-to-end system for acquisition, management, and integration of diverse data from sensor networks in watersheds: Lessons from a mountainous community observatory in East river, Colorado. *IEEE Access*, 7, 182796–182813. <https://doi.org/10.1109/access.2019.2957793>
- Wainwright, H. M., Uhlemann, S., Franklin, M., Falco, N., Bouskill, N. J., Newcomer, M., et al. (2021). Watershed zonation approach for tractably quantifying above-and-belowground watershed heterogeneity and functions. *Hydrology and Earth System Sciences Discussions*, 1–23. <https://doi.org/10.5194/hess-2021-228>
- Wan, J., Tokunaga, T. K., Brown, W., Newman, A. W., Dong, W., Bill, M., et al. (2021). Bedrock weathering contributes to subsurface reactive nitrogen and nitrous oxide emissions. *Nature Geoscience*, 14(4), 217–224. <https://doi.org/10.1038/s41561-021-00717-0>
- Wen, H., Brantley, S. L., Davis, K. J., Duncan, J. M., & Li, L. (2021). The limits of homogenization: What hydrological dynamics can a simple model represent at the catchment scale? *Water Resources Research*, 57(6), e2020WR029528. <https://doi.org/10.1029/2020wr029528>
- Williams, K., Beutler, C., Brown, W., Henderson, A., & Newman, A. (2020). Anion data for the East River watershed, Colorado (Tech. Rep.). Watershed Functionality scientific focus area. <https://doi.org/10.15485/1668054>
- Williamson, M. A., & Rimstidt, J. D. (1994). The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochimica et Cosmochimica Acta*, 58(24), 5443–5454. [https://doi.org/10.1016/0016-7037\(94\)90241-0](https://doi.org/10.1016/0016-7037(94)90241-0)
- Winnick, M. J., Carroll, R. W., Williams, K. H., Maxwell, R. M., Dong, W., & Maher, K. (2017). Snowmelt controls on concentration-discharge relationships and the balance of oxidative and acid-base weathering fluxes in an alpine catchment, east river, Colorado. *Water Resources Research*, 53(3), 2507–2523. <https://doi.org/10.1002/2016wr019724>
- Winter, C., Lutz, S. R., Musolff, A., Kumar, R., Weber, M., & Fleckenstein, J. H. (2021). Disentangling the impact of catchment heterogeneity on nitrate export dynamics from event to long-term time scales. *Water Resources Research*, 57(1), e2020WR027992. <https://doi.org/10.1029/2020wr027992>
- Xu, Z., Molins, S., Dwivedi, D., Özgen-Xian, I., Steefel, C. (2022). ATS (Advanced Terrestrial Simulator) integrated hydrology and reactive transport model output in Copper Creek, Colorado. Watershed Function SFA, ESS-DIVE repository. [Dataset]. <https://data.ess-dive.lbl.gov/datasets/doi:10.15485/1877377>
- Yang, J., Heidbüchel, I., Musolff, A., Reinstorf, F., & Fleckenstein, J. H. (2018). Exploring the dynamics of transit times and subsurface mixing in a small agricultural catchment. *Water Resources Research*, 54(3), 2317–2335. <https://doi.org/10.1002/2017wr021896>
- Zhi, W., & Li, L. (2020). The shallow and deep hypothesis: Subsurface vertical chemical contrasts shape nitrate export patterns from different land uses. *Environmental Science & Technology*, 54(19), 11915–11928. <https://doi.org/10.1021/acs.est.0c01340>
- Zhi, W., Li, L., Dong, W., Brown, W., Kaye, J., Steefel, C., & Williams, K. H. (2019). Distinct source water chemistry shapes contrasting concentration-discharge patterns. *Water Resources Research*, 55(5), 4233–4251. <https://doi.org/10.1029/2018wr024257>