

Water Resources Research

RESEARCH ARTICLE

10.1029/2025WR041597

Special Collection:

Key Hydrological Processes and Its Controlling Factors in Terrestrial Ecosystems

Key Points:

- Hydroclimatic events, especially snowmelt, increase carbonate weathering and soil-derived CO₂ drawdown in shale-underlain hillslopes
- Steeper slopes enhance the vertical transport of reactants, increasing dolomite and pyrite dissolution rates and enhancing CO₂ drawdown
- Shale weathering acts as a short-term CO₂ sink but is a long-term CO₂ source due to sulfuric acid-driven carbonate weathering

Supporting Information:

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

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Citation:

Stolze, L., Dwivedi, D., Steefel, C., Molins, S., Dong, W., Beutler, C., et al. (2026). Model-based interpretation of solute exports and carbon partitioning during shale weathering in a mountainous hillslope. *Water Resources Research*, 62, e2025WR041597. <https://doi.org/10.1029/2025WR041597>

Received 9 JUL 2025

Accepted 17 FEB 2026

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Model-Based Interpretation of Solute Exports and Carbon Partitioning During Shale Weathering in a Mountainous Hillslope

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Abstract The weathering of sedimentary rocks in high-elevation catchments influences freshwater quality and the global carbon cycle. While individual biogeochemical mechanisms involved in this process are relatively well understood, quantifying their contributions to solute export and carbon fluxes under natural, transient conditions remains challenging. Here, we implement a numerical multidimensional and multiphase model to simulate coupled hydrological and biogeochemical processes in a shale-underlain, snow-dominated hillslope in the Rocky Mountains, Colorado. The model captures the dynamic interplay between soil respiration, mineral weathering, and climate-driven hydrological forcing, reproducing observed soil CO₂ dynamics, groundwater chemistry, and subsurface flow. Our results reveal that seasonal snowmelt enhances carbonate weathering by promoting the infiltration of CO₂-rich water to depth, while pyrite oxidation is primarily sensitive to low water saturation that facilitates O₂ diffusion through the regolith. Topography modulates the spatial distribution of shale weathering, as steeper slopes enhance lateral drainage, favoring the delivery of reactants to greater depths. While shale weathering at our site acts as a transient carbon sink, with silicates and carbonates buffering acidity and promoting atmospheric CO₂ consumption (1% of soil-derived CO₂), the exported dissolved inorganic carbon is predominantly geogenic (~73%). Consequently, when accounting for long-term marine carbonate precipitation. The current weathering regime represents a net source of carbon to the atmosphere. The oxidation of pyrite and petrogenic organic carbon together release approximately 0.9 mol·m⁻²·yr⁻¹ of CO₂. Our findings highlight the role of topography, hydroclimate, and the coupling between acid-base reactions in shaping the carbon balance and the solute exports in mountainous critical zones.

Plain Language Summary The breakdown of rocks, or weathering, in mountain regions affects both water quality and the Earth's carbon cycle. Sedimentary rocks, such as shales, are important because they contain large amounts of carbon. However, it is difficult to assess how much weathering contributes to the movement of carbon in and out of the ground, since it involves many interconnected reactions influenced by changing environmental conditions. In this study, we use a computer model to understand how water, gases, and minerals interact beneath a snow-covered shale hillslope in Colorado and to calculate the contributions of the different reactions. The melting of snow in spring greatly affects how rocks break down and how CO₂ moves deeper in the ground, where it reacts with carbonate and silicate minerals. Steeper slopes enhance water movement, which accelerates weathering. Overall, shale weathering temporarily removes CO₂ from the atmosphere, making it a short-term carbon sink. However, over long times, it releases more CO₂ than it stores because much of the carbon comes from the rocks.

1. Introduction

Chemical weathering in mountainous watersheds regulates headwater quality (Arora et al., 2020; Carroll et al., 2018; Manning et al., 2024; Tipper et al., 2006; Todd et al., 2012) and governs carbon partitioning between the subsurface and the atmosphere (Bufe et al., 2021; Gaillardet et al., 1999; Horan et al., 2019; Roylands et al., 2022). At global scales, this process plays a pivotal role in determining freshwater availability (Immerzeel et al., 2020; Li et al., 2023) and long-term climate trajectory (Beaulieu et al., 2012; Brantley et al., 2023; Bufe et al., 2024; Hilton & West, 2020; Maher & Chamberlain, 2014; Torres et al., 2014; Zondervan et al., 2023). Accordingly, understanding the interactions between subsurface biogeochemical and hydrological processes is critical for modeling Earth's evolution, predicting watershed responses to external forcing, and mitigating the

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impacts of anthropogenic perturbations, including climate change (Brooks et al., 2015; Krause et al., 2017; Li et al., 2023; Manning et al., 2024; Siirila-Woodburn, 2021; Todd et al., 2012).

Hillslopes are prominent geomorphic features that control water residence time and dictate the hydrochemical behavior of high-elevation catchments (Carroll et al., 2018; Jencso et al., 2009; Maher, 2011; McGuire et al., 2005; Torres et al., 2015). Over geological timescales, weathering transforms bedrock into regolith and soil, producing vertical gradients in organic matter content, mineral reactivity, porosity, and permeability near the surface of hillslopes (Brantley et al., 2017; Lebedeva & Brantley, 2020; Maher et al., 2009; Maher & Navarre-Sitchler, 2019; Navarre-Sitchler et al., 2019; Rempé & Dietrich, 2014; Stolze et al., 2023b). These gradients create strong contrasts in hydrogeological and biogeochemical properties, which in turn influence modern biogeochemical fluxes.

Substantial efforts have focused on understanding how subsurface structure and climate forcing modulate flow, transport, and reaction pathways within hillslopes (Brantley et al., 2017; Golla et al., 2022; Hopp & McDonnell, 2009; McGuire & McDonnell, 2010; Salve et al., 2012; Thiros et al., 2024; Uhlemann et al., 2024). For example, numerous studies have examined the interplay between depth-distributed chemical signatures and subsurface hydrologic connectivity in determining solute exports (e.g., Herndon et al., 2018; Stewart et al., 2021; Tokunaga et al., 2022; Winnick et al., 2017). These studies show that the relative contributions of different subsurface horizons (i.e., soil, saprolite, bedrock) to stream solute fluxes vary with hydrologic conditions. During baseflow, exports primarily reflect the biogeochemical composition of deeper horizons due to limited lateral connectivity in the variably saturated zone. In contrast, during storm events or snowmelt, rising water tables activate shallower flow-paths, increasing the contribution of near-surface horizons (Herndon et al., 2018; McGuire & McDonnell, 2010; Stewart et al., 2021; Tokunaga et al., 2022).

While this conceptual representation of shallow versus deep end-members helps explain the integrated hydrogeochemical behavior of many catchments (Botter et al., 2020; Torres et al., 2015; Zhi et al., 2019), it does not capture the full intricacy of terrestrial fluxes. Weathering involves dynamic, spatially heterogeneous interactions among biological, hydrological, and geochemical processes, all of which respond to climate forcing. For example, soil respiration generates carbonic acid, a key weathering agent, and exhibits strong seasonality tied to precipitation and temperature (Calmels et al., 2014; Carbone et al., 2011; Davidson & Janssens, 2006; Manzoni et al., 2016; Moyano et al., 2013; Winnick et al., 2020). Moreover, the downward percolation of water and the diffusion of gases modulate the delivery of atmospheric and biogenic reactants to weathering zones (Ameli et al., 2016; Brantley et al., 2017; Xiao et al., 2021). Consequently, hydroclimatic fluctuations shape weathering dynamics by altering flow paths and fluid phase distributions (Ahmadi et al., 2024; Angert et al., 2015; Hodges et al., 2021; Olshansky et al., 2019; Sanchez-Canete et al., 2018; Stolze et al., 2024; Tune et al., 2020), while temperature variations influence the thermodynamics and kinetics of the weathering reactions (Brantley et al., 2023; Roylands et al., 2022; Soulet et al., 2021).

Much of our understanding of hillslope weathering comes from analyses of stream chemistry and discharge relationships (i.e., Arora et al., 2020; Carroll et al., 2018; Godsey et al., 2009; Pinder & Jones, 1969; Tipper et al., 2006; Winnick et al., 2017). While such analyses are valuable for inferring solute sources and broad-scale processes, streamwater integrates flow paths that experience considerable spatiotemporal variations, limiting a detailed mechanistic understanding of weathering processes (Herndon et al., 2018; Knapp et al., 2022; Slosson et al., 2025; Torres & Baronas, 2021). To develop generalizable descriptions of watershed hydrogeochemical functioning (Beaulieu et al., 2012; Godderis et al., 2006; Kerins et al., 2024; Stewart et al., 2024; Xu et al., 2022; Zhi et al., 2019), there is a pressing need for intermediate-scale studies that bridge watershed and laboratory-scale observations, target specific landscape components and provide direct insights into subsurface processes.

This is especially true in catchments underlain by sedimentary rocks undergoing active exhumation and erosion. These rocks often host a variety of reactive mineral phases (e.g., carbonates, sulfides, and petrogenic organic matter) that weather rapidly upon exposure to atmospheric oxygen (O_2) and carbon dioxide (CO_2) (Fox et al., 2022; Keller & Bacon, 1998; Roylands et al., 2022; Soulet et al., 2021). Therefore, these reactions frequently dominate solute exports (Arora et al., 2020; Carroll et al., 2018; Manning et al., 2024; Winnick et al., 2017) and significantly affect terrestrial carbon fluxes (Amiotte Suchet et al., 2003; Bufe et al., 2021; Gaillardet et al., 2019; Hilton & West, 2020; Petsch et al., 2005; Zondervan et al., 2023). In particular, carbonate and silicate minerals favor the dissolution of atmospheric and/or biogenic CO_2 in groundwater by buffering carbonic acid (Calmels et al., 2014; Hodges et al., 2021; Jin et al., 2014), whereas the oxidative weathering of

sulfide minerals and petrogenic OM represent major pathways of CO₂ release into the atmosphere (Beaulieu et al., 2011; Bufer et al., 2021; Hemingway et al., 2018; Hilton et al., 2021; Torres et al., 2014).

Despite detailed knowledge of individual weathering reactions, their relative contributions in complex natural settings remain poorly constrained. This is in part due to the transient nature of near-surface environments and the nonlinear interactions among acid-sensitive and/or redox-sensitive biogeochemical mechanisms that complicate the quantitative understanding of these systems (Jin et al., 2014; Maher et al., 2009; Muniruzzaman et al., 2021; Roylands et al., 2022; Stolze et al., 2022). To better quantify biogeochemical fluxes during sedimentary rock weathering, process-based models capable of describing hydrological, multiphase transport, and biogeochemical processes under realistic environmental conditions are needed. In particular, numerical models honoring rigorous reactive transport principles provide a robust framework for integrating these processes and for analyzing how physical transport and geochemical mechanisms shape terrestrial fluxes (Godderis et al., 2019; Li et al., 2017; Maher & Navarre-Sitchler, 2019; Rolle et al., 2025; Steefel et al., 2019).

A few studies have applied reactive transport models to investigate sedimentary rock weathering (Bao et al., 2017; Bolton et al., 2006; Heidari et al., 2017; Maher et al., 2009; Stolze et al., 2023b, 2024). However, these models have largely remained limited to one-dimensional representations and are primarily designed to simulate the evolution of near-surface conditions over millennia. Some two-dimensional models have explored hillslope-scale processes, such as the co-evolution of weathering fronts and hydrological pathways (Anderson et al., 2018; Dontsova et al., 2009; Harman & Cosans, 2019; Lebedeva & Brantley, 2020), as well as the sensitivity of solute exports to mineral reactivity, flow path distribution, and fluid residence time (Ameli et al., 2017; Xiao et al., 2021). Yet, many of these efforts simplify critical aspects of subsurface processes, limiting their ability to provide a mechanistic understanding of sedimentary rock weathering. In particular, existing hillslope models often rely on simplified biogeochemical reaction networks that do not capture the full range of interactions among multiple mineral phases and dissolved species. The influence of transient soil respiration is generally omitted despite its strong influence on weathering rates via carbonic acid generation. Furthermore, most models assume steady-state conditions, neglecting the impact of transient climatic forcing, and do not incorporate a full multiphase treatment, including partially-saturated flow and gas exchange. These omissions are significant as such processes strongly govern the availability of weathering agents in the near-surface. As a result, a comprehensive, process-based description of sedimentary rock weathering and associated biogeochemical fluxes in mountainous hillslopes is still lacking.

In this study, we address how transient near-surface processes and climatic variability shape the weathering of sedimentary rocks along a mountainous hillslope and regulate both aqueous solute exports to the adjacent floodplain and CO₂ flux partitioning between the subsurface and atmosphere. Our focus is on shale, a widespread sedimentary rock that strongly influences watershed-scale biogeochemical fluxes (Arora et al., 2020; Fox et al., 2022; Winnick et al., 2017) and plays a central role in the global cycling of carbon (Amiotte Suchet et al., 2003; Petsch et al., 2005). We consider a well-instrumented hillslope located in a snow-dominated mountainous watershed of Colorado and underlain by Cretaceous Mancos shale, a formation rich in nitrogen and broadly distributed across the Rocky Mountains. Using a comprehensive data set that capture the hydrological, biological, and geochemical conditions of the hillslope, we develop a multidimensional multiphase reactive transport model to simulate the weathering of shale under transient conditions and the associated biogeochemical fluxes along the hillslope. This model enables us to quantitatively evaluate the individual and coupled influence of the physical, biological, and geochemical processes on the hydrochemical fluxes. To disentangle these complex interactions, we perform targeted sensitivity analyses that systematically test the influence of key biogeochemical reactions, hydroclimatic transients, and hillslope topography on solute exports and carbon partitioning.

2. Study Site and Data Set Description

The hillslope is located in the East River watershed, which is part of the Rocky Mountains in Colorado, USA. This high-elevation watershed serves as a testbed for the Watershed Science Focus Area (SFA), led by Lawrence Berkeley National Laboratory, to advance our understanding of the ecological, hydrological, and biogeochemical functioning of mountainous watersheds, as well as the response and resilience of headwater catchments to climate (Dwivedi et al., 2022; Hubbard et al., 2018). This section outlines key characteristics of the hillslope and summarizes the data collection that informed the model implementation. Instrumentation, field sampling, and

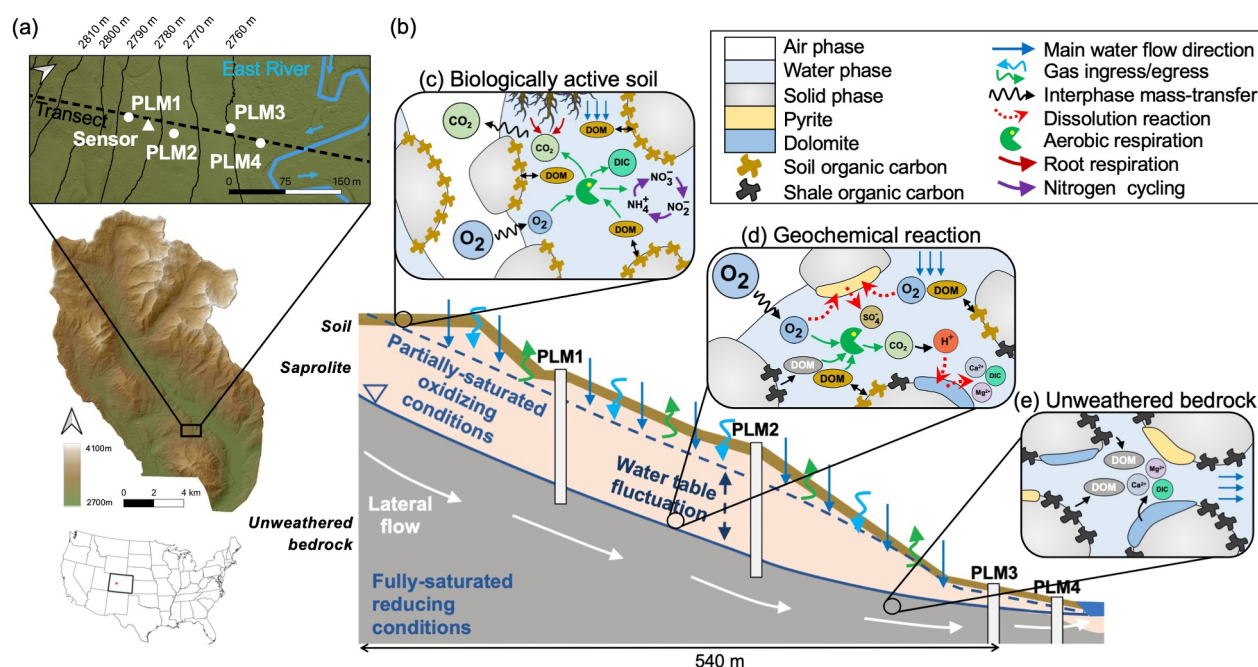


Figure 1. Schematic illustration of the hillslope: (a) Location of the East River Watershed and topographic map showing the positions of the monitoring wells (PLM1–4 represented as dots) and the CO_{2(g)} flux sensor (represented as a triangle); (b) conceptual cross section view showing the groundwater flow, the geochemical reaction fronts of the most reactive minerals (i.e., pyrite and dolomite), the locations of the monitoring wells, and the exchange of gases between the atmosphere and the subsurface; (c)–(e) zoom-in panels showing the conceptual model for the key biogeochemical reactions and the main water flow direction in the three functional zones making up the hillslope: the biologically active soil, the geochemical reaction front, and the unweathered shale.

measurements relevant to this study have been described in detail elsewhere (Sorensen et al., 2020; Stolze et al., 2023b, 2024; Tokunaga et al., 2019, 2022; Wan et al., 2021, 2024a, 2024b).

The hillslope faces northeast with an average slope of 28% and drains into a floodplain along the East River. Its elevation ranges between 2,760 m and 2,910 m over a total length of 540 m. The climate is continental subarctic, characterized by a mean annual temperature of 1°C, with long, cold winters and short, cool summers. The average annual precipitation between 2016 and 2020 was ~850 mm. About half of the total annual precipitation occurs as snowfall and the total annual evapotranspiration (ET) amounts to 500 mm. Snow cover generally persists from mid-November to June, and rising temperatures drive snowmelt from April to June, resulting in rapid change in the hydrological conditions and increasing solute exports to streams (Arora et al., 2020; Carroll et al., 2018). The hillslope features a relatively uniform 1-m-thick soil horizon underlain by Mancos shale. The dominant vegetation is typical of lower montane meadows, comprising grasses, forbs, and shrubs with roots primarily concentrated within the top 20 cm of soil. The regolith thickness ranges between 2 and 4 m, closely corresponding to the lowest position of the water table, which lies deeper in upslope areas.

In September 2016, a 140-m transect aligned to the groundwater flow direction and consisting of three monitoring wells (PLM1 to PLM3 with PLM3 located at the toe slope) was installed in the lower portion of the hillslope to characterize the hydrological and biogeochemical properties of the subsurface and to monitor the hydrochemical exports (Tokunaga et al., 2019; Wan et al., 2021). Each well was equipped to a depth of 10 m with sensors to measure variations in water pressure, water content, matric potential, and temperature. In addition, the wells included depth-resolved pore gas and water samplers to monitor the temporal and spatial evolution of the hydrochemical conditions. A similar monitoring well (PLM4) was installed in the floodplain, 50 m from the East River but could only be operated to a depth of 1.28 m. Figure 1a shows the locations of the monitoring wells.

Water table time series were acquired in the four wells from November 2016 to October 2021 (Tokunaga et al., 2019). Discrete solid phase sampling and analyses were carried out down to a depth of 10 m to map the distribution of the bulk biogeochemical properties and to characterize the spatial extent of the weathering front (Stolze et al., 2023b; Wan et al., 2021). Core samples were separated by intervals ranging from 0.1 to 3 m, with spacing between samples progressively increasing at greater depths. The samples were analyzed for bulk

mineralogy (i.e., mineral mass fractions via X-ray diffraction), solid-associated total organic carbon (TOC), and total organic nitrogen across the soil, saprolite, and bedrock layers.

Pore water and gas samples were collected at multiple depths on a weekly to monthly basis from November 2016 to October 2021. This was achieved using nested suction lysimeters installed in the wells at depths ranging from 0.2 to 7.8 m (Wan et al., 2021, 2024a, 2024b). The vertical spacing between sampling ports increased with depth, with $\Delta z = 0.2$ m within the upper 1 and $0.7 \text{ m} \leq \Delta z \leq 3.58$ m below 1 m. Additional gas samples were collected from lysimeters placed near the PLM transect at depths of 25, 91, and 152 cm below ground surface (Stolze et al., 2023b). Gas samples were collected year-round, while water samples were collected from spring to fall. A higher sampling frequency was adopted from spring to late summer (weekly) to capture the impact of snowmelt on the hydrochemical conditions. Water samples were analyzed for major cations, major anions, trace elements, dissolved organic carbon, and dissolved inorganic carbon (DIC) (Wan et al., 2021, 2024a, 2024b). Complementary to the measured $\text{CO}_{2(g)}$ concentrations in the gas phase, daily measurements of $\text{CO}_{2(g)}$ flux from the soil to the atmosphere (Stolze et al., 2024) as well as the seasonal change in soil microbial biomass reported by Sorensen et al. (2020) were used to characterize the impact of transient climate forcing on soil respiration. pH profiles were measured in the monitoring wells in May 2019.

3. Modeling Approach

3.1. Conceptual Model of Shale Weathering in a High Elevation Hillslope

The infiltration of meteoric water, ingress of atmospheric gases, and biological activity near the Earth's surface collectively drive the exchange of CO_2 and O_2 between the atmosphere and the subsurface, promote chemical weathering, and regulate solute exports from hillslopes (Maher & Navarre-Sitchler, 2019). Figures 1b–1d illustrate our conceptual model of the key processes governing biogeochemical fluxes within shale-dominated hillslopes, highlighting three characteristic zones of the shallow subsurface. Each zone exhibits a distinct nexus of hydrological flow, physical transport, and biogeochemical mechanisms.

In the biologically active soil (Figure 1c), respiration by heterotrophic microbes and autotrophic plant roots generates substantial CO_2 (Carbone et al., 2011; Davidson & Janssens, 2006; Keller & Bacon, 1998; Winnick et al., 2020). Although this layer is depleted in the most reactive shale minerals (dolomite and pyrite in our case), it is enriched in OM and remains unsaturated for most of the year. Low water saturation enhances gas exchange with the atmosphere, maintaining oxic conditions that support microbial decomposition of surface-derived OM (Moyano et al., 2013). Soil respiration is strongly modulated by climate forcing across environments including snow-dominated mountainous watersheds (Rindt et al., 2023; Sorensen et al., 2020; Stolze et al., 2024; Winnick et al., 2020). Pulse-wetting events driven by snowmelt or rainfall stimulate microbial activity by increasing access to DOM (Carbone et al., 2011; Manzoni et al., 2016), while variations in temperature and water saturation control seasonal root respiration dynamic (Winnick et al., 2020).

Although most CO_2 generated in the soil is released back to the atmosphere, a fraction percolates into deeper layers and influences geochemical reactions in the underlying regolith. Within the geochemical reaction front (Figure 1d), silicate and carbonate minerals consume CO_2 and buffer porewater acidity, contributing to long-term atmospheric CO_2 drawdown (Heidari et al., 2017; Jin et al., 2014; Olshansky et al., 2019; Stolze et al., 2024). Concurrently, oxygen penetration into the subsurface promotes the oxidative weathering of petrogenic OM (referred to as georespiration in our study; Keller & Bacon, 1998) and pyrite. These oxidation reactions generate CO_2 and represent important sources of atmospheric emissions at regional to global scales (Hilton et al., 2021; Torres et al., 2014). Pyrite oxidation, in particular, produces sulfuric acid, which lowers pH, enhances carbonate dissolution, and influences the speciation and fate of DIC.

These biogeochemical reactions are tightly coupled with hydrological transients. Variations in water fluxes affect pH and redox conditions by modulating the transport of reactive gases and solutes. For example, higher water saturation restricts gas diffusion due to the much lower diffusivity of CO_2 and O_2 in water compared to air (Ahmadi et al., 2024). Conversely, percolating water enhances the downward advective transport of dissolved species, delivering acids and electron donors to mineral surfaces. However, as infiltration increases and lateral flow paths develop, vertical transport may be reduced, altering the magnitude and direction of the biogeochemical fluxes. Additionally, subsurface temperatures influence reaction thermodynamics and kinetics, thus affecting the

rates of mineral transformation and hydrochemical fluxes (Brantley et al., 2023; Davidson & Janssens, 2006; Soulet et al., 2021).

In the deeper, permanently saturated zone (Figure 1e), chemical weathering is limited and shale is not significantly altered. High water content inhibits gas diffusion from the surface, and most of the dissolved CO₂ and O₂ is consumed in the overlying regolith. Lateral flow dominates in this zone, but the overall flow rate remains low due to the low porosity and permeability of the parent rock.

These three zones form an integrated system where hydrologic forcing, gas exchange, and biogeochemical processes collectively shape terrestrial hydrochemical fluxes. To simulate these fluxes at the study hillslope, we implement a numerical model that mathematically describes the dynamic coupling between water flow, multi-phase transport, and biogeochemical reactions. The model explicitly represents the geomorphological structure of the hillslope, including soil, saprolite, and bedrock by distributing the biogeochemical and physical properties over a continuous two-dimensional domain.

3.2. Biogeochemical Model

The reaction network integrated into our model is based on two recent studies that quantitatively examined (a) the long-term weathering and development of regolith in shale (Stolze et al., 2023b) and (b) the impact of climatic events on the connection between soil respiration and chemical weathering (Stolze et al., 2024). The conceptual model for the biogeochemical processes controlling the weathering of shale and the partitioning of carbon between the atmosphere and the subsurface includes: (a) the primary components of soil respiration (i.e., the mineralization of soil OM and the autotrophic respiration of roots), (b) the mineralization of petrogenic OM associated with shale, (c) the growth and decay of microbial biomass, (d) the oxidative dissolution of pyrite and the subsequent precipitation of iron (hydr)oxides, (e) the weathering of carbonate, silicate, and clay minerals, and (f) the exchange of cations at solid surfaces. Table 1 lists the kinetically-controlled biogeochemical reactions defined in the model.

We defined two pools of OM to represent the differing reactivities of soil OM and the more recalcitrant shale-associated OM. Both pools consist of solid-associated and dissolved OM (SOM and DOM, respectively). Soil DOM (DOM_{soil}) accounts for (a) the DOM derived from litter that percolates from the ground surface during infiltration events, (b) the DOM mobilized from solid-associated OM (SOM_{soil}) via depolymerization, and (c) the exudates released from roots. The DOM derived from litter is incorporated by specifying a concentration of DOM_{soil} in the infiltrating water (Table S7 in Supporting Information S1). Mobilization of DOM_{soil} from SOM_{soil} is described as a two-step mechanism in order to simulate the low accessibility of microorganisms to labile DOM_{soil} under dry conditions (Manzoni et al., 2016; Moyano et al., 2013). First, enzymatic catalyzed depolymerization from SOM_{soil} and the formation of an intermediate and microbially-inaccessible pool of dissolved organic matter DOM_{soil,0} was described using a 1st order rate expression:

$$R_{\text{SOM}_{\text{soil}}} = k_{\text{SOM}_{\text{soil}}} A_{\text{SOM}_{\text{soil}}} \quad (1)$$

where $k_{\text{SOM}_{\text{soil}}}$ [mol·m⁻²·s⁻¹] is the rate constant, $A_{\text{SOM}_{\text{soil}}}$ [m²] is the exposed surface area of SOM. DOM_{soil,0} is assumed immobile and non-reactive.

The mobility and bioavailability of labile DOM_{soil} increases upon rewetting. Therefore, the conversion of DOM_{soil,0} to DOM_{soil} was computed with a dependency on the liquid saturation (n_w [-]; Liu et al., 2019; Stolze et al., 2024; Zhang et al., 2022):

$$R_{\text{DOM}_{\text{soil}}} = k_{\text{DOM}_{\text{soil}}} C_{\text{DOM}_{\text{soil},0}} f(n_w) \quad (2)$$

where $k_{\text{DOM}_{\text{soil}}}$ [mol·mol⁻¹·s⁻¹] is the rate constant and $C_{\text{DOM}_{\text{soil},0}}$ [mol] is the amount of DOM_{soil,0}. $f(n_w)$ expresses the dependency of DOM_{soil} release from SOM on the liquid saturation:

Table 1

Biogeochemical Reactions Simulated in the Reactive Transport Model

Processes	Reaction stoichiometry
Aqueous reactions	
Aerobic respiration ^a	$(\text{CH}_2\text{O})(\text{NH}_3)_x + \text{O}_2 = \text{H}^+ + \text{HCO}_3^- + x\text{NH}_3$
Ferrous iron oxidation	$\text{Fe}^{2+} + 0.25\text{O}_2 + \text{H}^+ = \text{Fe}^{3+} + 0.5\text{H}_2\text{O}$
Biomass	
Growth	$(\text{CH}_2\text{O})(\text{NH}_3)_x + (y - x)\text{NH}_4^+ = X + (y - x)\text{H}^+$
Minerals	Reaction stoichiometry
Mineral phase dissolution/precipitation reactions	
Dolomite	$\text{MgCa}(\text{CO}_3)_2 + 2\text{H}^+ = \text{Mg}^{2+} + \text{Ca}^{2+} + 2\text{HCO}_3^-$
Albite ^b	$\text{Na}_{0.95}\text{K}_{0.05}\text{AlSi}_3\text{O}_8 + 4\text{H}^+ + 4\text{H}_2\text{O} = \text{Al}^{3+} + 0.95\text{Na}^+ + 0.05\text{K}^+ + 3\text{H}_4\text{SiO}_4$
Quartz	$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$
Pyrite	$\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$
Iron (hydr)oxide	$\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{FeOOH} + 3\text{H}^+$
Calcite	$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3$
Chlorite ^c	$\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 16\text{H}^+ = 5\text{Fe}^{2+} + 2\text{Al}^{3+} + 3\text{H}_4\text{SiO}_4 + 6\text{H}_2\text{O}$
Illite	$\text{Al}_{2.85}\text{K}_{0.85}\text{Si}_{3.15}\text{O}_{10}(\text{OH})_2 + 9.4\text{H}^+ + 0.6\text{H}_2\text{O} = 2.85\text{Al}^{3+} + 0.85\text{K}^+ + 3.15\text{H}_4\text{SiO}_4$
Organo-mineral interactions	
Soil OM depolymerization	$\text{SOM}_{\text{soil}} \rightarrow \text{DOM}_{\text{soil},0}$
Soil DOM release	$\text{DOM}_{\text{soil},0} \rightarrow \text{DOM}_{\text{soil}}$
Shale DOM release	$\text{SOM}_{\text{shale}} = \text{DOM}_{\text{shale}}$

Note. DOM is defined with the general stoichiometry $(\text{CH}_2\text{O})(\text{NH}_3)_x$ with x the N:C ratios equal to 0.07 and 0.1 for soil-derived and shale-associated OM, respectively. y is the N/C ratio of biomass and equal to 0.07. ^aAerobic respiration was defined for soil and shale OM. ^bAlbite was assumed to contain 5% of potassium to reproduce the measured concentration of K^+ . ^cThe stoichiometry of chamosite was adopted based on the XRD analyses showing a Fe^{2+} -rich chlorite.

$$f(n_w) = \begin{cases} f(n_w > n_{1,2}) = \left(\frac{1}{1 + \left(\frac{n_{1,1}}{n_w} \right)^{m_1}} \right) \\ f(n_w \leq n_{1,2}) = \left(\frac{1}{1 + \left(\frac{n_{1,1}}{n_{1,2}} \right)^{m_1}} \right) \end{cases} \quad (3)$$

where $n_{1,1}$, $n_{1,2}$, and m_1 [–] are empirical constants used to express the dependency of the reaction kinetics on the liquid saturation n_w . These parameters were calibrated to reproduce the observed soil respiration data, including $\text{CO}_{2(\text{g})}$ concentrations, surface $\text{CO}_{2(\text{g})}$ flux, and microbial biomass.

Based on the experimental observations of Schillawski and Petsch (2008), the release of $\text{DOM}_{\text{shale}}$ from shale during water-rock interaction was represented as a simple dissolution reaction. The kinetics of the reaction was described based on the transition state theory (Helgeson et al., 1984; Lasaga, 1998):

$$R_{\text{DOM}_{\text{shale}}} = k_{\text{DOM}_{\text{shale}}} A_{\text{SOM}_{\text{shale}}} \left(1 - \frac{C_{\text{DOM}_{\text{shale}}}}{K_{\text{eq,DOM}_{\text{shale}}}} \right) \quad (4)$$

where $k_{\text{DOM}_{\text{shale}}}$ [$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$] is the rate constant, $A_{\text{SOM}_{\text{shale}}}$ [m^2] is the exposed surface area of shale OM, $C_{\text{DOM}_{\text{shale}}}$ [$\text{mol}\cdot\text{L}^{-1}$] is the concentration of dissolved shale organic matter, and $K_{\text{eq,DOM}_{\text{shale}}}$ [–] is the equilibrium constant.

The mineralization of DOM_{soil} and $\text{DOM}_{\text{shale}}$ and the associated production of CO_2 were described using double Michaelis-Menten rate expressions (Van Cappellen & Gaillard, 1996), including a first order dependence on the concentration of microbial biomass and an exponential dependence on the temperature:

$$R_S = \mu_{\text{max},S} X \frac{C_S}{K_{m,S} + C_S} \frac{C_{\text{TEA}}}{K_{m,\text{TEA}} + C_{\text{TEA}}} \exp\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{REF}}}\right)\right) \quad (5)$$

where $\mu_{\text{max},S}$ [$\text{mol}\cdot\text{mol biomass}^{-1}\cdot\text{s}^{-1}$] is the maximum rate of the reaction for substrate S , X [$\text{mol}\cdot\text{m}^{-3}$] is the microbial biomass concentration. C_S and $K_{m,S}$ [$\text{mol}\cdot\text{L}^{-1}$] are the concentration and half-reaction constant of the substrate used in the reaction, respectively. C_{TEA} and $K_{m,\text{TEA}}$ [$\text{mol}\cdot\text{L}^{-1}$] are the concentration and half-reaction constant of the terminal electron acceptor considered in the reaction, respectively. The temperature dependence of the reaction rate was expressed with an Arrhenius relationship where T_{REF} is the reference temperature (298.15 K), R is the gas constant ($8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), E_a [$\text{kJ}\cdot\text{mol}^{-1}$] is the activation energy specific to the reaction. We set E_a equal to $50 \text{ kJ}\cdot\text{mol}^{-1}$ for both soil heterotrophic respiration and the oxidation of shale-associated organic matter. This temperature dependency is equivalent to a Q_{10} value of 2.1 lying in the range of typical values reported for soil organic matter respiration (Davidson & Janssens, 2006) and rock organic matter oxidation (Soulet et al., 2021).

Biomass growth was coupled to the microbially-mediated decomposition of soil and shale organic matter through the definition of anabolic pathways (Molins et al., 2015). The simulated growth yield was assumed constant and calibrated to reproduce the temporal change in microbial biomass concentration in the top 30 cm of soil, as measured at the site by Sorensen et al. (2020) using the chloroform-fumigation extraction method. The stoichiometries of the anabolic pathways account for the different C/N ratio of soil and shale DOM and use ammonium as the nitrogen source (Table 1). Microbial biomass was assumed immobile and the decay of biomass was described via a first-order rate expression $R_d = -k_d X$.

The release of CO_2 and exudates (i.e., DOM_{soil}) associated with root respiration was simulated over the rooting depth (0.2 m) and described by a kinetic rate expression that accounts for the local temperature and liquid saturation conditions (Carbone et al., 2011; Simunek & Suarez, 1993; Winnick et al., 2020):

$$R_{\text{root}} = k \exp\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{REF}}}\right)\right) \frac{1}{1 + \left(\frac{n_2}{n_w}\right)^{m_2}} \quad (6)$$

where k [$\text{mol}\cdot\text{s}^{-1}$] is the rate constant, E_a is the activation energy equal to $75 \text{ kJ}\cdot\text{mol}^{-1}$ (Suarez & Šimůnek, 1993; i.e., equivalent $Q_{10} = 3.1$) and n_2 and m_2 [–] are empirical constants. Two different rate constants k_r and k_{ex} were used to describe the release of CO_2 and exudates, respectively.

The model includes eight abiotic dissolution/precipitation reactions for the solid mineral phases identified in the shale (i.e., dolomite, pyrite, calcite, iron (hydr)oxide, albite, quartz, chlorite, and illite; Table 1). Silicate, carbonate, and clay minerals reactions were simulated using transition state theory rate law and their kinetic rate expressions account for pH and CO_2 concentration using parallel rate expressions (Palandri & Kharaka, 2004):

$$R_m = A_m \left(\begin{aligned} &k_{m,\text{H}_2\text{O}} \exp\left(\frac{-E_{a,m,\text{H}_2\text{O}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{REF}}}\right)\right) + \\ &k_{m,\text{H}^+} [\text{H}^+]^{x_{1,m}} \exp\left(\frac{-E_{a,m,\text{H}^+}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{REF}}}\right)\right) + \\ &k_{m,\text{OH}^-} [\text{OH}^-]^{x_{2,m}} \exp\left(\frac{-E_{a,m,\text{OH}^-}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{REF}}}\right)\right) + \\ &k_{m,\text{CO}_2(\text{aq})} [\text{CO}_2(\text{aq})]^{x_{3,m}} \exp\left(\frac{-E_{a,m,\text{CO}_2(\text{aq})}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{REF}}}\right)\right) \end{aligned} \right) \left(1 - \frac{\text{IAP}_m}{K_{\text{eq},m}}\right) \quad (7)$$

where A_m [m^2] is the total exposed surface area of the mineral m , $k_{m,\text{H}_2\text{O}}$, k_{m,H^+} , k_{m,OH^-} , and $k_{m,\text{CO}_2(\text{aq})}$ [$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$] are the effective rate constants for the reaction accounting for its dependency to water, protons, hydroxide, and/or carbon dioxide at 25°C, $E_{a,m,\text{H}_2\text{O}}$, E_{a,m,H^+} , E_{a,m,OH^-} , and $E_{a,m,\text{CO}_2(\text{aq})}$ [$\text{kJ}\cdot\text{mol}^{-1}$] are the respective activation energies to account for the temperature dependency of the reaction, IAP_m and $K_{\text{eq},m}$ [–] are the ion activity product and equilibrium constant of the reaction, respectively. The quantities in brackets (e.g., $[\text{H}^+]$, $[\text{OH}^-]$) represent the activities of dissolved species.

The oxidative dissolution of pyrite was assumed abiotic and driven by the presence of oxygen. We used the empirical rate law proposed by Williamson and Rimstidt (1994) that accounts for the local pH conditions and concentration of oxygen:

$$R_{\text{pyr},\text{O}_2} = k_{\text{pyr},\text{O}_2} A_{\text{pyr}} [\text{O}_2]^{x_{\text{pyr},1}} [\text{H}^+]^{x_{\text{pyr},2}} \quad (8)$$

where $k_{\text{pyr},\text{O}_2}$ [$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$] is the rate constant, A_{pyr} [m^2] is the total exposed surface area of pyrite, $x_{\text{pyr},1}$ and $x_{\text{pyr},2}$ [–] are exponents.

The oxidation of ferrous iron generated by the dissolution of pyrite and chlorite to ferric iron upon reaction with dissolved oxygen was kinetically controlled according to the rate (Singer & Stumm, 1970):

$$R_{\text{Fe}} = k_{\text{Fe}} [\text{Fe}^{2+}] [\text{O}_2] [\text{H}^+]^{-2} \quad (9)$$

where k_{Fe} [$\text{mol}\cdot\text{s}^{-1}$] is the rate constant. The subsequent precipitation of ferrous iron into iron (hydr)oxide was described with a rate expression accounting for the degree of saturation:

$$R_{\text{FeO}} = k_{\text{FeO}} A_{\text{FeO}} \left(1 - \frac{\text{IAP}_{\text{FeO}}}{K_{\text{eq,FeO}}}\right) \exp\left(\frac{-E_{a,\text{FeO}}}{RT}\right) \quad (10)$$

where k_{FeO} [$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$] is the rate constant, A_{FeO} [m^2] is the total exposed surface area of iron (hydr)oxide, IAP_{FeO} , and $K_{\text{eq,FeO}}$ [–] are the ion activity product and equilibrium constant of the reaction, $E_{a,\text{FeO}}$ [$\text{kJ}\cdot\text{mol}^{-1}$] is the activation energy of the reaction. For this reaction, we specifically considered the thermodynamic and kinetic properties of goethite.

Note that our model represents chlorite dissolution via a congruent mechanism that releases Fe(II). However, recent work has shown that chlorite weathering in the field can be incongruent, initiated by the oxidation of structural Fe(II) followed by interlayer dissolution (Liao et al., 2022). While our current framework captures the redox control on the overall reaction via the oxidation of Fe(II) in the aqueous phase, it does not explicitly represent this stepwise mechanism. Developing kinetic formulations that move beyond traditional Transition State Theory to more accurately capture such complex mineral dissolution pathways remains an important area for future research.

The model parameters describing the soil respiration and DOM mobilization, except the activation energies (Equations 1–6), were calibrated to reproduce the seasonal change in microbial biomass measured in soil, the temporally varying flux of $\text{CO}_2(\text{g})$ emitted to the atmosphere, as well as the $\text{CO}_2(\text{g})$ concentrations and DOM concentrations measured in the subsurface (Stolze et al., 2024). In contrast, the thermodynamic parameters, including equilibrium constants and activation energies, as well as kinetic rate constants controlling the mineral reactions were taken from the literature. Model parameters used to simulate the biogeochemical processes as well as details regarding ion exchange reactions and cation exchange capacity are reported in Section S5 in Supporting Information S1.

3.3. Variably Saturated Flow and Reactive Transport

The flow of water in the partially-saturated subsurface was simulated by solving the Richards' equation (Bandai et al., 2024; Richards, 1931):

$$\theta_t \frac{\partial n_w(h)}{\partial t} = \nabla \cdot \left[\frac{K^* \rho g}{\mu} k_r(h) (\nabla h - 1) \right] + q_s \quad (11)$$

where θ_t [–] is the porosity, n_w [–] is the water saturation (i.e., $n_w = 1 - n_g$ with n_g the gas phase saturation), h [m] is the pressure head, z [m] is the vertical coordinate, K^* [m²] is the intrinsic permeability of the porous medium, ρ [kg·m^{−3}], g [m·s^{−2}], and μ [kg·m^{−1}·s^{−1}] are the water density, the gravitational acceleration, and the water viscosity, respectively, k_r [–] is the relative permeability with respect to the water phase, and q_s [s^{−1}] is a source/sink term describing water input through infiltration and removal via evapotranspiration.

The water retention and conductivity properties of the subsurface were described with the van Genuchten-Mualem model which combines the van Genuchten saturation function (Equation 12; van Genuchten, 1980) and the Mualem relative permeability function (Equation 13; Mualem, 1976):

$$\frac{n_w - n_{w, \text{res}}}{1 - n_{w, \text{res}}} = \left(\frac{1}{1 + |\alpha h|^{m_{vG}}} \right)^{m_{vG}} \quad (12)$$

where $n_{w, \text{res}}$ [–] is the residual water saturation and α [m^{−1}], n_{vG} [–], and m_{vG} [–] are empirical parameters describing the soil hydraulic properties with $m_{vG} = 1 - 1/n_{vG}$.

$$k_r = n_w^\tau \left(1 - \left(1 - n_w^{\frac{1}{m_{vG}}} \right)^{m_{vG}} \right)^2 \quad (13)$$

where τ [–] is the tortuosity set to 0.5. When the porous medium is saturated (i.e., $h \geq 0$), $n_w = 1.0$ and $k_r = 1.0$.

The reactive transport of solutes involving advection-dispersion for aqueous solutes and diffusion of gas species was described by the governing multicomponent mass conservation equation:

$$\frac{\partial(\theta_w C_{w,i} + \theta_g C_{g,i})}{\partial t} = \nabla \cdot (\theta_w \mathbf{D}_w \nabla C_{w,i}) + \nabla \cdot (\theta_g D_p^g \nabla C_{g,i}) - \nabla \mathbf{q}_w C_{w,i} - \sum_{k=1}^{N_k} v_{i,k} R_k - \sum_{m=1}^{N_m} v_{i,m} R_m \quad (14)$$

where the indices w and g refer to the water and gas phases, respectively, $C_{w,i}$ [mol·L^{−1}] and $C_{g,i}$ [mol·L^{−1}] are the concentrations of component i , $\mathbf{D}_w$ is the diagonal hydrodynamic dispersion tensor and D_p^g [m²·s^{−1}] is the effective diffusion coefficient for gases. θ_w [–] is the total water content ($\theta_w = n_w \cdot \theta_t$ with n_w and θ_t the water saturation and porosity, respectively) and θ_g [–] is the gas-filled porosity ($\theta_g = \theta_t - \theta_w$). $v_{i,k}$ [–] is the stoichiometric coefficient for species i in the aqueous reaction k proceeding at a rate R_k [mol^{−1}·L^{−1}·s^{−1}], $v_{i,m}$ [–] is the stoichiometric coefficient for species i in the mineral transformation reaction m proceeding at a rate R_m [mol^{−1}·L^{−1}·s^{−1}]. $\mathbf{q}_w$ [m·s^{−1}] is the specific discharge described using Darcy's law as defined in the Richards' equation:

$$\mathbf{q}_w = - \frac{K^* \rho g}{\mu} k_r (\nabla h - 1) \quad (15)$$

The diffusive/dispersive transport in the gas and water phases was described using Fick's law. The diagonal hydrodynamic dispersion tensor for aqueous species with principal axes (x and y) parallel and perpendicular to the principal directions of flow was expressed as:

$$\mathbf{D}_w = D_p^w + \alpha_T \bar{V} \delta_{xy} + (\alpha_L - \alpha_T) \frac{\bar{V}_x \bar{V}_z}{\bar{V}} \quad (16)$$

where D_p^w [m²·s^{−1}] is the effective pore water diffusion coefficient, α_L and α_T [m] are the longitudinal and transverse dispersivities, respectively, with $\alpha_L = 0.1$ m (Bao et al., 2017; Jardine et al., 1999; Zhou et al., 2007) and $\alpha_T = 0.1 \times \alpha_L$, $\bar{V}$ [m²·s^{−1}] is the average velocity magnitude, $\bar{V}_x$ and $\bar{V}_z$ [m²·s^{−1}] are the velocity magnitudes, δ_{ij} [–] is the Kronecker delta.

We used the semi-empirical formulation of Millington and Quirk (1961), which accounts for the local tortuosity, to calculate the effective pore diffusion coefficients in the water and gas phases:

$$D_p^w = D_0^w \theta_t^{1/3} n_w^{7/3} \quad (17)$$

$$D_p^g = D_0^g \theta_t^{1/3} n_g^{7/3} \quad (18)$$

where D_0^w [$\text{m}^2\cdot\text{s}^{-1}$] and D_0^g [$\text{m}^2\cdot\text{s}^{-1}$] are the molecular diffusion coefficients for the aqueous and gas species, respectively. The partitioning of chemical species between aqueous and gas phase was calculated using Henry's law:

$$H_i = \frac{C_{g,i}}{C_{w,i}} \quad (19)$$

where H_i is the Henry's law coefficient [–] of species i .

3.4. Spatial Distribution of the Biogeochemical and Physical Properties

The 2-D hillslope model represents the physical and biogeochemical heterogeneity of the subsurface, as characterized at the field site. Figure 2 displays the spatial distribution of the hydrostratigraphic units, mineral concentrations, and organic matter prescribed within the numerical domain.

The hillslope topography was derived from airborne LiDAR data acquired in 2015 with a resolution of 0.5 m and vertical accuracy of 10 cm (USGS's QL1 standard; Wainwright & Williams, 2017). The model domain extends to a depth of 30 m, adopting a terrain-following lower boundary. This configuration was chosen to maintain computational efficiency across the numerous scenarios evaluated. To ensure this boundary condition did not bias our results, we performed a sensitivity analysis comparing the base case model to a configuration with a deeper, horizontal lower boundary. As detailed in Supporting Information S1, this comparison showed no significant differences in the simulated hydrological and geochemical behavior, confirming that the 30 m terrain-following domain adequately captures the dominant processes at our field site.

We defined four hydrostratigraphic units (Figure 2a) considering the soil thickness at the hillslope (~1 m), the shallow subsurface bulk resistivity distribution based on electrical resistivity tomography reported by Falco et al. (2019), and the hydrological model of Tokunaga et al. (2019). In particular, the resistivity distribution was used to delineate the depth marking the limit between the regolith and the bedrock. The zone located between the soil and the bedrock was subdivided into two units: a weathered shale layer and an underlying fractured shale horizon. For each unit, we assumed homogeneous hydrogeological properties, including the empirical parameters defined in the van Genuchten-Mualem model (α , n_{vG} , $n_{w, res}$), and isotropic permeability. These hydrogeological parameters and the thickness of the weathered shale horizon were calibrated to reproduce the variations in water table and water content measured in the monitoring wells. Table 2 lists the calibrated hydrogeological model parameters assigned to the stratigraphic units. Reflecting the weathered subsurface environment, permeability shows a net decline with depth due to the lower degree of weathering at greater depth.

The model also integrates the distributions of the minerals and solid organic matter that were characterized from the soil and rock analyses (Figures 2b–2g). At our site, the Mancos shale is dominated by quartz, albite, illite, and chlorite and contains 13.7 wt% dolomite, 0.9 wt% pyrite, and 1.25 wt% petrogenic organic carbon (a summary of the mineral composition of the parent rock is provided in Table S2 in Supporting Information S1). In this system, dolomite and pyrite represent the most reactive minerals, as evidenced by their significant depletion in the regolith and the formation of secondary minerals such as goethite and calcite (Stolze et al., 2023b; Figure S1 in Supporting Information S1). Such geochemical heterogeneities were represented spatially in the 2-D numerical domain by interpolating the mass fraction profiles [wt%] determined in the four monitoring wells (Stolze et al., 2023a). We used a Gaussian process regression model (i.e., Kriging interpolation method) with an exponential kernel covariance function using the MATLAB® function *fitrgp*. The model was trained for each mineral using the measured mineral concentration profile as the response variable. For each model cell, the depth from the ground surface to the cell center, the longitudinal coordinate at the cell center, the hydrostratigraphic unit corresponding to the cell, and the water saturation simulated during baseflow (i.e., January) were used as predictor variables.

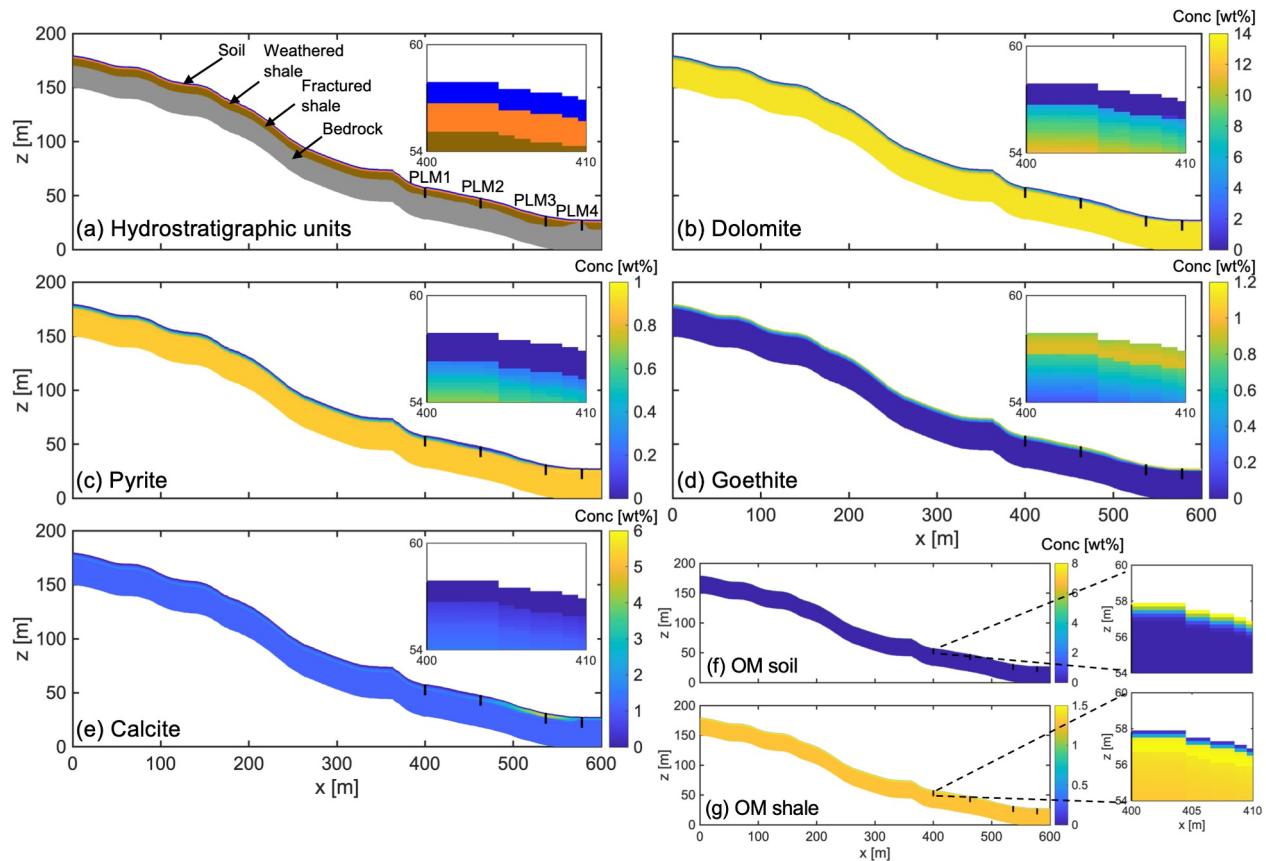


Figure 2. Spatial distribution of the hydrogeological and biogeochemical properties defined in the continuum 2-D model domain representing the shallow subsurface of the hillslope. (a) Hydrostratigraphic units used to simulate the groundwater flow; (b)–(e) mineral concentrations showing significant degree of heterogeneity; (f)–(g) soil and shale organic matter concentrations. The insets show the distributions close to the surface within $x = [400 - 410]$ m and $z = [54 - 60]$ m.

Mass fractions of the other minerals that showed low spatial variability (i.e., albite, quartz, chlorite, illite) were assumed homogeneous over the model domain using the average measured mass fractions. Comparison between measured and model mass fractions is shown in Figure S1 in Supporting Information S1.

Amount and surface area of a given mineral m were inserted in the numerical grid using cell-indexed data sets of volume fraction θ_m [$\text{m}^3 \cdot \text{m}^{-3}$] and bulk surface area A_m [$\text{m}^2 \cdot \text{m}^{-3}$]. These gridded data sets were computed from the

Table 2
Model Input Parameters Used to Simulate the Flow of Water and the Transport of Gas and Aqueous Solutes

Hydrostratigraphic units		Soil	Weathered shale	Fractured shale	Bedrock
Average Thickness	[m]	1.10	1.40	6.65	—
Permeability, K^*	[m^2]	1.58×10^{-09}	8.82×10^{-12}	1.21×10^{-14}	2.82×10^{-15}
Porosity, θ_i	[—]	0.40	0.22	0.29	0.04
van Genuchten parameter, α	[m^{-1}]	3.33	4.54	4.37	4.59
van Genuchten parameter, n_{vG}	[—]	2.00	1.98	1.68	1.52
Residual water content, θ_r	[—]	0.19	0.10	0.10	0.50
Aqueous diffusion coefficient, D_0^w	[$\text{m}^2 \text{s}^{-1}$]	1.00×10^{-9}			
Gas diffusion coefficient, D_0^g	[$\text{m}^2 \text{s}^{-1}$]	1.32×10^{-5}			
Longitudinal dispersivity, α_L	[m]	0.1			
Transverse dispersivity, α_T	[m]	0.01			

interpolated mass fractions using the molar masses M_m [g·mol⁻¹], molar volumes V_m [m³·mol⁻¹], and specific surface areas $A_{m,s}$ [m²·g⁻¹] of the respective minerals (literature values are provided in Supporting Information S1) following the approach applied in Stolze et al. (2023b). Because lower interfacial surface area (Navarre-Sitchler et al., 2011; Pandey & Rajaram, 2016) and passivated mineral surfaces (Battistel et al., 2021; Stolze et al., 2022) in natural systems typically lower weathering rates compared to that measured under well-controlled laboratory conditions, we applied a scaling factor to reduce the bulk surface area of the minerals composing the shale ($S_f = 1.61 \times 10^{-3}$ Navarre-Sitchler et al., 2011). Hence, the bulk surface area for a given mineral m in the bedrock was calculated as:

$$A_{m,0} = S_f \frac{A_{m,s} M_m}{V_m} \theta_{m,0} \quad (20)$$

The bulk surface areas in the other hydrostratigraphic units (soil, weathered shale, and fractured shale) were derived from the bulk surface areas calculated in the bedrock using the shrinking sphere model:

$$A_{m,x} = A_{m,0} \left(\frac{\theta_{t,x}}{\theta_{t,0}} \right)^{2/3} \left(\frac{\theta_{m,x}}{\theta_{m,0}} \right)^{2/3} \quad (21)$$

where $\theta_{t,x}$ and $\theta_{m,x}$ are the porosity and a mineral volume fraction in a given hydrostratigraphic unit x , and $\theta_{t,0}$ and $\theta_{m,0}$ are the porosity and the mineral volume fraction for mineral m in the bedrock.

The distributions of SOM_{soil} and SOM_{shale} concentrations shown in Figures 2f and 2g were based on the TOC profiles measured in the four monitoring wells (Figure S1 in Supporting Information S1), combined with the modeled fractions of soil-derived and shale-derived OM from Stolze et al. (2023b). In this system, SOM_{soil} dominates the upper 1 m of the profile, where SOM_{shale} is markedly depleted. Below this depth, SOM_{shale} makes the majority of the organic matter and shows relatively homogeneous concentrations. Given the consistent TOC profiles across the wells and the relatively uniform soil thickness along the hillslope, SOM_{soil} and SOM_{shale} were assumed to be spatially heterogeneous in the vertical direction but homogeneous in the longitudinal direction. Consistent with the approach used for the minerals, the volume fractions and bulk surface areas of SOM_{soil} and SOM_{shale} were scaled according to the porosity distribution, assuming $A_{m,0}$ equal to 1 m²/m³.

3.5. Climate Forcing and Boundary Conditions

Transient groundwater recharge was implemented as a spatially uniform flux boundary condition applied to the surface of the model domain. To capture the site-specific hydroclimatic dynamics, we generated a time series of meteoric water infiltration that accounts for both rainfall and snowmelt contributions. Snowmelt was estimated using the point energy balance model ESCIMO.spread v2 (Marke et al., 2016), which simulates snowpack drainage based on energy and mass balance principles. The model integrates hourly meteorological data, including total precipitation [mm·h⁻¹], temperature [K], relative humidity [%], wind speed [m·s⁻¹], global radiation [W·m⁻²], and incoming longwave radiation [W·m⁻²]. These meteorological parameters were collected between 1 October 2015 and 30 September 2020 at the Billy Bar meteorological station, located 5.7 km from the hillslope and at a similar elevation (2,900 m; Faybischenko, 2020). Simulated snow water equivalent time series were validated against measurements from the SNOTEL Butte site (elevation 3,100 m), located 2.96 km from the hillslope (USDA, 2021). For this study, we selected the year 2016 to represent climate forcing conditions, as it corresponds to average annual precipitation for the study period (850 mm, 51% of which occurring as snowfall) and typical snowpack dynamics.

Evapotranspiration (ET) was implemented as a transient sink term in the top cells of the domain. ET time series were computed from land surface simulations performed by Chen et al. (2021) using the *Community Land Model* (Oleson et al., 2013). ET was assumed to influence only water content, not solute mass. Time series of both meteoric water infiltration and ET are shown in Figure 3a, while snowpack model validation results are provided in Supporting Information S1.

Hydrological boundary conditions were specified as follows: no-flux boundaries were assigned to the bottom and upslope sides of the domain, while the downslope boundary was treated as a dynamic seepage face. The latter was defined using time series of the adjacent East River's stage.

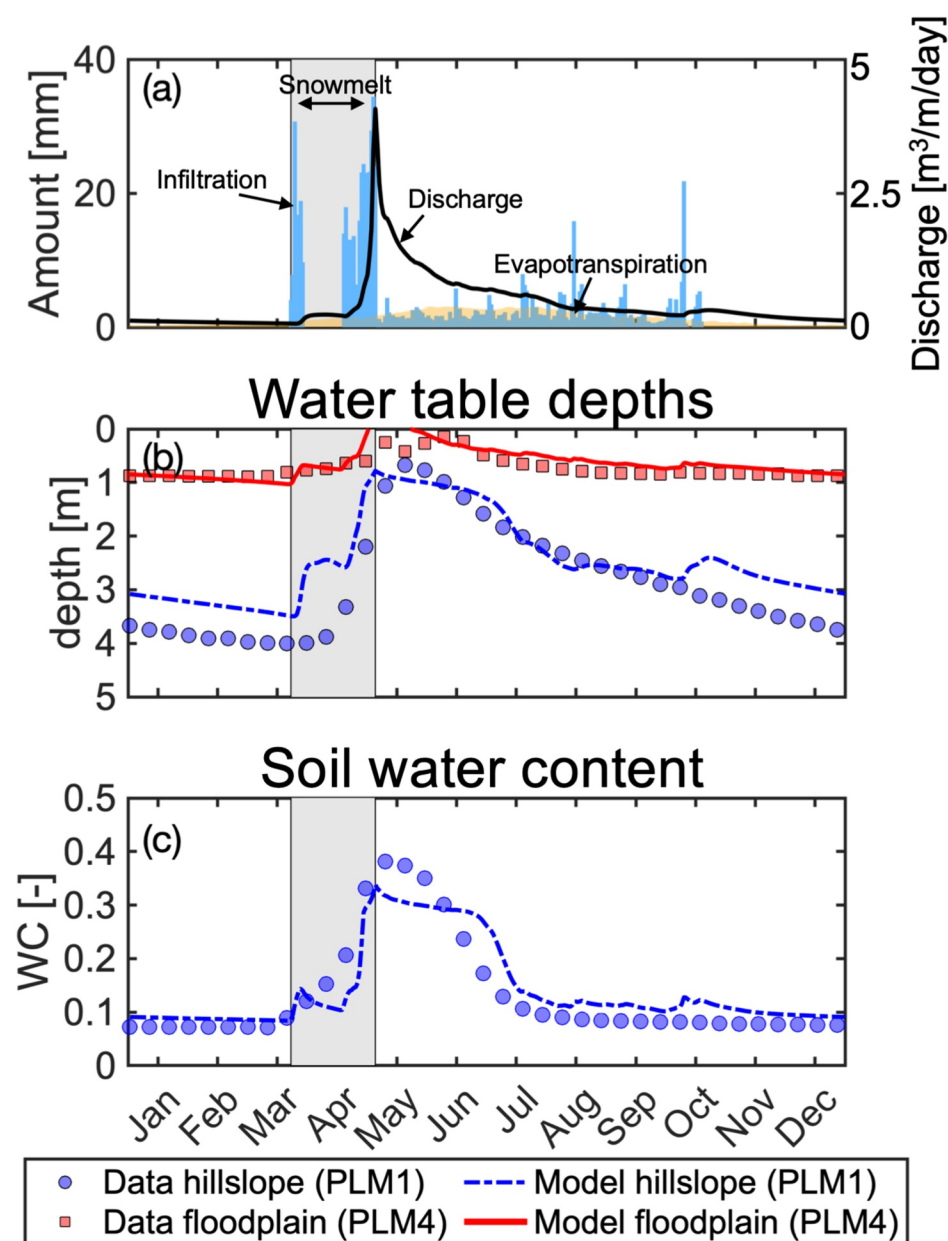


Figure 3. Measured and simulated temporal evolution of the hydrological conditions at the hillslope. (a) Infiltration and evapotranspiration time series monitored at the field site and simulated discharge at the hillslope toe (PLM3); (b) Depth to the water table in the monitoring wells PLM1 and PLM4 located on the hillslope and in the floodplain, respectively; (c) Soil water content within the depth interval [0.6 – 1.1] m in the monitoring well PLM1.

Subsurface temperature dynamics were captured using daily temperature records collected from monitoring wells equipped with vertically distributed sensors (depth intervals ranging from 0.2 to 1 m, increasing with depth). As the temporal trends at each depth were consistent across wells, we assumed lateral homogeneity in temperature. The domain was discretized into nine depth intervals following hillslope topography, each assigned with a distinct temperature time series. These series reflect clear seasonal fluctuations, with maximum temperatures in July and minimum in January (Figure S2 in Supporting Information S1). Due to the low thermal diffusivity of the rock, temperature amplitude decreases with depth. Temperature was assumed constant below 7 m, where temporal variations are minimal.

To simulate gas and solute fluxes at the atmosphere-subsurface interface (top boundary) and at the downslope outlet to the East River (downslope boundary), we applied Dirichlet boundary conditions for chemical species concentrations. Infiltrating water chemistry at the surface was defined using rainwater composition reported by the National Atmospheric Deposition Program. Gas concentrations (O_2 , N_2 , and CO_2) in the infiltrating water were determined via equilibrium calculations based on atmospheric partial pressures at the site elevation ($p_{O_2} = 1.68 \times 10^{-1}$ bar, $p_{N_2} = 6.24 \times 10^{-1}$ bar, and $p_{CO_2} = 1.67 \times 10^{-4}$ bar). These values were also used to model diffusive exchange of gases between the atmosphere and the subsurface. Chemical compositions of both meteoric water and East River water are provided in Table S7 in Supporting Information S1.

3.6. Model Implementation

Transient simulations of coupled subsurface processes including variably saturated water flow, multiphase transport, and biogeochemical reactions were performed using the finite volume flow and reactive transport code PFLOTRAN (Hammond et al., 2014). PFLOTRAN solves the partially-saturated flow and multicomponent reactive transport equations sequentially using a fully implicit Newton-Raphson nonlinear solver.

The hillslope domain was discretized into 92,880 active elements using a structured grid with horizontal resolution (Δx) of 1 m and vertical resolution (Δz) of 0.2 m. The high vertical resolution was necessary to capture key near-surface dynamics, including gas-water exchange, sharp geochemical reaction fronts (e.g., pyrite oxidation zones), and flow variability in the vadose zone.

The model includes 20 primary species, 26 secondary aqueous species, and 4 gaseous species: $O_{2(g)}$, $CO_{2(g)}$, $N_{2(g)}$, and $N_2O_{(g)}$ (see Table S8 in Supporting Information S1 for a comprehensive list of all modeled species). The mass conservation equations were solved for the primary species (Equation 14), while the secondary species were involved in aqueous speciation and mineral precipitation/dissolution calculations. Aqueous speciation was computed under the assumption of local equilibrium using the mass action law and thermodynamic data from the Thermoddem database (Blanc et al., 2012). Activity coefficients were calculated using the extended Debye-Hückel equation (Helgeson et al., 1984).

Biogeochemical processes, including mineral dissolution/precipitation, microbially-mediated reactions, and root respiration, were implemented through the PFLOTRAN's Reaction Sandbox framework (Hammond, 2022). Kinetic rate expressions (Equations 1–10) were incorporated by implementing analytically derived Jacobian terms to increase numerical efficiency and solution stability. To further reduce the computational burden of simulating fully coupled flow and multicomponent transport over a large domain, simulations were performed on the Perlmutter supercomputer at NERSC. Specifically, we leveraged PFLOTRAN's massive parallelization capabilities through domain decomposition using PETSc libraries (Balay et al., 1997) with runs distributed across five CPU nodes (640 processors in total).

Initial conditions were defined by setting the water table parallel to the land surface at a depth of 4 m and by assuming that the pore water was in equilibrium with the local shale mineral assemblage. The flow and biogeochemical conditions were then dynamically initialized using a 50-year transient spin-up simulation before initiating the primary 1-year simulation considered in this work. The maximum time step was set to 1h for all simulations to ensure temporal resolution of hydrological and reaction dynamics.

3.7. Sensitivity Analyses

To systematically investigate the controls on shale weathering and associated biogeochemical fluxes, we performed three sets of numerical experiments. These experiments were designed to isolate and quantify the influence of distinct biogeochemical, hydroclimatic, and topographic controls, using the calibrated transient model as our base case.

First, to quantify the influence of individual biogeochemical processes, we ran six modeling scenarios in which key reactions from the base case were individually inhibited. Second, to isolate the impact of hydroclimatic forcing, we compared the base case against three simulations with simplified climate conditions. Finally, to assess the role of topography, we evaluated the sensitivity of weathering fluxes to the average slope angle.

For all scenarios, the results were compared against the base case by analyzing the domain-integrated mineral reaction rates, cumulative solute export fluxes at the hillslope toe, and the net CO_2 exchange with the atmosphere.

4. Results and Discussion

4.1. Transients in Hydroclimatic Forcing and Subsurface Hydrological Conditions

In the East River watershed, spring snowmelt dominates the hydrological cycle and represents the primary mechanism of annual groundwater recharge. This seasonal influx induces strong responses in the hillslope subsurface hydrology, as illustrated in Figure 3.

During winter, snow cover prevents infiltration, resulting in a deeper water table and lower soil water content (baseflow). As temperature rises in spring, snowmelt leads to rapid infiltration and a marked response in subsurface conditions. The impact of snowmelt infiltration on the hydrological conditions is evidenced by the rapid increase in water table and soil water content between April and June (peak flow; Figures 3b and 3c). In the monitoring well PLM1 located on the hillslope, the water table is shallowest at the end of the snowmelt period, in May, with a depth of ~ 1 m below ground surface. In comparison, the monitoring well PLM4 located in the floodplain shows fully saturated conditions from May to June, as the water table tends to be shallower downslope.

Following snowmelt, the water table gradually recedes (falling limb). It stabilizes at different depths depending on landscape position, remaining relatively constant from December to March (~ 4 m in the hillslope, ~ 1 m in the floodplain). Soil water content (Figure 3c) follows a similar seasonal pattern but recovers to baseflow conditions more rapidly than the water table. The smooth decline in both water table and water content during summer indicates that intermittent monsoonal rainfall events do not substantially affect the subsurface flow as ET limits water infiltration.

The 2-D hillslope model captures the subsurface hydrodynamics, reproducing the different positions of the water table in the hillslope and the floodplain as well as the timing and magnitude of hydrologic responses (Figures 3b and 3c). The simulated discharge at the toe slope (integrated vertically in monitoring well PLM3) rapidly increases during spring, reaching a maximum of $4.08 \text{ m}^3/\text{m}/\text{day}$ at the end of snowmelt, nearly tenfold higher than the annual mean ($0.42 \text{ m}^3/\text{m}/\text{day}$; Figure 3a). In addition, the model results allow us to visualize the evolution of the subsurface hydrological conditions. Figure 4 illustrates the spatial distributions of the water saturation and discharge as well as the simulated streamlines. The results are displayed for three times (January, May, and September) representative of the seasonal hydrologic regimes observed at our site (baseflow, peak flow, and falling limb, respectively).

The 2-D maps illustrate the evolution of the subsurface hydrological conditions over time and highlight the significant impact of spring snowmelt on the water flow dynamics. In January, conditions are driest due to the absence of water infiltration beneath the snowpack and therefore both water saturation and specific discharge are lowest (Figures 4a and 4d). In May, these metrics increase markedly at shallow depths across the hillslope, reflecting snowmelt-driven infiltration (Figures 4b and 4e). In September, conditions have returned to near baseflow (Figures 4c and 4f).

Discharge patterns reveal consistently higher flow rates in shallow layers throughout the year (Figures 4d–4f). In particular, lateral flow paths preferentially develop at the interface between the soil horizon and the weathered shale due to the higher permeability of the regolith and the ponding of water at the interface with the impeding bedrock (Figure 4e). These pathways are especially active during snowmelt, as shown by the sharp discharge peak ($\sim 294 \text{ m}^3/\text{yr}$) at 1.1 m depth in PLM1 (Figure 4h).

Furthermore, the irregular streamline patterns displayed in Figures 4a–4c highlight topographic influences on near-surface flow, especially where the slope steepens abruptly between 350 and 400 m, causing divergence of flow lines.

4.2. Seasonal Responses in Soil Respiration

Seasonal warming and snowmelt infiltration not only affect the hydrological conditions but also lead to significant responses in soil biological processes as indicated by the increased CO_2 production and microbial biomass in the soil between March and August (Figure 5).

$\text{CO}_{2(g)}$ flux from soil to atmosphere remains positive year-round and shows considerable temporal variations from spring to late summer (Figure 5a). In particular, the $\text{CO}_{2(g)}$ flux increases significantly during snowmelt, reaching a maximum in June ($85.55 \text{ mol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$), before declining as the soil dries out. Soil $\text{CO}_{2(g)}$ concentrations,

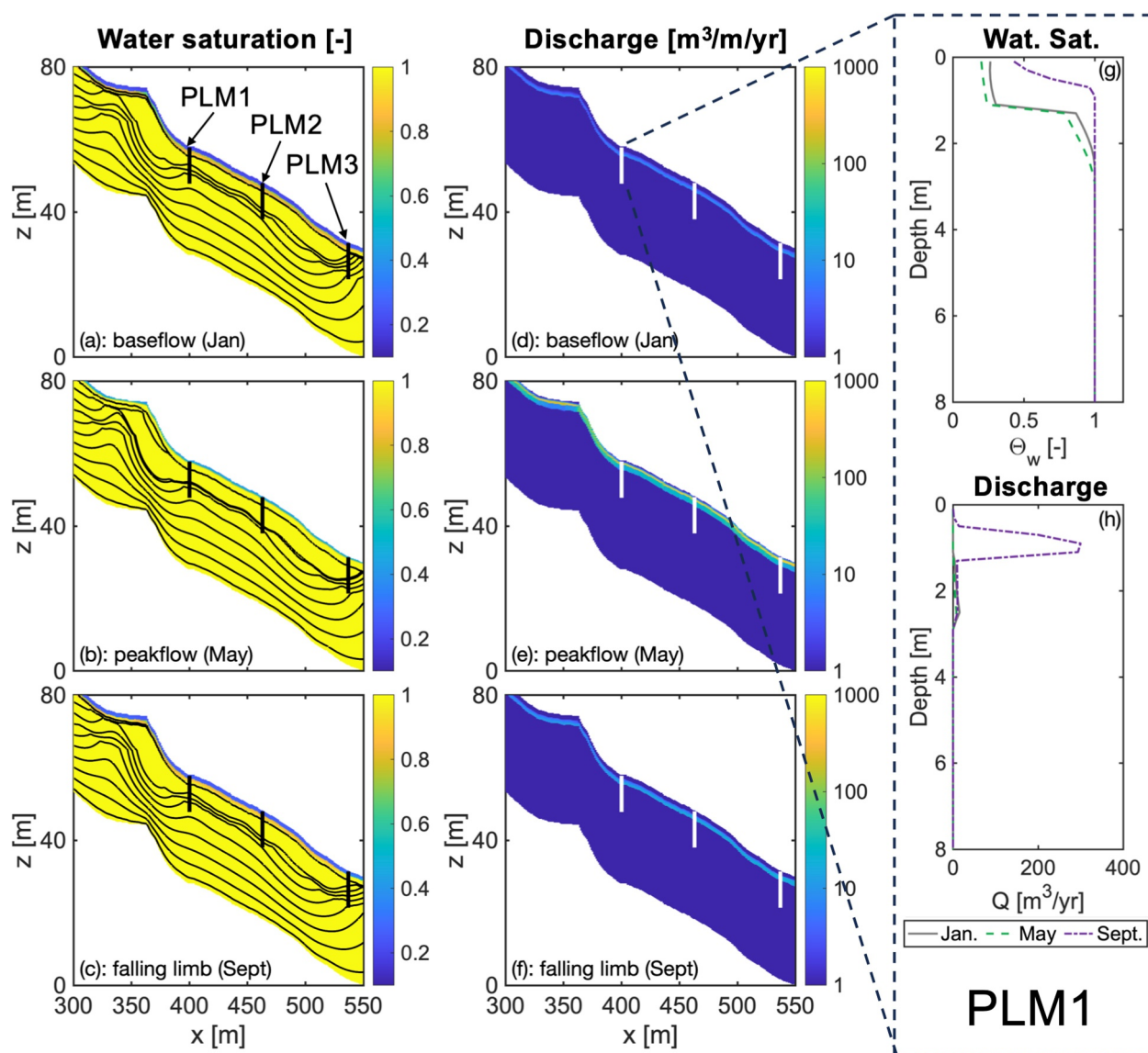


Figure 4. Simulated spatial distributions of the subsurface hydrological conditions at three times representative of the key water flow regimes. (a–c) 2-D maps of the water saturation; (d–f) 2-D maps of the magnitude of the specific discharge; (g–h) Vertical distributions of the water saturation and specific discharge in the monitoring well PLM1. 2-D maps are shown for the interval $x = [300 - 550]$ m for ease of visualization.

measured at multiple depths and locations, follow similar patterns (Figures 5c–5e), with average and maximum values of 6,340 ppm and 19,070 ppm between April and July.

The sharp increase in soil microbial biomass during snowmelt (Figure 5b) indicates a surge in heterotrophic microbial respiration, which contributes significantly to the increase in $\text{CO}_{2(g)}$ production early in the season (Stolze et al., 2024). This phenomenon, known as the Birch effect (Birch, 1958), is largely driven by the increased availability of labile DOM for microorganisms during soil rewetting (Manzoni et al., 2016; Moyano et al., 2013). Later, during the growing season, root respiration becomes the primary source of CO_2 due to optimal temperature and water saturation conditions (Stolze et al., 2024; Winnick et al., 2020). During winter, heterotrophic respiration persists beneath the snowpack (Brooks et al., 1996; Rindt et al., 2023; Sorensen et al., 2020), maintaining $\text{CO}_{2(g)}$ levels (averaging 1,406 ppm; Figures 5c–5e) above atmospheric concentrations (211 ppm at the altitude of the field site), and sustaining a positive $\text{CO}_{2(g)}$ flux to the atmosphere (averaging $13.12 \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$; Figure 5a).

The simulation results agree well with the measured seasonal variations in CO_2 emissions to the atmosphere (Figure 5a) and the soil microbial biomass concentrations (Figure 5b). In addition, the model reproduces the soil

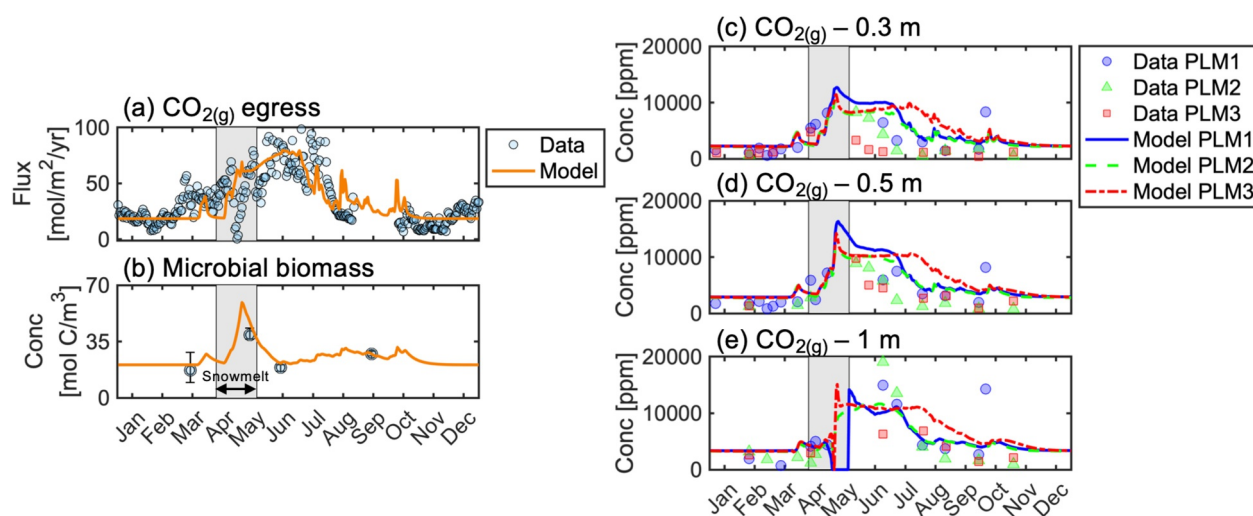


Figure 5. Soil respiration response to climate forcing. Comparison between the measured and simulated temporal evolution of (a) $\text{CO}_{2(g)}$ flux emitted from the soil to the atmosphere, (b) microbial biomass concentration in the top 30 cm of soil (data from Sorensen et al., 2020), and (c)–(e) $\text{CO}_{2(g)}$ concentrations measured at various depths of the soil layer.

CO_2 concentrations at various depths (Figures 5c–5e) although it slightly overestimates these concentrations at shallow depths (0.3–0.5 m below ground) during summer in the wells PLM2 and PLM3 located downslope. This strong agreement indicates that the model not only captures the effects of climate forcing on soil respiration rates but also that it adequately describes the impact of transient water dynamics on the multiphase CO_2 exchange in the near surface.

4.3. Spatial Variability in Pore Water Chemistry

Atmospheric forcing and soil respiration drive mineral weathering in the regolith, shaping the spatial distribution of pore water chemistry. Figure 6 displays the simulated concentrations of DIC, Ca, SO_4 , and Na. We focus on these solutes because they dominate the ionic composition of the pore water at our site and are mobilized by the dissolution of the most reactive mineral phases composing the Mancos shale (i.e., dolomite, pyrite, and albite). A comprehensive overview of the hydrochemical conditions is included in Supporting Information S1.

The distributions of the aqueous species highlight the considerable spatial variability in the hydrochemical conditions of the critical zone. Specifically, solute concentrations increase below ~1 m depth, reflecting the depletion of reactive minerals in the soil horizon and enhanced reaction rates at depth. Vertical profiles vary by solute: DIC concentration remains relatively uniform below the soil profile because the pore water equilibrates with dolomite ($M = 4.50 \text{ mM}$, $\text{SD} < 5 \times 10^{-1} \text{ mM}$; Figures 6a–6c and 6m). Similarly, pH is buffered by dolomite and therefore remains relatively uniform below the soil profile (Figure 6q). In contrast, Ca, SO_4 , and Na are highest between 1–4 m, then decline with depth (Figures 6d–6l, 6n, and 6p). These higher concentrations reflect the position of the geochemical reaction front where the dissolution of the minerals is enhanced due to their exposure to atmospheric and biogenic reactants, including oxygen (O_2) and carbon dioxide (CO_2). SO_4 concentrations are particularly low below the water table ($< 0.5 \text{ mM}$; Figures 6g–6i and 6o) due to limited availability of O_2 which restricts pyrite oxidation. In contrast, concentrations of Ca and Na remain relatively elevated in the saturated zone as the pore water equilibrates with the carbonate and silicate minerals (i.e., 1.2–1.5 mM; Figures 6d–6f, 6j–6l, 6n, and 6p).

Figures 6m–6q show that the simulation generally captures the primary features of the vertical concentration and pH profiles measured in PLM1. Similar agreement was obtained in the other monitoring wells (PLM2 and PLM3) and for other key inorganic solutes including Mg, K, and Si (i.e., a detailed comparison is provided in Section S7 in Supporting Information S1). However, some systematic model-data discrepancies are apparent. For instance, the model tends to overpredict Ca and Mg concentrations in the soil ($< 1 \text{ m}$ depth) following snowmelt, which may be caused by an over-representation of the concentrating effect of evapotranspiration. Furthermore, a consistent overestimation of Mg across all wells suggests that the model may not fully resolve the complexities of dolomite

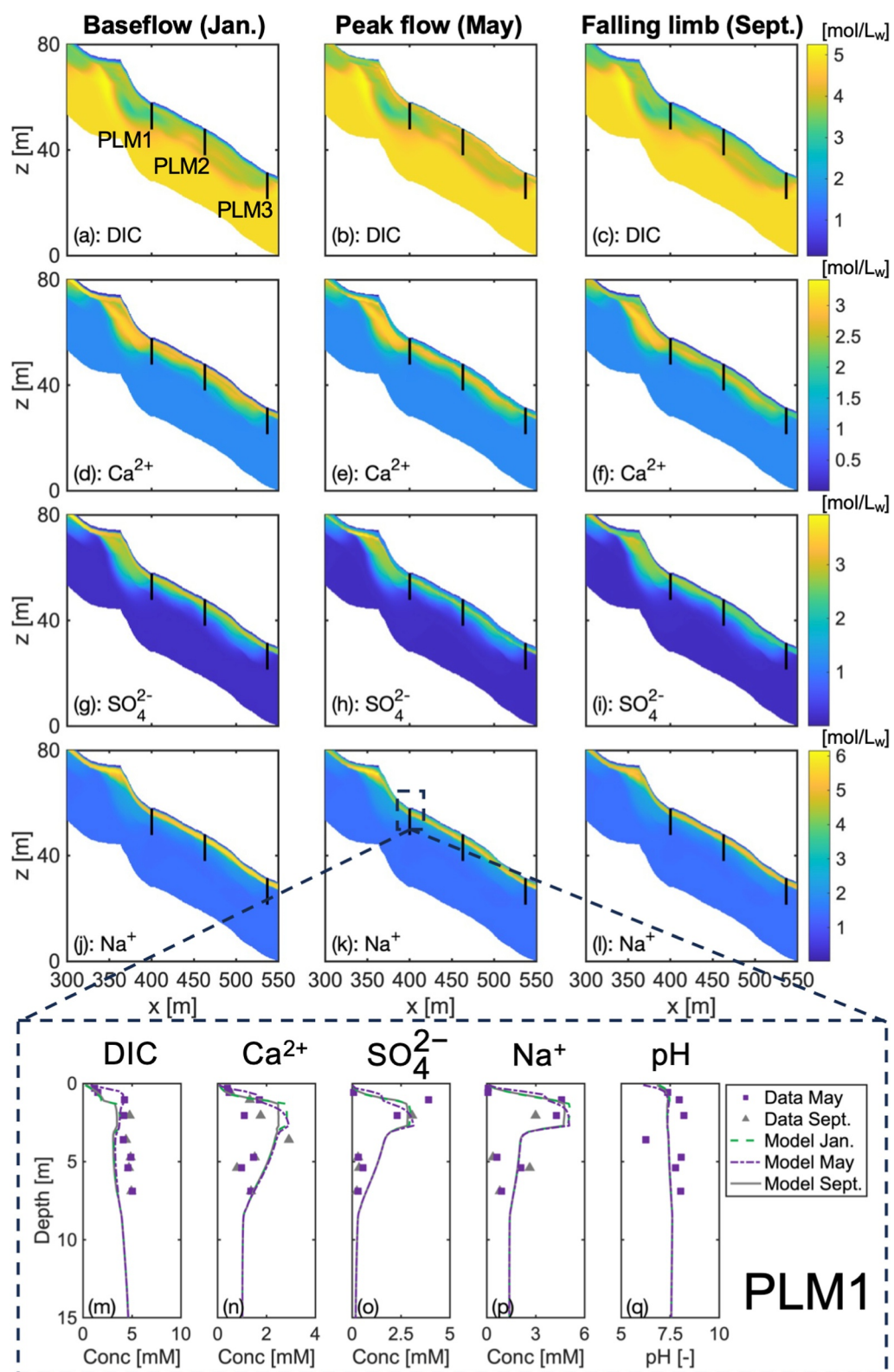


Figure 6. Spatial distributions of the dissolved inorganic carbon, Ca, SO₄ and Na concentrations and pH in the hillslope at three times representative of the seasonal hydrological conditions: 2-D maps of the aqueous species concentrations computed over the lower part of the hillslope (a–l) and comparison between measured (symbols) and simulated (lines) vertical concentration and pH profiles in the monitoring well PLM1 (m–q).

weathering. This discrepancy could stem from a non-ideal Ca:Mg stoichiometry in the parent shale's dolomite, or from complex reaction dynamics like incongruent dissolution and secondary mineral precipitation pathways. Finally, underestimation of DIC and Na at the toe slope (PLM3) likely points to biogeochemical heterogeneity at the hillslope floodplain interface that is not fully captured by the 2D hillslope model. Despite these localized discrepancies, the model successfully reproduces the overall spatial distribution of the major aqueous solutes. These results indicate that the model effectively captures the dominant spatiotemporal variations in biogeochemical reaction rates and resulting solute exports.

Despite the large change in hydrological conditions driven by snowmelt, the concentrations of inorganic solutes at a given depth remain remarkably steady at both seasonal and decadal scales (i.e., a year-to-year comparison of measured concentration time series for the period 2016 – 2021 is provided in Figures S15–S17 in Supporting Information S1). Furthermore, while the vertical patterns in aqueous species concentrations are relatively well preserved along the hillslope, the simulated 2-D maps displayed in Figures 6a–6l indicate significant fluctuations in the vertical extent of the zone characterized by higher concentrations of base cations and sulfate. For instance, this zone is significantly broader in the interval $x = [350 - 400]$ m (Figures 6d–6l), which coincides with the sharp steepening of slope and the occurrence of diverging streamlines discussed in Section 4.1. This result indicates that topographic features can significantly modulate the vertical distribution of aqueous species mobilized from chemical weathering by enhancing their advective transport to depth.

Figure 7 shows the seasonal dynamics and vertical distribution of DIC, Ca, SO_4 , and Na exports at the toe slope. All solutes exhibit pronounced pulse behavior, with concentrations peaking sharply during snowmelt, followed by gradual declines. This pattern reflects both the chemostatic nature of these species and the seasonal hydrologic regime of the East River watershed, where discharge peaks in May. The simulations indicate that most solute export originates within the weathered shale layer (blue bars in Figure 7), aligning with the vertical discharge distribution and the concentration profiles described above. Annual export rates for DIC and SO_4 (1.21 and $0.57 \text{ mol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively) are consistent with field measurements from the East River (1.43 and $0.28 \text{ mol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$; Winnick et al., 2017), suggesting that the model outputs are representative at the catchment scale.

4.4. Hydroclimatic and Topographic Controls on Geochemical Reaction Rates

We used the model to map and visualize the distributions and temporal evolutions of the dissolution rates of dolomite, pyrite, and albite because these minerals represent the main geogenic sources of aqueous solutes in the Mancos shale. Figure 8 compares the spatial distributions of the reaction rates simulated during baseflow (January) and peak flow (May). For completeness, similar results for the other mineral phases are presented in Supporting Information S1.

The model results show that the dissolution of pyrite, dolomite, and albite primarily occur within a depth interval of $[1 - 3]$ m (Figures 8a–8i), reflecting the vertical distributions of the inorganic solutes discussed in Section 4.3. In particular, dolomite dissolution is relatively localized with a maximum dissolution rate simulated at 1.5 m below the ground surface (Figures 8b, 8e, and 8h). In contrast, pyrite and albite dissolution rates are more uniformly distributed across the saprolite (e.g., Figures 8a and 8c).

Comparing the geochemical reaction rates simulated between peak flow and baseflow periods shows that mineral dissolution is significantly enhanced during snowmelt, although the response differs between the various minerals. Dolomite dissolution shows the largest relative change, with an average 357% increase estimated between January and May (i.e., $0.58 - 2.65 \text{ mol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$; Figure 8b). In comparison, the response of pyrite and albite are lower (Figures 8a and 8c, respectively). These transients highlight the significant impact of snowmelt on shale weathering as the percolating water enhances the vertical transport of dissolved atmospheric O_2 and soil CO_2 to the geochemical reaction front.

The longitudinal distribution of the geochemical reaction rates displayed in Figures 8j–8l indicates that the dissolution rates of pyrite and dolomite also vary along the hillslope, while albite reaction rate is more uniformly distributed. For example, the dissolution rates of pyrite and dolomite are characterized by a sharp increase at $x = 370$ m. This location is particularly interesting as it corresponds to the sharp steepening of the slope and the zone enriched in base cations and sulfate concentrations displayed in Figure 6. This overlap indicates that diverging streamlines induced by abrupt changes in slope angle can locally enhance the weathering of shale and

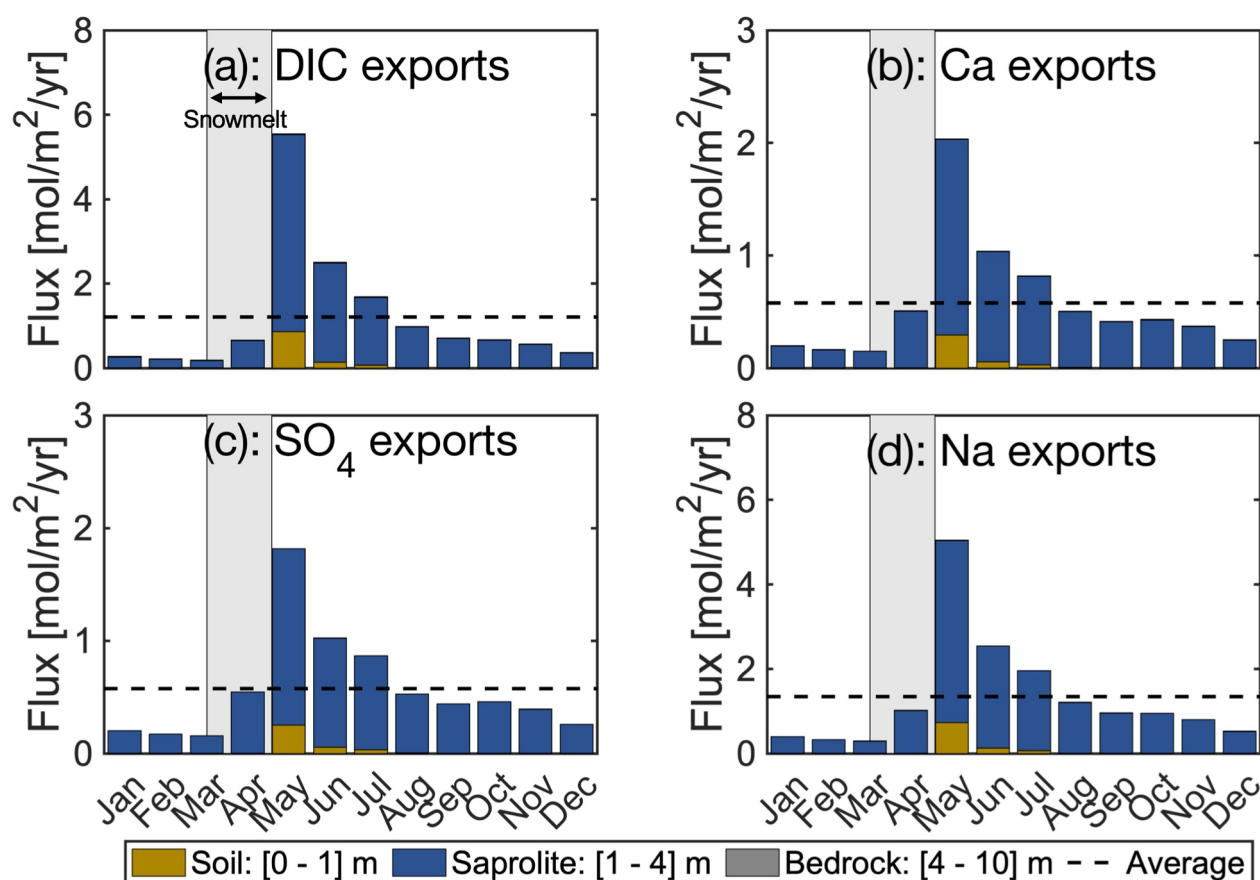


Figure 7. Simulated temporal and vertical variations of solute fluxes from hillslope to floodplain at the toe-slope ($x = 537$ m), aggregated monthly and by hydrogeological unit.

the associated mobilization of inorganic solutes by favoring the downward transport of reactive species that drive the geochemical reactions at depth.

Despite this similar local enhancement in the rates of pyrite and dolomite dissolution, the model highlights important differences in the sensitivities of pyrite and dolomite dissolutions to the surface topography. For example, the longitudinal distribution of the pyrite oxidation rate remains relatively consistent throughout the year as shown by the similar computed profiles in January and May (Figure 8j). In contrast, the influence of topography on dolomite dissolution is only evident during snowmelt (Figure 8k). Moreover, during peak flow, dolomite and pyrite dissolution rates exhibit an inverse spatial pattern between 400 and 450 m (as seen in the comparison between Figures 8j and 8k). Such differences underscore the distinct sets of coupled physical and biogeochemical processes governing the spatial and temporal behavior of pyrite and dolomite dissolutions.

To further evaluate the sensitivity of the geochemical reactions to the hillslope topography, we analyze the spatial distributions and temporal evolutions of the mineral dissolution rates in relation to topographic surface attributes and subsurface flow (Figure 9). The topographic metrics considered include slope angle and curvature.

Figures 9b and 9c reveal that the slope angle exerts a strong control on the spatial distribution of pyrite and dolomite weathering. Specifically, the simulated pyrite oxidation rate increases linearly with the slope up to a terrain gradient of 45%, above which the rate remains relatively constant (Figure 9b). This relationship is strong and consistent across all flow conditions (Pearson's $R > 0.73$). In comparison, the impact of the slope angle on dolomite dissolution is more moderate during baseflow and becomes notably stronger during spring snowmelt. In contrast to the slope angle, the curvature has no apparent influence on the geochemical reactions (Figures 9e–9h).

To better understand the mechanisms underlying the impacts of the slope angle, we analyze the relationships between hydrological variables and mineral dissolution rates (Figures 9i–9p). Here, the steep and variable

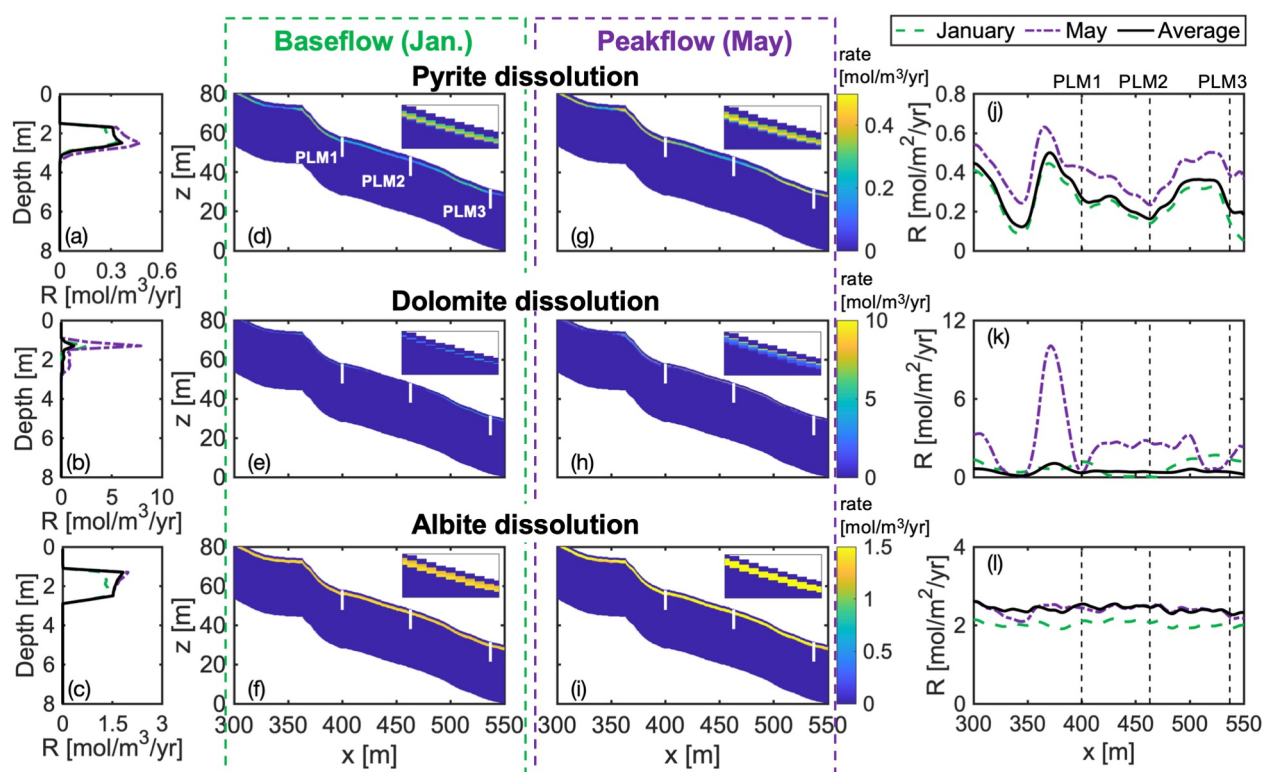


Figure 8. Simulated spatial distributions of the geochemical reaction rates under baseflow (January) and peak flow (May) conditions: vertical profiles (a–c); 2-D maps (d–i); longitudinal profiles (j–l). The insets in panels (d–i) show the distributions of the geochemical reaction rates close to the surface within $x = [370 - 380]$ m. The vertical profiles plotted in panels (a–c) were computed by averaging the model results along the hillslope from the upslope boundary to the toe-slope (PLM3; $x = 537$ m). The longitudinal profiles plotted in panels (j–l) were calculated by integrating the model results vertically from the top to the bottom of the model domain. Each row corresponds to a given mineral reaction, as indicated in bold.

topography results in significant spatial variability in both water saturation and vertical water percolation within the regolith (Figures 9i and 9m). When plotted against these hydrological variables, the dissolution rates of pyrite and dolomite exhibit clear dependencies on near-surface flow conditions (Figures 9j–9l, 9n, and 9p). Pyrite oxidation shows a strong inverse relationship with water saturation (Figure 9j), indicating that its dissolution is enhanced under drier conditions that facilitate the diffusion of atmospheric oxygen. Conversely, dolomite dissolution shows a particularly strong positive correlation with vertical flow velocity, especially during snow-melt (Figure 9k), highlighting the critical role of reactant delivery via the percolating water.

Because the water table tends to decline toward the ridgetop (Figure 9i), pyrite oxidation rates linearly increase with elevation, showing a negative correlation with longitudinal position (Figure S21 in Supporting Information S1). To isolate the role of slope angle, we removed the first-order trend between pyrite oxidation and water saturation and re-evaluated the correlation between the detrended pyrite oxidation rates and slope angle. The resulting correlations confirmed the direct influence of slope angle on pyrite oxidation ($R > 0.73$).

These results collectively demonstrate that the spatial variability of shale weathering is shaped by slope-induced differences in subsurface hydrology. Steeper slopes promote more efficient drainage, resulting in persistently lower water tables and enhanced vertical percolation during snowmelt (Figure S23 in Supporting Information S1). The lower water saturation conditions favor the gaseous diffusion of atmospheric $O_{2(g)}$ into the subsurface and, thus, maximize the oxidation of pyrite. Because O_2 does not directly influence dolomite weathering, while the egress of soil-derived CO_2 to the atmosphere is maximized under lower water saturation, the observed inverse relationship between dolomite dissolution and water saturation suggests that a substantial fraction of the sulfuric acid produced by pyrite oxidation is subsequently buffered by dolomite. In addition, increased vertical water flux facilitates the advective transport of dissolved CO_2 and O_2 to deeper reactive zones, accelerating geochemical reactions, in particular carbonic acid-driven dissolution of dolomite.

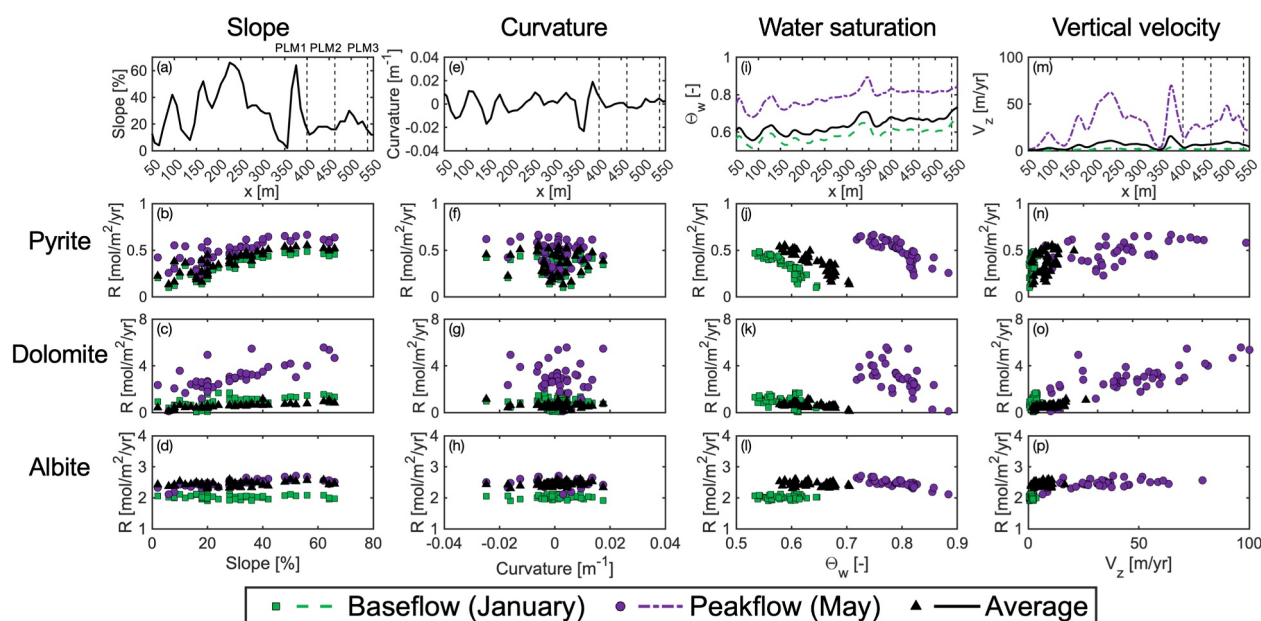


Figure 9. Impacts of topography and near-surface hydrological conditions on the dissolution of pyrite, dolomite, and albite. Relationships between mineral reaction rates and slope (a–d), curvature (e–h), water saturation (i–l), and vertical flow velocity (m–p). Results are computed by slicing the model domain in 10 m sections along the longitudinal direction of the hillslope. Slope and curvature are calculated as the first and second derivatives of the elevation profile, respectively. Porosity-weighted averages of the water saturation and average vertical flow velocity were computed by integrating the results within the top 5 m of the model domain.

4.5. Controls of Biogeochemical Processes on Solute Exports and Carbon Partitioning

To quantify the influence of individual biogeochemical processes on hydrochemical fluxes, six modeling scenarios were defined in which we excluded key mechanisms from the base case model while retaining all other processes: (a) soil respiration, (b) dolomite dissolution, (c) pyrite dissolution, (d) albite dissolution, (e) georespiration, and (f) both dolomite and albite dissolutions. These mechanisms were removed by setting their associated kinetic rates to zero.

Figure 10 compares the cumulative solute exports from the hillslope to the floodplain and the partitioning of CO_2 between the subsurface and the atmosphere simulated for each scenario and the base case. These simulations underscore the central role of acid–base interactions in regulating the hydrochemical behavior of shale-dominated landscapes.

Figure 10a shows that the exported DIC is primarily governed by soil respiration and the dissolution of dolomite and albite. Removing soil respiration (scenario A) and dolomite dissolution (scenario B) leads to substantial decreases in DIC export (–66% and –45%, respectively). In contrast, removing albite dissolution (scenario D) increases the DIC export by 13%, as albite consumes protons but does not generate carbon. In its absence, the resulting excess acidity enhances dolomite dissolution (Figures S25 and S26 in Supporting Information S1), thereby increasing DIC release. The greatest reduction in DIC export (–83%) occurs when both dolomite and albite weathering are inhibited (scenario F), underscoring the important role of silicate-derived alkalinity in retaining biogenic CO_2 in the subsurface.

Interestingly, removing pyrite oxidation (scenario C) has only a minor effect on DIC export despite reducing dolomite dissolution by 57% ($0.66 \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$; Figures S25 and S26 in Supporting Information S1). Based on a mass balance approach, this suggests that pyrite oxidation primarily enhances CO_2 emissions from the subsurface to the atmosphere, rather than significantly contributing to downslope DIC export. The impact of this process on carbonate weathering becomes apparent when examining Ca export (Figure 10b), which declines by 38% when pyrite oxidation is excluded. By comparison, removing soil respiration (scenario A) results in a 16% reduction in Ca export.

Acid–base reactions also influence SO_4 and Na exports (Figures 10c and 10d). In Scenario F, inhibiting both dolomite and albite dissolution reduces SO_4 export by 56%, indicating that carbonate and silicate alkalinity

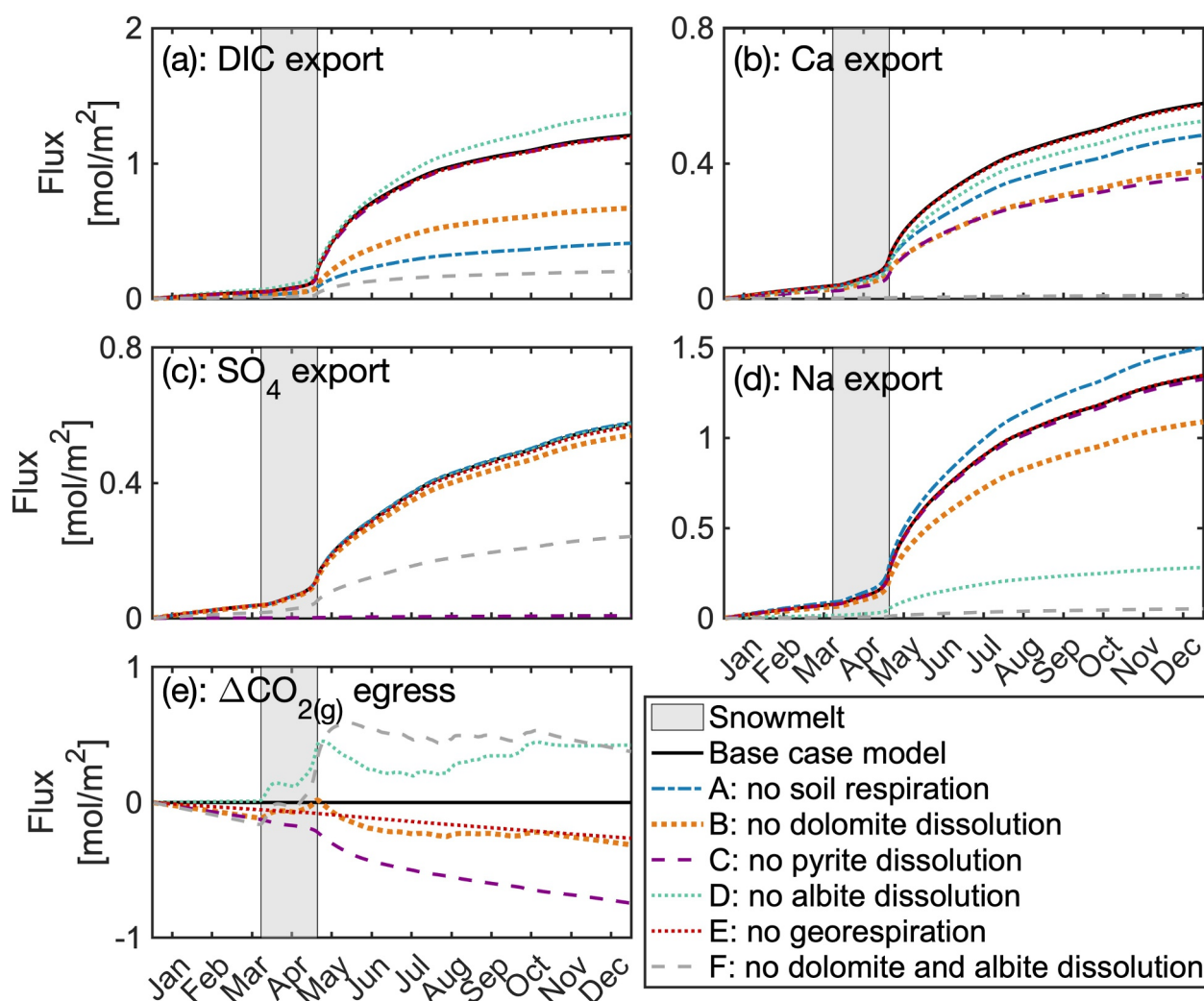


Figure 10. Simulated temporal change in cumulative mass of solutes exported to the adjacent floodplain (a–d) and cumulative $\text{CO}_2(\text{g})$ egress to the atmosphere (e). The simulations were performed using the base case model and six modeling scenarios (A–F) in which key biogeochemical mechanisms were individually inhibited from the base case model. Cumulative fluxes of $\text{CO}_2(\text{g})$ emissions to the atmosphere were integrated along the upper boundary of the model domain and normalized to the $\text{CO}_2(\text{g})$ flux simulated with the base case model in order to facilitate the comparison of the impacts of the weathering reactions on the partitioning of CO_2 . Cumulative fluxes of the aqueous solutes were calculated at the toe-slope ($x = 537$ m).

enhance pyrite oxidation, consistent with its pH-dependent dissolution kinetics (Equation 7; Williamson & Rimstidt, 1994). The response of Na export is controlled by the U-shaped pH-dependency of albite weathering, where the dissolution rate is minimal near neutral pH and increases under both alkaline and acidic conditions. In our base case, dolomite buffers the system to a slightly alkaline pH. Removing soil respiration (Scenario A) reduces carbonic acid, allowing the pH to become even more alkaline, thereby accelerating albite dissolution and maximizing Na^+ export. Conversely, excluding dolomite dissolution (scenario B) allows the background acidity to drive the pH down from this alkaline state toward the circumneutral minimum, which slows albite dissolution (Figures S25 and S26 in Supporting Information S1) and decreases Na export. This behavior highlights a key difference from carbonate-poor systems, where near-surface biological activity is the primary driver of silicate weathering by supplying acidity (Osorio-Leon et al., 2025). Moreover, our results show that sulfuric acid derived from pyrite oxidation has a limited effect on albite dissolution (Figures S25 and S26 in Supporting Information S1) and by extension Na export (scenario C; Figure 10d) because of the rapid buffering of carbonate. This is in agreement with Bufe et al. (2021) who reported limited enhancement of silicate weathering by sulfuric acid in the presence of carbonate minerals in Taiwan.

Furthermore, ion exchange reactions play a significant role on the cation fluxes in the different scenarios. For example, despite the removal of albite dissolution and a resulting increase in dolomite dissolution in scenario D (Figures S25 and S26 in Supporting Information S1), Ca export is not significantly altered in comparison to the base case model (Figure 10b), while Na export remains significant (Figure 10d). This discrepancy reflects enhanced Ca adsorption and Na release from the exchanger under reduced albite weathering. Conversely, desorption of Ca through Na adsorption is evident in scenario B, where removing carbonate weathering decreases Ca export by only 34%. This competitive exchange is eliminated in scenario F, where simultaneous removal of dolomite and albite weathering leads to 98% and 96% declines in Ca and Na exports, respectively. The impact of ion exchange reactions on Mg behavior is similar to that of Ca (Figure S27 in Supporting Information S1). The temporal change in concentration of species sorbed on the exchanger simulated in the different scenarios is provided in Supporting Information S1 (Figure S28).

Figure 10e explores the influence of individual weathering reactions on CO₂ partitioning between the subsurface and the atmosphere. Among all mechanisms, albite dissolution most effectively reduces CO_{2(g)} emissions through silicate alkalinity. Excluding this reaction (scenario D) leads to marked increase in CO_{2(g)} emissions relative to the base case (+0.43 mol·m⁻²·yr⁻¹). Removing carbonate together with albite in scenario F slightly alters the dynamics of the CO₂ consumption but does not substantially change the annual CO₂ budget compared to Scenario D (+0.38 mol·m⁻²·yr⁻¹). These simulations also show that CO₂ drawdown peaks during snowmelt, reflecting the importance of vertical percolation in transporting soil-respired CO₂ to the geochemical reaction front at greater depth where it can react with the minerals.

Balancing the uptake of CO₂ by alkaline reactions, the simulations show that pyrite oxidation and georespiration act as significant sources of CO₂, contributing 0.72 and 0.20 mol·m⁻²·yr⁻¹, respectively (Scenarios C and E; Figure 10e). In particular, the rate of georespiration is directly taken from Hilton et al. (2021) who estimated this rate based on measured rhenium fluxes in the East River. Moreover, the simulated pyrite-driven CO₂ flux is consistent with that derived from C-Q relationships by Winnick et al. (2017; 0.79 mol·m⁻²·yr⁻¹) and supports independent evidence for elevated pyrite oxidation in the East River. For comparison, sulfuric acid-driven CO₂ fluxes are lower in the Mackenzie River Basin, an important sedimentary rock-dominated watershed of the Rockies (0.058 mol·m⁻²·yr⁻¹; Calmels et al., 2007; Beaulieu et al., 2011), and in Southwest China (0.092 mol·m⁻²·yr⁻¹; Li et al., 2008), but substantially higher in the Gaoping River catchment in Taiwan (2.38 mol·m⁻²·yr⁻¹; Blattman et al., 2019).

Despite these CO₂ sources, our simulations indicate that shale weathering currently results in a net atmospheric CO₂ uptake of 0.33 mol·m⁻²·yr⁻¹. This net sink arises from the combined buffering effects of carbonate and silicate weathering, which retain a portion of soil CO₂ within the subsurface. Although only ~1.5% of soil-derived CO₂ is retained, it accounts for 27% of the DIC export due to the disproportionately large soil-atmosphere CO₂ exchange relative to deeper fluxes. This is consistent with previous estimates of biogenic DIC contributions in the Mackenzie River ([24 – 38]%; Calmels et al., 2007; Beaulieu et al., 2011).

On geological timescales (10⁴ – 10⁶ year), however, approximately 50% of the carbon exported to the ocean is released to the atmosphere during marine carbonate precipitation (Beaulieu et al., 2011). Because less than half of the DIC export at our site is biogenic, the current weathering regime functions as a net CO₂ source, with estimated emissions of 0.27 mol CO₂·m⁻²·yr⁻¹. In contrast, silicate-dominated catchments such as Coal Creek located near the East River exhibit higher biogenic DIC fractions (57%; Kerins et al., 2024), emphasizing the role of lithological heterogeneity in shaping carbon budgets at the watershed scale. In particular, silicate-rich regions serve as long-term CO₂ sinks, offsetting emissions from carbonate- and shale-dominated functional zones.

4.6. Impacts of Transient Forcing on Shale Weathering and Biogeochemical Fluxes

To quantify the impact of climatic variability on shale weathering and associated biogeochemical fluxes, we performed three additional simulations under distinct climate forcing scenarios:

- *Steady-state forcing*: Constant water infiltration (850 mm·yr⁻¹) and evapotranspiration (500 mm·yr⁻¹), matching the 2016 – 2020 averages, and a fixed vertical temperature gradient representative of present-day average subsurface conditions.
- *Constant hydrologic forcing with transient temperature*: Water infiltration and evapotranspiration remain constant, while temperature varies spatially and temporally, as in the base case model.

- *Transient hydrologic forcing with constant temperature:* Water infiltration and evapotranspiration vary seasonally as in the base case, while temperature remains constant.

The annual reaction rates and hydrochemical fluxes quantified in these scenarios are summarized in Figure 11 and show that temporal variations in water infiltration are a dominant driver of carbonate weathering intensity, DIC export, and CO₂ partitioning.

A comparison of the different mineral reaction rates reveals their distinct sensitivities to hydroclimatic forcing, providing insight into their unique controlling mechanisms. Dolomite dissolution is the most sensitive weathering reaction to transient forcing (Figures 11a–11d). Its rate decreases substantially under constant water infiltration (~40% decline), which highlights that carbonate weathering in this system is primarily limited by the transport of soil-derived carbonic acid to the weathering front. In contrast, pyrite oxidation shows a much more limited sensitivity to the hydroclimatic variability (~10% decline under constant infiltration). This limited sensitivity is consistent with the findings that the primary control for the oxidative dissolution of pyrite is the water saturation, which governs gaseous O₂ diffusion, rather than the magnitude of the water flux (Section 4.4). Georespiration rates are moderately affected by both hydrologic and thermal transients (Figure 11d). Lower oxidation of petrogenic organic matter under constant temperature conditions is primarily due to the dampened summer peak in georespiration (Figure S31 in Supporting Information S1). This result aligns with Soulet et al. (2021), who reported enhanced rock OC oxidation at elevated temperatures in shallow shale outcrops in the Laval catchment, France.

The most significant change in hydrochemical fluxes obtained under steady-state conditions compared to the transient model is the reversal of the hillslope's net carbon balance. Without transient infiltration events, the annual soil CO₂ drawdown becomes negative ($-0.08 \text{ mol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$), effectively turning shale weathering into a CO₂ source. This result underscores the critical role of infiltration events in transporting atmospheric CO₂ to depth, where it is efficiently retained by mineral alkalinity. In fact, during snowmelt, elevated water saturation suppresses gas exchange with the atmosphere, promoting CO₂ transport into the subsurface, which enhances carbonate weathering. Conversely, constant infiltration leads to persistently dry surface conditions, which limit CO₂ drawdown and favor atmospheric loss. The lower CO₂ drawdown and dolomite dissolution under constant water infiltration translate into a substantial decrease in DIC export (Figure 11e), while other aqueous solute fluxes are not significantly altered under transient conditions (Figures 11f–11h).

Taken together, these results emphasize the importance of seasonal hydrologic pulses, particularly snowmelt events, in transferring soil-derived CO₂ to the subsurface, which in turn enhances carbonate weathering. While silicate weathering contributes significantly to acid buffering and long-term CO₂ consumption, it is comparatively less sensitive to infiltration dynamics. This supports observations by Tipper et al. (2006), who documented stronger monsoonal response of carbonates versus silicates in the Marsyandi catchment, Nepal. Our findings highlight that the transient hydrologic connectivity between soil respiration and carbonate dissolution occurring during snowmelt is a key mechanism shaping the carbon balance and the DIC export associated with shale weathering in mountainous watersheds.

4.7. Effects of Slope Angle on Weathering Fluxes and Carbon Partitioning

Slope angle exerts a key control on hillslope hydrology, influencing flow pathways, residence times, and thus weathering reaction rates and carbon fluxes. Here, we assess the sensitivity of weathering reactions and CO₂ partitioning to variations in average slope angle ([14 – 55]%) using a synthetic model with a regular surface topography (i.e., without the local slope variations as present in the base case). All other aspects of the base case model are kept identical, including domain size, boundary conditions, and geochemical/hydrogeological conditions. Figure 12 illustrates the strong influence of the slope angle on subsurface carbon fluxes and weathering dynamics.

As the slope increases, the model predicts a substantial increase in the transfer of soil-derived CO₂ into the subsurface (Figure 12a). Specifically, the fraction of soil CO₂ retained belowground rises from 1.36% to 4.45% as the slope increases from 14% to 55%. This trend is well described by an exponential function, reflecting a non-linear system response where steeper slopes become progressively more efficient at promoting the transfer of soil-derived CO₂ into the subsurface. Concurrently, CO₂ emissions associated with pyrite oxidation also increase from 0.50 to 0.75 mol·m⁻²·yr⁻¹ over the same slope interval, following a power-law relationship (Figure 12b).

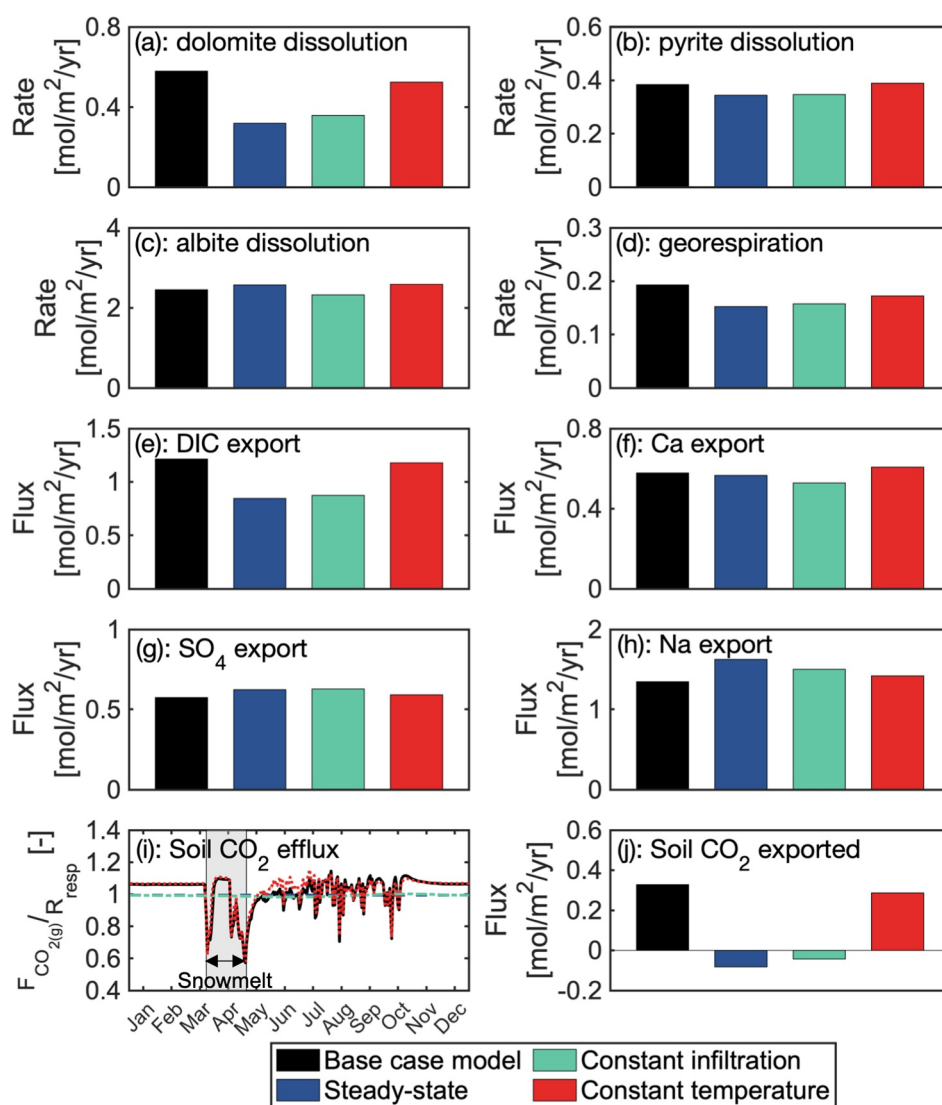


Figure 11. Comparison of mineral reaction rates and biogeochemical fluxes simulated under transient and steady-state climate forcing conditions: (a–d) average mineral reaction rates; (e–h) average fluxes of geogenic species exported from the hillslope to the floodplain; (i) temporal evolution of the ratio between CO_2 emitted from the subsurface to the atmosphere and CO_2 produced by soil respiration; (j) annual amount of soil CO_2 exported downslope. Total solute exports were calculated at the toe-slope ($x = 537$ m).

Consistent with the findings presented in Section 4.4, these trends reflect the more efficient water drainage under steeper terrain leading to a lower water table and deeper percolation of meteoric water during infiltration events (Figures S34 and S35 in Supporting Information S1). Drier conditions under steeper slopes favor $\text{O}_{2(\text{g})}$ diffusion into the subsurface. In turn, pyrite oxidation rises from 0.24 to $0.39 \text{ mol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ (Figure 12d), thereby enhancing sulfuric acid-driven carbonate weathering and associated CO_2 release (Figure 12b).

Conversely, enhanced drainage during snowmelt favors the drawdown of soil-derived CO_2 , leading to greater buffering by carbonate and silicate minerals. As illustrated in Figure 12c, this effect is most evident in the change in dolomite dissolution, which is more responsive to acid pulses from infiltrating snowmelt. Dolomite weathering increases from 0.38 to $0.92 \text{ mol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ as slope increases from 14% to 55% . In contrast, albite weathering shows a more modest response, rising from 2.36 to $2.88 \text{ mol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, and is not markedly enhanced during snowmelt, consistent with the lower sensitivity of silicates to short-term carbonic acid influxes (Figure 12e). Georespiration remains largely unaffected by slope angle (Figure 12f).

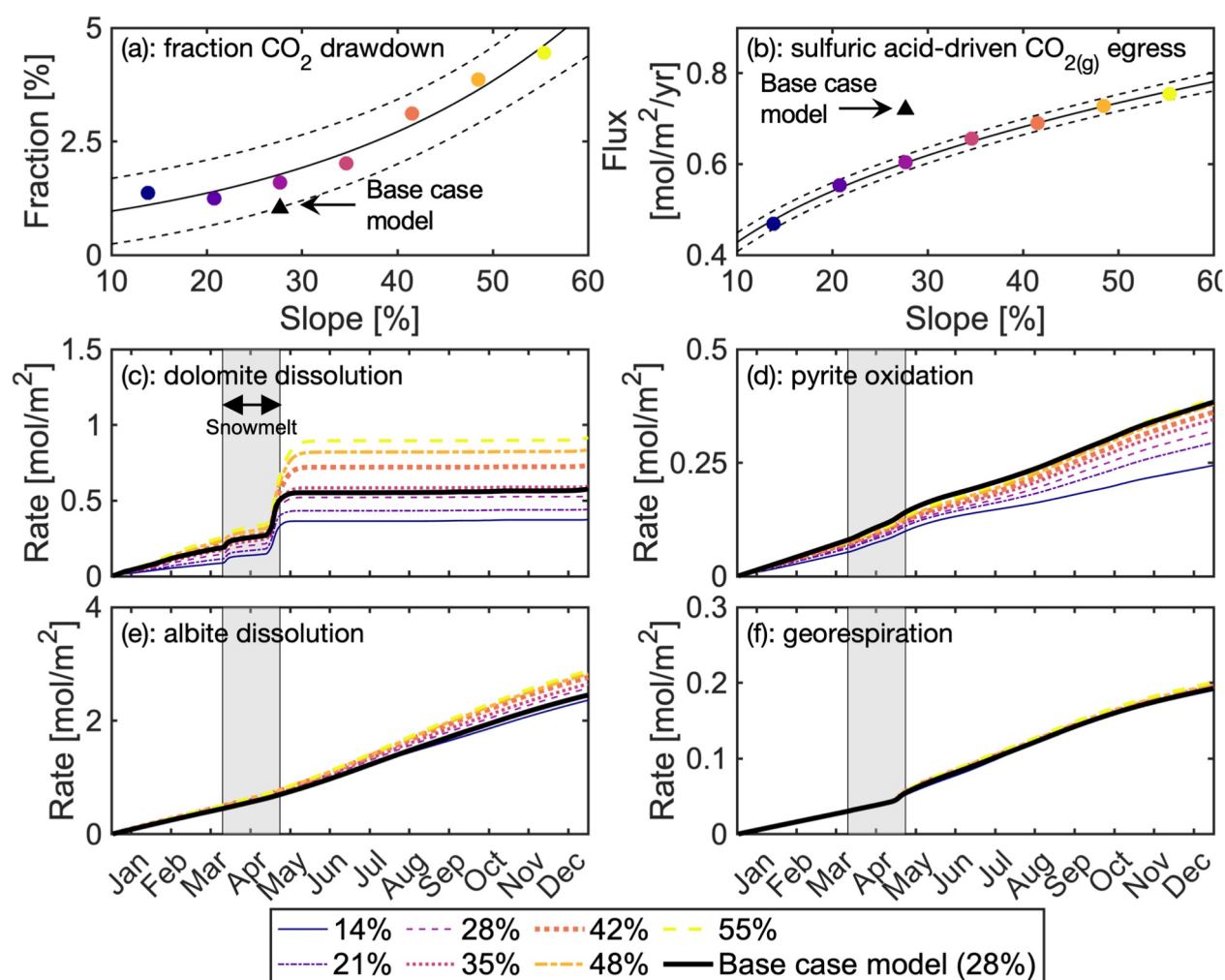


Figure 12. Controls of slope angle on CO₂ partitioning and weathering rates. (a) Fraction of soil CO₂ transferred to the subsurface at an annual timescale; (b) CO_{2(g)} flux associated with pyrite oxidation; (c)–(d) cumulative geochemical reaction rates. Simulated CO₂ drawdown and mineral dissolution rates are integrated over the entire hillslope domain. The contribution of sulfuric acid derived from pyrite oxidation to the CO₂ emissions shown in panel (b) was quantified by repeating the simulations in the absence of pyrite. In panels (a) and (b), solid lines represent best-fit functions (exponential and power law, respectively) and dashed lines indicate the associated 95% confidence intervals. The exponential function in panel (a) follows the form $y = a \cdot \exp(b \cdot x)$, with best-fit coefficients $a = 0.68$ (95% CI: 0.42 – 0.95) and $b = 0.035$ (95% CI: 0.026 – 0.043). The power-law expression in panel (b) follows the form $y = a \cdot x^b$ with best-fit coefficients $a = 0.20$ (95% CI: 0.18 – 0.21) and $b = 0.34$ (95% CI: 0.31 – 0.36).

Interestingly, at an equal slope of 28%, the synthetic model with regular topography predicts a higher CO₂ drawdown (1.59%) and lower pyrite-derived CO₂ emissions (0.60 mol·m^{−2}·yr^{−1}) compared to the base case (1.03% and 0.72 mol·m^{−2}·yr^{−1}, respectively; Figures 12a and 12b). This discrepancy is primarily attributed to enhanced pyrite oxidation in the base case, driven by local topographic irregularities, as evidenced by the lower oxidation rate in the corresponding flat-topography scenario (Figure 12d). In contrast, dolomite and albite dissolution rates are comparable between the two models at this slope (Figures 12c and 12d).

Overall, these results demonstrate that both the average slope angle and local topographic variations exert a critical influence on CO₂ partitioning and weathering dynamics along hillslopes, highlighting the importance of topographic heterogeneity in regulating biogeochemical fluxes in mountainous terrain.

5. Conclusions

The weathering of sedimentary rocks has been recognized as a critical process influencing both water quality and the global carbon cycle. However, the absence of models that simultaneously capture transient near-surface

conditions driven by climatic forcing, multiphase transport of reactants, the interplay of multiple biogeochemical processes, and subsurface heterogeneity has hindered a rigorous understanding and quantification of terrestrial biogeochemical fluxes associated with sedimentary rocks. In this study, we addressed this gap by conducting a detailed process-based analysis of the subsurface biogeochemical fluxes in a soil-mantled hillslope underlain by shale within a high-elevation mountainous watershed of Colorado. Based on experimental characterization of the subsurface, we implemented a multiphase and multidimensional reactive transport model that mathematically describes the dynamic coupling between soil respiration, geochemical reactions, and hydrological processes during shale weathering under transient hydrological and thermodynamic conditions. This framework enables us to quantitatively evaluate the relative contributions and interactive controls of co-occurring biogeochemical processes on aqueous solute exports to the adjacent floodplain and on the partitioning of CO₂ between the subsurface and the atmosphere.

Our results show that near-surface hydrological conditions exert a dominant yet complex influence on the reactivity of the shale mineral assemblage. In particular, hydroclimatic forcing events affect soil respiration dynamics and dictate the delivery of reactants from the atmosphere to the geochemical reaction fronts. We find that mineral reactions respond differently to such forcing due to specific seasonal coupling between physical and chemical processes, variable reactant transport pathways, and mineral-specific sensitivities to the hydrochemical conditions. Specifically, dolomite dissolution is disproportionately high during spring snowmelt as significant infiltration of meteoric water following dry conditions beneath the snowpack stimulates soil respiration and enhances the transport of biogenic carbonic acid to the mineral weathering front. In contrast, pyrite oxidation is primarily driven by lower near-surface water saturation that facilitates oxygen penetration via gaseous diffusion, while plagioclase feldspar (albite, in this case) is less sensitive to hydrologic variability.

Surface topography influences water flow in the near-surface, and consequently has important implication for the magnitude, dynamics, and spatial distribution of the mineral reaction rates. Our findings highlight two important topographic features that favor sulfide and carbonate minerals weathering. First, streamlines divergence under sharp topographic features can promote the downward advective transport of dissolved O₂ and CO₂ to reactive minerals. Second, steeper terrain enhances water drainage, lowering near-surface water saturation and enhancing vertical infiltration during recharge events such as snowmelt. These conditions favor O₂ diffusion and CO₂ delivery to the weathering front. Because of these topographic controls, we find that slope variations along the hillslope result in localized zones experiencing higher weathering rates. While previous studies have highlighted the influence of small-scale topographic variation on runoff (Özgen-Xian et al., 2020) and soil biogeochemistry (Frei et al., 2012), and that of large-scale topographic relief on mixing dynamics (Bandopadhyay et al., 2018), this study is the first to directly link topographic controls to the spatial distribution of weathering rates. This spatial heterogeneity has important implications for the carbon balance, particularly through increased CO₂ emissions from pyrite oxidation in areas of enhanced reactivity.

Our model also highlights the importance of explicitly capturing acid-base interactions between biogeochemical reactions for rigorously describing the reactivity of sedimentary rocks and associated biogeochemical fluxes. Under current field conditions, shale weathering acts as a short-term net CO₂ sink (0.33 mol-m⁻²·yr⁻¹), with alkaline silicate weathering consuming more atmospheric CO₂ than is generated by oxidation reactions. Pyrite-driven carbonate weathering is the largest CO₂ source (0.72 mol-m⁻²·yr⁻¹), while georespiration represents a secondary but significant source (0.20 mol-m⁻²·yr⁻¹). We demonstrate that a key aspect of the carbon balance associated with shale weathering in snow-covered environments is its high sensitivity to spring snowmelt, which maximizes the drawdown of CO₂. This CO₂ is subsequently buffered by mineral alkalinity and transported as DIC to the river system. However, because the exported DIC under present-day conditions is predominantly geogenic, shale weathering at our field site ultimately serves as an atmospheric carbon source when considering marine carbon precipitation occurring over longer time-scale. This quantitative estimate should be viewed as a conceptual classification of the current system. A true long-term projection would require a dynamic model that accounts for the critical roles of erosion, uplift, and climatic shifts, which determine the evolution of weathering fluxes (e.g., West et al., 2005). For instance, our sensitivity analysis highlights that, in the absence of snowmelt, shale weathering would shift from a transient CO₂ sink to a direct CO₂ source, underscoring the sensitivity of this balance to the prevailing climate regime.

This process-based analysis represents a critical step toward a comprehensive understanding of the factors and processes that control headwater quality and carbon balance in shale-rich mountainous watersheds. The flexible

mechanistic modeling approach presented in this study can be adapted to other landscape units where the distinct impacts of geomorphologic features, vegetation cover, and climatic forcing conditions on biogeochemical fluxes cannot be easily extrapolated (Calmels et al., 2014; Slosson et al., 2025). Moreover, the detailed insights gained at such an intermediate scale, focusing on specific landscape components such as hillslopes, are of interest for the development of a generalizable description of watershed hydrochemistry (Bao et al., 2017; Beaulieu et al., 2012; Duffy et al., 2014; Godderis et al., 2006; Kerins et al., 2024; Li, 2019; Xu et al., 2022; Zhi et al., 2019). Integrating subsurface-surface hydrology, ecosystem dynamics, and geochemical reactions across lithologies will improve predictions of watershed hydrochemical responses to climate forcing and enable quantification of contributions from distinct landscape units. Such integrated modeling is essential for designing effective mitigation strategies to address the rapid evolution of high-elevation watersheds driven by climate change.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Input files for the two-dimensional (2D) base case reactive transport model, along with the simulation results used for quantitative analysis and figure generation are available through the ESS-DIVE database (Stolze et al., 2025a, <https://doi.org/10.15485/3005940>). Field measurements data set used to evaluate the model performance, including aqueous chemistry (Dong et al., 2025a, <https://doi.org/10.15485/1660459>; Williams et al., 2025, <https://doi.org/10.15485/1668054>; Dong et al., 2025b, <https://doi.org/10.15485/1668055>), gas chemistry (Wan et al., 2024b, <https://doi.org/10.15485/2322567>; Wu et al., 2025, <https://doi.org/10.15485/3007697>), hydrological parameters (Wan et al., 2024b, <https://doi.org/10.15485/2322567>), and soil microbial biomass (Sorensen et al., 2019, <https://doi.org/10.15485/1577267>), are also publicly available on ESS-DIVE. The augmented PFLOTRAN source code required to reproduce the simulations presented in this study are permanently archived in a Zenodo repository (Stolze et al., 2025b). The code modifications include the implementation of depth-dependent temperature variations and the integration of Reaction Sandboxes (Hammond, 2022) to simulate the biogeochemical reactions. The repository is available at: <https://doi.org/10.5281/zenodo.17923668>.

Acknowledgments

This work was supported by the Watershed Function Science Focus Area project at Lawrence Berkeley National Laboratory funded by the U.S. Department of Energy, Office of Science, Biological and Environmental Research under Contract No. DE-AC02-05CH11231. This research used resources of the National Energy Research Scientific Computing Center (NERSC), a department of Energy Office of Science User Facility using NERSC awards BER-ERCAP28550 and BER-ERCAP33789, for the allocation years 2024 and 2025, respectively. We thank Madison Burrus and Dylan O'Ryan for their technical assistance in preparing and publishing the data set on the ESS-DIVE repository. Constructive comments and suggestions of three anonymous reviewers helped improving the quality of the manuscript.

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