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## From Soils to Streams: Connecting Terrestrial Carbon Transformation, Chemical Weathering, and Solute Export Across Hydrological Regimes

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# Water Resources Research®

## RESEARCH ARTICLE

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### Key Points:

- Numerical experiments show droughts enhance vertical CO<sub>2</sub> export to the atmosphere, whereas storms promote lateral carbon export into streams
- Carbonate precipitation reduces inorganic carbon (IC) in water under dry conditions while dissolution adds IC in water under wet conditions
- Subsurface structures exert smaller influence on the rates of carbon transformation and chemical weathering than hydrological conditions

### Supporting Information:

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

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## From Soils to Streams: Connecting Terrestrial Carbon Transformation, Chemical Weathering, and Solute Export Across Hydrological Regimes

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**Abstract** Soil biota generates carbon that exports vertically to the atmosphere (CO<sub>2</sub>) and transports laterally to streams and rivers (dissolved organic and inorganic carbon, DOC and DIC). These processes, together with chemical weathering, vary with flow paths across hydrological regimes; yet an integrated understanding of these interactive processes is still lacking. Here we ask: *How and to what extent do subsurface carbon transformation, chemical weathering, and solute export differ across hydrological and subsurface structure regimes?* We address this question using a hillslope reactive transport model calibrated using soil CO<sub>2</sub> and water chemistry data from Fitch, a temperate forest at the ecotone boundary of the Eastern temperate forest and mid-continent grasslands in Kansas, USA. Model results show that droughts (discharge at 0.08 mm/day) promoted deeper flow paths, longer water transit time, carbonate precipitation, and mineralization of organic carbon (OC) into inorganic carbon (IC) (~98% of OC). Of the IC produced, ~86% was emitted upward as CO<sub>2</sub> gas and ~14% was exported laterally as DIC into the stream. Storms (8.0 mm/day) led to carbonate dissolution but reduced OC mineralization (~88% of OC) and promoted DOC production (~12% of OC) and lateral fluxes of IC (~53% of produced IC). Differences in shallow-versus-deep permeability contrasts led to smaller difference (<10%) than discharge-induced differences and were most pronounced under wet conditions. High permeability contrasts (low vertical connectivity) enhanced lateral fluxes. Model results generally delineate hillslopes as active CO<sub>2</sub> producers and vertical carbon transporters under dry conditions, and as active DOC producers and lateral carbon transporter under wet conditions.

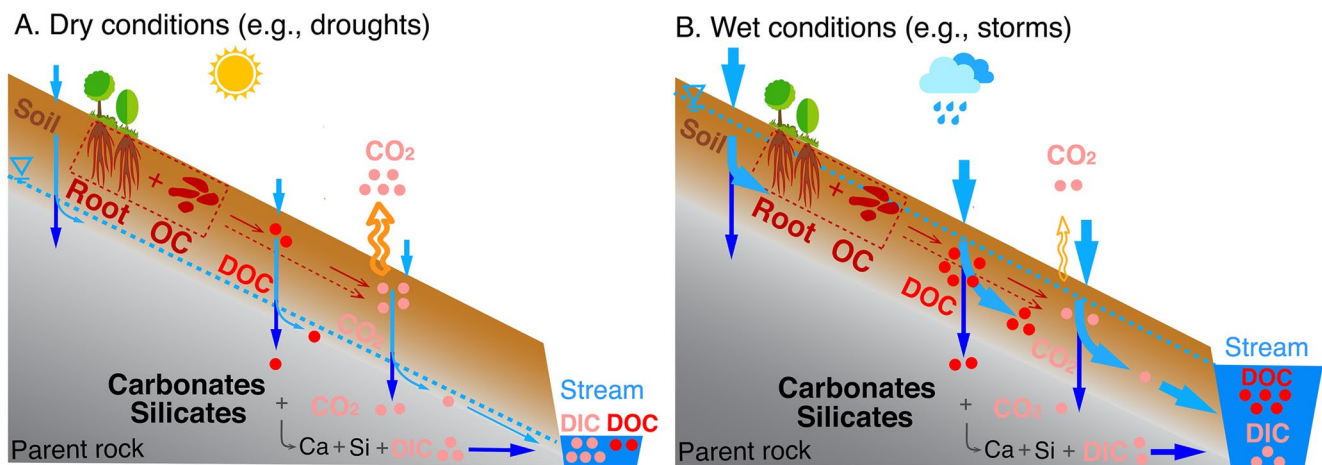
## 1. Introduction

Soil is the largest terrestrial carbon pool (Batjes, 2014). Vertical fluxes of CO<sub>2</sub> into the atmosphere have been extensively studied (e.g., Bond-Lamberty et al., 2020; Chapin et al., 2006; Jian et al., 2021). Lateral fluxes of dissolved organic and inorganic carbon (DOC and DIC) from terrestrial to aquatic systems have been increasingly recognized for emitting substantial amounts of CO<sub>2</sub> along river corridors (e.g., Barnes et al., 2018; Battin et al., 2009; Regnier et al., 2013). Vertical and lateral carbon fluxes, however, are often studied separately within disciplinary boundaries (Brookfield et al., 2021; Grimm et al., 2003). Their connections, partitioning, and relationship to carbon transformation across gradients of hydroclimatic and subsurface conditions have remained poorly understood. As a result, quantifications of carbon transformation rates and fluxes have remained highly uncertain (Duvert et al., 2018).

Organic carbon (OC) transformation and chemical weathering (i.e., carbonate dissolution and precipitation) are key processes that produce dissolved and gaseous carbon and drive terrestrial carbon dynamics. Their rates depend on hydroclimatic conditions (Figure 1) that are bound to change under future climates with intensifying hydrological extremes including droughts and storms (Ault, 2020; Mastrotheodoros et al., 2020). Soil respiration rates often increase with temperature (Lloyd & Taylor, 1994) but peak at 50%–70% water saturation (Yan et al., 2018).

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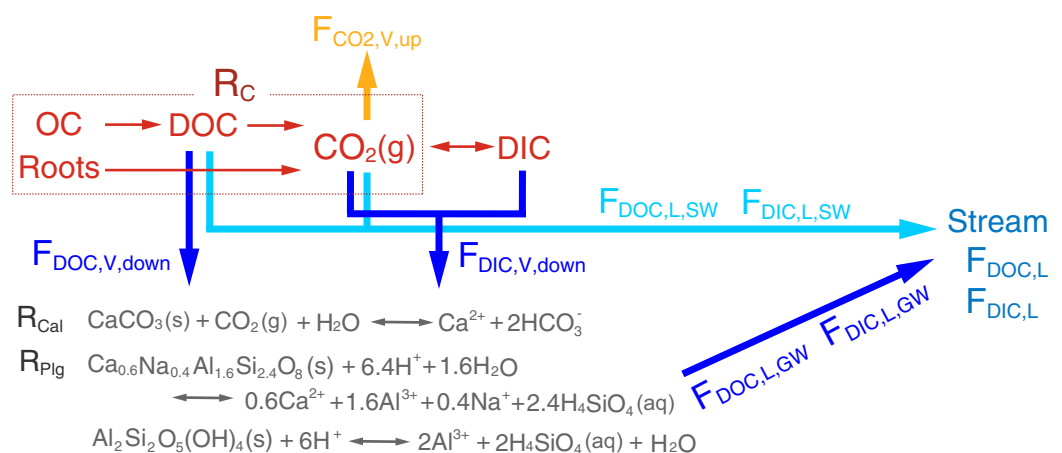
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**Figure 1.** Conceptual diagrams of reactions and fluxes under dry and wet conditions. (a) Under dry conditions (e.g., droughts), deeper flow paths (dashed blue lines), slower flow (thin blue arrows), and longer water transit times promote soil  $\text{CO}_2(\text{g})$  production and vertical carbon export to the atmosphere (yellow arrows) but reduce lateral export of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) via shallow and deeper groundwater flow paths. (b) Under wet conditions (e.g., storms), shallow flow paths and fast flow in OC-rich soils (thick blue arrows) and shorter water transit times reduce carbon mineralization, soil  $\text{CO}_2(\text{g})$  production, and vertical  $\text{CO}_2$  fluxes but promote lateral carbon fluxes to streams and rivers.

Overly wet conditions can induce anoxic conditions and limit soil respiration (Vasconcelos et al., 2004); overly dry conditions, although with abundant oxygen, can limit microbial metabolism and reduce respiration rates by increasing physical protection of OC and reducing carbon-enzyme contact (Li, Maher, et al., 2017). Droughts can also induce anaerobic metabolism and hypoxic conditions, especially in headwater streams (Gómez-Gener et al., 2020).

Hydrological events and flow regimes regulate flow paths and solute export from terrestrial to aquatic systems. Large storms enhance land-river hydrological connectivity and mobilize stored DOC (Raymond & Saiers, 2010; Wen et al., 2020). Riverine DOC concentrations increase with river discharge in approximately 80% of watersheds in the U.S. (Zarnetske et al., 2018). Wetter conditions and resultant predominance of shallow soil water flow often facilitates the export of solutes enriched in shallow soils. Soil water charged with high  $\text{CO}_2$  and DOC



**Figure 2.** Reactions (red arrows) and fluxes (blue and yellow arrows) considered in this work. The reactions include soil respiration (root respiration and microbial OC mineralization) to produce dissolved inorganic carbon (DIC),  $\text{CO}_2(\text{g})$ , and dissolved organic carbon (DOC). Gaseous  $\text{CO}_2$  can vertically emit to the atmosphere ( $F_{\text{CO}_2,\text{V},\text{up}}$ ), dissolve in water to become DIC, or precipitate to become carbonate minerals. Dissolved carbon (DIC and DOC) can flow laterally via shallow water path (SW,  $F_{\text{DOC,L,SW}}$ ,  $F_{\text{DIC,L,SW}}$ ), entering streams via a shorter path with shorter transit time, or vertically recharge to the depth and eventually enter streams via groundwater (GW) discharge via a longer flow path. Note that  $F_{\text{DIC,L}} = F_{\text{DIC,L,SW}} + F_{\text{DIC,L,GW}}$  and  $F_{\text{DOC,L}} = F_{\text{DOC,L,SW}} + F_{\text{DOC,L,GW}}$ . Detailed reactions and reaction rate laws are in Table 1 and Text S2 in Supporting information S1.

can also recharge more into the deeper subsurface under wet conditions, thereby enhancing weathering and DIC lateral fluxes (Clow & Mast, 2010; Wen et al., 2021). In contrast, droughts reduce DOC export not only by reducing water fluxes but also by drought-induced acidification and decreasing DOC solubility (Clark et al., 2010). Under dry conditions, streams are often sustained by deeper groundwater flow that is characterized by low DOC and elevated geogenic solutes.

Subsurface flow paths and solute export also depend on subsurface physical structures, particularly the vertical distribution of permeability over depth, or vertical connectivity (Figure 1). Permeability typically decreases with depth following an exponential- or power-law form (Cardenas & Jiang, 2010; Saar & Manga, 2004). Soil permeability is generally orders-of-magnitude higher than that of weathered or parent rocks at depth (Welch & Allen, 2014), leading to water fluxes that sharply decrease with depth (Harman & Cosans, 2019). The vertical distribution of permeability therefore regulates water flow partitioning via shallow versus deep paths and new and old water transit times (Harman & Sivapalan, 2009; Sprenger et al., 2018; Xiao et al., 2021). Subsurface structure and shallow versus deeper water partitioning is often reflected in stream chemistry, as older waters from deeper subsurface often carry highly concentrated weathering products such as silica and cations (Benettin et al., 2015; Torres & Baronas, 2021), whereas younger waters are often enriched with solutes that are abundant in shallow soils (Benettin et al., 2020; Li et al., 2021).

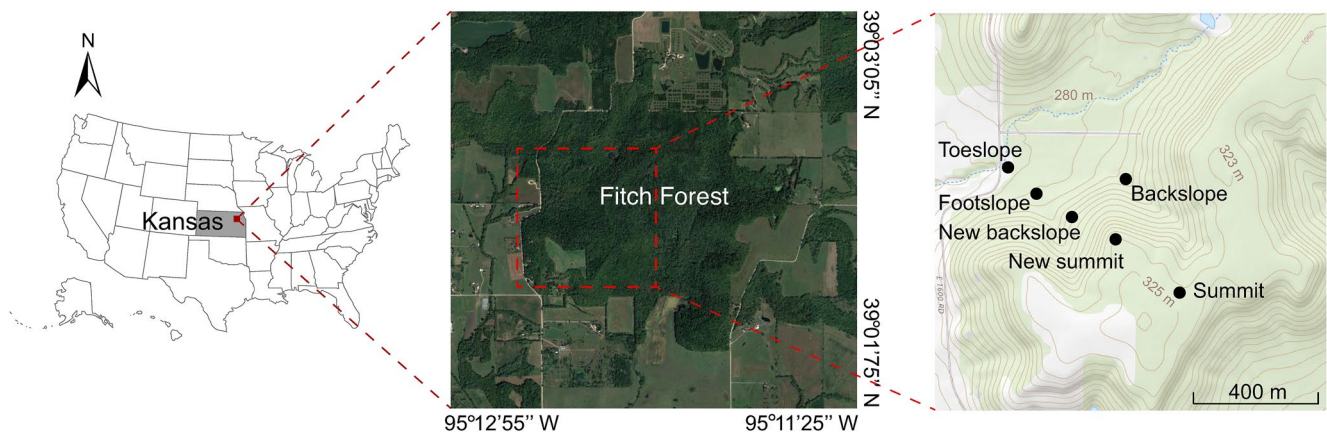
The linkage between subsurface flow paths and reactions, including soil carbon transformation and chemical weathering at depth, however, is generally poorly understood. Soil CO<sub>2</sub> effluxes are typically quantified using localized, small-scale CO<sub>2</sub> vertical fluxes measured at ground surface (Barba et al., 2018; Carey et al., 2016; Kuz'yakov, 2006; Richter & Billings, 2015). Concerted measurements of DIC, <sup>13</sup>C isotopes, and instantaneous river discharge have revealed the connections between source waters (shallow soil water and deeper groundwater) and their delivery to streams (Duvert et al., 2020; Horgby, Boix Canadell, et al., 2019; Horgby, Gómez-Gener, et al., 2019). The entangled interactions among multiple factors however challenge the differentiation of individual effects. We generally lack an integrated view on the connections and regulation of soil respiration and chemical weathering and solute and gas export fluxes.

Here we begin to address this knowledge gap by asking the question: *How and to what extent do subsurface carbon transformation, chemical weathering, and solute export differ across hydrological and subsurface structure regimes?* To answer this question, we draw upon the rich foundation of reactive transport modeling (RTM) that has been widely used to understand hydrological and biogeochemical coupling (Ackerer et al., 2021; Dwivedi et al., 2022; Jung & Navarre-Sitchler, 2018; Li, Bao, et al., 2017; Wen et al., 2020). Here we first developed a hillslope-scale RTM using soil CO<sub>2</sub> and soil water chemistry data from the Fitch Forest, a temperate forest at the ecotone boundary of the Eastern temperate forest and mid-continent grasslands in Kansas (Fitch, 2006). We then fixed reaction parameters and conditions at Fitch (e.g., hillslope topography, organic carbon content, mineralogy) and carried out numerical experiments by varying conditions across hydrological extremes from droughts to storms (mean discharge from 0.08 to 8.0 mm/day) in three scenarios of shallow-versus-deep permeability contrasts. By doing so we can differentiate and quantify the impacts of hydrological conditions and permeability contrasts on reactions and solute export.

## 2. Research Site, Field Measurements, and Data

The Fitch Forest (hereafter Fitch) at the University of Kansas Field Station (Figure 3) is located at the ecotone boundary of the Eastern temperate forest and mid-continent grasslands in Kansas. The mean annual temperature and precipitation are 13.3°C and 945 mm, respectively. The majority of rainfall occurs in the spring and summer (Brunsell & Wilson, 2013). The elevation ranges from 274 to 326 m and slope from 2.0% to 57.5%. The bedrock is mainly composed by the Upper and Middle Pennsylvania limestone, sandstone, and shale (Ashok & Sophocleous, 2008; Dickey et al., 1977). At an ecotone boundary, Fitch is highly sensitive to climate conditions; relatively small decreases in mean annual precipitation could push the system to more savannah-like land cover. The observed daily range of mean discharge at Fitch varies from 0.04 to 8.3 mm/day.

Fitch has extensive measurements of soil properties, water table, and water chemistry data. We specifically focused on a planar hillslope covered by temperate forests to reduce topographic complexity; dominant vegetation is composed of mature oak (*Quercus* spp.), hickory (*Carya* spp.), elm (*Ulmus americana*), white ash (*Frax-*



**Figure 3.** Location of the study site. Subsurface characterization data of physical and chemical properties from four hillslope locations (summit, backslope, footslope, and toeslope) were used for model setup. To better align the transect, two of the piezometers (backslope and summit) were moved to different locations on the topographic position, labeled “New Backslope” and “New Summit.”

*inus americana*), trees with walnut (*Juglans nigra*), hackberry (*Celtis occidentalis*), and other hardwood species contributing some canopy cover. Data from four hillslope positions (summit, backslope, footslope, and toeslope) encompass the variations across the entire hillslope and were used in RTM, as detailed later.

Soils at these four topographic positions were excavated, described, and sampled by the Natural Resources Conservation Service (NRCS) to a depth of 1 m. The soil order is Mollisols in general while soils at the summit, backslope, and footslope/toeslope were mapped as the Oska series (Vertic Argiudolls), Rosendale (Typic Eutrudepts)-Bendena (Lithic Hapludolls) complex, and Martin series (Aquertic Argiudolls), respectively (Soil Survey Staff, 2022). Soils at all locations were classified as silty clay loam (Soil Survey Staff, 2010), with an average proportion of ~42.4% clay, 52.8% silt, and 4.8% sand (Table S1 in Supporting Information S1). Soil porosity decreases from ~0.57 at surface to ~0.43 at a depth of 1.0 m.

We used soil CO<sub>2</sub> data from the National Ecological Observatory Network at depths of 10, 40, and 120 cm in the mineral soil along an adjacent hillslope transect. These data were collected at the same time period as the soil water samples. To quantify the water-extractable organic carbon (EOC), soils were collected using a bucket auger and segmented in 10 cm depth intervals. EOC contains a suite of carbon-rich compounds, including organic acids, important biotic weathering agents (Herbert & Bertsch, 1995), as well as compounds with a high potential of undergoing microbial mineralization to CO<sub>2</sub> (Buscot & Varma, 2005) (more details in Supporting Information S1).

Hydrologic conditions were quantified using PVC piezometers installed at all hillslope positions to a depth of ~160 cm (small variations exist in installation depth due to varied depth of auger refusal). Two of the piezometers were immediately adjacent to the soil pits (toeslope and footslope) while two were moved to different locations on the topographic position to better align the transect (backslope and summit; see sites labeled “New Backslope” and “New Summit” in Figure 3). The water table elevations and water chemistry in the piezometers were measured weekly or after precipitation events, an approach also implemented for soil water chemistry measurements using ceramic suction cup lysimeters (SK-20s Meter with ~1.0% uncertainties, at depths 30, 60, and 90 cm). Water samples were filtered using 0.45 μm nylon syringe filters. Alkalinity and major cations (e.g., Ca) were analyzed using an auto-titrator and an inductively coupled plasma optical emission spectroscopy (~1.0%–5.0% uncertainties), respectively.

The rainfall chemistry was based on data from the National Atmospheric Deposition Program (*nadp.sws.uiuc.edu*) and from Konza Prairie (*lter.konza.ksu.edu/station-keywords/precipitation-chemistry*), the closest data site from Fitch (~145 km west). The rainfall has a pH of 6.1, with DOC, DIC, Ca, Na, H<sub>4</sub>SiO<sub>4</sub>(aq), Al, and Cl<sup>-</sup> at 60.0, 12.0, 38.0, 78.0, 10.0, 0.2, and 10.0 μmol/L, respectively. The initial soil water was set in the model using the averaged soil water concentrations, which has a pH of 7.0, with DOC, DIC, Ca, Na, H<sub>4</sub>SiO<sub>4</sub>(aq), Al, and Cl<sup>-</sup> at 2.0 × 10<sup>-4</sup>, 7.0 × 10<sup>-4</sup>, 5.0 × 10<sup>-4</sup>, 1.0 × 10<sup>-4</sup>, 3.0 × 10<sup>-4</sup>, 1.0 × 10<sup>-9</sup>, and 1.0 × 10<sup>-4</sup> mol/L, respectively.

### 3. Hillslope Reactive Transport Model

#### 3.1. The Model Setup

##### 3.1.1. Governing Equations

A two-dimensional (2D) hillslope RTM was set up using the code CrunchTope (Steeffel et al., 2015). CrunchTope has been extensively used in understanding chemical weathering, biogeochemical reactions, and physical property evolution (Deng et al., 2017; Druhan et al., 2021; Jung & Navarre-Sitchler, 2018; Lawrence et al., 2014; Li et al., 2010; Maher et al., 2006; Xiao et al., 2021). These applications use 1D or 2D rectangular domains except that Xiao et al. (2021) also adopt a hillslope model. The code integrates advective and diffusive/dispersive transport and biogeochemical reactions. For a representative solute  $i$ , it solves the following mass conservation equations,

$$\frac{\partial}{\partial t} (\phi C_i) = \nabla \cdot \{ \phi \mathbf{D}_i \nabla C_i - \mathbf{u} C_i \} + r_i \quad (1)$$

where  $\phi$  is porosity,  $C_i$  is the concentration of solute  $i$  (mol/m<sup>3</sup> water),  $\mathbf{D}_i$  is the hydrodynamic dispersion tensor (m<sup>2</sup> porous media/s),  $\mathbf{u}$  is the Darcy flow velocity (m<sup>3</sup> water/m<sup>2</sup> porous media/s), and  $r_i$  is the reaction rate (mol/m<sup>3</sup> water/s) described further in Section 3.2.

##### 3.1.2. Domain Setup

The 2D hillslope domain (450.0 × 58.0 m) was set up using the average slope (6.5°) of the Fitch hillslope. The spatial resolution was 4.5 and 0.5 m in the horizontal and vertical directions, respectively. We assumed that the soil and substratum extended through the upper 3.0 m based on observations at the site. Below 3.0 m, the subsurface generally consists of weathered bedrock (3.0–6.0 m) and parent rock (below 6.0 m), which often harbors the groundwater (GW).

##### 3.1.3. Subsurface Physical Properties and Flow Field

The porosity–depth relationship in the top 6.0 m was assumed to follow the exponential function  $\phi = \phi_0 e^{-\alpha_\phi z}$  (Gleeson et al., 2016), where  $\phi_0$  is the porosity at the ground surface and  $\alpha_\phi$  quantifies the steepness of the porosity gradient. Values of  $\phi_0$  and  $\alpha_\phi$  were estimated to be 0.53 and 0.17, respectively (Figure 4a1), based on soil porosity data in the top 1.0 m (Table S1 in Supporting Information S1) and an assumed value of 0.2 at 6.0 m for typical parent rocks. The porosity below 6.0 m (i.e., parent rocks) was assumed to be constant at 0.2.

The permeability in the top 6.0 m was prescribed using the widely used power law function  $\kappa = \kappa_0 z^{b_\kappa}$  (Cardenas & Jiang, 2010; Saar & Manga, 2004), where  $\kappa_0$  is the intrinsic permeability (m<sup>2</sup>) at the ground surface,  $z$  is the depth from the ground surface (m), and  $b_\kappa$  is the power law exponent that quantifies the steepness of the permeability gradient. The values of  $\kappa_0$  and  $b_\kappa$  were estimated to be  $1.7 \times 10^{-11}$  m<sup>2</sup> and  $-0.4$ , respectively (Figure 4a2), based on the averages of soil permeability in the top 1.0 m calculated from porosity data using the Kozeny-Carman equation (Carman, 1997; Rawls et al., 1998) and an assumed value of  $10^{-12}$  m<sup>2</sup> at 6.0 m for parent rocks. This is consistent with field observations that permeability contrast between the shallow soil and parent bedrock is about 1–3 orders of magnitude (Elhakim, 2016). The parent rock permeability below 6.0 m was kept constant at  $10^{-12}$  m<sup>2</sup>.

The model assumes that all water entering the soil eventually leaves as discharge. The mean annual discharge at Fitch is 0.8 mm/day (or 0.3 m/a), essentially the difference between mean annual precipitation (2.6 mm/day) and evapotranspiration (1.8 mm/day). The average water table depth (WTD) in the soil was estimated to be 1.5 m at the discharge of 0.8 mm/day (Figure S1 in Supporting Information S1). The unsaturated–saturated interface was prescribed in the model as the depth of WTD. In the unsaturated zone (i.e., above WTD), the vertical flow rate was assumed to equal the infiltration rate (0.8 mm/day) with zero lateral flow. In the saturated zone, the flow field was calculated based on Darcy's law following the permeability distribution. As will be detailed in Section 3.3, water table depth was assumed to vary with discharge to mimic the rising and falling water tables under wet and dry conditions.

### 3.1.4. Subsurface Biogeochemical Properties

The abundance of OC and roots typically decreases exponentially with depth (Murphy et al., 2019), with the volume percentage (v/v) of OC and roots following the exponential function  $VF_{OC} = VF_{OC,0}e^{-\alpha_{oc}z}$ , where  $VF_{OC,0}$  is the average volume fraction at the ground surface. This value was set at 0.04 based on the measured root/soil volume ratio (0.01–0.05) and the typical OC content of 0.01–0.07 in forest soils (Foth, 1978; Sorenson et al., 2020). The coefficient  $\alpha_{oc}$  quantifies the steepness of the decline with depth; it was set at  $-0.5$  following the observations that the totals of OC and roots in the second meter are  $\sim 50\%$  of that in the top meter of forested soils (Jobbagy & Jackson, 2000). Similarly, biomass was assumed to be  $\sim 5 \times 10^{-5}$  (v/v) in the soil surface (Michelsen et al., 2004) and decreased exponentially to  $\sim 10^{-7}$  (v/v) at the weathered rock–parent rock interface (6.0 m). Below this interface, OC and root volumes were assumed constant and two-orders-of-magnitude lower than those at the ground surface (Billings et al., 2018). Soil water chemistry indicates that the mineralogy is primarily calcite and plagioclase (Figure S2 in Supporting Information S1). Calcite increased with depth from zero (volume fraction) in soils to 0.10 (v/v) in the parent rock. Plagioclase was assumed constant (0.22, v/v), based on reported mineral volumes in Kansas (Dickey et al., 1977; Ransom et al., 1998).

### 3.2. Reaction Network and Rate Laws

The biotic reactions include OC decomposition and root respiration (Figure 2 and Table 1). OC is transformed into DOC and  $CO_2$  through microbial activities (Reactions 1–2). Roots can respire to produce  $CO_2$  (Reaction 3); they can also release exudates as DOC, the mineralization of which releases  $CO_2$  (Ekblad & Högberg, 2001; Jones et al., 2004). We do not have data to differentiate these detailed reaction mechanisms so Reaction 3 represents the “bulk”  $CO_2$  production from roots (i.e., root respiration + mineralization of associated root exudates). The organic carbon has three forms in the model: soil OC, microbial community represented as  $C_5H_7O_2N$ , and DOC (Ahrens et al., 2015; Riley et al., 2014). Produced  $CO_2$  can become  $CO_2(g)$  when reaching solubility (Reaction 5) and emit to the atmosphere (Reaction 4); dissolved  $CO_2$  is DIC, the sum of  $CO_2(aq)$ ,  $HCO_3^-$ , and  $CO_3^{2-}$  (Reactions 6–7). The dissolution of  $CO_2$  acidifies water and accelerates weathering (Reactions 9–11). Produced DOC can sorb on solid surfaces (Reaction 8), which affects its availability for mineralization. The reaction parameters were calibrated by reproducing water chemistry data (Sections 3.3 and 4.1).

Produced  $CO_2(g)$  can emit vertically to the atmosphere, which is represented by a “diffusion” or “release” rate  $r_{D,CO_2(g)} = D_{CO_2(g)}A \left(1 - \frac{C_{CO_2(g)}}{K_{eq,4}}\right)$ . Here  $C_{CO_2(g)}$  is the soil  $CO_2$  gas concentration, and  $K_{eq,4}$  ( $4 \times 10^{-4}$  atm) represents the atmospheric  $CO_2$  level. That is, diffusion only occurs when soil  $CO_2(g)$  concentration is higher than the atmospheric  $CO_2$  level.  $D_{CO_2(g)}$  is the diffusion rate ( $mol/m^2/s$ ), calibrated by fitting measured  $CO_2(g)$  over depth, and  $A$  is the surface area ( $m^2$ ). Because diffusion rates are highest in top soil,  $D_{CO_2(g)}$  was set the highest at the soil surface ( $2.5 \times 10^{-4}$   $mol/m^2/s$ ) and exponentially decreased to  $2.5 \times 10^{-9}$   $mol/m^2/s$  in the deep zone. In CrunchTope, this rate was set up in the form of the Transition State Theory rate law (Plummer et al., 1978). The approximation for diffusion here aims to capture the first-order dynamics with data constraints and to avoid overburdening the model with multiphase flow dynamics without relevant data. Similar approximations have been used in Heidari et al. (2017) and Wen et al. (2021).

The model does not include the rate dependence of carbon transformations on temperature and soil moisture; thus, the overall rates are similar across hydrological gradients. Although not ideal, this approach enables the differentiation of the effects of varying flow paths and permeability distribution on reactions and export fluxes without the confounding effects of temperature and soil moisture. In addition, variations in water table depth and flow paths reflect the wetness condition at the site.

### 3.3. Model Calibration

Reaction parameters in the model for shallow soil processes were calibrated with constraints from direct field observations. They include averaged soil pore water chemistry data (DOC, alkalinity, Ca, Si, and Na concentrations) and soil  $CO_2$  (Pabich et al., 2001; Sullivan et al., 2019). Most parameters for deep subsurface processes were taken from literature (e.g., porosity and permeability, mineral percentage, and OC abundance), due to the lack of measurements at the site. The reaction parameters for deep subsurface processes were calibrated by comparing simulated water chemistry to literature values with similar lithology and land cover (“+” in Figure 4)

**Table 1**  
Key Reactions and Kinetic and Thermodynamic Parameters<sup>a</sup>

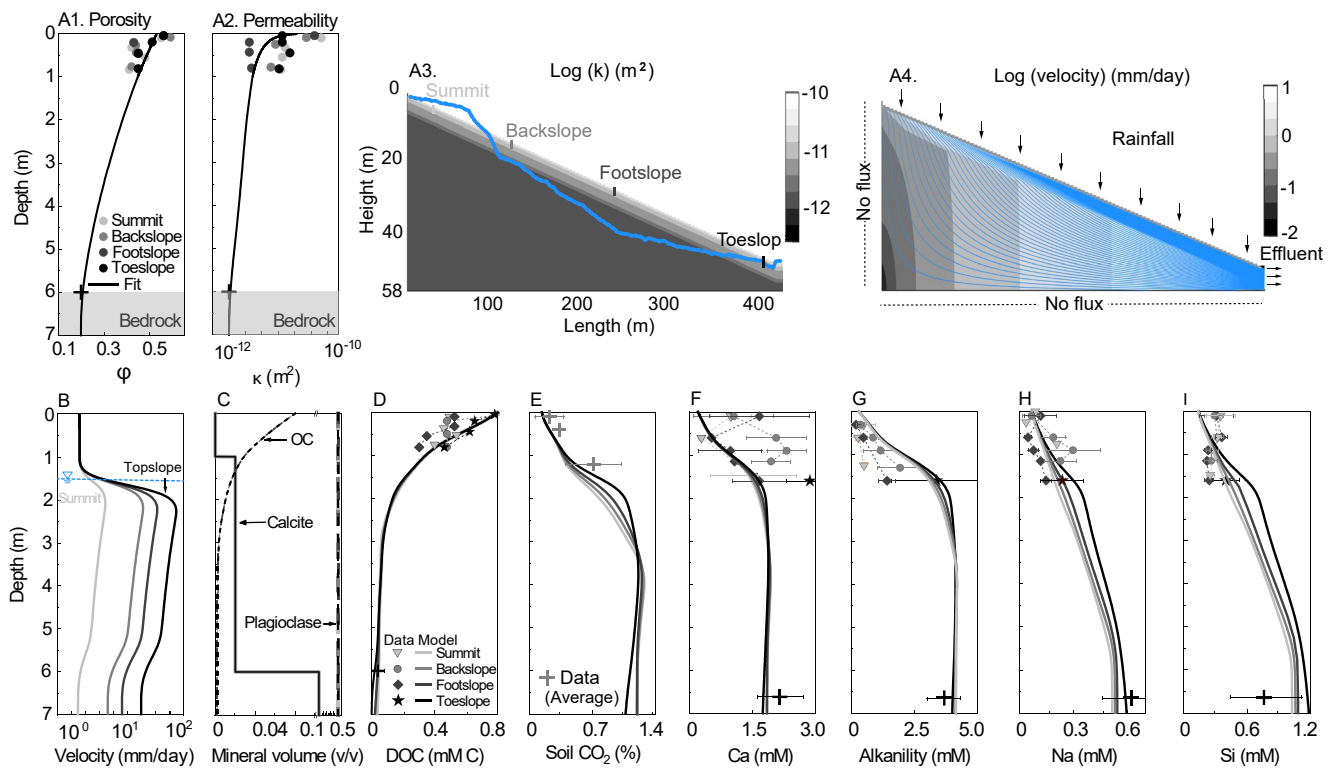
Reaction	$\log_{10} K_{eq}$ <sup>b</sup>	$\log_{10} k$ (mol/m <sup>2</sup> /s) <sup>c,d</sup>	Specific surface area (m <sup>2</sup> /g) <sup>d</sup>
<b>Bio-mediated reactions: Root respiration + OC decomposition<sup>b</sup></b>			
(1) OC(s) → 500DOC	–	10 <sup>–6.7</sup>	5.0
(2) DOC → 4.8CO <sub>2</sub> (aq)	–	10 <sup>–4.5</sup>	1.0
(3) Roots → CO <sub>2</sub> (aq)	–	–	–
<b>CO<sub>2</sub> partitioning in gas and water phases<sup>c</sup></b>			
(4) CO <sub>2</sub> (g) → CO <sub>2</sub> (g *)	–3.40	10 <sup>–5.0</sup>	1.0
(5) CO <sub>2</sub> (aq) ↔ CO <sub>2</sub> (g)	–1.50	–	–
(6) CO <sub>2</sub> (aq) + H <sub>2</sub> O ↔ H <sup>+</sup> + HCO <sub>3</sub> <sup>–</sup>	–6.35	–	–
(7) HCO <sub>3</sub> <sup>–</sup> ↔ H <sup>+</sup> + CO <sub>3</sub> <sup>2–</sup>	–10.33	–	–
<b>Sorption</b>			
(8) ≡ X + DOC ↔ ≡ XDOC	10 <sup>0.2</sup>	Soil sorption capacity 7.5 × 10 <sup>–5</sup> mol/g soil	
<b>Chemical weathering<sup>f</sup></b>			
(9) CaCO <sub>3</sub> (s) + CO <sub>2</sub> (aq) + H <sub>2</sub> O ↔ Ca <sup>2+</sup> + 2HCO <sub>3</sub> <sup>–</sup>	–4.52	–6.69	0.84
CaCO <sub>3</sub> (s) ↔ Ca <sup>2+</sup> + CO <sub>3</sub> <sup>2–</sup>			
CaCO <sub>3</sub> (s) + 2H <sup>+</sup> ↔ Ca <sup>2+</sup> + 2HCO <sub>3</sub> <sup>–</sup>			
(10) Ca <sub>0.613</sub> Na <sub>0.387</sub> Al <sub>1.613</sub> (SiO <sub>4</sub> ) <sub>2.387</sub> (s) + 6.452H <sup>+</sup> + 1.548H <sub>2</sub> O ↔ 0.613Ca <sup>2+</sup> + 1.613Al <sup>3+</sup> + 0.387Na <sup>+</sup> + 2.387H <sub>4</sub> SiO <sub>4</sub> (aq)	18.11	–11.30	6.70 × 10 <sup>–4</sup>
Ca <sub>0.613</sub> Na <sub>0.387</sub> Al <sub>1.613</sub> (SiO <sub>4</sub> ) <sub>2.387</sub> (s) + 8.000H <sub>2</sub> O ↔ 0.613Ca <sup>2+</sup> + 1.613Al <sup>3+</sup> + 0.387Na <sup>+</sup> + 2.387H <sub>4</sub> SiO <sub>4</sub> (aq) + 6.452OH <sup>–</sup>			
(11) Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> (s) + 6H <sup>+</sup> ↔ 2Al <sup>3+</sup> + 2H <sub>4</sub> SiO <sub>4</sub> (aq) + H <sub>2</sub> O	6.81	–12.97	17.50

<sup>a</sup>Detailed descriptions about rate laws were included in Text S2 in Supporting Information S1. All parameters refer to the condition at 15°C. <sup>b</sup>The molecular formula of OC and DOC is assumed to follow the general form of (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)<sub>1000</sub>(s) and C<sub>12</sub>H<sub>24</sub>O<sub>12</sub>(aq), respectively (Riley et al., 2014). <sup>c</sup>The rate constant *k* in the microbe mediated reactions 1 and 2 refers to  $\mu$  in Equations S1–S2 in Supporting Information S1 (mol C/m<sup>2</sup>/s and mol C/mol biomass/s), respectively; For the local CO<sub>2</sub> production from roots (Reaction 3), with no explicit rate law, *k* is not defined and its local rate is directly assumed to be the same with that from OC (Equation S4 in Supporting Information S1). That is, root respiration was assumed to contribute 50% of the total soil respiration at the annual scale, which is within the reported range of 40%–60% in forest ecosystems (Hanson et al., 2000; Subke et al., 2006). <sup>d</sup>Values of *K<sub>eq</sub>* were interpolated using the EQ3/6 database (Wolery et al., 1990), except Reactions 4–5, and Reaction 8 (i.e., *K<sub>eq,4</sub>*, *K<sub>eq,5</sub>*, and *K<sub>eq,8</sub>*). *K<sub>eq,4</sub>* is used to represent the atmospheric CO<sub>2</sub> level; *K<sub>eq,5</sub>* is equal to the coefficient *K<sub>H</sub>* in the Henry's law for CO<sub>2</sub>. The value for *K<sub>eq,8</sub>* and the soil sorption capacity was from Oren and Chefetz (2012) and Jin et al. (2010), respectively. <sup>e</sup>Reaction 4 approximates the process of the gas CO<sub>2</sub> diffusing into atmosphere by having a solid phase “CO<sub>2</sub>(g\*)” that acts as an atmospheric sink that can infinitely take in the released CO<sub>2</sub>(g). <sup>f</sup>The kinetic rate parameters and specific surface areas for mineral dissolution and precipitation (Reactions 9–11) were from Palandri and Kharaka (2004).

(McElwee et al., 1995; Pabich et al., 2001; Whittemore et al., 2014). As summarized in Table 2, this encapsulates our best efforts to constrain the model based on our knowledge of the Fitch site. One limitation is the lack of time-resolved water chemistry data, which limits the extent to which the model can capture the dynamics.

The model performance was evaluated using the Nash-Sutcliffe efficiency (NSE) that quantified the residual variance of model outputs compared to measurements (Moriassi et al., 2007). To reproduce soil CO<sub>2</sub> and pore water chemistry data to the satisfactory NSE level (>0.5), we first set the rate constant of OC decomposition ( $\mu_{OC}$ ) using literature values (Ahrens et al., 2015; Wang et al., 2015) and then adjusted CO<sub>2</sub> production rates ( $\mu_{CO_2,OC}$ ) based on the reported ranges for forests (Carey et al., 2016). Lastly, we calibrated the CO<sub>2</sub>(g) diffusion rate (*D<sub>CO2(g)</sub>*) with reported soil CO<sub>2</sub> fluxes from 10<sup>–5</sup>–10<sup>–6</sup> mol C/m<sup>2</sup>/s (Heinemeyer et al., 2007) at the soil surface to 10<sup>–9</sup> mol C/m<sup>2</sup>/s in deep layers. All these calibrations ultimately lead to the reproduction of the depth profiles of measured soil CO<sub>2</sub>, alkalinity, Ca, Si, and Na concentrations (depicted later in Figure 4).





**Figure 4.** Top row: (a1) Depth profiles of porosity (field measurements), (a2) depth profile of permeability, estimated from Kozeny-Carman equation, (a3) hillslope permeability distribution, (a4) simulated flow velocity distribution. Blue lines in (a4) are flow paths. Areas with more blue lines indicate converging flow paths and therefore higher flow velocities. Bottom row: (b) Depth profiles of flow velocities, (c) mineral volume fraction ( $v/v$ ), (d) DOC (mM C), (e) soil  $\text{CO}_2$  (%), (f) Ca, (g) alkalinity, (h) Na, and (i) Si. Units of all solute concentrations are mM. Symbols are the average of field data; error bars are for one standard deviation; solid lines are model outputs. The dash line in (b) represents the prescribed water table depth (WTD) in the model based on field data. Overall, the top 6 m of the subsurface contributed >91% of stream water and was the most hydrologically active.

### 3.4. Numerical Experiments

To differentiate the impacts of hydrological conditions and subsurface physical structures, we designed numerical experiments with different flow regimes and shallow-versus-deep permeability contrasts while using the same reaction parameters and conditions as the base case at Fitch (e.g., organic carbon content, and mineralogy).

#### 3.4.1. Subsurface Physical Structures

Three shallow-versus-deep permeability contrast scenarios were set up with different  $b$  values in  $\kappa = \kappa_0 z^{b\kappa}$  for the layers above the bedrock (<6 m). The scenario without a shallow-versus-deep permeability contrast, named LContrast (for Low contrast), has a  $b_\kappa$  value of 0, such that permeability is homogeneous over depth. The scenario with median shallow-versus-deep contrast (MContrast for medium) has a  $b_\kappa$  value of  $-0.4$ , the same set up as the base case at Fitch. The high contrast case (HContrast for High) has a  $b_\kappa$  value of  $-2.0$  and a steep permeability decline over depth. The value of  $\kappa_0$  are the same  $1.7 \times 10^{-11} \text{ m}^2$  in all three cases. The permeability of the parent rock (below 6.0 m) was kept constant at  $1.7 \times 10^{-11} \text{ m}^2$ ,  $1.0 \times 10^{-12} \text{ m}^2$ , and  $7.8 \times 10^{-14} \text{ m}^2$  in LContrast, MContrast, and HContrast, respectively, based on typical ranges in literature (Elhakim, 2016). All other parameters (e.g., hillslope topography, reaction rate parameters, OC and mineral content) are the same in all three cases. The hillslope model was set up with no flow at the left and bottom boundaries such that all water entering the hill eventually leaves the hill via the toeslope (Figure 4a4).

#### 3.4.2. Rising and Falling Water Tables Across Hydrological Gradients

This work focused on changing hydrological conditions and set the temperature at  $15^\circ\text{C}$  in all simulation cases. Field observations (Figure S1 in Supporting Information S1) indicate different water table depths at different rain-

**Table 2**  
Main Model Input Parameters and Corresponding Data Constraints

	Parameters	Source for constrain	Description
Domain	Size (length, height, slope)	Fitch observation	Section 3.1
Physical properties	Porosity	Fitch observation	Section 3.1
	Permeability		
Hydrological conditions	Discharge	Fitch observation	Section 3.1
	Water table depth (WTD)		
Subsurface chemical properties	Water saturation		
	Rainwater (injecting)	Fitch observation	Sections 2 & 3.1
	CO <sub>2</sub> (initial)		
	Subsurface water chemistry (initial)		
	OC and root abundance		
	Mineralogy abundance		
	OC decomposition rate constant $\mu_{OC}$	Fitch observation: soil CO <sub>2</sub> and water chemistry	Sections 2, 3.2 and S2
	CO <sub>2</sub> production rate constant $\mu_{CO_2,OC}$		
	CO <sub>2</sub> (g) diffusion rate $D_{CO_2(g)}$		
	Chemical weathering, including kinetic rate constant, equilibrium constant, and mineral surface area	Literature-derived (Jin et al., 2010; Oren & Chefetz, 2012; Palandri & Kharaka, 2004; Wolery et al., 1990)	Sections 3.2 and S2

fall events, from 2.5 m at 0.08 mm/day (very dry) to 0.5 m at 8.0 mm/day (very wet). We therefore prescribed the unsaturated–saturated interface to be from 2.5 to 0.5 m in the model, depending on the corresponding discharge conditions. Five hydrological conditions were run in each permeability contrast scenario, yielding to a total of 15 cases. Each case was run until steady state, when concentrations at the domain outlet became relatively constant with time (within  $\pm 5\%$ ).

### 3.5. Water Transit Time, Concentrations, Rates, and Fluxes at the Hillslope Scale

#### 3.5.1. Water Transit Time

We used a “smart” tracer that goes through the decay process following zero-order kinetics  $\frac{dC}{dt} = -k_{decay}$ , where  $k_{decay}$  is the decay rate ( $=10^{-4}$  mol/L/a). The transit time ( $\tau_i$ ) of water arriving at a grid cell  $i$  can be estimated through the local tracer concentration following the solution of the equation  $\tau_i = t - 0 = \frac{C_0 - C_i}{k_{decay}}$ , where  $C_0$  and  $C_i$  are the tracer concentration in the rainfall and pore water in the grid cell  $i$  at time  $t$ . The tracer was simulated with a concentration in the rainfall ( $C_0$ ) of 0.9 mol/L and an initial zero concentration. The mean transit times in stream ( $\tau_{stream}$ ), shallow soil ( $\tau_{SW}$ ), and deep groundwater ( $\tau_{GW}$ ) were calculated using mean concentrations (averaged over depth) coming out of the soil zone (upper 3.0 m), groundwater zone (below 3.0 m), and stream using  $\tau_{SW} = \frac{C_0 - C_{SW}}{k_{decay}}$ ,  $\tau_{GW} = \frac{C_0 - C_{GW}}{k_{decay}}$ , and  $\tau_{stream} = \frac{C_0 - C_{stream}}{k_{decay}}$ , respectively.

#### 3.5.2. Solute Concentrations in Soil Water, Deep Groundwater, and Stream

We define the top 3.0 m as the shallow soil water zone (SW); the water below 3.0 m was considered as the deeper GW. Mean solute concentrations in SW ( $C_{SW}$ ) were calculated as  $\frac{\sum(C_{i,SW} \times u_i)}{\sum u_i}$ , where  $u_i$  is flow velocity and  $C_{i,SW}$  is the solute concentration in grid block  $i$  in soil zone (10 grid blocks away from the toeslope outlet to avoid mixing effects at the outlet). Similarly, mean solute concentrations in GW ( $C_{GW}$ ) were calculated as  $\frac{\sum(C_{i,GW} \times u_i)}{\sum u_i}$ , where  $C_{i,GW}$  is the local concentration in the grid block  $i$  of the GW zone close to the hillslope outlet. The stream concentration  $C_{stream}$  is the average effluent concentration at the hillslope outlet, calculated as  $\frac{\sum(C_i \times u_i)}{\sum u_i}$  with the solute concentration  $C_i$  and flow velocity  $u_i$  in the grid block  $i$  at the effluent. We also tested 2.0 and 4.0 m as soil depths. The calculated mean soil water and groundwater chemistry varied but the trend remained the same.

### 3.5.3. Hillslope Reaction Rates

Reaction rates  $R$  at the hillslope scale are the sum of the local rates in individual grids ( $r_i$ ) multiplied by the corresponding water volume in each grid ( $V_i$ ). The rate of net DOC production is  $R_{\text{DOC}} = \sum (r_{i,\text{DOC}} \times V_i)$ , where  $r_{i,\text{DOC}}$  is the difference between OC decomposition and DOC mineralization rates (Reactions 1–2, Equation S3 in Supporting Information S1). The net  $\text{CO}_2$  production rate is  $R_{\text{CO}_2} = \sum (r_{i,\text{CO}_2} \times V_i)$ , where  $r_{i,\text{CO}_2}$  includes both DOC decomposition (Reaction 2) and root respiration (Reaction 3) in the grid  $i$  (Equation S4 in Supporting Information S1). Mineral weathering rates are  $R_{\text{cal}} = \sum (r_{i,\text{cal}} \times V_i)$  and  $R_{\text{plg}} = \sum (r_{i,\text{plg}} \times V_i)$ . They follow the transition-state theory rate law (Equation S6 and Equation S7 in Supporting Information S1, respectively). The overall carbon production rate ( $R_c$ ) from OC and roots equals the sum of  $R_{\text{DOC}}$  and  $R_{\text{CO}_2}$  (Figure 2).

### 3.5.4. Biogeochemical Export Fluxes

The export fluxes  $F$  (Figure 2) include the vertical upward flux of  $\text{CO}_2$  to the atmosphere ( $F_{\text{CO}_2,V,\text{up}}$ ) and the lateral fluxes of dissolved organic and inorganic carbon into the stream ( $F_{\text{DOC,L}}$  and  $F_{\text{DIC,L}}$ ). The vertical flux ( $F_{\text{CO}_2,V,\text{up}}$ ) is the sum of local  $\text{CO}_2$  diffusion rates  $r_{i,D,\text{CO}_2(g)}$  (Equation S5 in Supporting Information S1) across the entire hillslope (i.e.,  $F_{\text{CO}_2,V,\text{up}} = \sum r_{i,D,\text{CO}_2(g)}$ ). Normally, only the top soil layer releases  $\text{CO}_2$  to the atmosphere and  $\text{CO}_2$  in deeper depths transport  $\text{CO}_2$  to the top layer. Gas transport however was not explicitly simulated in the model. The summation of gas diffusion in deeper grids, albeit with much lower upward diffusion rates, counts for  $\text{CO}_2$  diffusion from depths to shallow soils that eventually emit  $\text{CO}_2$  to the atmosphere. The lateral fluxes are the product of discharge ( $Q_T$ ) and concentrations at the outlet grids. The lateral export of DOC ( $F_{\text{DOC,L}}$ ) is the summation of outlet lateral fluxes from the shallow soil ( $F_{\text{DOC,L,SW}}$ ) and from deeper GW ( $F_{\text{DOC,L,GW}}$ ). Similarly,  $F_{\text{DIC,L}}$  is the summation of lateral SW fluxes ( $F_{\text{DIC,L,SW}}$ ) and GW fluxes ( $F_{\text{DIC,L,GW}}$ ). DIC came from both soil respiration and carbonate weathering. The soil respiration rates ( $F_{\text{DIC,SoilResp,L}}$ ) were estimated following  $F_{\text{DIC,SoilResp,L}} = F_{\text{DIC,L}} - R_{\text{cal}}$ . The overall carbon lateral export flux from biogenic carbon  $F_c$  was calculated as  $F_c = F_{\text{DIC,SoilResp,L}} + F_{\text{DOC,L}} + F_{\text{CO}_2,V,\text{up}}$ . The total carbon export flux from both soil respiration and carbonate weathering ( $F_{c,T}$ ) is the sum of  $F_{\text{DOC,L}}$ ,  $F_{\text{DIC,L}}$ , and  $F_{\text{CO}_2,V,\text{up}}$ . The geogenic solute fluxes ( $F_{\text{Ca,L}}$  and  $F_{\text{Si,L}}$ ) were calculated as the production of discharge and concentrations of Ca and Si, respectively. For Si,  $F_{\text{Si,L}}$  is the same as the overall silicate weathering rates (Reactions 10–11) at the hillslope scale. For Ca,  $F_{\text{Ca,L}}$  is the summation of calcite and silicate weathering rates multiplying corresponding stoichiometric coefficients.

## 4. Results

### 4.1. Effects of Hydrological Conditions

#### 4.1.1. The Fitch Base Case (MContrast)

Simulated flow velocities (Figure 4a1-3) at Fitch varied laterally and decreased with depth (Figure 4a4). At 0.8 mm/day (0.3 m/a), the infiltrated water propagated vertically until reaching the shallow water table at 1.5 m and then flowed laterally into the stream (Figure 4b). The toeslope “collected” water from the entire hillslope such that flow velocities were much higher (~80.0 mm/day) than those at the summit (~2.4 mm/day). The depth profile of DOC almost overlapped at the four sampling locations (Figure 4d). They decreased with depth from ~0.8 to <0.1 mM C, consistent with common observations of higher carbon concentrations in shallow soils (Pabich et al., 2001; Sullivan et al., 2019). Soil  $\text{CO}_2$ , Ca, alkalinity, Na, and Si concentrations generally increased with depth in the upper 2.0 m of soil (Figures 4e–4i). The model captured these variations in shallow soils (NSE > 0.5), indicating the model includes key processes that control soil water chemistry patterns. Concentrations below 2.0 m were not measured but the simulated concentrations were consistent with literature values for Kansas (Macpherson, 2009; McElwee et al., 1995; Pabich et al., 2001; Whittimore et al., 2014). Soil  $\text{CO}_2$  increased from 0.2% to ~1.3%, much higher than 0.04% in the atmosphere. Soil  $\text{CO}_2$  concentrations were similar in the upper 1.5 m in all hillslope positions. The depth profiles of Ca and alkalinity mirrored those of soil  $\text{CO}_2$ , indicating soil  $\text{CO}_2$  drove the concentration levels of these solutes. Although not included in the model, sulfate concentration increased from ~0.05 mM at 0.3 m to ~0.38 mM at 0.9 m, at least a half-order of magnitude lower than Ca and alkalinity concentrations at the same depth, indicating that carbonic acid is the major acid for mineral weathering. The dissolution of plagioclase elevated Na and Si concentrations both vertically (from soil to parent rock) and horizontally (from summit to toeslope).

Several parameters tuned during the model calibration were important in reproducing data. They include rate constants of OC decomposition ( $\mu_{OC}$  in Equation S1 in Supporting Information S1) that generated DOC, and rate constants of  $CO_2$  production ( $\mu_{CO_2,OC}$  in Equation S2 in Supporting Information S1). The depth profiles of soil  $CO_2$  data were essential to capture the depth profiles of alkalinity and Ca data. In addition,  $D_{CO_2(g)}$ , a proxy for rates of  $CO_2$  diffusion out of the domain (Equation S5 in Supporting Information S1), was important as it controlled the upward export of  $CO_2$  into the atmosphere ( $F_{CO_2,v,up}$ ). Mineral compositions of calcite and plagioclase were critical in reproducing Ca, Na, and Si concentrations. The soil water had abundant Ca, Na, and Si (Figure S2), suggesting a plagioclase formula of  $Ca_{0.61}Na_{0.39}Al_{1.61}(SiO_4)_{2.39}(s)$  (i.e., An60) and the dominant control of carbonate mineral. Other forms of plagioclase (e.g., An40 and 80) were tested but cannot reproduce Na and Si data.

#### 4.1.2. Biogeochemical Spatial Profiles

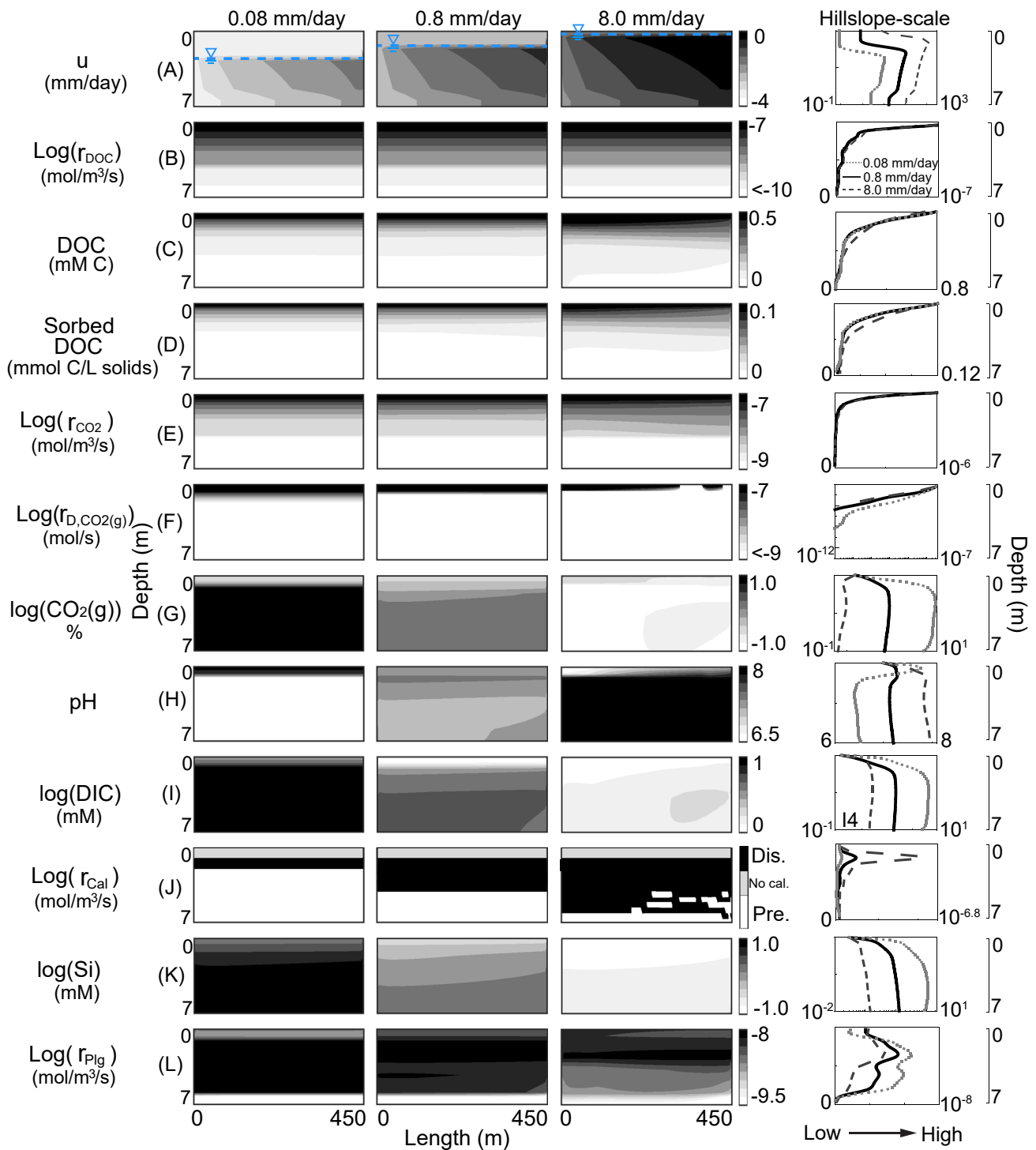
Most reactions occurred in the upper 7.0 m of the subsurface and are therefore shown in Figure 5. Flow velocities generally peaked at the unsaturated–saturated interface (Figure 5a). As conditions became wetter, the water table was set to be increasingly shallower. Across different hydrological conditions, DOC production rates  $r_{DOC}$  were highest ( $\sim 10^{-7}$  mol/m<sup>3</sup>/s) in the topsoil with abundant OC (Figures 5b and 4c) and lowest ( $\sim 10^{-11}$  mol/m<sup>3</sup>/s) at 7.0 m. This pattern generally led to higher DOC and sorbed DOC in shallow soils. At 8.0 mm/day, high flow flushed more DOC into the stream and deeper subsurface, leading to higher sorbed DOC at depth (Figure 5d). Similarly, soil  $CO_2$  production rates  $r_{CO_2}$  peaked in shallow soils and decreased with depth (Figure 5e). Topsoil  $CO_2$  however was the lowest because of the highest vertical upward fluxes to the atmosphere (Figures 5f and 5g). The  $CO_2$  production rates were not influenced as much by flow conditions, but  $CO_2$  concentrations depended on flow conditions because of the flow influence on export. Under dry conditions, diffusion exported soil  $CO_2$  upward but lateral export of DIC was slow such that soil  $CO_2$  levels remained high (Cueva et al., 2019; Olshansky et al., 2019); under wet conditions, concentrations were lower because of rapid water flow and higher DIC lateral export (Figures 5f and 5g).

The pH generally increased with discharge whereas concentrations of Ca and DIC concentrations decreased with discharge (Figures 5h and 5i). At 0.08 mm/day, high soil  $CO_2$  level and carbonate precipitation lowered pH ( $\sim 6.5$ ). At 8.0 mm/day, fast flow led to rapid lateral export of soil  $CO_2$  and carbonate dissolution, such that pH was much higher ( $\sim 8.0$ ). Calcite dissolution rates peaked at the calcite–no calcite interface when calcite was in contact with relatively young water still at disequilibrium (Figure 5j). Calcite precipitated in the deep subsurface as Ca and carbonate built up and approached equilibrium. The dissolving–precipitating interface (black vs. white color) progressively deepened from  $\sim 2.0$  m at 0.08 mm/day to  $\sim 6.5$  m at 8.0 mm/day, as the faster flow also replenished the deeper subsurface rapidly with water at disequilibrium (Figure 5j). Plagioclase weathering was much slower than carbonate weathering and depended on pH. With pH increasing from low to high discharge, plagioclase dissolution rates decreased (Figures 5k and 5l).

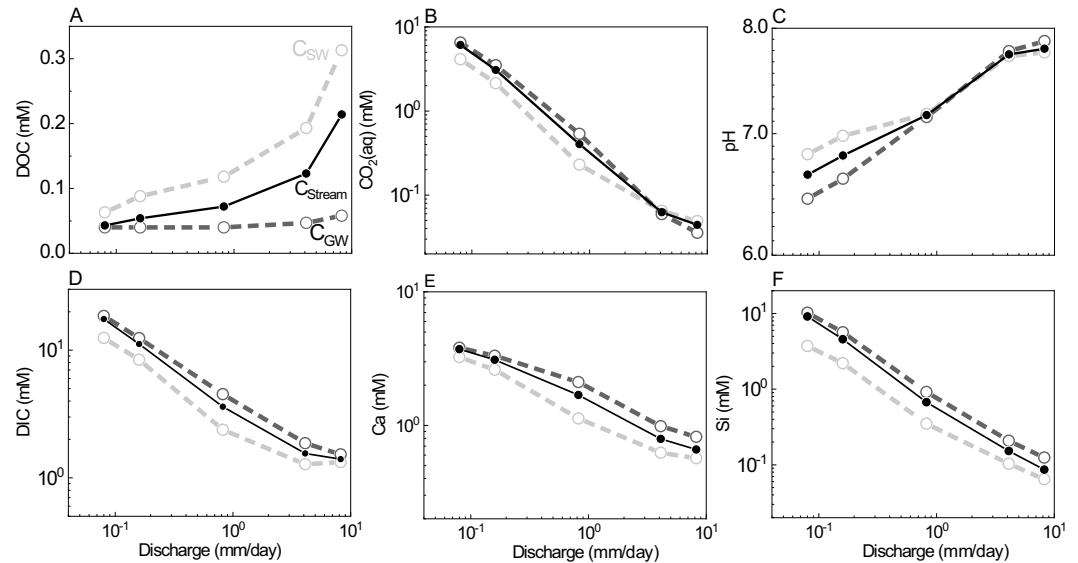
#### 4.1.3. Solute Concentrations in Different Waters

Soil and groundwater solute concentrations varied with discharge. For DOC, both soil and groundwater concentrations increased with discharge; Soil water concentrations ( $C_{SW}$ ) were higher than groundwater concentrations ( $C_{GW}$ ) (Figure 6a). The  $C_{SW}$  versus  $C_{GW}$  difference was small under dry conditions and increased under wet conditions, due to the flushing of DOC via top soils with more abundant DOC. Conversely, the  $C_{SW}$  and  $C_{GW}$  difference of other solutes ( $CO_2$ ,  $H^+$ , DIC, Ca, and Si) was generally higher under dry conditions and lower under wet conditions (Figures 6b–6f). The elevated water tables at high flow enhanced flow mixing at the toeslope and led to similar  $C_{SW}$  and  $C_{GW}$  before they entered the stream.

Stream water was a mixture of soil water and groundwater. Under wet conditions, soil water dominated stream water; under dry conditions, groundwater dominated streamflow. The stream concentration therefore approximated  $C_{GW}$  under dry conditions and mirrored  $C_{SW}$  under wet conditions. Stream DOC concentrations increased as discharge increased (flushing pattern, Figure 6a). Stream DIC, Ca, and Si concentrations decreased with increasing discharge, exhibiting a dilution pattern (Figures 6d–6f). Stream  $CO_2(aq)$  decreased from 6.8 to 0.04 mM, as stream pH increased and DIC decreased from dry to wet conditions. Generally,  $CO_2(aq)$  reached the highest level at the highest DIC and lowest pH.



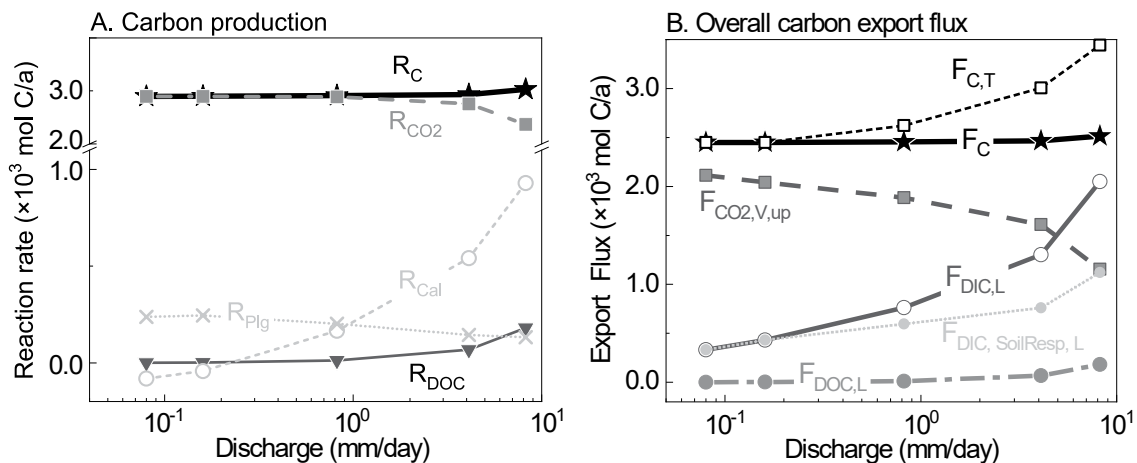
**Figure 5.** Simulated spatial profiles of (a) flow velocity, (b) DOC production rate,  $r_{\text{DOC}}$ , (c) DOC, (d) sorbed DOC, (e)  $\text{CO}_2$  production rate,  $r_{\text{CO}_2}$ , (f)  $\text{CO}_2$  vertical flux, (g) soil  $\text{CO}_2(\text{g})$  (%), (h) pH, (i) DIC, (j) carbonate weathering (calcite) rate,  $r_{\text{cal}}$ , (k) Si, and (L) silicate weathering (plagioclase) rate,  $r_{\text{plg}}$  at discharge of 0.08, 0.8, and 8.0 mm/day. All figures are for the top 7 m from the ground surface. The hillslope outlet is at the right. The right column shows horizontally-averaged quantities over depth at 0.08 mm/day (dotted), 0.8 mm/day (black), and 8.0 mm/day (dashed), respectively. The blue dash line in (a) is the prescribed unsaturated-saturated interface in the model following WTD data at Fitch. Soil  $\text{CO}_2(\text{g})$  (%) was calculated using Henry's law based on  $\text{CO}_2(\text{aq})$  and Henry's law constant.



**Figure 6.** Simulated soil water ( $C_{SW}$ ; gray dash) and groundwater ( $C_{GW}$ ; black dash) solute concentrations (at the toeslope before entering the stream) as a function of discharge ( $X$ -axis): (a) DOC, (b)  $CO_2(aq)$ , (c) pH, (d) DIC, (e) Ca, and (f) Si. Stream DOC ( $C_{stream}$ ; solid black line) exhibited a flushing pattern (increasing concentration with discharge) whereas the inorganic carbon ( $CO_2$  and DIC), Ca, and Si showed a dilution pattern (decreasing concentration with discharge). These solutes also have higher groundwater concentrations compared to soil water, the opposite of DOC.

#### 4.1.4. Carbon Rates and Fluxes at the Hillslope Scale

The rates of net DOC production (i.e.,  $R_{DOC} = R_{OC} - R_{CO_2,OC} = F_{DOC,L}$ ) increased from  $\sim 1.0$  to  $284 \text{ mol C/a}$  (from  $<0.1\%$  to  $12\%$  of the total processed carbon) when discharge increased from  $0.08$  to  $8.0 \text{ mm/day}$  (Figure 7), because higher discharge flushed DOC out quickly and lessened the mineralization of DOC to DIC and/or  $CO_2$  ( $R_{CO_2,OC}$ ). For the same reason, the rates of soil respiration or the net  $CO_2$  production ( $R_{CO_2} = R_{CO_2,rt} + R_{CO_2,OC}$ ) decreased from  $\sim 2,412$  to  $2,152 \text{ mol C/a}$  with increasing discharge. The rates of  $R_{CO_2}$  are generally more than an order of magnitude higher than  $R_{DOC}$ . In addition, more inorganic carbon was produced under dry conditions compared to wet conditions. The hillslope carbon transformation rate ( $R_C$ ) from OC and roots, which is the sum



**Figure 7.** (a) Hillslope-scale soil respiration rates ( $R_C$ ), production rates of DOC and  $CO_2$  ( $R_{DOC}$ ,  $R_{CO_2}$ ), and calcite and plagioclase weathering rates ( $R_{cal}$  and  $R_{plg}$ ); (b) DOC and DIC export fluxes.  $F_{DIC,L}$  is the total lateral DIC flux;  $F_{DIC,SoilResp,L}$  is the flux of carbon originated from soil respiration, excluding those from carbonate dissolution. Dry conditions favored the production and vertical fluxes of  $CO_2$  and calcite precipitation; Wet conditions enhanced the production of DOC, lateral export of DIC (especially via shallow soil water), and calcite dissolution (also see Figure S3 in Supporting information S1 for Ca and Si export fluxes, and Tables S2 and S3 in Supporting information S1 for reaction and export rates of MContrast case under different discharge conditions).

of  $R_{\text{DOC}}$  and  $R_{\text{CO}_2}$ , increased with discharge slightly but remained close to  $\sim 2,400$  mol C/a under different hydrological conditions.

Calcite weathering rates increased considerably from  $-80$  mol/a (precipitation) at  $0.08$  mm/day to  $\sim 916$  mol/a (dissolution) at  $8.0$  mm/day. This is expected as calcite dissolves quickly and depends on rapid water flow to maintain disequilibrium. The plagioclase weathering rates did not vary as much with discharge, because plagioclase dissolves slowly (Reaction 10 in Table 1) and is typically at disequilibrium. In addition, plagioclase weathering depended on pH, which increased with discharge and offset the enhanced dissolution rates from rapid flow. In summary, dry conditions produced more DIC, less DOC, and precipitated carbonate; wet conditions produced less DIC, more DOC, and dissolved carbonate.

As soil respiration remained similar, the fluxes of carbon from soil respiration,  $F_C (= F_{\text{CO}_2, V, up} + F_{\text{DIC, SoilResp, L}} + F_{\text{DOC, L}})$ , also remained similar across hydrological gradients. Total carbon fluxes ( $F_{C, T} = F_{\text{CO}_2, V, up} + F_{\text{DIC, L}} + F_{\text{DOC, L}}$ ), the carbon from both soil respiration and carbonate weathering, however, increased with flow (Figure 7b) due to the higher rates of carbonate weathering at high flow that contributed more geogenic carbon. At  $0.08$  mm/day, the vertical upward  $\text{CO}_2$  flux was  $2,084$  mol C/a ( $\sim 86\%$ ); DOC ( $F_{\text{DOC, L}} = F_{\text{DOC, L, SW}} + F_{\text{DOC, L, GW}}$ ) and DIC ( $F_{\text{DIC, L}} = F_{\text{DIC, L, SW}} + F_{\text{DIC, L, GW}}$ ) exported laterally at  $\sim 1.0$  mol C/a and  $\sim 259$  mol C/a, respectively. Almost all lateral DIC fluxes were from soil respiration and via deeper groundwater flow paths ( $83\%$ , or  $214$  mol C/a, Figure S3 in Supporting Information S1). The lateral DOC flux was close to zero ( $F_{\text{DOC, L, SW}}$ , Figure 7b).

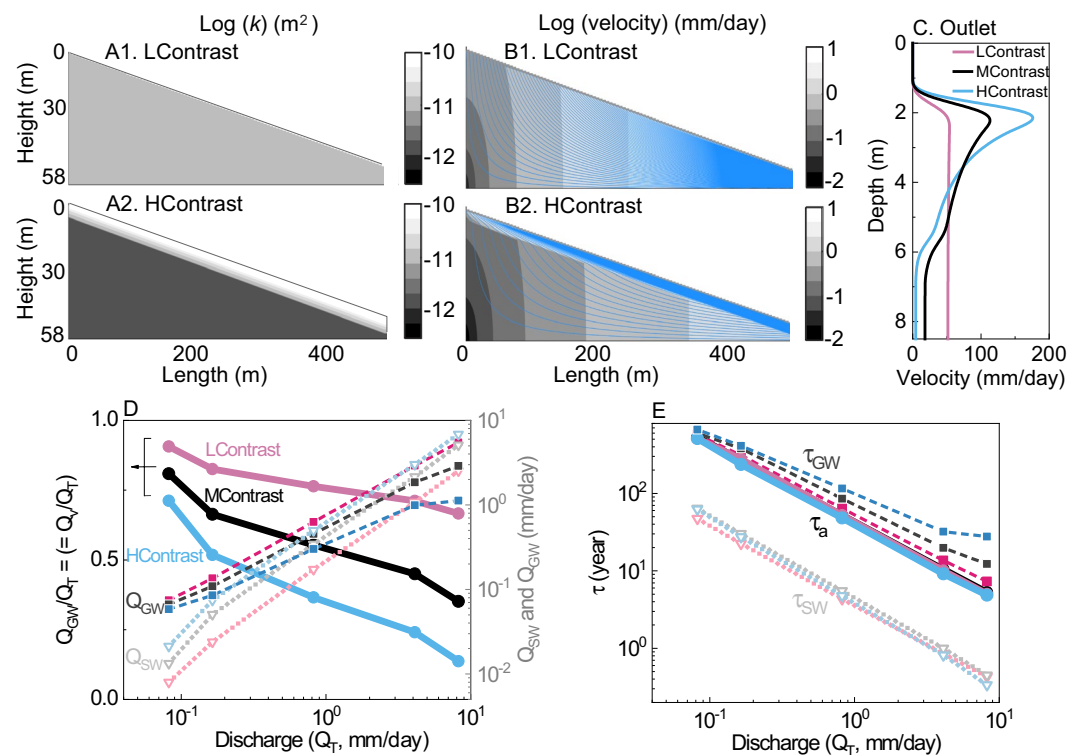
At  $8.0$  mm/day,  $\text{CO}_2$  vertical fluxes,  $F_{\text{CO}_2, V, up}$ , were  $1,138$  mol C/a. The lateral DOC fluxes increased to  $284$  mol C/a,  $90\%$  of which exported via SW due to much higher water fluxes and higher DOC concentrations in shallow soils. The overall DIC lateral flux was also much higher ( $F_{\text{DIC, L}} = 2,019$  mol C/a), with carbonate dissolution and soil respiration contributing  $\sim 916$  mol C/a and  $\sim 1,103$  mol C/a, respectively (Figure 7b). Although not shown here, cation fluxes (Ca and Si) generally followed similar trends as their weathering rates ( $R_{\text{Cal}}$  and  $R_{\text{Plg}}$ , Figure 7a and Figure S3 in Supporting Information S1). In summary, dry conditions exported more  $\text{CO}_2$  vertically to the atmosphere but less DIC and DOC laterally; wet conditions exported less  $\text{CO}_2$  vertically to the atmosphere but more laterally.

## 4.2. Effects of Shallow-Versus-Deep Permeability Contrast

### 4.2.1. Water Partitioning and Transit Times

The depth distribution of permeability determines the relative proportions of water fluxes from different depths. In HContrast, steep permeability decline (soil surface-bedrock permeability contrast of  $\sim 10^2$ ) resulted in about  $48\%$  of total water fluxes to discharge from the upper  $3.0$  m of subsurface (Figure 8a2–b2). In contrast, about  $15\%$  of total water fluxes came out of the upper  $3.0$  m in LContrast (homogeneous) (Figure 8a1–b1). The corresponding values for the upper  $6.0$  m were  $96\%$  and  $65\%$  in HContrast and LContrast, respectively.

The stream water is a mixture of soil water and groundwater from different depths. The depth profiles of shallow and deep flow entering the stream followed similar trends among cases with different permeability distribution (Figure 8c). At  $0.8$  mm/day, flow rates increased with depth before peaking at the shallow water table ( $\sim 1.5$  m) and declined below that depth. The vertical contrasts in flow rates were highest in HContrast. The proportion of SW versus GW varied with discharge because of the rising and falling water table (Figure S4 in Supporting Information S1). This variation in water table depths led to different water partitioning between soil water and groundwater under different scenarios (Figure 8d). In MContrast, at  $Q_T = 0.08$  mm/day, water table was deep and the deeper groundwater dominated, contributing to  $83\%$  of the stream flow ( $Q_{\text{GW}}/Q_T = 0.83$ ). At  $Q_T = 8.0$  mm/day, deep groundwater contributed about  $36\%$  of the streamflow. The GW proportions to streamflow varied most in HContrast, decreasing from  $0.73$  to  $0.14$  from very dry to very wet conditions, compared to persistently high GW proportion ( $0.93$ – $0.73$ ) in LContrast. LContrast also had the youngest GW. The mean SW age varied from  $\sim 0.4$  to  $47$  years, and the GW age varied from  $\sim 7.3$  to  $571$  years. The stream water age ( $\tau_{\text{stream}}$ ) varied from  $\sim 5.2$  to  $531$  years, generally younger under wet conditions (Figure 8e). Larger permeability contrast at different depths resulted in larger variations in GW age compared to SW.



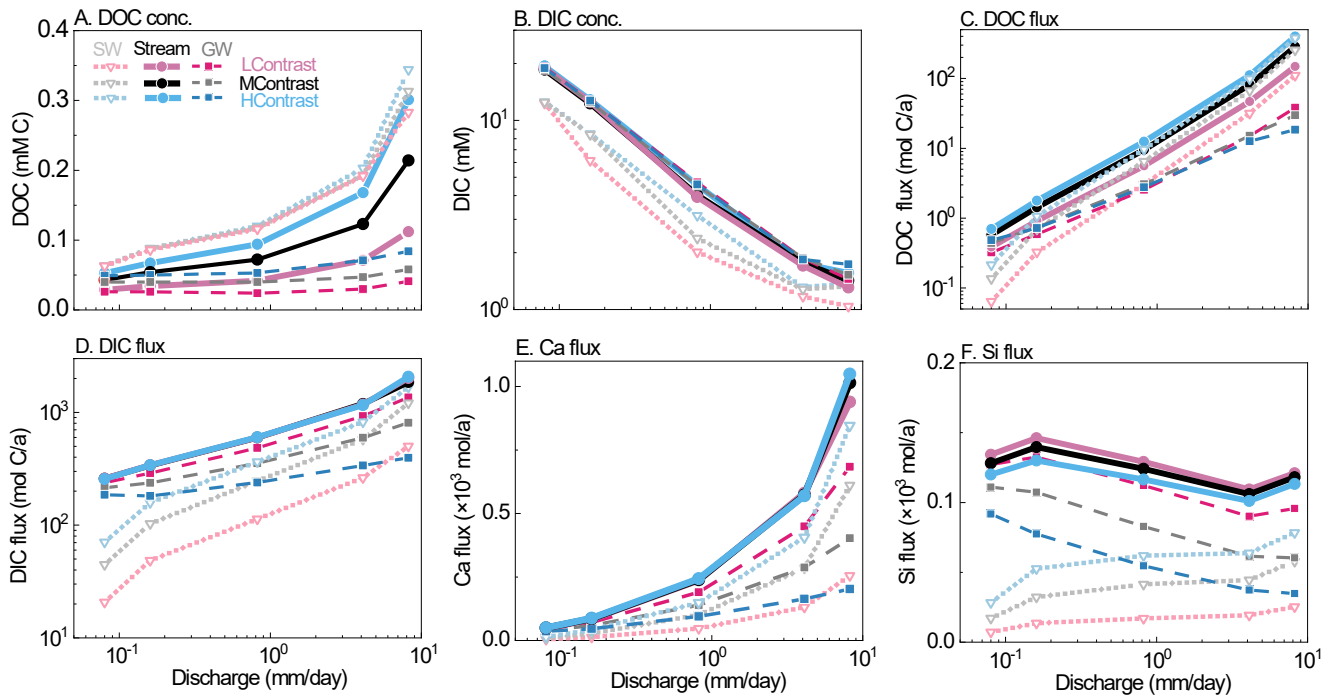
**Figure 8.** (a–b) Spatial profiles of permeability and flow velocities at a discharge of 0.8 mm/day in LContrast with homogeneous permeability distribution (top) and in HContrast with steep decline in permeability (bottom). The thin blue lines represent the flow lines. In LContrast, much more water flows through the deeper zone compared to HContrast. (c) Depth profiles of flow velocities at the hillslope outlet. (d) Flow rates of shallow soil water ( $Q_{SW}$ , dotted lines) and groundwater ( $Q_{GW}$ , dashed lines) that enters stream, and the corresponding relative contribution of groundwater to stream ( $Q_{GW}/Q_T$ , thick solid lines). (e) Mean transit time of stream water  $\tau_{stream}$ , soil water  $\tau_{SW}$ , and groundwater  $\tau_{GW}$  under different permeability contrast and discharge conditions. The GW proportion was generally highest in LContrast and lowest in HContrast, and decreased as discharge increased.

#### 4.2.2. Biogeochemical Measures

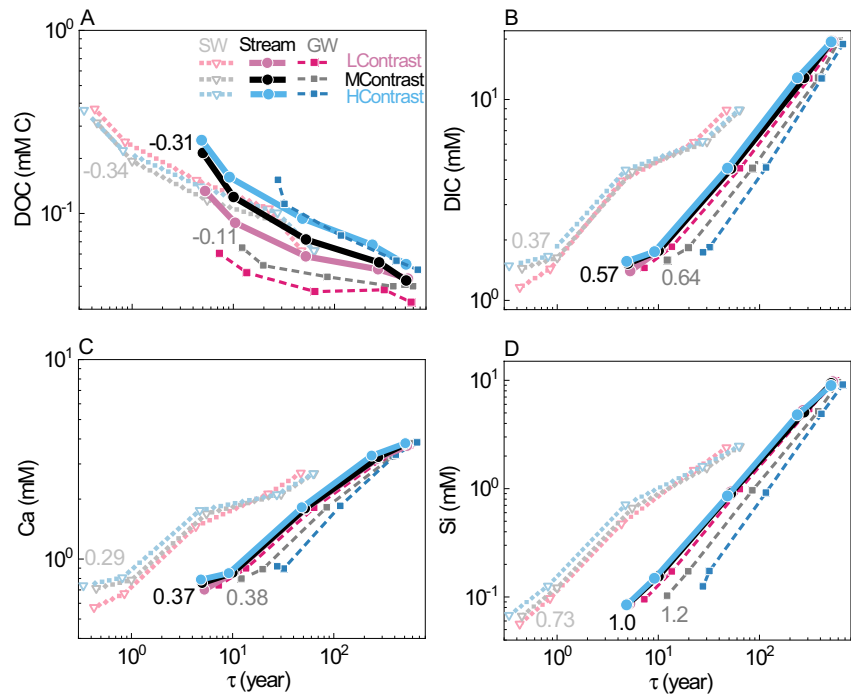
The vertical profiles of geochemical variables were similar in different permeability contrast scenarios (Figure S5 in Supporting Information S1). Likewise, DOC and DIC concentrations were similar in different waters (SW, DW, and stream in Figures 9a and 9b) except under extreme wet conditions. Stream DOC concentrations were highest in HContrast because more water flows via the shallow organic-rich zone (Figure 9a). Stream concentrations of DIC, Ca, and Si were similar among all three cases (Figure 9b, Ca and Si are not shown here). The permeability contrast was more influential in determining lateral SW versus GW export fluxes. LContrast generally had the highest GW fluxes. For all solutes, GW fluxes were higher than SW fluxes under dry conditions (Figures 9c–9f). As the system became wetter, SW fluxes increased faster than GW fluxes such that they eventually dominated under wet conditions. HContrast had the most significant increase in SW fluxes, leading to the highest SW flux percentage, or lowest GW flux proportion under wet conditions.

Reaction rates and fluxes exhibited the largest differences across permeability contrast scenarios under extreme wet conditions (Figure S6 and Table S2 in Supporting Information S1). At 8.0 mm/day,  $R_{CO_2}$  in HContrast decreased from  $\sim 2,412$  mol C/a at 0.08 mm/day to  $\sim 2,047$  mol C/a at 8.0 mm/day. Correspondingly,  $F_{CO_2, V, up}$  was  $\sim 2,084$  mol C/a at 0.08 mm/day and  $\sim 1,064$  mol C/a at 8.0 mm/day. The vertical upward  $CO_2$  fluxes were highest in LContrast and lowest in HContrast. This is because HContrast has the highest SW that rapidly exported DOC and DIC out of the system, leaving less  $CO_2$  for vertical export. The difference among cases however was relatively small, about  $\sim 8\%$  between extreme wet conditions. The differences in carbonate weathering rates across permeability contrast scenarios were also negligible except under very wet conditions (Figure S6 and Table S2 in Supporting Information S1). At 8.0 mm/day, HContrast had the fastest carbonate weathering rates

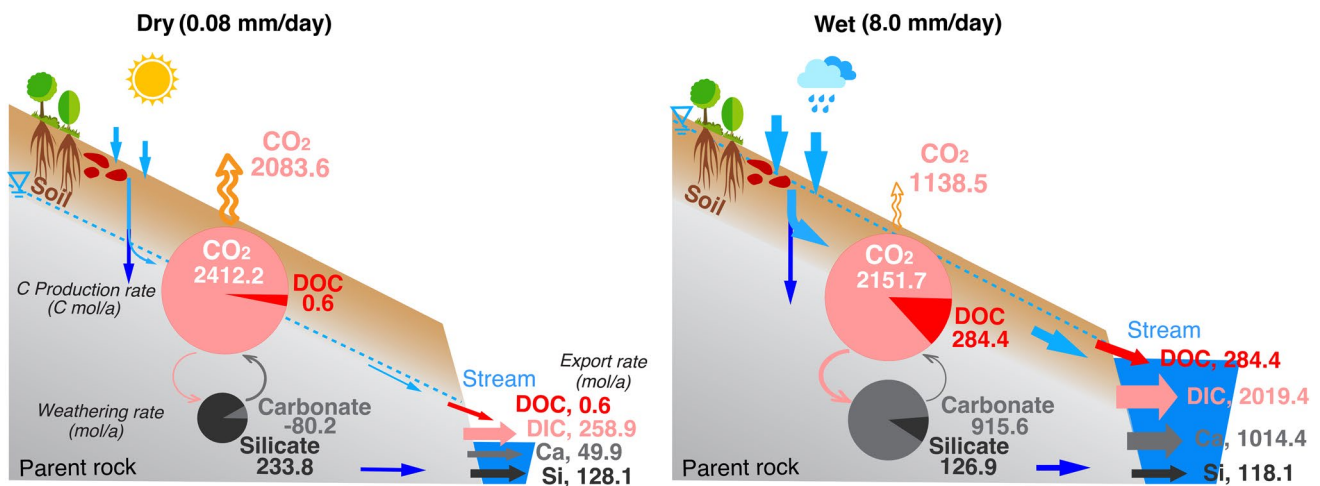




**Figure 9.** (a–b) Concentrations and (c–f) fluxes under different hydrological and permeability contrast conditions: (a) DOC, (b) DIC, (c) DOC fluxes, (d) DIC fluxes, (e) Ca fluxes, and (f) Si fluxes. Differences across permeability contrast scenarios were smaller than discharge-induced differences and were most pronounced under wet conditions. Higher permeability in shallow soil (HContrast) promoted solute lateral fluxes.



**Figure 10.** Concentrations versus water transit time: (a) DOC, (b) DIC, (c) Ca, and (d) Si. DOC concentrations were generally higher in younger waters. All other solutes had higher concentrations in older waters. The concentrations–transit time relationship approximated power law relationships (linear in loglog scale). The numbers are the average slopes of the  $C-t$  relationship ( $C = at^b$ ) in log-log scale.



**Figure 11.** Quantification of rates and fluxes from hillslope RTM under dry and wet conditions. All carbon rates and fluxes are in units of C mol/a; all weathering rates are in units of mol/a. Droughts (0.08 mm/day, left) promoted upward emission of CO<sub>2</sub> gas, deeper flow paths, carbonate precipitation, and mineralization of organic carbon into inorganic carbon. Storms (8.0 mm/day) reduced CO<sub>2</sub> upward emission to the atmosphere and OC mineralization but promoted shallow flow paths, carbonate dissolution, DOC production, and lateral fluxes of IC into streams.

( $R_{Ca}$ ), about ~10% higher than LContrast. The differences in silicate weathering rates in the three permeability contrast scenarios were less than 2%.

### 4.3. Concentration Dependence on Water Transit Time

The concentrations of all solutes strongly relate to water transit time, although the relationship differed for different solutes and different waters (Figure 10). DOC concentrations generally increased with decreasing water age, as younger water and higher water table carried more DOC in shallow soil. In contrast, DIC, Ca, and Si concentrations increased with water age, as weathering occurred to a large extent in the old water in deeper zones.

## 5. Discussion

This work examines (a) the rarely explored linkage among carbon transformation reactions, vertical and lateral carbon fluxes, and their intertwined connections with flow paths at the hillslope scale, and (b) the significance of hydrological extremes (e.g., from droughts to storms) and internal structure (vertical permeability contrast) in regulating reaction rates, fluxes, and stream chemistry. This work delineates an integrated “picture” for carbon cycling and terrestrial-aquatic connections demanded in literature (Keller, 2019; Tank et al., 2018). Existing terrestrial biosphere models account for vertical CO<sub>2</sub> transport but not lateral IC transport to streams and rivers, which ultimately evades to the atmosphere. Existing models therefore overestimate subsurface carbon storage and underestimate CO<sub>2</sub> emission (Butman et al., 2016). Results here indicate that the extent of errors may be more significant under wet conditions where higher proportions of terrestrial carbon are exported laterally in dissolved forms. The reactive transport model developed here can be considered as a basis for further studies constrained by time-resolved field data to explore terrestrial carbon cycling.

### 5.1. Connecting Carbon Transformation, and Vertical and Lateral Transport

Results here delineate an integrated framework that connects terrestrial carbon and cation production to solute export into streams (Figure 1 and Figure 11). Production of CO<sub>2</sub> in the top 1.0 m contributed >90% of total soil respiration. Carbon transformation rate (i.e.,  $R_C$  in Figure 2) was ~5.6 mol C/m<sup>2</sup> (drainage area)/a at intermediate flow (0.8 mm/day), within the typical range of 2.0–50.0 mol C/m<sup>2</sup>/a reported for forest ecosystems under similar temperature conditions (Fang & Moncrieff, 2001; Raich & Schlesinger, 1992).

The results underscore the predominance of hydrological conditions in controlling the relative magnitude of vertical and lateral carbon fluxes: droughts enhance carbon mineralization and vertical upward carbon fluxes back to the atmosphere, and storms and flooding promote lateral export of dissolved carbon into streams and rivers (Figure 11). Under dry (0.08 mm/day) and wet (8.0 mm/day) conditions, vertical carbon fluxes were about 86% and 51% of total soil respiration, respectively. Correspondingly, about 14% of inorganic carbon from soil respiration ( $F_{\text{DIC,SoilResp,L}}$ ) was laterally exported under dry conditions, compared to 49% under wet conditions (Figure 7b). This explains two observations: first, a considerable portion of DIC fluxes originates from soil respiration under dry conditions; second, riverine DIC fluxes from soil respiration positively correlates with discharge (Campeau et al., 2017; Zhong et al., 2017), and CO<sub>2</sub> evasion from rivers can be substantial, especially in headwater streams (Hotchkiss et al., 2015; Raymond et al., 2013). The reactions and transport dynamics under dry and wet conditions resemble the dynamics under arid versus humid climates across United States (Li et al., 2022).

The projected DOC lateral fluxes can vary by two orders of magnitude ( $2 \times 10^{-3}$  to  $6 \times 10^{-1}$  mol C/m<sup>2</sup>/a) across hydrological conditions, similar to the reported range of  $6 \times 10^{-3}$  mol C/m<sup>2</sup>/a (Mulholland, 1997) to  $4 \times 10^{-1}$  mol C/m<sup>2</sup>/a in temperate forests (Raymond & Saiers, 2010). The fluxes increase with discharge (Figure 7), echoing observations of elevated DOC export during storms potentially arising from enhanced connectivity and DOC desorption under wet conditions (Campeau et al., 2019; Piney et al., 2018). Results here however underscore two additional mechanisms: (a) less DOC may undergo transformation into inorganic carbon due to shorter water transit times under wet conditions (Figures 7a and 8e); and (b) high DOC fluxes can arise from rising water tables that flush out more DOC-enriched water in shallow soils (Figures 5c and 6a) (Barnes et al., 2018; Seibert et al., 2009; Zhi & Li, 2020; Zhi et al., 2019). Results here also support the observation that discharge, among many climate indexes, can be the single most important control on DOC fluxes (Worrall et al., 2004, 2008).

Soil respiration rates are often measured on the ground surface based on vertical fluxes (Bond-Lamberty & Thomson, 2010; Soper et al., 2017). Results here indicate that such measurements may underestimate respiration rates, because they do not count for the lateral transport of DIC. Similarly, because soil carbon storage is often inferred from vertical efflux from soil, not counting DIC lateral fluxes can overestimate terrestrial ecosystem carbon stocks (Liu et al., 2010). The extent of underestimation and overestimation may be particularly large under wet conditions, when the lateral DIC fluxes constitute about half of total produced IC.

The influence of permeability contrast and vertical connectivity on carbon transformation rates is generally higher under wet conditions, although its influence is overall small. This is because soil respiration mostly occurs in shallow soils: >90% of the total annual efflux occurs in the top meter of soil. The deeper subsurface generally has orders-of-magnitude lower carbon transformation rates than those in surface soils such that reaction rates at depth do not influence the overall rates as much (Figure 5 and S5 in Supporting Information S1). Permeability distribution, however, regulates flow partitioning and therefore the amount of dissolved carbon via deeper subsurface. Total DOC and DIC fluxes via the GW route maximized in LContrast (Figures 9c and 9d), whereas those via the SW route peaked in HContrast, as more DOC-enriched soil water flowed out of the shallow zone in HContrast.

## 5.2. Chemical Weathering at Hydrological Extremes

### 5.2.1. The Differential Dependence of Carbonate and Silicate Weathering Rates on Hydrological Conditions

Hydrological conditions influence carbonate and silicate weathering via different mechanisms. Carbonate weathering is fast and transport controlled such that it largely depends on water flow to drive the reaction to disequilibrium. The opposite is true for the slower silicate weathering (Reactions 9 and 10 in Table 1). Its rate is pH rather than flow dependent. Under dry conditions, the low flow rates and DIC export sustained soil CO<sub>2</sub> at higher levels and resulted in acidic soil water (pH ~6.5 at 0.08 mm/day) that accelerates silicate weathering.

Silicate weathering slowed down at high pH under wet conditions (pH = ~8.0 at 8.0 mm/day). The dependence of silicate weathering on CO<sub>2</sub> and pH has been well documented in theoretical and experimental work (Golubev et al., 2005; Penman et al., 2020; Winnick & Maher, 2018). Direct field observations addressing the relationship between soil CO<sub>2</sub>, pH, and weathering rates under varied hydrological conditions are limited due to confounding environmental factors. Elevated soil pCO<sub>2</sub> at high temperature and low soil moisture have been observed to amplify silicate weathering (Andrews & Schlesinger, 2001). This work suggested that Si fluxes and silicate

weathering rates were highest under dry conditions and decreased with discharge. Note that this may only hold true for the slow, kinetic-controlled weathering (i.e., transport time/reaction time  $<1$ ). In tropical regions or during monsoons when transport time/reaction time  $\gg 1$ , silicate weathering rates might be directly proportional to precipitation or runoff (Tipper et al., 2006; West et al., 2005; White & Blum, 1995).

### 5.2.2. Carbonate Releasing or Storing CO<sub>2</sub>?

The direction of the carbonate reaction ( $\text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$ ), whether dissolution or precipitation, highly depends on hydrological conditions. When carbonate dissolves, it transforms soil CO<sub>2</sub> into DIC; when carbonate precipitates, it releases gaseous CO<sub>2</sub>. Model results here show that carbonate dissolved in shallow soils (1–2 m) when in direct contact with fresh rainwater (Figure 5j), but quickly reached equilibrium and precipitated with cations from plagioclase dissolution at higher pH and DIC in the deep subsurface (below 2 m). Under wet conditions, fast flow drove dissolution to rates as high as  $\sim 900$  mol/a, contributing more than a third of the overall inorganic carbon lateral fluxes (Figures 7a and 7b). Such calcite dissolution in shallow zones and precipitation at depth has been observed in calcite-dominated sites, especially when silicates provide extra cations (Monger et al., 2015; Wan et al., 2019; Zamanian et al., 2016). Pedogenic carbonate as soil inorganic carbon stocks is widely observed in arid and semi-arid regions (Stanbery et al., 2017; Zamanian et al., 2016). These results suggest that inorganic carbon can be stored under dry conditions as carbonate precipitates but can be released into water again during storms (Sagi et al., 2021).

These findings shed lights on the decade-long debate of whether soil carbonates and groundwater act as active carbon sinks or source (Ma et al., 2014; Sagi et al., 2021; Schlesinger, 1982; Schlesinger & Amundson, 2019; Schlesinger et al., 2009). Results here indicate that transition from droughts to storms can shift carbonate between a carbon sink and source via changing the carbonate reaction direction. Similar conclusions have been drawn in studies for Karst catchments (Liu et al., 2018; Zeng et al., 2019). In other words, soil carbonate can be both sources and sinks, depending on hydrologic regimes.

### 5.2.3. The Influence of Permeability Contrasts on Weathering Is Surprisingly Small

Contrasting the expectation that vertical connectivity is a dominant control on weathering deep in the subsurface (Xiao et al., 2021). Silicate weathering rates in LContrast and HContrast differed only by about 3%–7% under dry conditions. For carbonate weathering, its influence increased with discharge but still below 10% even under wet conditions, much smaller than the structure heterogeneity effects observed at the pedon scale (10s of centimeters) and meter scale (Wen & Li, 2018; Wen et al., 2021). At the pedon scale, the deeper flow facilitated by deepening roots can elevate carbonate weathering by 17%–207% (Wen et al., 2021). Carbonate weathering rates in heterogeneous and homogenous media can differ by more than an order of magnitude (Wen & Li, 2017, 2018). This relatively low impact of permeability contrasts could arise from several mechanisms. In previous studies (Wen & Li, 2017, 2018), carbonate dissolution only occurs in the low permeability zone, whereas in the current work carbonate and plagioclase occurs in both shallow and deep zones such that in effect only permeability heterogeneity existed. Physical heterogeneity alone has been shown to have limited impacts on mineral weathering (Jung & Navarre-Sitchler, 2018). In addition, the hillslope scale examined here is much larger in spatial scale than the pedon or meter scales, such that a longer transit time can promote carbonate weathering equilibrium.

The dependence of weathering on subsurface structure is also likely lithology-dependent and reflects the co-occurrence of carbonate and silicates. In shale-dominated sedimentary rocks, for example, oxidation of sulfides (e.g., pyrite) can produce acids and accelerate weathering (Bufe et al., 2021; Gu et al., 2020; Torres et al., 2014). Sulfide oxidation often occurs in deeper subsurface and is highly dependent on water table depth that regulates O<sub>2</sub> availability. Conditions that lead to deeper water tables have been observed to accelerate weathering in alpine mountains (Crawford et al., 2019). Shale weathering might have stronger dependence on subsurface structure than the lithology explored here. Vertical connectivity has also been shown to have much higher impact on silicate weathering without the presence of carbonates (Xiao et al., 2021). The fast carbonate reactions and the close-to-equilibrium conditions may be overwhelming such that it masks the effects of subsurface structure on silicate weathering.

### 5.3. Stream Chemistry, Subsurface Structure, and Water Age

Numerical experiments show distinct depth profiles for different solutes. DOC concentrations generally decreased with depth, as organic carbon is less abundant and reactive at depth. In addition, DOC from shallow soils can continue to become mineralized at deeper depths. In contrast, concentrations of cations increased with depth (Figure 5), because of longer travel times, near-equilibrium conditions, or lower flow and export (Maher, 2011; Winnick & Maher, 2018). These different depth profiles led to distinct export patterns: DOC consistently shows flushing patterns with increasing concentration with discharge, whereas other solutes show consistent dilution patterns. This echoes observations in the literature that solute export patterns are shaped by their depth profiles (Stewart et al., 2022; Zhi & Li, 2020; Zhi et al., 2019).

Correspondingly, high DOC concentrations positively correlate with younger water fractions whereas other solutes positively correlate to older water (Figure 10). In particular, stream DOC exhibited more pronounced differences across flow regimes in HContrast with high permeability contrasts and lower vertical connectivity (Figure 10), which resembles observations in cations (Xiao et al., 2021). This alludes to the potential of establishing benchmark relationships between stream chemistry and subsurface structure characteristics such as permeability contrast and vertical connectivity. Stream chemistry has been used to infer shallow soil and deeper groundwater chemistry with satisfactory accuracy, especially for locations close to streams (Stewart et al., 2022). That is, the dynamics of stream chemistry may reveal subsurface structure such that we can use stream chemistry to mirror subsurface characteristics, infer reaction rates, and reveal structure-function relationships.

### 5.4. Model Assumption, Limitation, and Extrapolation Beyond Fitch

The model made several simplifications. The biogeochemical properties, including the abundance of organic matter and mineralogy, were kept constant. Neither do we consider topographic difference, for example, more OC in toeslopes than other positions. The rates of soil respiration do not include dependence on temperature and soil moisture, such that the rates represent “averages” across temperate and soil moisture conditions. Such choice permits differentiation among the effects of hydrological conditions and permeability contrasts without the confounding effects of soil moisture and temperature driving changes in soil CO<sub>2</sub> production.

The model also made simplifying assumptions for subsurface structure due to the lack of data. Permeability was assumed to decline with depth (Cardenas & Jiang, 2010). Although a common observation, permeability distribution can be complicated by the presence of fractures and roots that enable deeper penetration of acidic soil water and promote weathering at depth (Sullivan et al., 2022). This can happen especially when fractures and roots are the primary water conduits (Ackerer et al., 2021; Wen et al., 2021). The OC content typically declines with depth, as we assumed here (Hauser et al., 2020). This entails that maximum CO<sub>2</sub> production in shallow soil. Rates of OC respiration at depth however cannot be ignored (Soulet et al., 2021). For example, in an old-growth forest in Northern California (Tune et al., 2020), ~80% of CO<sub>2</sub> was produced from bedrock during the wet season; in the dry season, bedrock respiration continued but a greater fraction was emitted as soil CO<sub>2</sub>. These observations echo conclusions here and underscore the predominance of vertical CO<sub>2</sub> emission under dry conditions and lateral transport under wet conditions.

Note that the lack of subsurface structure and function data are common, as the subsurface characterization remains challenging and expensive. Except for a few Critical Zone Observatories (Brantley et al., 2017), subsurface structure and function have remained largely unknown. Detailed structural data, including images for fractures and root distributions, and functional data such as soil and groundwater chemistry and gas concentrations, are direly needed to reveal processes at depth and their connections to observed dynamics in surface water.

Despite model simplification and the model employment of Fitch idiosyncrasy, results here exhibit patterns similar to those observed in other places. For example, large-scale meta-analyses have indicated widespread CQ patterns (Botter et al., 2020; Ebeling et al., 2021). DOC exhibits flushing patterns in more than 90% of sites in the United States (Zarnetske et al., 2018). DIC and weathering-derived cations often exhibit dilution patterns (Bluth & Kump, 1994; Najjar et al., 2020). All these are similar to the model predictions here (Figure 6). In addition, soil CO<sub>2</sub> has long been observed to increase with depth (Davidson & Trumbore, 1995; Fierer et al., 2005), which is consistent with depth profiles of solutes and soil CO<sub>2</sub> from the model output here (Figures 4 and 5). Such consistency between data and model indicates the representation of key process dynamics. Under different

climate, vegetation cover, and geology conditions, subsurface structure such as abundance of organic matter and permeability contrast will differ from Fitch site, which can lead to differing concentrations and fluxes. We however expect the general patterns and trends remain similar, as the key processes could remain similar.

## 6. Conclusions

We leverage a 2D hillslope reactive transport model to understand and quantify the rarely-explored linkages among flow paths, soil OC transformations, chemical weathering, and solute export across hydrological and subsurface structure gradients. The model integrates hydrological flow, solute transport, and biogeochemical reactions. The model was set up using measured discharge (i.e., precipitation – ET), water table depth, and soil properties (e.g., porosity and OC abundance). It was calibrated using soil CO<sub>2</sub> and soil water chemistry data from the Fitch Forest in Kansas (USA).

The results delineate a hillslope conceptual model that connects terrestrial carbon transformation and chemical weathering with vertical and lateral fluxes across gradients of hydrological conditions and subsurface permeability contrasts. Results demonstrate that dry conditions (0.08 mm/day) promoted deeper flow paths and longer water transit time, which enhanced carbon precipitation, production of inorganic carbon (IC, ~98% of OC), and vertical CO<sub>2</sub> export (~86% of produced IC); they also reduced DOC production and lateral carbon export. Conversely, storms (8.0 mm/day) promoted shallow flow and shorter water transit time, carbonate dissolution, DOC production, lateral carbon export, but reduced IC production (~88% of OC) and vertical carbon export (~53% of produced IC). Carbonate precipitated under dry conditions and dissolved under wet conditions as the fast flow drove the reaction to disequilibrium. Silicate weathering rates are not as sensitive to hydrological conditions because of its slower dissolution kinetics; its rates are higher under dry conditions with relatively high acidity. Permeability contrasts exert smaller influence on reaction rates than hydrological conditions but regulate the partitioning between water and solute fluxes via shallow and deeper flow paths. High permeability contrasts (low vertical connectivity) promote lateral fluxes. These results have important implications for understanding carbon production and export and chemical weathering under changing climate conditions.

## Data Availability Statement

Data from this work are archived in the Consortium of Universities for the Advancement of Hydrologic Science, Inc. (CUAHSI) data website (<https://www.hydroshare.org/resource/48991c1a1e14442a8f1ad98001469e29/>). The link contains not only field data used in this work, but also simulation data. The simulation data include files for numerical experiments under the five discharge conditions in the three permeability contrast scenarios.

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