Vertical Connectivity Regulates Water Transit Time and Chemical Weathering at the Hillslope Scale

Dacheng Xiao,1,2, Susan L. Brantley,3, and Li Li2

1Department of Energy and Mineral Engineering, The Pennsylvania State University, University Park, PA, USA, 2Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA, USA, 3Earth and Environmental Systems Institute and Department of Geosciences, The Pennsylvania State University, University Park, PA, USA

Abstract How does hillslope structure (e.g., hillslope shape and permeability variation) regulate its hydro-geochemical functioning (flow paths, solute export, chemical weathering)? Numerical reactive transport experiments and particle tracking were used to answer this question. Results underscore the first-order control of permeability variations (with depth) on vertical connectivity (VC), defined as the fraction of water flowing into streams from below the soil zone. Where permeability decreases sharply and VC is low, >95% of water flows through the top 6 m of the subsurface, barely interacting with reactive rock at depth. High VC also elongates mean transit times (MTTs) and weathering rates. VC however is less of an influence under arid climates where long transit times drive weathering to equilibrium. The results lead to three working hypotheses that can be further tested. H1: The permeability variations with depth influence MTTs of stream water more strongly than hillslope shapes; hillslope shapes instead influence the younger fraction of stream water more. H2: High VC arising from high permeability at depths enhances weathering by promoting deeper water penetration and water-rock interactions; the influence of VC weakens under arid climates and larger hillslopes with longer MTTs. H3: VC regulates chemical contrasts between shallow and deep waters (C\textsubscript{shallow}/C\textsubscript{deep}) and solute export patterns encapsulated in the power law slope b of concentration-discharge (CQ) relationships. Higher VC leads to similar shallow versus deep water chemistry (C\textsubscript{shallow}/C\textsubscript{deep} ~1) and more chemostatic CQ patterns. Although supporting data already exist, these hypotheses can be further tested with carefully designed, co-located modeling and measurements of soil, rock, and waters. Broadly, the importance of hillslope subsurface structure (e.g., permeability variation) indicate it is essential in regulating earth surface hydrogeochemical response to changing climate and human activities.

1. Introduction

Hillslope structure characteristics, including topography and permeability variation with depth, develop as tectonics, climate, lithology, and biota interact over geological time scales (Beering & Berner, 2005; Berner, 1992; Brantley et al., 2017; Riebe et al., 2017; West, 2012). Hillslope topography and associated “horizontal” connectivity from uphill to streams have been extensively studied. They are known to determine water flow paths and transit time distributions (TTDs) (Buttle et al., 2004; Jencko et al., 2009; Leibowitz et al., 2018; McGuire et al., 2005; Seeger & Weiler, 2014; Tetzlaff et al., 2009), streamflow generation (Bracken et al., 2013; Jencko et al., 2010; McGlynn & McDonnell, 2003; Tromp-van Meerveld & McDonnell, 2006; Wlostowski et al., 2016; Xiao et al., 2019), water storage (McGuire et al., 2005), and solute export and weathering (Herndon et al., 2015; Lebedeva & Brantley, 2013; Sullivan, Stops, et al., 2019; Torres et al., 2015). Comparatively, the influence of subsurface structure, in particular permeability variation with depth and vertical connectivity (VC) between shallow and deeper zones, has received less attention (Ameli, McDonnell, & Bishop, 2016; Hale & McDonnell, 2016; Hopp & McDonnell, 2009; Li et al., 2021; Zimmer & McGlynn, 2017; Zimmer & Gannon, 2018). This VC is regulated by subsurface permeability distribution and is not as easily accessible for characterization. Recent Critical Zone research has directed concerted efforts for subsurface characterization (Brantley, Holleran, et al., 2013; Holbrook et al., 2019; Radke et al., 2019; Rempe & Dietrich, 2014), yet our understanding of its effect remains limited. Quantifying the impacts of VC is however essential, because it links the shallow and deeper subsurface. The shallow subsurface is often
responsive to changing climate and human activities; the deeper subsurface is not as sensitive to surface variations but can offer much-needed "capacity that buffers surface perturbations.

Subsurface properties vary significantly with depth. Shallow soils are weathered materials that are depleted in geogenic solutes such as Ca and Mg (Brantley, Holleran, et al., 2013; Jin et al., 2010) but are organic-rich with plant roots, leaves, and microbiota (Billings et al., 2018; Herndon et al., 2015; Jobbágy & Jackson, 2000). The deeper subsurface includes parent and partially weathered bedrocks that are enriched with geogenic elements. Shallow soils generally have orders of magnitude higher permeability compared to the deeper, unweathered bedrock (Welch & Allen, 2014). As the incipient rainwater enters the subsurface, it tends to flow through the very thin surficial soil, leading to water ages of a few months (Jasechko et al., 2016; Kirchner, 2016b). In contrast, deeper zones harbor much older water, with ages ranging from hundreds of years to millennia (Jasechko et al., 2017).

These distinct shallow and deep characteristics have strong implications for connecting stream chemistry, reaction rates, flow paths, and solute depth profiles (Benettin et al., 2020; Godsey et al., 2009b; Li, Bao, et al., 2017; Torres et al., 2015). Concentrations of geogenic solutes often increase with depth and their concentration-discharge (CQ) relationship exhibit dilution patterns, often become more pronounced with the presence of sharp contrasts between shallow and deep subsurface (Ameli et al., 2017; Zhi et al., 2019). Aged dissolved organic carbon (DOC) in arid basins and base flow often associate with deeper flows paths (Barnes et al., 2018), whereas concentrations of weathering products (e.g., Si) typically decrease with increasing stream discharge (Clow & Drever, 1996; Johnson, 1969). Concentrations of silica have been observed to positively correlate with groundwater age (Burns et al., 1998; Burns et al., 2003) but not with the age of younger stream water estimated using surface water dating techniques (e.g., Frisbee, Wilson, et al., 2013), raising the question of whether surface water dating have largely missed the long tail of TTDs. Along similar lines of ideas, the end-member mixing analysis (EMMA) have long been used by the hydrology community to differentiate the contributions from different source waters to streamflow (Hooper et al., 1990; Pinder & Jones, 1969) (Klaus & McDonnell, 2013). Recent meta analysis further support the shallow and deep hypothesis that vertical chemical contrasts in shallow and deep waters regulateThis idea however has emerged from studies of individual catchments much earlier (Boyer et al., 1997; Creed et al., 1996).

Reactive transport modeling of homogeneous systems have emphasized the importance of the Damköhler number, the relative time scales of reactions versus water flow in regulating weathering and solute chemistry (e.g., Lebedeva et al., 2015; Maher, 2010; Salehikhoo & Li, 2015). The water transit time here reflects the time that water interacts with the omnipresent reacting minerals in homogeneous systems. In heterogeneous systems where reacting minerals are present only in specific locations, additional reactive transit times or exposure times are needed in the upscaled rate laws in order to account for the water-mineral interactions (Wen & Li, 2017, 2018). Causal and quantitative linkages among hillslope geomorphic and subsurface structure, transit time, and chemical weathering however have not been established (Benettin et al., 2020; Harman & Cosans, 2019; Sanz-Prat, Lu, Finkel, & Cirpka, 2016; Sanz-Prat, Lu, Amos, et al., 2016; van der Velde et al., 2010).

Here we ask the questions: how and to what extent does hillslope structure (hillslope shape and subsurface permeability) regulate its hydrogeochemical functioning (water transit times, VC, solute export, and weathering)? Which characteristics exert a stronger control for what function? We focus on weathering systems that involve the dissolution of primary minerals (silicates) and precipitation of secondary minerals (kaolinite). In contrast to recent hillslope studies that use a single component (Ameli et al., 2017; Brantley & Lebedeva, 2021; Harman & Cosans, 2019), this work uses a multi-component model. Numerical experiments were carried out for hillslopes of the same homogenous mineralogy but different shape and subsurface permeability. The mean discharge conditions range from 0.02 to 2.00 mm/d, representing arid (annual mean discharge of 7 mm/yr) to wet (700 mm/yr) climate. Comparison among cases can identify the most influential factors for hydrogeochemical functioning.

2. Methods

2.1. The Hillslope Model

In the hillslope model illustrated in Figure 1, infiltrating water (=annual rainfall and snow fall − annual evapotranspiration, or P − ET) can flow laterally through the shallow subsurface to the stream, or vertical-
Water flows into the hillslope and flows into the stream via the shallow and deep flow paths, dissolving soils and rocks along the way. The flow paths (light gray lines) and velocity fields (colors) are model outputs from two cases with permeability distribution following the equation \( \kappa(z) = \kappa_0 e^{-\alpha z} \), where \( \kappa \) is permeability, \( \kappa_0 \) at the ground surface, \( z \) is depth (mbls, meters below land surface), \( \alpha \) quantifies how fast permeability decreases with depth (see Table 1 in Section 2). The orange line illustrates the position of soil-weathered rock interface. In the homogeneous case with high vertical connectivity (\( \alpha = 0 \)), the flow lines are relatively evenly distributed with depth and > 55% stream water is from depths deeper than 6 m; in the heterogeneous case where permeability decreases sharply (\( \alpha = 0.6 \)), vertical connectivity is low and the flow lines mostly concentrate in the shallow soil and less 5% of stream water is from depths deeper than 6 m. High permeability at depth (high VC) enhances deeper water penetration and increases flow velocities at depth, therefore promoting weathering at depths and more dissolved solutes in stream water.

2.1.1. Numerical Experiments

To tease apart the influence of permeability distribution and hillslope shape, we designed 12 cases with different combinations of these two variables (Table 1). All cases have homogeneous minerals. They have linear or non-linear hillslope shapes and variable permeability distribution (\( \alpha \) from 0 to 0.6) (Table 1). In natural systems, permeability typically decreases with depth (Welch & Allen, 2014). Here we used \( \kappa_0 = 10^{-12} \text{ m}^2 \) based on observations at Shale Hills (Kuntz et al., 2011). Values of \( \kappa \) quickly drop to
Water Resources Research

\(10^{-14}\) m\(^2\) at 6 m depth when \(\alpha = 0.6\), but remain at \(\kappa_0\) in the homogeneous case (Figure 1b). The heterogeneous cases (with non-zero \(\alpha\) values and permeability decreasing with depth) represent characteristics of natural systems with low permeability at depth. In the homogeneous case, permeability at depth is the same as in shallow soil, representing conditions where high permeability can develop in deeper zones, for example, in karst formations (Hartmann et al., 2014), or systems with dense fractures at depth (Somers & McKenzie, 2020) or deepening roots (Nippert et al., 2012). In all cases, model results show that >95% of water flow comes out from the top 6 m (as observed at Shale Hills (Sullivan et al., 2016)) and the remaining water is from depths below 6 m. Five numerical experiments were run with discharge from 0.02 to 2.00 mm/d, representing very dry (annual mean discharge about 7 mm/yr) to wet (700 mm/yr) conditions.

### 2.1.2. Weathering Reactions

The model considered a generic set of weathering reactions, which includes plagioclase feldspar as the primary dissolving mineral, kaolinite as the precipitating mineral, and quartz as an inert mineral (Table 2). The net weathering reaction for plagioclase dissolution and kaolinite precipitation is

\[
\begin{align*}
\text{Ca}_{0.613}\text{Na}_{0.387}\text{Al}_{1.613}[\text{SiO}_4]_{2.387} (\text{Plagioclase}) + 6.452 \text{H}^+ + 2.774 \text{H}_2\text{O} &= 0.387\text{Na}^+ \\
+ 0.613\text{Ca}^{2+} + 0.387\text{SiO}_2 (aq) + 0.548 \text{H}^+ + \text{HCO}_3^- + \text{Al}_2\text{Si}_3\text{O}_8(\text{OH})_4 (\text{Kaolinite})
\end{align*}
\]

The reaction consumes Al and \(\text{CO}_2(aq)\) and releases Na, Ca, and Si. Chloride (Cl) is conservative and originates from rainfall and snowfall. Because of the rate difference between plagioclase dissolution and kaolinite precipitation, Al produced from plagioclase dissolution is not consumed right away. Soil organic carbon (OC) was used as a “proxy” acidity source for the production of \(\text{CO}_2\) through soil respiration and the presence of organic acid (Brantley, Lebedeva, & Bazilevskaya, 2013; Li, Maher, et al., 2017). Previous reactive

### Table 1

| Cases | Hillslope shape | Permeability \(\kappa(z) = \kappa_0 e^{-az}\) | \(\kappa_0 = 10^{-12}\) m\(^2\) |
|-------|----------------|-----------------------------------------------|----------------------------------|
| 1     | Linear         | \(\alpha = 0\)                                |                                  |
| 2     | Linear         | \(\alpha = 0.1\)                              |                                  |
| 3     | Linear         | \(\alpha = 0.2\)                              |                                  |
| 4     | Linear         | \(\alpha = 0.3\)                              |                                  |
| 5     | Linear         | \(\alpha = 0.45\)                             |                                  |
| 6     | Linear         | \(\alpha = 0.6\)                              |                                  |
| 7     | Convex         | \(\alpha = 0.0\)                              |                                  |
| 8     | Convex         | \(\alpha = 0.6\)                              |                                  |
| 9     | S-shape        | \(\alpha = 0.0\)                              |                                  |
| 10    | S-shape        | \(\alpha = 0.6\)                              |                                  |
| 11    | Concave up     | \(\alpha = 0.0\)                              |                                  |
| 12    | Concave up     | \(\alpha = 0.6\)                              |                                  |

*Each case was run with five values of discharge (0.02, 0.2, 1.0, 1.5, 2.0 mm/d) and with the same initial and boundary conditions (supporting information, Table S1).

### Table 2

| Mineral reactions | \(\log_10K_{eq}\) | Rate law (mol/m\(^2\)/s) | Specific surface area (m\(^2\)/g) |
|-------------------|-------------------|-----------------------------|----------------------------------|
| **Weathering reaction (kinetic controlled)** | | | |
| \(\text{Ca}_{0.613}\text{Na}_{0.387}\text{Al}_{1.613}[\text{SiO}_4]_{2.387} (\text{Plagioclase}) + 6.452 \text{H}^+ + 2.774 \text{H}_2\text{O} = 0.387\text{Na}^+ \\
+ 0.613\text{Ca}^{2+} + 0.387\text{SiO}_2 (aq) + 0.548 \text{H}^+ + \text{HCO}_3^- + \text{Al}_2\text{Si}_3\text{O}_8(\text{OH})_4 (\text{Kaolinite})\) | 18.11\(^a\) | \(a_{\text{H}^+}^{6.14}10^{-9.0}\) | 0.0067\(^a\) |
| \(\text{H}_2\text{O} + 0.387 \text{Na}^+ + 0.613 \text{Ca}^{2+} + 1.613 \text{Al}^{3+} + 2.387 \text{SiO}_2 (aq)\) | 7.65\(^a\) | \(a_{\text{H}^+}^{6.55}10^{-12.2}\) | 0.0816\(^a\) |
| **Aqueous complexation (at equilibrium)** | | | |
| \(\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-\) | −14.00 | | |
| \(\text{CO}_2 (aq) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-\) | −6.35 | | |
| \(\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}\) | −10.33 | | |

\(^a\)Navarre-Sitchler et al. (2011). \(^b\)The reaction equilibrium and kinetic parameters were calibrated based on pH distribution in Shale Hills (Jin et al., 2010; Sullivan et al., 2016).
transport modeling has shown that weathering rates without soil CO$_2$ can be orders of magnitude lower and cannot reproduce soil water chemistry observations (Heidari et al., 2017; Moore et al., 2012). The OC(s) was set at a volume fraction of 5% in the top 2 m and 1% below 2 m with much lower specific surface area ($10^{-3}$ times the number for the top 2 m), as organic matter is typically more abundant and reactive in shallow soils. We assumed isovolumetric weathering that ignores contraction or compaction processes. The model outputs of concentrations are within the concentration ranges of soil water, groundwater, and streams in literature (Heidari et al., 2017; Jin et al., 2014; Zhi et al., 2019).

2.2. Reactive Transport Model

CrunchFlow has been used previously for one-dimensional systems with constant flow velocities (Heidari et al., 2017; Hubbard et al., 2014; Maher, 2010; Navarre-Sitchler et al., 2011; Navarre-Sitchler et al., 2009), and two-dimensional domains (Bao et al., 2014; Wen et al., 2016). To our knowledge, this is the first time CrunchFlow is used for hillslope simulation. The code solves mass conservation equations, considering advection, diffusion/dispersion, and weathering reactions. A representative equation for solute $j$ in grid $i$ is as follows:

$$
\frac{\partial}{\partial t} \left( \phi C_{j,i} \right) + \nabla \cdot \left[ -\phi D \nabla (C_{j,i}) + u C_{j,i} \right] = r_{j,i} \quad (j = 1, 2, ..., N)
$$

where $t$ is time (s), $\phi$ is porosity, $C_{j,i}$ is the concentration of primary species $j$ in grid $i$ (mol·m$^{-3}$ water), $D$ is the hydrodynamic dispersion tensor (m$^2$ porous media·s$^{-1}$), $u$ is the Darcy flow velocity (m$^2$ water·m$^{-2}$ porous media·s$^{-1}$), $r_{j,i}$ is the total rate of species $j$ (mol·m$^{-3}$ porous media·s$^{-1}$) in multiple reactions, and $N$ is the total number of primary species.

Weathering rates follow Transition state theory (Lasaga, 1998)

$$
r = \left( k_1 a_{H^+}^n + k_2 a_{OH^-}^n + k_3 \right) A \left( 1 - \frac{\text{IAP}}{K_{eq}} \right)
$$

where $k_1$, $k_2$, $k_3$ are the kinetic rate constants (mol·m$^{-2}$·s$^{-1}$), $a_{H^+}$ and $a_{OH^-}$ represent activities (product of activity coefficient and concentrations) of the hydrogen and hydroxyl ions, $n1$ and $n2$ describe the rate dependence on activities, $A$ is the surface area per unit volume of porous media (m$^2$·m$^{-3}$), IAP is the ion activity product, and $K_{eq}$ is the equilibrium constant. The term $\text{IAP}/K_{eq}$ quantifies the distance from equilibrium. The model outputs include concentrations of individual solutes and reaction rates in time and space.

2.3. Particle Tracking

We followed a previously published particle tacking approach (Ameli et al., (2017); Ameli et al., (2016b)) to track flow paths and to quantify water age. Particles enter the subsurface at time $t_0$ and follow the flow field, eventually leaving the hillslope at the outlet at time $t_{out}$ (Figure 1). A total of 250 particles was injected into the hillslope at the ground surface. For each particle $p$, its coordinates at any time step $k$ depend on its coordinates at the previous step $k-1$, flow velocities in the $x$ and $z$ direction $v_x$ and $v_z$, and the size of the time step (set as one hour). The coordinates of particle $p$ at the time step $k$ ($x_p^k$ and $z_p^k$) are:

$$
x_p^k = x_p^{k-1} + \left( V_{x,p} \right)_p^k \Delta t
$$

$$
z_p^k = z_p^{k-1} + \left( V_{z,p} \right)_p^k \Delta t
$$

With the random movement of particles, $v_{x,p}$ and $v_{z,p}$ are random numbers sampled from an exponential distribution with the means of $v_x$ and $v_z$ being the flow velocities at $x_p^{k-1}$ and $z_p^{k-1}$.

The $t_{out}$ of each particle at the stream outlet quantifies its total travel time across the hillslope. The distribution of $t_{out}$ for the 250 particles was considered to follow a Gamma distribution that has been extensively used for TTD (Ameli, Amvrosiadi, et al., 2016; Harman, 2015; McGuire & McDonnell, 2006):
Here $p(t)$ is the probability density function of Gamma distribution, $A$ is the shape parameter. Note that here $A$ is often referred to as $\alpha$ in the Gamma distribution equation. We use $A$ instead of $\alpha$ to avoid confusion. The models were run to steady state when solute concentrations no longer change with time. Plagioclase is weathered to kaolinite during exposure to water flowing through the hillslope. Except in homogeneous hillslopes ($\alpha = 0$), the majority of the water (>95%) flows through the top 6 meters of the subsurface. Water chemistry in the top 6 m is therefore most influential in determining stream chemistry. The concentrations of Na, Ca, and Si are lower in shallow zones (top 2 m), and Al concentrations are higher in shallow soils. Chloride concentrations are relatively similar within the top 6 meters.
with $\alpha$ in the permeability distribution equation. The $\beta$ is the rate parameter (the reciprocal of the scale parameter), $t$ is the transit time, and $\Gamma(A) = \int_0^\infty t^{A-1}e^{-t}dt$ is the Gamma function. The product of $A$ and $\beta$ is the statistically mean of $t$, that is, the mean transit time (MTT). The Gamma distribution is positive and skewed. The shape parameter $A$ describes the weight in the tails of the distribution. The smaller $A$, the larger variability in transit times with higher proportions of young and old waters.

### 2.4. Emergent Concepts and Quantifications at the Hillslope Scale

#### 2.4.1. Transit Time, Young and Old Water Fractions, and Water Age

The transit time is defined as the difference between the time when a particle enters and the time when a particle leaves the hillslope and enters the stream (McGuire & McDonnell, 2006; Rodhe et al., 1996). The TTD is the probability density function of the transit times of all particles (McGuire & McDonnell, 2006). The MTT is the product of the two parameters ($\mu = A \times \beta$) in Equation 5. The Water age is the average transit time of particles in particular locations (e.g., stream). The young water fraction ($F_{yw<1yr}$) is defined as the fraction of particles (out of all 250 particles) in the stream with transit times shorter than 1 year. The corresponding old water fraction is $F_{yw>1yr} = 1 - F_{yw<1yr}$. Note that this differs from the typical young water fraction defined as less than 2.3 months, or 0.2 years (Kirchner, 2016a; Kirchner, 2016b). As discussed later, this one year cutoff for young and old water fractions is somewhat arbitrary but roughly matches the cutoff between fast- and slow-flow through Shale Hills (Sullivan et al., 2016). The threshold of 0.2 and 5 years were also used, as shown in Figure S2 in the supporting information and discussed in the Results section.

#### 2.4.2. Vertical Connectivity

Vertical connectivity is a measure of the connection between shallow soil and deeper groundwater. Their values were quantified as the water fluxes below the soil-rock interface (deeper than the soil zone, averaged across the entire hillslope) divided by the total water fluxes at all depths (into the stream). Higher VC means higher water fluxes into (and out of) the deeper zone. The top few meters of the subsurface were considered as soil. Three depths (1 m, 2 m, and 3 m) were used as the depths of the soil-rock interface for analysis. As will be shown later, different soil depths lead to similar VCs. We therefore show the analysis for the 2 m soil depth in the Results section. The results for 1 and 3 m are in supporting information, Figure S1.

#### 2.4.3. Concentration-Discharge Relationships

Stream concentrations ($C_{stream}$) were calculated as the flux-weighted average over the entire depth. The grids within 10 m from the outlet were used to avoid boundary effects (Figure 1). Stream CQ relationships describe concentration variations responding to changes in mean streamflow (Godsey et al., 2009a; Herndon et al., 2018; Moatar et al., 2017). The simple power law $C = aQ^b$ was used to classify CQ patterns of chemostatic ($b \sim 0$), dilution ($b < 0$), and flushing ($b > 0$) patterns.

#### 2.4.4. Solute Concentrations in Shallow and Deep Zones

The model output includes solute concentrations in individual grids. Shallow soil water concentrations ($C_{sw}$) were calculated as the volume-weighted average concentrations from the top 2 m of the soil; groundwater concentrations ($C_{gw}$) were computed as the volume-weighted average concentrations from below 2 m. The concentration contrast $C_{ratio}$ was calculated as $C_{sw}/C_{gw}$. Analysis was also done using 1 and 3 m as the soil depth but did not yield significantly different MTT and $C_{ratio}$ values (supporting information, Figure S2).

#### 2.4.5. Hillslope Weathering Rates

The summation of solute fluxes ($= concentration (C) \times discharge (Q)$) at the stream outlet quantifies weathering fluxes at the hillslope scale. Some may argue that these quantities are solute fluxes instead of weathering rates. In natural systems where other geochemical processes (e.g., sorption or ion exchange) occur, the two quantities can differ. They may also differ at the event or daily scales with transient flow fields. Here as we simulate weathering without other reactions and under steady state flow conditions, the solute fluxes and weathering rates are expected to be the same. This is further confirmed by the resultant same values arising from $C \times Q$ at the outlet and the sum of local rates at individual grids.
3. Results

3.1. Flow Partitioning and Transit Time Distribution

3.1.1. Effects of Permeability Distribution

Here we discuss two linear hillslopes with different permeability distributions. In each hillslope, water particles that enter the valley generally have shorter flow paths compared to those that enter the ridge top. In the homogeneous case ($\alpha = 0$), permeability remains high at depth; in the heterogeneous case ($\alpha = 0.6$), permeability decreases by two orders of magnitude within the top 5 meters. The flow lines in the heterogeneous case are concentrated in the shallow, high-permeability subsurface (Figure 2). The flow lines in the homogeneous case, especially those starting at the ridge top, penetrate much deeper. These flow paths are much longer and water travels through a much larger volume of the subsurface than those in the heterogeneous case.

In the homogeneous hillslope, water fluxes are homogeneous with depth; in the heterogeneous hillslope, water fluxes concentrate mostly within the top 5 m (Figure 3). Water fluxes decrease and water ages increase with depth. Much more water exits the hillslope at shallow depths in the heterogeneous case. The water fractions exiting the top 2 m are 11% and 64%, respectively, in the cases of $\alpha = 0$ versus $\alpha = 0.6$. The corresponding water fractions for the top 6 m are 38% and 95%, respectively. The water leaving via shallow flow paths is considerably younger than that via deeper paths. The TTDs differ significantly in different cases (Figures 3c and 3d). The heterogeneous hillslopes have short transit times with much larger fractions of young water compared to the homogeneous hillslopes.

3.1.2. Effects of Hillslope Shape

The hillslope shape does not have as much influence as permeability variations. The Concave case has the highest fraction of younger water ($F_{yw<1yr}$), and the Convex case has the lowest $F_{yw<1yr}$ (Figures 3g and 3h). The differences among different hillslope shapes, however, are much smaller than the differences among different permeability distributions with the same hillslope shape (Figures 3c and 3d). The hillslope shapes generally have much stronger influences in the homogeneous case, and in younger water end of the TTD (below 1 year). The older water end of the TTD almost overlaps among different hillslopes.

3.1.3. Shallow Versus Deeper Water Partitioning, and Vertical Connectivity

Figure 4a shows that as $\alpha$ values vary from 0.6 to 0.0, VC increases. This is expected because more water penetrates to greater depths at low $\alpha$ values. The VC values however are almost identical in hillslopes of different shapes but identical $\alpha$ values, indicating negligible impacts of hillslope shape. Values of MTT (Equation 5), increase from ~1 year to ~10 years as $\alpha$ decreases. In the homogeneous cases ($\alpha = 0$) with high VC, the hillslope shape has large impact on MTT: The Concave case has an MTT value of 4.1 years compared to 9.5 years for the Convex case. At $\alpha = 0.6$, however, MTT values in these hillslopes overlap, indicating negligible impact of hillslope shape (Figure 4b). The younger water fraction $F_{yw<1yr}$ generally is much more influenced by hillslope shape than old water. Different hillslope shapes lead to distinct young water fractions, with the Convex and Concave cases resulting in the highest and lowest values, respectively. Supporting information, Figure S1 show similar trends for MTT versus VC at soil depths of 1 m, 2 m, and 3 m. The young water fractions with different threshold values (0.2, 1, and 5 years) also show similar trends with respect to dependence on VC (supporting information, Figure S2).

3.2. Weathering and Solute Export

3.2.1. Hillslope Distribution of Weathering Rates and Solutes

Figure 2 shows negligible effects of hillslope shape: weathering rates and solute concentrations are similar among the linear, concave and convex cases (Figures 2b–2d). The permeability distribution however strongly regulates flow paths, weathering rates, and solute distribution. The flow lines penetrate as deep as...
Water Resources Research

20 meters in the homogeneous hillslope, but only to ~5 meters in the heterogeneous case (Figure 2, row 1). Plagioclase generally dissolves faster in shallow compared to deeper zones, because newly infiltrated water in the shallow zones are farther away from equilibrium conditions (row 2, plagioclase rates). With the faster release of weathering products in shallow zones, kaolinite precipitation also occurs at faster rates (row 3). The shallow zones are therefore where weathering rates are highest; reaction rates plummet by orders of magnitude beneath the shallow zones. With deeper water penetration, weathering can occur at greater depths in the homogeneous hillslope.

Weathering transforms plagioclase to kaolinite (Equation 1). Plagioclase dissolution releases Na, Si, Al, and Ca, but kaolinite precipitation consumes Si and Al. Plagioclase releases more Si and less Al than the amounts consumed in kaolinite precipitation, as indicated in the Si:Al stoichiometry in Equation 1. The net weathering reaction therefore consumes Al but releases Si, Na, and Ca. Transforming one mole of plagioclase to one mole of kaolinite consumes 0.387 mole of Al and generates 0.387 moles of Na, Si, and Ca. As such, concentrations of Na, Ca, and Si increase along flow paths, leading to higher concentrations at depth in the top 6 meters (Figures 5a and 5b). Si decreases with depth beyond 6 m in some of the most heterogeneous hillslopes, indicating plagioclase dissolution rates are lower than kaolinite precipitation rates under these conditions with very low flow. In contrast, Al is consumed as kaolinite precipitates along flow paths such that its concentrations decrease with depth (Figure 5c). The non-reactive Cl is homogeneously distributed over all depths in the homogeneous cases and in the top 6 meters of the heterogeneous cases (Figure 5d).
3.2.2. Effects of Discharge

As discharge decreases from 1.0 to 0.2 mm/day (Figures 2 and 5), weathering rates decrease but solute concentrations increase. In addition, at lower discharge, the effects of permeability on depth profiles lessen. Figure 6a shows that plagioclase dissolution rates increase as discharge increases. Kaolinite precipitation rates mirror those of plagioclase dissolution, although at a slightly lower magnitude. The net weathering rates are positive and increase with discharge, because shorter transit times under high discharge maintain the system away from equilibrium. The homogeneous cases generally yield higher weathering rates and higher concentrations of Na, Si, and Ca compared to heterogeneous cases. Solute concentrations vary less as discharge varies. Concentrations of Al increase with discharge in the heterogeneous cases. The concentrations are at levels commonly observed in natural systems. For example, Al can reach as high as tens of μmol/L that is, within the high end of observed concentration ranges (Herndon et al., 2015; Zhi et al., 2020).

The concentrations of Na, Si, and Ca exhibit dilution CQ patterns with higher concentrations at low discharge (Figure 6). The Al concentrations demonstrate flushing patterns with high concentrations at high discharge, because the mobilized solutes are flushed out rapidly without as much kaolinite precipitation under high discharge. The concentrations of Cl exhibit a chemostatic pattern (invariable C with Q) at high discharge. Figure 5a suggests that total weathering fluxes (C × Q, the same as export rates) are higher at higher discharge, although stream concentrations of Na, Si, and Ca are lower in these cases.

The CQ patterns do not change under different permeability distributions or hillslope shape, although the extent of dilution or flushing (the value of the slope b) may differ (Figure 7). For example, Na exhibits a dilution pattern in all cases but with much steeper CQ at higher α values (lower VC), indicating more negative b values (Figure 7a). This may be due to increasing water fluxes through the top zone soil at high Q. Similarly, Al exhibits flushing patterns in all cases but exhibit more positive b values in the more heterogeneous cases. The heterogeneous cases generally have
more pronounced, steeper CQ relationships. Compared to the effect of variations in the distribution of permeability, variation in hillslope shape results in negligible changes in CQ patterns. The Concave hillslope notably has a more significant impact than other hillslope shape.

The CQ power law slope values \( b \) vary with different measures of transit time and VC (Figure 8). In all cases, Na, Al, and Cl exhibit dilution, flushing, and chemostatic patterns, respectively, regardless of the permeability distributions. The \( b \) values are negative at low \( C_{sw}/C_{gw} \) ratios (<1.0), are close to zero at \( C_{sw}/C_{gw} \) ratios roughly equal to 1, and are positive at high \( C_{sw}/C_{gw} \) ratios (>1.0) (Figure 8a). As VC increases, the shallow and deep contrasts decrease such that the \( b \) values approach 0 (Figure 8b). Similarly, when MTT and \( F_{sw} \) increase, \( b \) values approach 0. In other words, high VC indicates more connected shallow and deeper zones, reduced shallow-versus-deep contrast, and more chemostatic CQ relationships.

Figure 9 shows that weathering rates generally increase with VC and discharge. The magnitude of the increase depends on discharge. Under dry conditions (0.02 mm/d), weathering rates vary negligibly (Figures 9b and 9c). As conditions get wetter, the dependence on VC becomes more significant. At each \( Q \), weathering rates increase with \( F_{sw} \) (Figure 9b) and with MTT (Figure 9c). The stream concentrations of Na and Si correlate with MTTs under non-arid conditions (\( Q > 0.2 \) mm/day) via a power law relationship \( C_{stream} = C_0(MTT)^{0.58} \) (Figure 10). For Na, \( C_0 = 10^{-3.4} \) mol/L and \( \nu = 0.58 (R^2 = 0.90) \); for Si, \( C_0 = 10^{-3.1} \) mol/L and \( \nu = 0.53 (R^2 = 0.88) \). These correlation equations do not include concentrations under arid conditions (\( Q \leq 0.02 \) mm/day). Under these arid conditions, concentrations become relatively constant at \( 10^{-2.6} \), \( 10^{-2.0} \), \( 10^{-6.9} \), and \( 10^{-1.8} \) mol/L.

### 3.2.3. Weathering Over Geological Time

To explore the effects of permeability distributions over geological time, the models were run at 1.00 mm/d for 10,000 years for the Convex, homogeneous (\( \alpha = 0 \)) and heterogeneous (\( \alpha = 1.0 \)) cases. Note that here we simulate a “stationary” hillslopes where supply from below or uplift equals soil erosion such that these two competing processes “cancel” each other and are not considered in the model. Figure 11 shows the \( \tau \) values (mass transfer coefficient) for plagioclase dissolution, where \( \tau = 0 \) indicates the same plagioclase abundance as the parent bedrock and \( \tau = -1.0 \) represents 100% depletion of plagioclase compared to the parent rock (isovolumetric weathering). In the homogeneous hillslope, water penetrates deeply and has longer water-rock contact times, therefore generating a deeper reaction front where \( \tau \) value change from −1 to 0. The depths of the weathering front at 10,000 years are 11 m, 10 m, and 4 m, for the ridge top, mid slope, and valley position, respectively. In contrast, in the heterogeneous case, most water flows through a thin soil layer of high permeability. After 10,000 years, weathering fronts are situated at 4 m, 5 m, and 7 m, for ridge top, mid slope, and valley floor, respectively. In other words, the weathering fronts are shallower in the heterogeneous hillslopes. Overall, the total weathered mass for the entire hillslope is \( 3.70 \times 10^5 \) mol in the homogeneous case, compared to \( 1.99 \times 10^5 \) mol in the heterogeneous case. In other words, weathering rates almost doubled in the homogeneous case. In addition, the homogeneous Hillslope develops the deepest weathering front at the ridge top, as the water penetrates deepest there; the heterogeneous case develops the deepest front in the valley, where all water is eventually channeled.
This work used numerical thought experiments to understand the relative importance of different hillslope structure (permeability variation with depth and hillslope shape) in regulating hydrogeochemical functioning. The experiments made a few simplification assumptions. The hillslopes were modeled using relatively simplified, albeit multicomponent weathering reaction with dissolving primary mineral (plagioclase) and precipitating secondary mineral (kaolinite). The minerals were homogeneously distributed with depth in order to focus on effects of physical structure. The experiments used steady state flows that represent average hydrodynamic conditions and ignored details of unsaturated and saturated flows. The experiments therefore do not represent event-scale dynamics such as transient horizontal connectivity, antecedent conditions, and variable storm sizes (Hopp & McDonnell, 2009; Tromp-van Meerveld & McDonnell, 2006; Zimmer & McGlynn, 2017). Instead, they represent more of hillslopes of same homogeneous distributed mineralogy but different shape and permeability distribution under different hydroclimate conditions from arid to wet climates. These experiments linked hillslope horizontal and vertical structure with their hydrological (flow paths and transit times) and geochemical functioning (weathering and solute export).

As we discuss below, the model predictions are consistent with many field observations in literature, indicating the model represents essential processes that captured first-order dynamics at the hillslope scale. Here we distill the results into three hypotheses, discuss existing supporting evidence, and lay out future work that can test these hypotheses.

4.1. Hypothesis 1

The variations of permeability with depth more strongly influence the mean transit times of stream water than hillslope shape does; hillslope shapes instead influence more of the younger water fractions of stream water.

Existing Evidence and Implications

In hillslopes with high permeability at depth ($\alpha = 0$), more water penetrates deeper, leading to more evenly distributed water fluxes from different depths, high VC, high MTT, and low $F_{ow}$ (Figures 3 and 4). About 40% of infiltrated water enter the stream via the top 6% and and 12% via top 2 meters of the subsurface, respectively. Where permeability decreases sharply ($\alpha = 0.6$), ~95% of infiltrated water enters the stream via the top
6 meters and ~65% via the top 2 meters (Figure 4). These fractions of deeper water, or the complementing percentages that add up to one, are within the range of base flow indices reported in literature (Somers & McKenzie, 2020). The results underscores the essential roles of permeability variation as regulators of shallow and deep water partitioning.

MTTs have been shown to reflect the long tails of skewed TTDs and are not good predictors of seasonal cycles of non-reactive tracers such as Cl (Kirchner, 2016a; Kirchner, 2016b). Instead, $F_{yw<0.2\text{ yrs}}$ has been shown to be a better measure of seasonal variations and topographic characteristics (Kirchner, 2016a; Kirchner, 2019; von Freyberg et al., 2018). Results here underscore that $F_{yw}$ and MTTs in fact reflect different metrics of TTDs and distinct flow paths. Values of $F_{yw}$ reflect more of the shallow, fast flows shaped by hillslope shape whereas MTTs signal more of deep flow paths regulated by subsurface permeability variation. These observations corroborate existing literature on interacting controls of topography and permeability on transit times and flow paths. For example, steep catchments have been observed to have lower transit times; such topographic control weakens in flat and subdued terrains, where transit times depend more on subsurface permeability (Tetzlaff et al., 2009).

The correlations between MTTs and permeability distribution indicate that MTTs can be a good measure of the properties of hydrologically active soil and bedrock (Asano & Uchida, 2012). These correlations from modeling output echo observed correlations between MTTs, mean length of flow paths (McGuire & McDonnell, 2010), and Si concentrations that reflect water-rock contact time (Asano & Uchida, 2012; Frisbee, Phillips, et al., 2013). Low-permeability granite hillslopes have been observed to have a higher fraction of young, event water in the stream, as most water flows through the shallow layer. In contrast, hillslopes overlaying fractured, high-permeability shale had more older water due to the longer flow paths via deep bedrock (Onda et al., 2006). Similarly, longer MTTs have been observed in catchments with permeable, fractured sandstone bedrock compared to those with tight, volcanic bedrock (Hale & McDonnell, 2016; Pfister et al., 2017).

Over geological time, under similar tectonic and soil erosion conditions, thick soils can develop under high VC conditions (Figure 11). Deeper water penetration also connects a larger proportion of the subsurface to the stream and induces larger dynamic water storage (Berghuijs and Kirchner, 2017; Birkel et al., 2015; Buttle, 2016; McGuire & McDonnell, 2010; McNamara et al., 2011; Pfister et al., 2017; Remondi et al., 2018). Although not explicitly examined here, the relationship between subsurface permeability and dynamic storage can have important implications for storage-discharge relationships, streamflow generation, and the capacity to “buffer” external perturbations.

### 4.2. Hypothesis 2

High vertical connectivity (VC) arising from high permeability at depth enhances weathering because it promotes deeper water penetration and water-rock interactions in wet climates; the influence of VC weakens under arid conditions and in large hills with longer mean transit times.
Under wet conditions, weathering rates increase with both old water fractions $F_{ow}$ and with MTTs (Figure 9). Solute concentrations correlate to MTTs via a power law relationship (Figure 10). VC however is less of an influence under droughts and arid climates where slow flows and long transit times drive weathering to equilibrium. This hypothesis echoes the Wen and Li upscaled rate law that emphasizes two influential factors of weathering (Equation 14 and Figure 11 in Wen and Li (2018)). One is the total water flow, or the mean discharge in this work, that determines transit time and the Damköhler number (Ibarra et al., 2017; Maher & Chamberlain, 2014; Maher & Druhan, 2014; Salehikhoo & Li, 2015; Salehikhoo et al., 2013). As mean discharge is regulated by water input from precipitation (rainfall and snowfall) and water demand by evaporation and transpiration (discharge = precipitation–evapotranspiration) (Anderson et al., 2019; Wlóstowski et al., 2021; Zapata-Rios et al., 2015), this in fact reflects the first order control of hydroclimatic and vegetation conditions.

The other factor in the Wen and Li rate law is the water fraction that interacts with reacting minerals (Wen & Li, 2017; Wen & Li, 2018). This water fraction or water partitioning is determined by the heterogeneity factor, that is, permeability contrast between reactive and non-reactive zones (Wen & Li, 2017; Wen et al., 2021). In this work, the lateral versus vertical partitioning is quantified by VC values and is regulated by permeability variation with depth. High permeability at depth and VC enable the water contact with a larger volume of reacting minerals and reactive surface area, and therefore high weathering rates. Where more water can penetrate deep, stream water is older, resulting in higher concentrations of geogenic solutes (Figure 10). This concentration-water age relationship in fact echo many field observations that link water age dating to stream concentrations (Benettin et al., 2015; Frisbee, Wilson, et al., 2013; Rademacher et al., 2001). Natural conditions that can enhance water-conducting capabilities at depth include deepening plant roots (Beven, 2018; Hasenmueller et al., 2017; Wen et al., 2021), dense fractures (Brantley & Lebedeva, 2021; Brunet et al., 2016; Gu et al., 2020; Lebedeva & Brantley, 2017; Pandey & Rajaram, 2016; Wen et al., 2016), and large conduits in karst formation (Hartmann et al., 2014; Husic et al., 2019; Sullivan, Macpherson, et al., 2019).

The Wen and Li rate law also predicts that the influence of the heterogeneity factor (or VC) weakens when water transit times are high. Model results here show that permeability distribution does not matter much under arid condition (long MTTs) (Figure 8), which echoes the prediction from the rate law (Wen & Li, 2018). In large hillslopes with long flow paths, long MTTs can also drive weathering to equilibrium such that the control of VC diminishes. The Damköhler coefficient that explains CQ relationships of geogenic solutes (Ibarra et al., 2016; Maher & Chamberlain, 2014; Torres & Baronas, 2021; Wymore et al., 2017) indicate that long transit times lead to chemical equilibrium and chemostatic patterns. It implies that the dependence of weathering rates on VC and MTT will weaken as spatial scales increase. Some threshold spatial scales may

**Figure 11.** Weathering profile ($\tau$) of plagioclase dissolution in (a) homogeneous ($\alpha = 0.0$), and (b) heterogeneous ($\alpha = 1.0$) hillslopes. After 10,000 years, the homogeneous hillslope develops much deeper weathering fronts and has twice as fast weathering rates. The homogeneous case has the deepest weathering front at the ridge top, as the water can penetrate deepest there, whereas the heterogeneous case develops the deepest front in the valley, where all water eventually flow through.
exist, beyond which VC and subsurface permeability do not matter. Such threshold lengths will likely vary with minerals of distinct reaction thermodynamics and kinetics and specific conditions.

### 4.3. Hypothesis 3

*Vertical connectivity (VC) regulates chemical contrast between shallow and deep waters* ($C_{\text{ratio}}$) *and solute export patterns encapsulated in the concentration-discharge (CQ) power law slope $b$. Higher VC leads to similar shallow and deep water chemistry ($C_{\text{ratio}}$ $\sim$ 1), leading to more chemostatic CQ patterns.*

#### Existing Evidence and Implications

The solute export patterns, or CQ power law slope $b$ values, are generally consistent with solute depth profiles (Figures 2 and 5). Concentrations of Na, Si, and Ca increase with depth as weathering occurs along flow paths; Al concentrations decrease with depth, as Al continues to be depleted along flow paths by kaolinite precipitation. We therefore observe dilution patterns for Na, Si, and Ca and flushing patterns for Al. For Cl, its non-reactive nature and atmospheric source lead to relatively similar shallow and deep water chemistry and chemostatic patterns (Figure 7).

These results support the shallow and deep hypothesis arising from watershed reactive transport modeling and continental scale metaanalysis (Zhi & Li, 2020; Zhi et al., 2019). Namely, the shallow-versus-deep concentration contrasts determine solute export patterns, and CQ power law slope $b$ values can be predicted based on $C_{\text{ratio}}$. In general, solutes enriched in shallow zones demonstrate flushing patterns, whereas those abundant in deep zones show dilution patterns. This hypothesis echoes the use of EMMA and distinct geochemical signatures for hydrograph separation and source water differentiation (Hooper et al., 1990; Klaus & McDonnell, 2013; Pinder & Jones, 1969), although these approaches do not explicitly emphasize the depths of source waters and the deep and shallow water chemistry contrasts. The shallow and deep hypothesis is supported by extensive CQ data from individual sites and from across scale analysis (Creed et al., 1996; Ebeling et al., 2021; Moatar et al., 2017; Musolff et al., 2017). A recent global data analysis also shows the depth of solute generation, not climate drivers, determines CQ slope $b$ (Botter et al., 2020).

A natural follow-up question is then what determines the shallow-versus-deep concentration contrast ($C_{\text{ratio}}$). This work underscores the predominant role of physical heterogeneity (permeability distribution and VC), even in chemically homogeneous hillslopes. Low VC stratifies the flows via different depths, leading to distinct chemistry in older waters in deeper zones and in younger waters in shallow soils (Jin et al., 2014; Richardson et al., 2020; Sullivan et al., 2016). Large shallow and deep water contrast and non-chemostatic (dilution and flushing) patterns in these hillslopes suggest that chemical heterogeneity is required for non-chemostatic patterns, which is similarly observed in other studies (Torres & Baronas, 2021). This may appear surprising but align with reactive transport principles: Concentration gradients do develop even in idealized, homogeneous systems, as water continues to interact with minerals and dissolve out solutes along its flow paths, although mineral heterogeneity may intensify concentration gradients. In natural hillslopes where parent rocks are often at depth, CQ relationships may exhibit more pronounced dilution patterns with more negative $b$ values. Solutes that are enriched in shallow soils, such as DOC, almost always show flushing CQ patterns (Zarnetske et al., 2018). Metals that form complexes with DOC often exhibit flushing patterns (Herndon et al., 2015; Kiewiet et al., 2020; McIntosh et al., 2017).

The hillslope model here shows that long-term (e.g., annual) average CQ patterns of most geogenic solutes exhibit dilution patterns, similar to observations in recent global data (Godsey et al., 2019). Earlier CQ data have shown chemostatic patterns for geogenic solutes (Godsey et al., 2009b) and for nutrients (Basu et al., 2010). It is possible that chemostatic patterns from earlier data result from infrequent (often bimonthly) data mostly in low and intermediate flow regimes. Recent, more frequently sampled stream chemistry data rarely show chemostatic patterns (Knapp et al., 2020; Torres et al., 2015; Zhi et al., 2020). At minute and hourly time scales, highly resolved temporal solute data have demonstrated highly dynamic, contrasting CQ patterns in events of different size and antecedent conditions (Burns et al., 2019; Duncan et al., 2017). High frequency stream chemistry data may reflect distinct source water chemistry at different depths that relate to rising water table during the events. In other words, different storm events “sample” source waters with distinct chemistry from different depths of water table under different hydrological conditions. Broadly, it is possible that stream chemistry may “mirror” the subsurface water chemistry, and stream chemistry at
different time scales (events, seasonal, annual) may reflect subsurface water chemistry at different spatial resolutions.

### 4.4. Further Hypothesis Testing

Further testing of these hypotheses requires co-located measurements in individual sites with collated hydrogeochemical functioning data (stream chemistry and water age) and structure characterization (permeability distribution and hillslope shape). Water chemistry measurements will need to include soil water and groundwater at different depths as well as stream chemistry data at sufficient frequency covering the full spectrum of discharge regimes. Geophysical characterization, soil and rock chemistry, and physical measurements can help us “see” the subsurface, and they often require time-consuming and labor-intensive sampling campaigns (St. Clair et al., 2015). Multiple measures of TTD can be quantified using different tracers, with stable water isotopes targeting water fractions at the time scales of months to years, and groundwater dating techniques (e.g., radioactive carbon) and geochemical tracers for older water at ages ranging from tens to thousands of years (Frisbee, Wilson, et al., 2013). As indicated in the relationships between MTTs, stream chemistry, and VC, benchmark relationships can potentially be established between these data, such that stream chemistry can be used to mirror sparsely measured subsurface properties and weathering rates. The juxtaposition of different datasets can offer a multi-faceted view and reveal structure-function relationships in intensively measured sites.

The collation of data across different sites can then shed light on the first-order controls across distinct hillslope characteristics and climate conditions. Testing these hypotheses across sites requires carefully chosen catchments that differ in hillslope shape or permeability distribution but have similar conditions for other variables. Such studies have been done previously but are often challenging, as natural systems rarely differ only in one variable. Other variables, such as drainage area and soil properties, inevitably differ and mask the signature of compared variables (Hale & McDonnell, 2016; Li et al., 2018). Under such conditions, numerical thought experiments using process-based models, paired with carefully collected data, can help differentiate the effects of confounding variables, as has been shown before (Berghuijs & Kirchner, 2017; Remondi et al., 2018; Xiao et al., 2019).

### 5. Conclusions

We used a 2D hillslope reactive transport model and particle tracking to answer the question: How does hillslope structure (hillslope shape and permeability variation) influence hillslope hydrogeochemical functioning? Results show that permeability distribution is the first-order control over VC, flow paths, transit time, and MTT. In hillslopes with low permeability at depth, >65% of water is channeled through the top 2 m and >95% is channeled through the top 6 m of the subsurface, respectively (Figure 3). Where high permeability is sustained at depth, water penetrates deeper and interacts with parent rocks, leading to high VC, MTT, and larger fractions of old water (Fast > 50%). In contrast, the hillslope shape, a proxy to topography, more strongly influences the TTD of younger water that enters streams (Figure 4). These results imply that MTT and old water fractions, often considered poor metrics of watershed characteristics such as topography and hydroclimatic conditions, may encode essential information about subsurface structure and VC.

Model results also show the decisive role of permeability variation in influencing geochemical functioning. High permeability at depth and VC enhance weathering, especially under wet climate conditions. Higher VC reduces shallow versus deep solute chemistry contrast and leads to more chemostatic export patterns (Figures 5–8). The results support the shallow and deep hypothesis that vertical water chemistry contrasts regulate concentration discharge (CQ) patterns. Concentrations of Cl vary negligibly with depth, resulting in chemostatic CQ patterns. Concentrations of Na, Si, and Ca increase with depth, leading to dilution CQ patterns; Al concentrations decrease with depth, leading to flushing patterns. Higher VC can reduce the shallow and deeper water chemistry contrast, leading to CQ patterns toward chemostasis. These results underscore the important linkage between hillslope structure (permeability distribution) in regulating hydrological (flow paths and TTD), and geochemical functioning (weathering and solute export). They underscore the potential of using streams as mirrors to infer subsurface biogeochemical reactions and scarcely
measured subsurface physical and chemical properties. Establishing such linkage is essential for understanding and projecting the response of earth surface processes to future climate and human activities.

Data Availability Statement
Simulation data from this work will be archived in the Consortium of Universities for the Advancement of Hydrologic Science, Inc. (CUAHSI) data website (http://www.hydroshare.org/resource/8362807be163491dbf3df933c37a16ef).

Acknowledgments
This work was financially supported by funds from the National Science Foundation for the Susquehanna Shale Hills Critical Zone Observatory (SSHCZO) to S. L. Brantley (EAR 13-31726). D. Xiao was additionally supported by funds from the Penn State Earth and Environmental Systems Institute. This research was conducted in Penn State’s Stone Valley Forest, which is funded by the Penn State College of Agriculture Sciences and the Department of Ecosystem Science and Management and managed by the staff of the Forestlands Management Office. We acknowledge discussions with members in the SSHCZO and Brantley and Li Reactive Water research group. We are deeply grateful for the help from Brandon Forsythe for data organization and management. We are thankful for the careful text editing by Bryn Stewart from the Li Reactive Water Group. Constructive comments from two anonymous reviewers and the associate editor has significantly improved the manuscript. We particularly acknowledge Dr. Daniel Ibarra for his suggestion of framing the discussion into hypotheses, which has significantly sharpened the paper.

References
Ameli, A. A., Amvrosiadi, N., Grabs, T., Laidon, H., Creed, I. F., McDonnell, J. J., & Bishop, K. (2016). Hillslope permeability architecture controls on subsurface transit time distribution and flow paths. Journal of Hydrology, 543, 17–30. https://doi.org/10.1016/j.jhydrol.2016.04.071

Ameli, A. A., Beven, K., Erlandsson, M., Creed, I. F., McDonnell, J. J., & Bishop, K. (2017). Primary weathering rates, water transit times, and concentration-discharge relations: A theoretical analysis for the critical zone. Water Resources Research, 53(1), 942–960. https://doi.org/10.1002/2016wr19448

Ameli, A. A., McDonnell, J. J., & Bishop, K. (2016). The exponential decline in saturated hydraulic conductivity with depth: A novel method for exploring its effect on water paths and transit time distribution. Hydrological Processes, 30(14), 2438–2450. https://doi.org/10.1002/hyp.10777

Anderson, R. S., Rajaram, H., & Anderson, S. P. (2019). Climate driven coevolution of weathering profiles and hillslope topography generates dramatic differences in critical zone architecture. Hydrological Processes, 33(1), 4–19. https://doi.org/10.1002/hyp.13307

Asano, Y., & Uchida, T. (2012). Flow path depth is the main controller of mean base flow transit times in a mountainous catchment. Water Resources Research, 48(3), W30512. https://doi.org/10.1029/2011wr010906

Bao, C., Wu, H., Li, L., Newcomer, D., Long, P. E., & Williams, K. H. (2014). Uranium bioreduction rates across scales: Biogeochemical hot moments and hot spots during a biostimulation experiment at Rille, Colorado. Environmental Science & Technology, 48(17), 10161–10172. https://doi.org/10.1021/es501060d

Barnes, R. T., Butman, D. E., Wilson, H. F., & Raymond, P. A. (2018). Riverine export of aged carbon driven by flow path depth and residence time. Environmental Science & Technology, 52(3), 1028–1035. https://doi.org/10.1021/acs.est.7b04717

Basu, N. B., Destouni, G., Jawitz, J., Thompson, S., Loukinova, N., & Darraaq, A., et al. (2010). Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. Geophysical Research Letters, 37(23), L23J04. https://doi.org/10.1029/2010gl045168

Beerling, D. J., & Berner, R. A. (2005). Feedbacks and the coevolution of plants and atmospheric CO2. Proceedings of the National Academy of Sciences of the United States of America, 102(5), 1302–1305. https://doi.org/10.1073/pnas.0408724102

Benettin, P., Bailey, S. W., Campbell, J. L., Green, M. B., Rinaldo, A., Likens, G. E., et al. (2015). Linking water age and solute dynamics in streamflow at the Hubbard Brook Experimental Forest, NH, USA. Water Resources Research, 51(11), 9256–9272. https://doi.org/10.1002/2015wr017552

Benettin, P., Fovet, O., & Li, L. (2020). Nitrate removal and young stream water fractions at the catchment scale. Water Resources Research, 46(3), 1–14. https://doi.org/10.1029/2019wr023781

Bergbhiuji, W. R., & Kirchner, J. W. (2017). The relationship between contrasting ages of groundwater and streamflow. Geophysical Research Letters, 44(17), 8925–8935. https://doi.org/10.1002/2017gl074962

Berner, R. A. (1992). Weathering, plants, and the long-term carbon cycle. Geochimica et Cosmochimica Acta, 56(3), 3225–3231. https://doi.org/10.1016/0016-7037(92)90300-8

Beven, K. (2018). A century of denial: Preferential and nonequilibrium water flow in soils, 1864–1984. Vadose Zone Journal, 17(1). https://doi.org/10.2136/vzj2018.08.0153

Billings, S. A., Hirmas, D., Sullivan, P. L., Lehmeier, C. A., Bagchi, S., Min, K., et al. (2018). Loss of deep roots limits biogenic agents of soil development that are only partially restored by decades of forest regeneration. Elementa: Science of the Anthropocene, 6(1), 34. https://doi.org/10.1525/elementa.287

Birkel, C., Soulsby, C., & Tetzlaff, D. (2015). Conceptual modelling to assess how the interplay of hydrological connectivity, catchment storage and tracer dynamics controls nonstationary water age estimates. Hydrological Processes, 29(13), 2956–2969. https://doi.org/10.1002/hyp.10414

Bott, M., Li, L., Hartmann, J., Burlando, P., & Fatichi, S. (2020). Depth of solute generation is a dominant control on concentration-discharge relations. Water Resources Research, 56, e2019WR026695. https://doi.org/10.1029/2019WR026695

Boyer, E. W., Hornberger, G. M., Bengala, K. E., & McKnight, D. M. (1997). Response characteristics of DOC flushing in an alpine catchment. Hydrological Processes, 11(12), 1635–1647. https://doi.org/10.1002/(sici)1099-1085(19971015)11:12<1635::aid-hyp494>3.0.co;2-h

Bracken, L. J., Wainwright, J., Ali, G. A., Tetzlaff, D., Smith, M. W., Reaney, S. M., & Roy, A. G. (2013). Concepts of hydrological connectivity: Research approaches, pathways and future agendas. Earth-Science Reviews, 119, 17–34. https://doi.org/10.1016/j.earscirev.2013.02.001

Brantley, S. L., Holleran, M. E., Jin, L., & Bazilevskaya, E. (2013). Frothing deep weathering in the Shale Hills Critical Zone Observatory, Pennsylvania (USA): The hypothesis of nested chemical reaction fronts in the subsurface. Earth Surface Processes and Landforms, 38(11), 1280–1298. https://doi.org/10.1002/esp.3415

Brantley, S. L., Lebedeva, M., & Bazilevskaya, E. (2013). Relating weathering fronts for acid neutralization and oxidation to pCO2 and pO2. In J. Farquhar, J. Kasting, & D. Canfield (Eds.), Treatise of geochemistry. Amsterdam, The Netherlands. Elsevier.

Brantley, S. L., & Lebedeva, M. I. (2021). Relating land surface, water table, and weathering fronts with a conceptual model for headwater catchments. Hydrological Processes, 35(2), e14010. https://doi.org/10.1002/hyp.14010

Brantley, S. L., Lebedeva, M. I., Balashov, V. N., Singhla, K., Sullivan, P. L., & Stinchcomb, G. (2017). Toward a conceptual model relating chemical reaction fronts to water flow paths in hills. Geomorphology, 277, 100–117. https://doi.org/10.1016/j.geomorph.2016.09.027

Brantley, S. L., White, T., Pinto, A., Williams, J. Z., Forsythe, B., Shapich, D., et al. (2018). Susquehanna Shale Hills Critical Zone Observatory: Shale hills in the context of Shaver’s Creek watershed. Vadose Zone Journal, 17, 1–19. https://doi.org/10.2136/vzj2018.04.0092
Ibarza, D. E., Moon, S., Caves, J. K., Chamberlain, C. P., & Maher, K. (2017). Concentration–discharge patterns of weathering products from global rivers. *Acta Geochimica*, 36(3), 405–409. https://doi.org/10.1007/s11631-017-0177-z

Jasechko, S., Kirchner, J. W., Welker, J. M., & McDonnell, J. J. (2016). Substantial proportion of global streamflow less than three months old. *Nature Geoscience*, 9(2), 126–129. https://doi.org/10.1038/ngeo2636

Jasechko, S., Perrone, D., Belus, K. M., Bayani Cardenas, M., Ferguson, G., Gleeson, T., et al. (2017). Global aquifers dominated by fossil groundwater but wells vulnerable to modern contamination. *Nature Geoscience*, 10(6), 425–429. https://doi.org/10.1038/ngeo2943

Jenko, K. G., McGlynn, B. L., Gooseff, M. N., Bencala, K. E., & Wondzell, S. M. (2010). Hillslope hydrologic connectivity controls riparian groundwater turnover: Implications of catchment structure for riparian buffering and stream water sources. *Water Resources Research*, 46, W10524. https://doi.org/10.1029/2009WR008818

Jenko, K. G., McGlynn, B. L., Gooseff, M. N., Wondzell, S. M., Bencala, K. E., & Marshall, L. A. (2009). Hydrologic connectivity between landscapes and streams: Transferring reach- and plot-scale understanding to the catchment scale. *Water Resources Research*, 45, W04428. https://doi.org/10.1029/2008WR007225

Jin, L., Ogroń, N., Vesavage, T., Hasenmueller, E. A., Ma, L., Sullivan, P. L., et al. (2014). The CO₂ consumption potential during gray shale weathering: Insights from the evolution of carbon isotopes in the Susquehanna Shale Critical Zone Observatory. *Geochimica et Cosmochimica Acta*, 142, 260–280. https://doi.org/10.1016/j.gca.2014.07.006

Jin, L., Ravela, R., Ketchum, B., Bierman, P. R., Heaney, P., White, T., & Brantley, S. L. (2010). Mineral weathering and elemental transport during hillslope evolution at the Susquehanna/Shale Critical Zone Observatory. *Geochimica et Cosmochimica Acta*, 74(13), 3669–3691. https://doi.org/10.1016/j.gca.2010.03.036

Johng, R. G., & Jackson, R. B. (2000). The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecological Applications*, 10(2), 423–436. https://doi.org/10.1890/1051-0761(2000)10[4043:tvodse]2.0.co;2

Johnson, M. (1969). The delayed neurotoxic effect of some organophosphorus compounds. Identification of the phosphorylation site as an esterase. *Biochemical Journal*, 114(4), 711–717. https://doi.org/10.1042/bj1140711

Kiewiet, L., van Meerveld, I., Stähli, M., & Seibert, J. (2020). Do stream water solute concentrations reflect when connectivity occurs in a small, pre-Alpine headwater catchment? *Hydrology and Earth System Sciences Discussions*, 24(7), 3381–3398. https://doi.org/10.5194/hess-24-3381-2020

Kirchner, J. W. (2016a). Aggregation in environmental systems – Part 2: Seasonal tracer cycles quantify young water fractions, but not mean transit times, in spatially heterogeneous catchments. *Hydrology and Earth System Sciences Discussions*, 20(1), 279–297. https://doi.org/10.5194/hess-20-279-2016

Kirchner, J. W. (2019). Quantifying new water fractions and transit time distributions using ensemble hydrograph separation: Theory and benchmark tests. *Hydrology and Earth System Sciences*, 23(1), 303–349. https://doi.org/10.5194/hess-23-303-2019

Klaus, J., & McDonnell, J. J. (2013). Hydrograph separation using stable isotopes: Review and evaluation. *Journal of Hydrology*, 505, 47–64. https://doi.org/10.1016/j.jhydrol.2013.09.006

Knapp, J. L. A., von Freyberg, J., Studer, B., Kiewiet, L., & Kirchner, J. W. (2020). Concentration–discharge relationships vary among hydrological events, reflecting differences in event characteristics. *Hydrology and Earth System Sciences*, 24(5), 2561–2576. https://doi.org/10.5194/hess-24-2561-2020

Kunst, R. W., Rubin, S., Berkowitz, B., & Singha, K. (2011). Quantifying solute transport at the Shale Hills Critical Zone Observatory. *Vadose Zone Journal*, 10(3), 843–857. https://doi.org/10.2136/vzj2010.03.30

Lasaga, A. (1998), Reaction Kinetics in Geoscience, 811 p. edited, Princeton University Press, Princeton.

Lebedeva, M. I., & Brantley, S. L. (2013). Exploring geochemical controls on weathering and erosion of convex hillslopes: Beyond the empirical regolith production function. *Earth Surface Processes and Landforms*, 38(15), 1793–1807. https://doi.org/10.1002/esp.3424

Lebedeva, M. I., & Brantley, S. L. (2017). Weathering and erosion of fractured bedrock systems. *Earth Surface Processes and Landforms*, 42(13), 2090–2108. https://doi.org/10.1002/esp.4177

Lebedeva, M. I., Sak, P., Ma, L., & Brantley, S. (2015). Using a mathematical model of a weathering elast to explore the effects of weathering on chemical weathering. *Chemical Geology*, 404, 88–99. https://doi.org/10.1016/j.chemgeo.2015.03.027

Leibowitz, S. G., Wigington, P. J., Jr., Schofield, K. A., Alexander, L. C., Vanderhoof, M. K., & Golden, H. E. (2018). Connectivity of streams and wetlands to downstream waters: An integrated systems framework. *Journal of the American Water Resources Association*, 54(2), 298–322. https://doi.org/10.1111/1752-1688.12631

Li, L., Bao, C., Sullivan, P. L., Brantley, S., Shi, Y., & Duffy, C. (2017). Understanding watershed hydrogeochemistry: 2. Synchronized hydrological and geochemical processes drive stream chemostatic behavior. *Water Resources Research*, 53(3), 2346–2347. https://doi.org/10.1002/2016wr198935

Li, L., Dibiase, R. A., Vecchio, J. D., Marcon, V., Hoagland, B., Xiao, D., et al. (2018). Investigating the effect of lithology and agriculture at the Susquehanna Shale Hills Critical Zone Observatory (SSHZCO): The Garner Run and Cole Farm subcatchments. *Vadose Zone Journal*, 17(1), 18063. https://doi.org/10.2136/vzj2018.03.0063

Li, L., Maher, K., Navarre-Steecher, A., Druhan, J., Meile, C., Lawrence, C., et al. (2017). Expanding the role of reactive transport models in critical zone processes. *Earth Science Reviews*, 165, 280–301. https://doi.org/10.1016/j.earscirev.2016.09.003

Li, L., Sullivan, P. L., Benetton, P., Cirpka, O., Bishop, K., Brantley, S., et al. (2021). Toward Catchment hydro-biogeochemical theories. *WIREs Water*. 2021, 8, e1495. https://doi.org/10.1002/wat2.1495

Maher, K. (2010). The dependence of chemical weathering rates on fluid residence time. *Earth and Planetary Science Letters*, 294(1–2), 101–110. https://doi.org/10.1016/j.epsl.2010.03.010

Maher, K., & Chamberlain, C. P. (2014). Hydrologic regulation of chemical weathering and the geologic carbon cycle. *Science*, 344(6178), 1502–1504. https://doi.org/10.1126/science.1250770

Maher, K., & Druhan, J. (2014). Relationships between the transit time of water and the fluxes of weathered elements through the critical zone. *Proceedings of the National Academy of Sciences*, 10, 16–22. https://doi.org/10.1073/pnas.1405801110

McGlynn, B. L., & McDonnell, J. J. (2003). Quantifying the relative contributions of riparian and hillslope zones to catchment runoff. *Water Resources Research*, 39(11), 1310. https://doi.org/10.1029/2003wr002091

McGuire, K. J., & McDonnell, J. J. (2006). A review and evaluation of catchment transit time modeling. *Journal of Hydrology*, 330(3–4), 543–563. https://doi.org/10.1016/j.jhydrol.2006.04.020

McGuire, K. J., & McDonnell, J. J. (2010). Hydrologic connectivity of hillslopes and streams: Characteristic time scales and nonlinearities. *Water Resources Research*, 46(10), W10543. https://doi.org/10.1029/2010wr0099341
McGuire, K. J., McDonnell, J. J., Weiler, M., Kendall, C., McGlynn, B. L., Welker, J. M., & Selbert, J. (2005). The role of topography on catchment-scale water residence time. Water Resources Research, 41(5), W05002. https://doi.org/10.1029/2004wr003657

Mcintosh, J. C., Schaumberg, C., Perdrial, J., Harpold, A., Vázquez-Ortega, A., Rasmussen, C., et al. (2017). Geochemical evolution of the Critical Zone across variable time scales informs concentration-discharge relationships: Jemez River Basin Critical Zone Observatory. Water Resources Research, 53, 4169–4196. https://doi.org/10.1002/2016WR019712

McNamara, J. P., Tetzlaff, D., Bishop, K., Soulsby, C., Seyfried, M., Peters, N. E., et al. (2011). Storage as a metric of catchment comparison. Hydrological Processes, 25(21), 3364–3371. https://doi.org/10.1002/hyp.8113

Moat, F., Abbott, B. W., Minnau, C., Curie, F., & Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. Water Resources Research, 53(2), 1270–1287. https://doi.org/10.1002/2016wr019635

Moore, J., Lichtner, P. C., White, A. F., & Brantley, S. L. (2012). Using a reactive transport model to elucidate differences between laboratory and field dissolution rates in regolith. Geochimica et Cosmochimica Acta, 93, 235–261. https://doi.org/10.1016/j.gca.2012.03.021

Musolf, A., Fleckenstein, J. H., Rao, P. S. C., & Jawitz, J. W. (2017). Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. Geophysical Research Letters, 44(9), 4143–4151. https://doi.org/10.1002/2017gl072630

Navarre-Sitchler, A., Steefel, C. I., Sak, P. B., & Brantley, S. L. (2011). A reactive-transport model for weathering rind formation on basalt. Geochimica et Cosmochimica Acta, 75(23), 7644–7667. https://doi.org/10.1016/j.gca.2011.09.033

Navarre-Sitchler, A., Steefel, C. I., Yang, L., Tomatsu, L., & Brantley, S. L. (2009). Evolution of porosity and diffusivity associated with chemical weathering of a basalt clast. Journal of Geophysical Research, 114, F02016. https://doi.org/10.1029/2008jf001060

Nippert, J. B., Wieme, R. A., Ocheltree, T. W., & Craine, J. M. (2012). Root characteristics of C-4 grasses limit reliance on deep soil water in tallgrass prairie. Plant and Soil, 355(1–2), 385–394. https://doi.org/10.1007/s11104-011-1112-4

Onoda, Y., Tsujimura, M., Fujihara, J.-I., & Ito, J. (2006). Runoff generation mechanisms in high-relief mountainous watersheds with different underlying geology. Journal of Hydrology, 331(3), 659–673. https://doi.org/10.1016/j.jhydrol.2006.06.009

Pandey, S., & Rajaram, H. (2016). Modeling the influence of preferential flow on the spatial variability and time-dependence of mineral weathering rates. Water Resources Research, 52(12), 9344–9366. https://doi.org/10.1002/2016wr019026

Pilster, L., Martinez-Carreras, N., Hissler, C., Klaus, J., Carrer, G. E., Stewart, M. K., & McDonnell, J. J. (2017). Bedrock geology controls on catchment storage, mixing, and release: A comparative analysis of 16 nested catchments. Hydrological Processes, 31(10), 1828–1845. https://doi.org/10.1002/hyp.11134

Pinder, G. F., & Jones, J. F. (1969). Determination of the ground-water component of peak discharge from the chemistry of total runoff. Water Resources Research, 5(2), 438–445. https://doi.org/10.1029/WR005i002p00438

Rademacher, L. K., Clark, J. F., Hudson, G. B., Erman, D. C., & Erman, N. A. (2001). Chemical evolution of shallow groundwater as record of early weathering of a basaltic crust. Water Resources Research, 37(2), 371–373. https://doi.org/10.1029/2000wr900146

Richardson, C. M., Zimmer, M. A., Fackrell, J. K., & Paytan, A. (2020). Geologic controls on water source baseflow generation and carbon geochemistry: Evidence of nonstationary baseflow sources across multiple subwatersheds. Water Resources Research, 56(7), e2019WR026577. https://doi.org/10.1029/2019wr026577

Riebe, C. S., Nahm, W. J., & Brantley, S. L. (2017). Controls on deep critical zone architecture: A historical review and four testable hypotheses. Earth Surface Processes and Landforms, 42(1), 128–156. https://doi.org/10.1002/esp.4052

Rödhe, A., Nyberg, L., & Bishop, K. (1996). Transiti Times for water in a small till catchment from a step shift in the oxygen 18 content of the water input. Water Resources Research, 32(12), 3497–3511. https://doi.org/10.1029/95wr01806

Salekhkoo, F., & Li, L. (2015). The role of magnesite spatial distribution patterns in determining dissolution rates: When do they matter? Geochimica et Cosmochimica Acta, 155, 107–121. https://doi.org/10.1016/j.gca.2015.01.035

Saleikhkhoo, F., Li, L., & Brantley, S. L. (2013). Magnesite dissolution rates at different spatial scales: The role of mineral spatial distribution and flow velocity. Geochimica et Cosmochimica Acta, 108, 91–106. https://doi.org/10.1016/j.gca.2013.01.010

Sanz-Prat, A., Lu, C., Amos, R. T., Finkel, M., Blowes, D. W., & Cirpka, O. A. (2016). Exposure-time based modeling of nonlinear reactive transport in porous media subject to physical and geochemical heterogeneity. Journal of Contaminant Hydrology, 192, 35–49. https://doi.org/10.1016/j.jconhyd.2016.06.002

Sanz-Prat, A., Lu, C., Finkel, M., & Cirpka, O. A. (2016). Using travel times to simulate multi-dimensional bioreactive transport in time-periodic flows. Journal of Contaminant Hydrology, 187, 1–17. https://doi.org/10.1016/j.jconhyd.2016.01.005

Seeger, S., & Weiler, M. (2014). Reevaluation of transit time distributions, mean transit times and their relation to catchment topography. Hydrology and Earth System Sciences, 18(12), 4751–4771. https://doi.org/10.5194/hess-18-4751-2014

Somers, L. D., & McKenzie, J. M. (2020). A review of groundwater in high mountain environments. WIREs Water, 7, e1475. https://doi.org/10.1002/wat2.1475

St Clair, J., Moon, S., Holbrook, W. S., Perron, J. T., Riebe, C. S., Martel, S. J., et al. (2015). Geophysical imaging reveals topographic stress control of bedrock weathering. Science, 350(6260), 534–538. https://doi.org/10.1126/science.aab2210

Steele, C., Appelo, C., Arora, B., Jacques, D., Kalbacher, T., Kolditz, O., et al. (2015). Reactive transport codes for subsurface environmental simulation. Computational Geosciences, 19(3), 445–478. https://doi.org/10.1007/s10590-014-9443-x

Steele, C. L., & Lasaga, A. C. (1994). A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. American Journal of Science, 294(5), 529–592. https://doi.org/10.2475/ajs.294.5.529

Sullivan, P. L., Hynek, S. A., Gu, X., Singh, K., White, T., West, N., et al. (2016). Oxidative dissolution under the channel leads geomorphological evolution at the Shale Hills catchment. American Journal of Science, 316(10), 981–1026. https://doi.org/10.2475/10.2016.02

Sullivan, P. L., Macpherson, G. L., Martel, S. J., & Price, R. M. (2019). Evolution of carbonate and karst critical zones. Chemical Geology, 527, 119223. https://doi.org/10.1016/j.chemgeo.2019.06.023
Zhi, W., Williams, K. H., Carroll, R. W. H., Brown, W., Dong, W., Kerins, D., & Li, L. (2020). Significant stream chemistry response to topography. *Chemical Geology*, 527, 118989. https://doi.org/10.1016/j.chemgeo.2018.12.002

Tetzlaff, D., Seibert, J., McGuire, K. J., Laudon, H., Burns, D. A., Dunn, S. M., & Soulsby, C. (2009). How does landscape structure influence stream chemistry in different geomorphologic provinces? *Hydrological Processes*, 23(6), 945–953. https://doi.org/10.1002/hyp.724

Torres, M. A., & Baronas, J. J. (2021). Modulation of riverine concentration-discharge relationships by changes in the shape of the water surface. *Global Biogeochemical Cycles*, 35(1), e2020GB006694. https://doi.org/10.1029/2020GB006694

Torres, M. A., West, A. J., & Clark, K. E. (2015). Geomorphic regime modulates hydrologic control of chemical weathering in the Andes-Amazon. *Geochimica et Cosmochimica Acta*, 166, 105–128. https://doi.org/10.1016/j.gca.2015.06.007

Tromp-van Meerveld, H. J., & McDonnell, J. J. (2006). Threshold relations in subsurface stormflow: 2. The fill and spill hypothesis. *Water Resources Research*, 42(2), W02411. https://doi.org/10.1029/2004wr003800

van der Velde, T., de Rooy, G. H., Rozemeijer, J. C., van Geer, F. C., & Broers, H. P. (2010). Nitrate response of a lowland catchment: On the relation between stream concentration and travel time distribution dynamics. *Water Resources Research*, 46(11), W11534. https://doi.org/10.1029/2010wr010915

von Freyberg, J., Allen, S. T., Seeger, S., Weiler, M., & Kirchner, J. W. (2018). Sensitivity of young water fractions to hydroclimatic forcing and landscape properties across 22 Swiss catchments. *Hydrology and Earth System Sciences*, 22(7), 3841–3861. https://doi.org/10.5194/hess-22-3841-2018

Welch, L. A., & Allen, D. M. (2014). Hydraulic conductivity characteristics in mountains and implications for conceptualizing bedrock groundwater flow. *Hydrogeology Journal*, 22(5), 1003–1026. https://doi.org/10.1007/s10040-014-1121-5

Wen, H., & Li, L. (2017). An upscaled rate law for magensite dissolution in heterogeneous porous media. *Geochimica et Cosmochimica Acta*, 210, 289–305. https://doi.org/10.1016/j.gca.2017.04.019

Wen, H., & Li, L. (2018). An upscaled rate law for mineral dissolution in heterogeneous media: The role of time and length scales. *Geochimica et Cosmochimica Acta*, 235, 1–20. https://doi.org/10.1016/j.gca.2018.04.024

Wen, H., Li, L., Crandall, D., & Hakala, A. (2016). Where calcite abscission creates more alteration: enhanced rock matrix diffusivity induced by preferential dissolution. *Energy & Fuels*, 30(5), 4197–4208. https://doi.org/10.1021/acs.energyfuels.6b02932

Wen, H., Sullivan, P. L., Macpherson, G. L., Billings, S. A., & Li, L. (2021). Deepening roots can enhance carbonate weathering by amplifying CO2-rich recharge. *Biogeoosciences*, 18(1), 55–75. https://doi.org/10.5194/bg-18-55-2021

West, A. J. (2012). Thickness of the chemical weathering zone and implications for erosional and climatic drivers of weathering and for carbon-cycle feedbacks. *Geology*, 40(9), 811–814. https://doi.org/10.1130/g33041.1

Weyman, D. R. (1973). Measurements of the downslope flow of water in a soil. *Journal of Hydrology*, 20(3), 267–288. https://doi.org/10.1016/0022-1694(73)90065-6

Wlostowski, A. N., Gooseff, M. N., Brantley, S. L., Chorover, J., McKnight, D. M., & Anderson, S. P. (2016). Patterns of hydrologic connectivity in the McMurdo Dry Valleys, Antarctica: A synthesis of 20 years of hydrologic data. *Hydrological Processes*, 30(17), 2958–2975. https://doi.org/10.1002/hyp.10818

Wlostowski, A. N., Molotch, N., Anderson, S. P., Brantley, S. L., Chorover, J., Drale, D., et al. (2021). Signatures of hydrologic function across the critical zone observatory network. *Water Resources Research*, 57, e2019WR026635. https://doi.org/10.1029/2019WR026635

Wolery, T. J. (1992). EQ3/6, a software package for geochemical modeling of aqueous systems: Package overview and installation guide. Version 7.0.

Wyman, A. S., Bretozon, R. L., Ibarra, D. E., Mahon, K., & McDowell, W. H. (2017). Critical zone structure controls concentration-discharge relationships and solute generation in forested tropical montane watersheds. *Water Resources Research*, 53(7), 6279–6295. https://doi.org/10.1002/2016wr020016

Xiao, D., Shi, Y., Brantley, S. L., Forsythe, B., DiBiase, R., Davis, K., & Li, L. (2019). Streamflow generation from catchments of contrasting lithologies: the role of soil properties, topography, and catchment size. *Water Resources Research*, 55, 9234–9257. https://doi.org/10.1029/2019WR023736

Zapata-Rios, X., McIntosh, J., Rademacher, L., Troch, P. A., Brooks, P. D., Rasmussen, C., & Chorover, J. (2015). Climatic and landscape controls on water transit times and silicate mineral weathering in the critical zone. *Water Resources Research*, 51(8), 6036–6051. https://doi.org/10.1002/2015wr017018

Zarnetske, J. P., Bouda, M., Abbott, B. W., Saires, J., & Raymond, P. A. (2018). Generality of hydrologic transport limitation of watersheds of carbon flux across ecoregions of the United States. *Geophysical Research Letters*, 45(21), 702–711. https://doi.org/10.1029/2018gl000005

Zhi, W., & Li, L. (2020). The shallow and deep hypothesis: Subsurface vertical chemical contrasts shape nitrate export patterns from different land uses. *Environmental Science & Technology*, 54(19), 11915–11928. https://doi.org/10.1021/acs.est.0c01340

Zhi, W., Li, L., Dong, W., Brown, W., Kaye, J., Steele, C., & Williams, K. H. (2019). Distinct source water chemistry shapes contrasting concentration-discharge patterns. *Water Resources Research*, 55(5), 4233–4251. https://doi.org/10.1029/2018wr024257

Zhi, W., Williams, K. H., Carroll, R. W. H., Brown, W., Dong, W., Kerins, D., & Li, L. (2020). Significant stream chemistry response to temperature variations in a high-elevation mountain watershed. *Communications Earth & Environment*, 1(1), 43. https://doi.org/10.1038/s43247-020-00039-w

Zimmer, M. A., & Gannon, J. P. (2018). Run-off processes from mountains to foothills: The role of soil stratigraphy and structure in influencing run-off characteristics across high to low relief landscapes. *Hydrolological Processes*, 32(11), 1546–1560. https://doi.org/10.1002/hyp.11488

Zimmer, M. A., & McGlynn, B. L. (2017). Ephemeral and intermittent runoff generation processes in a low relief, highly weathered catchment. *Water Resources Research*, 53(8), 7055–7077. https://doi.org/10.1002/2016wr019742