Deepening roots can enhance carbonate weathering

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Abstract: Carbonate weathering is essential in regulating atmospheric CO2 and carbon cycle at the century time scale. Plant roots have been known to accelerate weathering by elevating soil CO2 via respiration. It however remains poorly understood how and how much rooting characteristics (e.g., depth and density distribution) modify flow paths and weathering. We address this knowledge gap using field data from and reactive transport numerical experiments at the Konza Prairie Biological Station (Konza), Kansas (USA), a site where woody encroachment into grasslands is surmised to deepen roots.

Results indicate that deepening roots potentially enhance weathering in two ways. First, deepening roots can control thermodynamic limits of carbonate dissolution by regulating how much CO2 transports downward to the deeper carbonate-rich zone. The base-case data and model from Konza reveal that concentrations of Ca and Dissolved Inorganic Carbon (DIC) are regulated by soil pCO2 driven by the seasonal fluctuation of soil respiration. This relationship can be encapsulated in equations derived in this work describing the dependence of Ca and DIC on temperature and soil CO2, which has been shown to apply in multiple carbonate-dominated catchments. Second, numerical experiments show that roots control weathering rates by regulating the amount of water fluxes that flush through the carbonate zone and export reaction products at dissolution equilibrium. Numerical experiments explored the potential effects of partitioning 40% of infiltrated water to depth in woodlands compared to 5% in grasslands. Soil CO2 data from wood- and grasslands suggest relatively similar soil CO2 distribution over depth, and only led to 1% to 12% difference in weathering rates if flow partitioning was kept the same between the two land covers. In contrast, deepening roots can enhance weathering by 17% to 207% as infiltration rates increased from $3.7 \times 10^{-2}$ to 3.7 m/yr. Numerical experiments also indicated that weathering fronts in woodlands propagated > 2 times deeper compared to grasslands after 300 years at the infiltration rate of 0.37 m/yr. These differences in weathering fronts are ultimately caused by the contact time of CO2-charged water with carbonate rocks. We recognize that modeling results are subject to limitations in representing processes and parameters, but we propose that the data and numerical experiments allude to the hypothesis that 1) deepening roots can enhance carbonate weathering; 2) the hydrological impacts of rooting characteristics can be more influential than those of soil CO2 distribution in modulating weathering rates. We call for co-located characterizations of roots, subsurface structure, soil CO2 levels, and their linkage to water and water chemistry. These measurements will be essential to improve models and illuminate feedback mechanisms of land cover changes, chemical weathering, global carbon cycle, and climate.

1 Introduction

About 7–12% of the Earth's continental area is carbonate based; about 25% of the global population completely or partially depend on waters from karst aquifers (Hartmann et al., 2014). Carbonate weathering has long been considered negligible as a long-term control of atmospheric CO2 (0.5 to 1 Myr; (Berner and Berner, 2012; Winnick and Maher, 2018). Recent studies
however have underscored its significance in controlling global carbon cycle at the century time scale that is relevant to modern climate change, owing to its rapid dissolution, fast response to perturbations, and the order of magnitude higher carbon store in carbonate reservoirs compared to the atmosphere (Gaillardet et al., 2019). Carbonate weathering is influenced by many factors, including temperature (Romero-Mujalli et al., 2019b), hydrological regimes (Romero-Mujalli et al., 2019a; Wen and Li, 2018), and soil CO\textsubscript{2} concentrations (Covington et al., 2015) arising from vegetation type (Calmels et al., 2014). Rapid alteration to any of these factors, either human or climate induced, may change global carbonate weathering fluxes and lead to a departure from the current global atmospheric CO\textsubscript{2} level.

Plant roots have long been recognized as a dominant biotic-driver of chemical weathering and global carbon cycle (Berner, 1992; Beerling et al., 1998; Brantley et al., 2017a). The growth of forests has been documented to elevate soil pCO\textsubscript{2} and amplify Dissolved Inorganic Carbon (DIC) fluxes (Berner, 1997; Andrews and Schlesinger, 2001). Rooting structure can influence weathering in two ways. First, rooting systems (e.g., grass-, shrub- and woodlands) may affect the distribution of soil carbon (both organic and inorganic), microbe biomass, and soil respiration at depth (Drever, 1994; Jackson et al., 1996; Billings et al., 2018). The relatively deep root distributions of shrublands compared to grasslands may lead to deeper soil carbon profiles (Jackson et al., 1996; Jobbagy and Jackson, 2000), which may help elevate CO\textsubscript{2} and acidity that determine carbonate solubility and weathering rates.

Second, plant roots may affect soil structure and hydrological processes. Root trenching and etching can develop porosity (Mottershead et al., 2003; Hasenmueller et al., 2017). Root death and decay can promote the generation of macropores, or more specifically, biopores with connected networks (Angers and Caron, 1998; Zhang et al., 2015). Root channels have been estimated to account for about 70\% of the total described macropores (Noguchi et al., 1997; Beven and Germann, 2013) and for >70\% of water fluxes through soils (Watson and Luxmoore, 1986). In grasslands, the lateral, dense spread of roots in top soils promote horizontal macropores that support near-surface, lateral flow (Cheng et al., 2011). Highly dense fine roots also increase the abundance of organic matter and promote granular or “sandy” texture soil aggregates that facilitate shallow, near-surface water flow (Oades, 1993; Nippert et al., 2012). In contrast, shrublands and forests with deep and thick roots tend to have a high proportion of macropores and high connectivity to the deep subsurface (Canadell et al., 1996; Nardini et al., 2016), enhancing the drainage of water to the depth (Pawlik et al., 2016).

It is generally known that rooting characteristics vary among plant species and are critical in regulating flow paths and storage (Nepstad et al., 1994; Jackson et al., 1996; Cheng et al., 2011; Brunner et al., 2015; Fan et al., 2017). Existing studies however have primarily focused on the role of soil CO\textsubscript{2} and organic acids (Drever, 1994; Lawrence et al., 2014; Gaillardet et al., 2019). Systematic studies on coupled effects of flow partitioning and soil CO\textsubscript{2} distribution are missing, owing to the limitation in data that detail rooting effects on flow partitioning and complex hydrological-biogeochemical interactions. Here we ask the questions: how and to what degree do rooting characteristics influence carbonate weathering when considering both flow partitioning and soil CO\textsubscript{2} distribution? Which factor (flow partitioning or soil CO\textsubscript{2} distribution) predominantly controls weathering? We hypothesized that deepening roots in woodlands enhance carbonate weathering by promoting deeper recharge and CO\textsubscript{2}-carbonate contact at depth (Figure 1).

We tested the hypotheses by a series of numerical experiments integrating reactive transport modelling and water chemistry data from an upland watershed in the Konza Prairie Biological Station, a tallgrass prairie and one of the Long-Term Ecological Research (LTER) sites in the US (Figure S1). We used the calibrated model to carry out numerical experiments for two end-members of vegetation covers, grasslands and woodlands, under flow-partitioning conditions that are characteristic of their rooting structure. These experiments differentiated the impact of biogeochemical and hydrological drivers and bracketed the range
of their potential impacts on weathering, thus providing insights on the missing quantitative link between rooting structure, flow paths, and chemical weathering.

2 Research site and data sources

Site description. Details of the Konza site are in the Supporting Information (SI) and references therein. Here we provide brief information most relevant to this work. Konza is a mesic native grassland where experimentally manipulated, long-term burning regimes have led to woody encroachment in up to 70% of the catchment area in some catchments. The mean annual temperature and precipitation are 13°C and ~ 835 mm, respectively (Tsypin and Macpherson, 2012). The bedrock contains repeating Permian couplets of limestone (1-2 m thick) and mudstone (2-4 m) (Macpherson et al., 2008). The limestone is primarily calcite with traces of dolomite while the mudstone is dominated by illite, chlorite, and mixed-layers of chlorite-illite and chlorite-vermiculite, varying in abundance from major to trace amounts. With an average thickness of 1-2 m in the lowlands, soils mostly have carbonate less than 25% (Macpherson et al., 2008). Data suggest that the Konza landscape is undergoing a hydrogeochemical transition that coincides with and may be driven by woody-encroachment. In parallel to these changes is a detectable decline in stream flow and an increase in weathering rates (Macpherson and Sullivan, 2019) and groundwater $p$CO$_2$ (Macpherson et al., 2008). Stream water concentration-discharge (C-Q) patterns have exhibited chemodynamic patterns (i.e., solute concentrations are sensitive to changes in discharge) for geogenic species (e.g., Mg and Na) in woody-encroached sites compared to grass sites. Sullivan et al. (2019) hypothesized that concentration-discharge relationships may be affected by woody species with deeper roots, which altered flow paths and mineral-water interactions (Figure 1). We focus on the upland watershed N04d in Konza (Figure S1) that has experienced a 4-year burning interval since 1990 and has seen considerable woody encroachment and changes in hydrologic fluxes (Sullivan et al., 2019).

Data sources. Daily total meteoric precipitation and evapotranspiration were from the Konza data website (liter.konza.ksu.edu/data). Wet chemistry deposition data was from the National Atmospheric Deposition Program NADP (nadp.sws.uiuc.edu). Monthly data of soil gases (16, 84 and 152 cm), soil water (17 and 152 cm), and groundwater (366 cm) from 2009-2010 were used for this work (Tsypin and Macpherson, 2012) (Figure 2A). The sampling points were about 30 m away from the stream. More information on field and laboratory methods were included in the SI.
3 Reactive transport modeling

3.1 Base case: 1D reactive transport model for the Konza grassland (calibrated with field data)

A 1-D reactive transport model was developed using the code CrunchTope (Steefel et al., 2015). The code solves mass conservation equations integrating advective and diffusive/dispersive transport and geochemical reactions. It has been extensively used in understanding mineral dissolution, chemical weathering, and biogeochemical reactions (e.g., Lawrence et al. (2014); Wen et al. (2016); Deng et al. (2017)). In this study, the base case had a porosity of 0.48 and a depth of 366.0 cm at a resolution 1.0 cm.

Soil temperature was assumed to decrease linearly from 17 °C at the land surface to 8°C at 366.0 cm, within typical ranges of field measurements (Tsypin and Macpherson, 2012). Detailed set up of domain, soil mineralogy, initial condition, and precipitation chemistry, are in the SI.

Representation of soil CO₂. The model does not explicitly simulate soil respiration (microbial activities and root respiration) that produces soil CO₂. Instead, it approximates these processes by having a solid phase “CO₂(g*)” that continuously releases CO₂(g) that dissolves into CO₂(aq) (and other relevant aqueous species) at a kinetic rate constant of 10⁻⁹ mol/m²/s (Reaction 0-1 in Table 1) that reproduced the observed soil pCO₂ levels. This value is at the low end of the reported soil respiration rates (10⁻⁹ ~ 10⁻⁵ mol/m²/s) (Bengtson and Bengtsson, 2007; Ahrens et al., 2015; Carey et al., 2016). The dissolution of CO₂(g*) via CO₂(g) into CO₂(aq) follows Henry’s law $C_{CO2(aq)} = K_1 pCO₂$. Here $K_1$ is the equilibrium constant of Reaction 1, essentially Henry’s law constant. The extent of CO₂(g*) dissolution (i.e., the mass change of the solid phase over time) was constrained by $C_{CO2(aq)}$, which was estimated using temperature-dependent $K_1$ (following the van’t Hoff equation in Eq. S1) and measured soil CO₂ data at different horizons (Table 2). These $C_{CO2(aq)}$ values were then linearly interpolated for individual grid blocks in the model. Finally, these
prescribed \( C_{CO_2(aq)} \) values were used as the equilibrium constants of the coupled Reaction 0-1 in the form of \( CO_2(g^*) \rightleftharpoons CO_2(aq) \), such that the soil CO\(_2\) at different depth were represented (Section 4.1). In the base case, the soil profile of \( C_{CO_2(aq)} \) values were updated monthly based on the monthly soil CO\(_2\) data (Table 2). More details about the implementation in CrunchTope are included in the SI.

Table 1. Key reactions and kinetic and thermodynamic parameters

| Reaction | \( \log_{10}K_{eq} \) at 25 °C \(^1\) | Standard enthalpy \( (\Delta H^r, \text{kJ/mol}) \) | \( \log_{10}(k) \) (mol/m\(^2\)/s) at 25 °C \(^1\) | Specific Surface Area \((\text{m}^2/\text{g})\) \(^1\) |
|----------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| **Soil CO\(_2\) production through CO\(_2(g^*)\) and dissolving into CO\(_2(aq)\)** | | | | |
| (0) \( CO_2(g^*) \rightleftharpoons CO_2(g) \)| - | - | -9.00 | 1.0 |
| (1) \( CO_2(g) \rightleftharpoons CO_2(aq) \)| -1.46\(^b\) | -19.98 | - | - |
| (2) \( CO_2(aq) + H_2O \rightleftharpoons H^+ + HCO_3^- \)| -6.35 | 9.10 | - | - |
| (3) \( HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \)| -10.33 | 14.90 | - | - |
| **Chemical weathering** | | | | |
| (4) \( CaCO_3(s) + CO_2(aq) + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \)| -5.12\(^c\) | -15.41 | -6.69 | 0.84 |
| (5) \( CaAl_2Si_2O_8(s) + 8H^+ \rightleftharpoons Ca^{2+} + 2Al^{3+} + 2H_2SiO_4(aq) \)| 26.58 | - | -11.00 | 0.045 |
| (6) \( KAlSi_3O_8(s) + 4H^+ + 4H_2O \rightleftharpoons Al^{3+} + K^+ + 3H_2SiO_4(aq) \)| -0.28 | - | -12.41 | 0.20 |
| (7) \( Al_2Si_3O_8(OH)_4(s) + 6H^+ \rightleftharpoons 2Al^{3+} + 2H_2SiO_4(aq) + H_2O \)| 6.81 | - | -12.97 | 17.50 |

a. Values of \( K_{eq} \) were interpolated using the EQ3/6 database (Wolery et al., 1990), except Reaction 1 and 4 (i.e., \( K_i \) and \( K_r \)).
b. By combining the temporal- and spatial-dependent soil pCO\(_2\) data, CO\(_2(aq)\) concentrations were calculated through \( C_{CO_2(aq)} = \%\text{pCO}_2 \). The prescribed \( C_{CO_2(aq)} \) values were used as equilibrium constants in CrunchTope to describe how much soil CO\(_2\) was available for weathering.
c. Calcite in the shallow soil (above Horizon B) is mixed with other minerals and has small particle size (Macpherson and Sullivan, 2019), relatively “impure” and therefore has a lower \( K_{eq} \) value than those at depth with relatively “pure” calcite. The \( K_{eq} \) of the “impure” calcite was calibrated by fitting field data of Ca and alkalinity.
d. The kinetic rate parameters and specific surface areas were from Palandri and Kharaka (2004), except Reaction 0. The kinetic rate constant of the solid phase CO\(_2(g^*)\) dissolution (i.e., soil CO\(_2\) production rate constant) was from (Bengtson and Bengtsson, 2007; Ahrens et al., 2015; Carey et al., 2016). The specific surface area was referred to that of soil organic carbon (Pennell et al., 1995).
e. These reactions were only used in the base case model as they occurred in shallow soils in Konza. In the later numerical experiments, these reactions were not included so as to focus on carbonate weathering.

Table 2. Measured CO\(_2(g)\) at different depths and corresponding estimated \( C_{CO_2(aq)} \)

| Time | Soil depth | Ways obtained\(^{a,b,c}\) |
|------|------------|---------------------|
| I. Grassland (Konza) cases | | |
| Soil T °C | Horizon A (h = 16 cm) | Horizon AB (84 cm) | Horizon B (152 cm) | Groundwater (366 cm) |
| Ki | 17 | 15 | 13 | 8 |
| 4.1×10\(^{-2}\) | 4.4×10\(^{-2}\) | 4.6×10\(^{-2}\) | 5.4×10\(^{-2}\) | Estimated |
| I. Base case with monthly updated CO\(_2(g)\) (%) and CO\(_2(aq)\) (mol/L) | | | |
| CO\(_2(g)\) | July | 3.6 | 6.8 | 6.6 | 2.2 | Measured |
| | August | 1.4 | 1.7 | 7.2 | 3.9 | Measured |
| | September | 0.6 | 1.2 | 3.9 | 4.9 | Measured |
| | October | 0.5 | 1.4 | 2.5 | 5.0 | Measured |
| | November | 0.6 | 1.1 | 2.2 | 4.0 | Measured |
| | January | 0.3 | 0.8 | 1.1 | 3.6 | Measured |
| | March | 0.2 | 0.3 | 0.5 | 3.0 | Measured |
| CO\(_2(aq)\) | July | 1.5×10\(^{-3}\) | 3.0×10\(^{-3}\) | 3.0×10\(^{-3}\) | 1.2×10\(^{-3}\) | Estimated |
| | August | 5.7×10\(^{-4}\) | 7.5×10\(^{-4}\) | 3.3×10\(^{-4}\) | 2.1×10\(^{-3}\) | Estimated |
| | September | 2.5×10\(^{-4}\) | 6.2×10\(^{-4}\) | 1.8×10\(^{-4}\) | 2.6×10\(^{-4}\) | Estimated |
| | October | 1.9×10\(^{-4}\) | 6.2×10\(^{-4}\) | 1.2×10\(^{-4}\) | 2.7×10\(^{-4}\) | Estimated |
| | November | 2.5×10\(^{-4}\) | 4.8×10\(^{-4}\) | 1.0×10\(^{-3}\) | 2.2×10\(^{-3}\) | Estimated |
The Keq of "impure" calcite (K4) was calibrated by fitting field data of Ca and alkalinity.  

3.2 Numerical experiments  
   a. Monthly measured soil CO2 data for the Konza grassland (base case) were from (Tsypin and Macpherson, 2012). The annual-averaged soil CO2 used in the grassland experiments was averaged from the corresponding monthly measurements. More information on measurements at the Konza grassland were detailed in the SI. The annual-average soil CO2 in the woodland experiments was from the Calhoun site in South Carolina where trees (forest) are dominant (Billings et al., 2018).  
   b. CO2(aq) were estimated using Henry’s law CCO2(aq) = K1pCO2. The temperature-dependent K1 was calculated following Eq. S1. The CCO2(aq) values at different soil depths were used to prescribe the available soil CO2 for chemical weathering.  
   c. Soil temperature was estimated from the soil water and shallow groundwater temperature (Tsypin and Macpherson, 2012; Billings et al., 2018).  

Reactions. The shallow soils have more anorthite (CaAl2Si2O8(s)) and K-feldspar (KAlSi3O8(s)) and deeper subsurface contains more calcite (Table S1). Table 1 summarizes reactions and thermodynamic and kinetic parameters. Soil CO2 increases pore water acidity (Reactions 0-2) and accelerates mineral dissolution (Reactions 3-6). Silicate dissolution leads to the precipitation of clay (represented by kaolinite in Reaction 7). These reactions were included in the base case to reproduce field data. The kinetics follows the transition state theory (TST) rate law (Plummer et al., 1978) r = kA \left(1 - \frac{\text{IAP}}{K_{eq}}\right), where k is the kinetic rate constant (mol/m²/s), A is the mineral surface area per unit volume (m²/m³), IAP is the ion activity product, and K_{eq} is the equilibrium constant. The term \text{IAP/}K_{eq} quantifies the extent of disequilibrium: values close to 0 suggest far from equilibrium whereas values close to 1.0 indicate close to equilibrium.  

Flow partitioning. Rainwater entered soil columns at the annual infiltration rate of 0.37 m/yr, estimated based on the difference between measured precipitation (0.88 m/yr) and evapotranspiration (0.51 m/yr). At 50 cm, a lateral flow Q_e (soil water) exited the soil column to the stream at 0.35 m/yr. The rest recharged the deeper domain beyond 50 cm (to the groundwater system) at 0.02 m/yr (~2% of precipitation) and became groundwater (Figure 1A), a conservative value compared to 2-15% reported in another study (Steward et al., 2011). The groundwater flow Q_w eventually came out at 366.0 cm and was assumed to enter the stream as part of discharge (= Q_e + Q_w). The flow field was implemented in CrunchTope using the “PUMP” option.  

Calibration. We used monthly measured alkalinity and Ca concentration data in different horizons (Horizon A, B and groundwater in Figure 2A) from 2009-2010 at the Konza grassland for model calibration. The monthly Nash-Sutcliffe efficiency (NSE), which quantified the residual variance of modeling output compared to measurements, was used for model performance evaluation (Moriasi et al., 2007). NSE values higher than 0.5 are considered acceptable. At Konza, calcite in the shallow soil (above Horizon B) is mixed with other minerals, has small particle size, and is considered “impure” (Macpherson and Sullivan, 2019) and therefore has a lower K_{eq} value than those at depth with relatively “pure” calcite. The K_{eq} of “impure” calcite (K_a) was calibrated by fitting field data of Ca and alkalinity.  

3.2 Numerical experiments
Numerical experiments were set up to understand how and to what extent roots regulate weathering rates and solute transport in grasslands and in woodlands. The base case from Konza was used to represent grasslands, and the Calhoun site (the Calhoun Critical Zone Observatory in South Carolina, USA) was used as a representative woody site (Billings et al., 2018). Grasslands are typically characterized by a high proportion of horizontal macropores induced by dense, lateral-spread of roots mostly at depths less than 0.8 m (Jackson et al., 1996; Frank et al., 2010). These characteristics promote lateral flow ($Q_L$) at the shallow subsurface (Figure 1A). At Konza, > 90% of grass roots were at the top 0.5 m, leading to high hydrologic conductivity in top soils (Nippert et al., 2012). In the woodland, a greater proportion of deep roots enhances vertical macropore development (Canadell et al., 1996; Nardini et al., 2016), reduces permeability contrasts at different depths (Vergani and Graf, 2016), and is thought to facilitate more vertical water flow to the depth ($Q_v$). At the Calhoun site, > 50% of roots are in the top 0.5 m in woodlands, with the rest penetrating deeper (Jackson et al., 1996; Eberbach, 2003; Billings et al., 2018).

The experiments aimed to compare the general, averaged behaviors rather than event-scale dynamics so the annual-average soil CO$_2$ data and corresponding prescribed CO$_2$(aq) concentrations were used (Table 2). The experiments focused on calcite weathering (Reaction 0-4) and excluded silicate weathering reactions (Reaction 5-7). The mineral-dissolution-related parameters from the base case were used for all experiments. We compared the relative significance of hydrological and biogeochemical effects (soil CO$_2$ level and distribution) of rooting depths.

**Hydrological and bigeochemical differences in grasslands and woodlands.** Flow partitioning between lateral shallow flow and vertical recharge flow is challenging to quantify and is subject to large uncertainties under diverse climate, lithology, and land cover conditions. The ratios of lateral flow in shallow soils versus the total flow inferred from a tracer study in a grassland vary from ~70% to ~95% (Weiler and Naef, 2003). Harman and Cosans (2019) found that the lateral flow rate at shallow soils over the overall infiltration can vary between 50% and 95%. Deeper roots in woodlands can increase deep soil permeability by > one order of magnitude (Vergani and Graf, 2016). Assuming that the vertical, recharged flow water ultimately leaves the watershed as baseflow, the ratio of the lateral versus vertical flow has been reported with a wide range. In forests such as Shale Hills in Pennsylvania and Coal Creek in Colorado, ~ 7%-20% of stream discharge is from groundwater, presumably recharged by vertical flow (Li et al., 2017; Zhi et al., 2019). Values of $Q_o/Q_r$ estimated through base flow separation vary from 20% to 90% in forest/wood-dominated watersheds (Price, 2011), often negatively correlating with the proportion of grasslands (Mazvimavi et al., 2004).

Soil respiration rates can vary between $10^{-9}$ ~ $10^{-5}$ mol/m$^2$/s for both grasslands and woodlands (Bengtson and Bengtsson, 2007; Ahrens et al., 2015; Carey et al., 2016). Soil CO$_2$ levels may vary by 2-3 orders of magnitude depending on vegetation type and climate conditions (Neff and Hooper, 2002; Breecker et al., 2010). Soil CO$_2$ levels are further complicated also by their dependence on topographic position, soil depth, and soil moisture, all of which determine the magnitude of microbial and root activities and CO$_2$ diffusion (Hasenmueller et al., 2015; Billings et al., 2018). There is however no consistent evidence suggesting which land cover exhibits higher soil respiration rate or soil CO$_2$ level. Below we describe details of the numerical experiments (Table 3) exploring the influence of hydrological versus biogeochemical impacts of roots.
Table 3. Physical and geochemical characteristics in numerical experiments

| Cases                     | Calcite distribution | Schematic | Hydrological and biogeochemical aspects | Flow partitioning | Soil CO$_2$ distribution |
|---------------------------|----------------------|-----------|----------------------------------------|-------------------|--------------------------|
| Scenario 1 with flow partitioning (PF) | Grass$_{PF}$         |           |                                        | $Q_L = 95\% Q_T$  | Annual average from the Konza grassland (red line) |
|                           | Wood$_{PF}$          |           |                                        | $Q_V = 5\% Q_T$   | Annual average from the Calhoun forest (blue line)  |
| Scenario 2 with 100% vertical flow (VF) | Grass$_{VF}$         |           |                                        | $Q_L = 0$         | Annual average from the Konza grassland (red line) |
|                           | Wood$_{VF}$          |           |                                        | $Q_V = Q_T$       | Annual average from the Calhoun forest (blue line)  |
| Scenario 3 with 100% lateral flow (HF) | Grass$_{HF}$         |           |                                        | $Q_L = Q_T$       | Annual average from the Konza grassland (red line) |
|                           | Wood$_{HF}$          |           |                                        | $Q_V = 0$         | Annual average from the Calhoun forest (blue line)  |

220 a. Diagrams represent the soil profiles of physical and geochemical properties; b. Calcite distribution (black line) in all cases increases with depth; c. The flow field was implemented in CrunchTope using the “PUMP” option; d. Annual-average soil CO$_2$ used for constraining the grassland (red line) was from the Konza grassland (Tsypin and Macpherson, 2012). The annual-average soil CO$_2$ in the woodland (blue line) was from the Calhoun forest (Billings et al., 2018).

Three scenarios. Each scenario in Table 3 includes a grassland and woodland case, with their respective profiles of calcite distribution and soil pCO$_2$ kept the same (column 3 and 4 in Table 3). The only difference in different scenarios is the flow partitioning (column 5 in Table 3). Soil pCO$_2$ in the grassland (red line in Table 3) were set to reflect the annual average of the Konza site. Soil pCO$_2$ (blue line) in the woodland is the annual average from the forest-dominant Calhoun site (Billings et al., 2018). In all scenarios, we assumed that grasslands and woodlands had the same total solid phase “CO$_2$(g*)” producing CO$_2$ gas and CO$_2$(aq) but differed in depth distributions. The CO$_2$(g*) served as the source of soil CO$_2$ and was constrained by CO$_2$(g) field data (Table 2). In grasslands, the modeled distribution of CO$_2$(g*) was steep, with higher density of roots and more abundant CO$_2$(g*) in the shallow soils; while the distribution was less steep in woodlands (Jackson et al., 1996). Below the rooting depth, CO$_2$(g*) was assumed to be smaller (by 10 times) to represent the potential soil CO$_2$ sources from microbial activities (Billings et al., 2018).

Scenario 1 considered flow partitioning (Table 3). With the large permeability contrast of soil and bedrock (over four orders of magnitude) in Konza (Macpherson, 1996), the Grass$_{PF}$ case (with $Q_L = 95\% Q_T$ and $Q_V = 5\% Q_T$) represents an end-member case for the grassland. The woodland (Wood$_{PF}$) case was set to have 60% lateral flow and 40% vertical flow into deeper subsurface. This groundwater percentage is at the high end of flow partitioning and serves as an end-member case for woodlands (Vergani and Graf, 2016). Scenarios 2 and 3 had no flow partitioning. Scenario 2 had two cases with 100% vertical flow via the bottom outlet (VF; Wood$_{VF}$ and Grass$_{VF}$); Scenarios 3 had two cases with 100% horizontal flow (HF; Wood$_{HF}$ and Grass$_{HF}$) via the shallow outlet at 50 cm. These cases represent the end-member flow cases with 100% lateral flow or 100% vertical flow. In addition, because the two cases have the same flow scheme, they enable the differentiation of effects of soil CO$_2$ distribution versus hydrology differences. All scenarios were run under infiltration rates from $3.7 \times 10^{-2}$ to 3.7 m/yr ($10^{-4}$ – $10^{-2}$ m/day), the observed daily variation range at Konza. This was to explore the role of flow regimes and identify conditions where most and least significant differences occur. To reproduce the observed soil CO$_2$ profile, the soil CO$_2$ production rate (mol/m$^2$/yr) at the domain scale (calculated by the mass change of the solid phase CO$_2$(g*) over time) was assumed to increase with infiltration rates (Figure S2).
This is consistent with field observations that soil CO$_2$ production rate and efflux may increase with rainfall in grassland and forest ecosystems (Harper et al., 2005; Patrick et al., 2007; Wu et al., 2011; Vargas et al., 2012; Jiang et al., 2013). For example, Zhou et al. (2009) documented soil CO$_2$ production rates increasing from 3.2 to 63.0 mol/m$^2$/yr when the annual precipitation increased from 400 to 1,200 mm. In addition, Wu et al. (2011) showed that increasing precipitation from 5 to 2,148 mm enhanced soil respiration by 40% and that a global increase in 2 mm precipitation per decade may lead to an increase of 3.8 mol/m$^2$/yr for soil CO$_2$ production. The simulated soil CO$_2$ production rates across different infiltration rates here (~0.1-10 mol/m$^2$/yr shown in Figure S2) were close to the reported belowground net primary production (belowground NPP) of typical ecosystems: ~0.8-100 mol/m$^2$/yr for grasslands (Gill et al., 2002) and ~0.4 - 40 mol/m$^2$/yr for woodlands (Aragao et al., 2009).

Each case was run until steady state, when concentrations at the domain outlet became constant (within ±5%) over time. The time to reach steady state varied from 0.1 to 30 yrs, depending on infiltration rates. The lateral flux (soil water, $M_l=Q_l\times C_l$) and vertical fluxes (groundwater, $M_w=Q_w\times C_w$) were calculated at 50 and 366 cm, in addition to total fluxes (weathering rates, $M_t$). These fluxes multiplied with unit cross-section area (m$^2$) convert into rates in units of mol/yr.

**Carbonate weathering over century time scales: soil property evolution.** To compare the propagation of weathering fronts over longer time scales, we carried out two 300-yr simulations for Scenario 1 with flow partitioning under the base-case infiltration rate of 0.37 m/yr (i.e., Grass$_{BP}$ and Wood$_{BP}$ in Table 3). During this long-term simulation, we updated calcite volume, porosity and permeability. The calcite volume changes were updated in each time step based on corresponding mass changes, which were used to update porosity. Permeability changes were updated based on changes in local porosity following the Kozeny–Carman equation:

$$k_i = k_{i,0} \left( \frac{\Phi_i}{\Phi_{i,0}} \right)^{3} \left( \frac{1-\Theta_{i,0}}{1-\Theta_i} \right)^{2}$$

(Kozeny, 1927; Costa, 2006), where $k_i$ and $\Phi_i$ is permeability and porosity in grid $i$ at time $t$, and $k_{i,0}$ and $\Phi_{i,0}$ are the initial permeability and porosity, respectively.

### 3.3 Quantification of weathering rates and their dependence on CO$_2$:carbonate contact

To quantify the overall weathering rates and CO$_2$:carbonate contact in each scenario, we used the framework from a previously-developed upscaled rate law for dissolution of spatially heterogeneously distributed minerals (Wen and Li, 2018). The rate law says that three characteristics times are important. The equilibrium time $\tau_0$ represents the characteristic timescale of mineral dissolution to reach equilibrium in a well-mixed system. The residence time $\tau_a$, i.e., the timescale of advection, quantifies the overall water contact time with the whole domain. It was calculated by the product of domain length ($L$) and porosity divided by the overall infiltration rate ($Q_w$): $\tau_a = \frac{L}{Q_w}$. The reactive transport time $\tau_{ad,r}$ quantified the water contact time with calcite as influenced by both advection and diffusion/dispersion. The upscaled rate law is as follows:

$$R_{calcite} = k_{calcite} A_r \left[ 1 - \exp \left( -\frac{\tau_a}{\tau_0} \right) \right] \left[ 1 - \exp \left[ -L \left( \frac{\tau_a}{\tau_{ad,r}} \right) \right] \right]$$

(1)

Here $k$ is the intrinsic rate constant measured for a mineral in a well-mixed reactor, $A_r$ is the total surface area, $L$ is domain length, $\alpha$ is geostatistical characteristics of spatial heterogeneity, and $\tau_{ad,r}$ is the reactive time ratio quantifying the relative magnitude of the water contact time with the whole domain versus the contact time with the reacting mineral. This rate law consists of two parts: the effective dissolution rates in homogeneous media represented by $k A_r \left[ 1 - \exp \left( -\frac{\tau_a}{\tau_0} \right) \right]$ and the heterogeneity factor $\left[ 1 - \exp \left[ -L \left( \frac{\tau_a}{\tau_{ad,r}} \right) \right] \right]^\alpha$ that quantifies effects of preferential flow paths arising from heterogeneous distribution of minerals. When
\( \frac{\tau_a}{\tau_{ad,r}} > 1 \), the water contact time with calcite zone is small, meaning the water is replenished quickly compared to the whole domain, leading to higher CO\(_2\)-carbonate interactions. In contrast, small \( \frac{\tau_a}{\tau_{ad,r}} \) ratio (<1) reflects water is replenished slowly in the reactive calcite zones, leading to less CO\(_2\)-carbonate contact. These different time scales were calculated for Scenarios 1-3 based on the flow characteristics and dissolution thermodynamics and kinetics, as detailed in the SI. Values of \( \tau_a \), \( \tau_{ad} \), and \( \tau_{ad,r} \) for all experiments are listed in Table S2.

4 Results

4.1 The thermodynamics of carbonate dissolution: grassland at Konza as the base case scenario

The calibrated model reproduced the temporal dynamics with a Nash-Sutcliffe efficiency (NSE) value > 0.6 and was considered satisfactory (Figure 2). Note that y axis is inverted to display shallow soils at the top and deep soils at the bottom to be consistent with their subsurface position shown in Figure 2A. The measured CO\(_2\)(g) varied between 0.24 – 7.30% (Figure 2B right axis), one to two orders of magnitude higher than the atmospheric level of 0.04%. The estimated CO\(_2\)(aq) (Figure 2B left axis) generally increased with depth except in July and August when horizon B was at peak concentration. The timing of the peaks and valleys varied in different horizons. The CO\(_2\)(aq) reached maxima in summer in soil horizons A and B and decreased to < 0.5 mM in winter and spring. The groundwater CO\(_2\)(aq) exhibited a delayed peak in September and October, and dampened seasonal variation compared to soil horizons. The temporal trends of alkalinity, DIC, and Ca in groundwater mirrored those of soil CO\(_2\) at their corresponding depths, indicating the predominate control of soil CO\(_2\) on carbonate weathering. The groundwater concentrations of these species were also higher than soil concentrations. The simulated groundwater DIC (approximately summation of CO\(_2\)(aq) and alkalinity) was > 6 times higher than that in shallow soil (~ 1.0 mM). The dissolved mineral volume was negligible for the simulation period (< 0.5% v/v). Sensitivity analysis revealed that changes in flow velocities influenced concentrations in Horizon A with anorthite as the dominating dissolving mineral (0 – 1.8 m); their effects are negligible in Horizon B and groundwater where fast-dissolving calcite has reached equilibrium.

Figure 2. (A) Schematic representation of sampling depths in the Konza grassland; Corresponding monthly dynamics of (B) CO\(_2\)(aq) and CO\(_2\)(g), (C) alkalinity, (D) DIC, and (E) Ca concentrations. Lines represent modelling outputs at the
corresponding sampling depth of monthly field measurements (dots), including soil water at Horizons A (16 cm) and B (152 cm), and groundwater (366 cm). The lines of CO$_2$(aq) and CO$_2$(g) in Figure B overlapped. Note that there are no DIC data so no dots in Figure D. The temporal trends of alkalinity, DIC, and Ca mirrored those of soil CO$_2$, indicating its predominant control on weathering.

Several measurements/parameters were important in reproducing data, especially soil CO$_2$ that determined the CO$_2$(aq) level and its spatial variation, and equilibrium constant ($K_{eq}$) of calcite dissolution. Imposition of monthly variations and depth distributions of soil CO$_2$ were essential to capture the variation of alkalinity and Ca data at different horizons. The imposition of calcite $K_{eq}$ was also critical for reproducing Ca concentrations. Impurities were suggested to affect $K_{eq}$ of natural calcite by a factor of ~2.0 (Macpherson and Sullivan, 2019). Calcite $K_{eq}$ in shallow soils had to be reduced by a factor of 3.8 in the model to reproduce concentrations in Horizon A. The alkalinity and Ca concentrations were not sensitive to kinetic parameters nor precipitation, because carbonate dissolution was fast and thermodynamically controlled.

4.2 Numerical experiments: the significance of potential hydrology differences

Scenario 1 for hydro-biogeochemical effects with flow partitioning (WoodPF and GrassPF). Figures 3A1-E1 show depth profiles of calcite and soil CO$_2$ production rates and steady-state concentrations of reaction products. Although the model did not explicitly simulate soil respiration, the soil CO$_2$ production rate was highest in the shallow soil at around $10^{-6.5}$ mol/s and decreased to ~ $10^{-9.5}$ mol/s at 366 cm (Figure 3B1), consistent with the decline with soil depth observed in natural systems. The CO$_2$(g) level (released from the solid phase CO$_2$(g*)) increased with depth due to autotrophic and heterotrophic respiration and downward fluxes of CO$_2$-charge water from the shallow soil (Figure 3C1). Concentrations of reaction products (Ca, DIC) were lower in the top 40 cm reflecting the lower carbonate-mineral background level and higher at depths > 60 cm. The transition occurred between 35 cm – 60 cm at the vicinity of calcite-no calcite interface at 55 cm, where concentrations of Ca and DIC increased abruptly until reaching equilibrium. This thin transition was driven by fast calcite dissolution and rapid approach to equilibrium, resulting in a short equilibrium distance. The equilibrated DIC and Ca concentrations below 60 cm followed the similar increasing trend of CO$_2$(g) with depth in the deep zone (Figure 3C1-E1).

Figures 3F1 show that Ca concentrations in soil water (light color) were lower than groundwater (dark color) and varied with infiltration rates. The difference between soil water and groundwater Ca concentrations was relatively small at low infiltration rates because both reached equilibrium but diverged at high infiltration rates. Higher infiltration rates diluted soil water but not as much for groundwater. As expected, stream concentrations, a mixture of soil water and groundwater (solid line), were in between these values but closely resembled soil water in the grassland. In both cases, stream concentration decreased as infiltration increased, indicating a dilution concentration-discharge relationship.
Figure 3. Simulated depth profiles of (A) calcite (vol %), (B) soil CO$_2$ production rate; (C) CO$_2$(g), (D) DIC, and (E) Ca at 0.37 m/yr, and (F) effluent Ca concentrations at different infiltration rates. From top to bottom rows are Scenario 1 (Grass$_{PF}$ and Wood$_{PF}$; with flow partitioning, first row), Scenario 2 (Grass$_{VF}$ and Wood$_{VF}$; 100% vertical flow, second row), and Scenario 3 (Grass$_{HF}$ and Wood$_{HF}$; 100% lateral flow, last row). Red and blue colors present grassland and woodland, respectively. Lines and empty circles represent modelling outputs while filled circles with error bar in Figure C are the annual average CO$_2$(g) data (in Table 2). Arrows in Figure A indicate flow conditions. In F, soil water and groundwater refer to concentrations at the lateral (50 cm) and vertical (366 cm) outlets, respectively. Higher fractions of vertical flow in Wood$_{VF}$ led to higher stream Ca concentration compared to Grass$_{VF}$. In Scenarios 2 and 3 without flow partitioning, stream Ca concentrations were similar. The concentrations of DIC versus discharge are very similar to the Ca concentrations in F.

**Scenarios 2-3 for biogeochemical effects (without flow partitioning).** Scenarios 2 and 3 were end-member cases that bracket the range of rooting effects. Calcite and soil CO$_2$ were distributed the same way as their corresponding PF cases (Table 3). The Wood$_{VF}$ and Grass$_{VF}$ cases had 100% flow going downward via the deeper calcite zone maximizing the CO$_2$-water-calcite contact.
In the WoodHF and GrassHF cases (Table 3), all water exited at 50 cm, bypassing the deeper calcite-abundant zone, minimizing the CO$_2$-water-calcite contact. Figures 3A2-F2 and 3A3-F3 show the VF (WoodVF and GrassVF) and HF (WoodHF and GrassHF) cases, respectively. Similar to the flow partitioning cases, the concentrations of reaction products were low in the shallow zone and increased over 10 times within a short distance ~ 5 cm at the depth of ~ 50 cm. The woodland cases increased slightly more than the grassland cases because of the slightly steeper soil CO$_2$ distribution (Figure 3C2 and 3C3). Figure 3F2 indicates that the effluent Ca concentrations were slightly higher in WoodVF due to the high soil CO$_2$ level at the bottom outlet. The GrassHF and WoodHF case almost had the same effluent Ca concentrations at the shallow soil (Figure 3F3).

**Concentration-discharge relationship and weathering rates in all cases.** The VF cases had the highest effluent concentrations and weathering rates, whereas the HF cases had lowest concentrations and weathering rates, and the GrassPF and WoodPF cases fell in between (Figure 4A-B). This is because the VF cases maximized the CO$_2$-calcite contact with 100% flow through the calcite zone, whereas the HF cases had minimum CO$_2$-calcite contact with water bypassing the calcite zone (column 3-4 in Table 3). The GrassPF and WoodPF cases allowed different extent of contact prescribed by the amount of flow via the calcite zone. A case run without soil respiration (i.e., no CO$_2$(g*), not shown) indicated that Ca and DIC concentrations were more than an order of magnitude lower than cases with soil respiration. In addition, the PF and HF cases generally showed dilution patterns with concentration decreasing with infiltration rates, as compared to the VF cases where a chemostatic pattern emerge with almost no changes with infiltration rates. This is because in the VF cases, the concentrations mostly reached equilibrium concentration. In PF and HF cases, a large proportion of water flow through soils with negligible calcite where the water becomes further away from equilibrium as infiltration rates increase.

![Figure 4](https://doi.org/10.5194/bg-2020-180)

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Within each pair with the same flow pattern, the difference was mainly due to the distribution of soil CO$_2$. The difference of weathering fluxes was 1-12% and 1-5% between HF cases and VF cases, respectively, much smaller than differences between the PF cases. Comparing the HF and VF cases, differences in weathering fluxes was 73% at 3.7 $\times$ 10$^{-2}$ m/yr and 721% at 3.7 m/yr, about 1-2 orders of magnitude higher than differences induced by soil CO$_2$ distribution. Between the Grass$_{PF}$ and Wood$_{PF}$ cases, the differences were in the range of 17%-207% at the flow range of 3.7 $\times$ 10$^{-2}$ - 3.7 m/yr. The DIC fluxes showed similar trends (Figure 4D).

Although weathering rates generally increased with infiltration rates, the woodland increased more (4.6 $\times$ 10$^{-2}$ to 2.4 mol/yr in Wood$_{PF}$). Estimates of the overall soil CO$_2$ production rate in Grass$_{PF}$ and Wood$_{PF}$ suggest that the values under the same infiltration rate were all within a difference of 10% (Figure S2), indicating that the difference of weathering rates are mainly driven by the flow partitioning. As a reference, the weathering rate in cases with soil respiration was up to 10 times higher compared to that without soil respiration.

**Development of reaction fronts at the century scale.** To explore the longer-term effects, we ran the PF cases at 0.37 m/yr for 300 years. More water flowing vertically through abundant calcite zones in Wood$_{PF}$ resulted in faster weathering and deeper reaction front at a depth of ~210 cm compared to ~95 cm in Grass$_{PF}$ (Figure 5A). The depletion of calcite led to an increase of porosity (Figure 5B), which was over one order of magnitude higher at the domain scale of the woodland than that in the grassland (Figure 5C). Permeability evolution had the similar trend with porosity (not shown here). This indicates that if deeper roots promoted more water into deeper soils, they would push reaction fronts deeper and controlled the position where chemically unweathered bedrock was transformed into weathered bedrock. At time scales longer than century scale, calcite may become depleted, which ultimately reduces weathering rates (White and Brantley, 2003) and lead to similar weathering fronts in grasslands and woodlands.

**Figure 5.** Predicted soil profiles of (A) calcite volume change ($\Delta$Calcite = initial calcite volume - current calcite volume) and (B) porosity after 300 years; (C) Predicted temporal evolution of domain-scale porosity in the grassland and woodland. The infiltration rate is 0.37 m/yr. Red and blue line represents the case Grass$_{PF}$ and Wood$_{PF}$, respectively.

**4.3 The regulation of weathering rates by CO$_2$-carbonate contact**

Natural systems are characterized by preferential flow paths such that flow distribution is not uniform in space. Weathering in such systems with preferential flow in zones of differing reactivities have been shown to hinge on the contact time
between water and the reacting minerals instead of all minerals that are present (Wen and Li, 2018) (Eq. 1). Here we contextualize the weathering rates in different scenarios (symbols) with predictions from an upscaled rate law developed by Wen and Li (2018) that incorporate the effects of heterogeneities in flow paths (Figure 6). The time ratio $\frac{\tau_a}{\tau_{ad,r}}$ compares the domain water contact time (or residence time) with the contact time with dissolving calcite. In GrassVF and WoodVF (open circles) where all CO$_2$-charged water flew through the deeper calcite zones, CO$_2$-calcite interactions reached maximum such that values of $\frac{\tau_a}{\tau_{ad,r}}$ approached 1.0, meaning all water interacted with calcite. Under this condition, weathering rates are the highest among all cases. In contrast, in WoodHF and GrassHF (open diamonds) where all CO$_2$-charged water bypassed the deeper calcite zone, $\frac{\tau_a}{\tau_{ad,r}}$ can be 1-3 orders of magnitude lower and weathering rates were at their minima. The $\frac{\tau_a}{\tau_{ad,r}}$ value in the water partitioning cases (GrassVF and WoodVF, filled circles) fell in between. At the same $\tau_a$, the WoodVF case with deepening roots promoted CO$_2$-water-calcite contact (i.e., larger $\frac{\tau_a}{\tau_{ad,r}}$), and dissolved calcite at higher rates.

The magnitude of rate difference also depends on the overall flow rates (or domain contact time $\tau_a$). At fast flow with small $\tau_a$ (large symbols and thick lines in Figure 6), flow partitioning has a larger influence. At $\tau_a$ of 0.47 year, the weathering rates in the VF cases were more than an order of magnitude higher than those in the PF cases. The weathering rate in the woodland was over 7 times that of the grassland. In contrast, at $\tau_a$ of 47 years, the rate differences between grass- and woody- cases were less than 25%, largely because the dissolution has reached equilibrium. In the VF and HF cases where flow conditions were the same, the soil CO$_2$ distribution in grassland and woodland differed only slightly, leading to similar values of $\frac{\tau_a}{\tau_{ad,r}}$ and weathering rates and indicating minimal impacts of soil CO$_2$ distribution. These rates from numerical experiments closely follow the prediction from the upscaled reaction rate law (grey lines, Eq. 1). The rate law predicted that weathering rates increased from HF cases with small $\frac{\tau_a}{\tau_{ad,r}}$ values to VF cases where $\frac{\tau_a}{\tau_{ad,r}}$ approached 1. It also showed that weathering rates reached their maxima in homogeneous domains without flow partitioning.

Figure 6. Calcite weathering rate as a function of the reactive time ratio $\frac{\tau_a}{\tau_{ad,r}}$. Symbols are rates from numerical experiments. Grey lines are predictions from the rate law equation at $\alpha = 0.8$ (Wen and Li, 2018). Large to small dots and thick to thin lines are for infiltration rates from $10^{-3}$ to $10^{-1.5}$ m/yr. The red filled stars represent the monthly rates in September (highest soil CO$_2$) and March (lowest soil CO$_2$) in the base case at $10^{-4}$ (0.37) m/yr; the black to grey dash lines represent predictions with increasing soil CO$_2$ level (i.e., larger $\tau_{eq}$) from Eq. (1). Grey filled star is for the case
without soil CO$_2$. At any specific infiltration rate or $r_\tau$, the VF and HF cases bracket the two ends whereas the PF cases fall in between. The Wood\textsubscript{WC} case with deeper roots enhanced the CO$_2$-water-calcite contact (i.e., larger $\frac{r_\tau}{r_{\text{ad}}} \text{ ratios}$), leading to higher calcite weathering rates compared to grasslands. The differences of weathering rates induced by different soil CO$_2$ level were relatively small compared to those hydrological changes induced by rooting depth.

5 Discussion

Because carbonate dissolution is thermodynamically controlled and transport limited, the overall weathering rates depend on how much CO$_2$-charged water flushes through the carbonate zone. This work indicates that the roots potentially enhance weathering rates in two ways. First, roots can control thermodynamic limits of carbonate dissolution by regulating how much CO$_2$ is transported downward and enters the carbonate-rich zone. In fact, the base-case grassland data and model reveal that the concentrations of Ca and DIC are regulated by seasonal fluctuation of pCO$_2$ and soil respiration. Second, roots control how much and how frequently water fluxes through the carbonate zone, exports reaction products at equilibrium such that more dissolution can occur. The numerical experiments indicate that carbonate weathering at depth hinges on the rate of delivery of CO$_2$-enriched water. Deepening roots in woodlands that channel more water into the unweathered carbonate can elevate weathering rates by more than an order of magnitude compared to grasslands. Below we elaborate and discuss these two messages.

5.1 The thermodynamics of carbonate weathering: control of temperature and pCO$_2$

The base case data and simulation showed that calcite dissolution reaches equilibrium rapidly and is thermodynamically controlled (Section 4.1), which echoes observations from other weathering studies (Tsypin and Macpherson, 2012; Gaillardet et al., 2019). The extent of dissolution, or solubility indicated in Ca and DIC concentrations, is determined by soil CO$_2$ levels that are a function of ecosystem functioning and climate. In hot, dry summer, soil respiration reaches its maximum rates in shallow soil horizons and pCO$_2$ peaks (Figure 2). In wet and cold winter, soil pCO$_2$ plummets, leading to much lower Ca and DIC concentrations. Based on Reactions 0-4 (Table 1) and temperature dependence of equilibrium constants, the following equations can be derived (detailed derivation in the SI) for Ca and DIC concentrations in carbonate-dominated landscapes:

$$C_{Ca} = \sqrt[3]{K_{\text{LC,25}} \exp \left( -\frac{\Delta H_{\text{f}}}{4R} \left( \frac{1}{T} - \frac{1}{273.15+25} \right) \right)} \cdot \text{pCO}_2$$  

(2)

$$C_{\text{DIC}} = 2 \sqrt[3]{K_{\text{LC,25}} \exp \left( -\frac{\Delta H_{\text{f}}}{4R} \left( \frac{1}{T} - \frac{1}{273.15+25} \right) \right)} \cdot \text{pCO}_2 + K_{\text{LC,25}} \exp \left( -\frac{\Delta H_{\text{f}}}{4R} \left( \frac{1}{7} - \frac{1}{273.15+25} \right) \right) \cdot \text{pCO}_2$$  

(3)

Here $K_{\text{LC,25}}$ is the total equilibrium constant $K_1 \left( = \frac{a_{\text{Ca}} + a_{\text{HCO}_3^-}}{p\text{CO}_2} = K_1 K_4 \right)$ of the combined reactions 1 and 4 at 25°C; $\Delta H_{\text{f}}$ is the corresponding standard enthalpy (-35.83 kJ/mol); $K_{\text{LC,25}}$ and $\Delta H_{\text{f}}$ are the equilibrium constant and standard enthalpy of Reaction 1 (in Table 1); $R$ is the gas constant ($=8.314 \times 10^{-3}$ kJ/K/mol). Eq. 2 and 3 imply that DIC and Ca in shallow soil water (0.2 m) are lower compared to groundwater (3.6 m) in the base case at Konza, due to lower dissolved CO$_2$(aq) arising from higher temperature and higher diffusion rates in shallow soil.

Eq. 2 and 3 were tested with compiled soil pCO2 and spring water chemistry data from 8 carbonate-dominated catchments (Dandurand et al., 1982; Lopez-Chicano et al., 2001; Moral et al., 2008; Ozkul et al., 2010; Kanduc et al., 2012; Calmels et al., 2014; Abongwa and Atekwana, 2015; Huang et al., 2015) (also see the SI for details). Plotting spring-water chemistry against pCO$_2$ indicates that spring water (as representing groundwater) DIC and Ca concentrations increase with pCO$_2$ (Figure 7), and Eq. 2-3
can describe these data and also DIC and Ca levels from numerical simulations from this work (empty dots in Figure 7). The lines of Eq. 2-3 describe the relationship at 10 °C, the mean annual temperature, confirming the thermodynamics-control of carbonate dissolution by soil CO\textsubscript{2} levels. The equation lines closely predicted Ca and DIC under high pH and lower pCO\textsubscript{2} conditions (< 8.0), because these conditions ensure the validity of the assumption of negligible CO\textsubscript{2}\textsuperscript{3} in the derivation. The presence of cations and anions other than Ca and DIC can complicate the solution and can bring significant variations of DIC and Ca concentrations under the same pCO\textsubscript{2} conditions.

Figure 7. (A) Ca and (B) DIC concentrations from field data in literature (gray dots) and prediction lines. Measured spring water chemistry are from calcite-dominant catchments in literature: Abongwa and Atekwana (2015); Lopez-Chicano et al. (2001); Moral et al. (2008); Huang et al. (2015); Ozkul et al. (2010); Dandurand et al. (1982); Calmel et al. (2014); Kanduc et al. (2012); and Tsypin and Macpherson (2012). Lines are predictions from the thermodynamic solutions (Eq. 2-3) at 10 (solid line) and 17 °C (dash line).

High temperature (T = 17°C) leads to lower DIC and Ca concentrations by about 10% due to the lower calcite and CO\textsubscript{2} solubility at higher T. Higher T also elevates pCO\textsubscript{2} due to higher soil respiration. Various equations exist for predicting soil pCO\textsubscript{2} based on climate and ecosystem functioning indicators such as Net Primary Production (NPP) (Goddéris et al., 2010; Romero-Muñalli et al., 2019a). These equations can be used together with Eq. 2-3 for the estimation of Ca and DIC concentrations in carbonate-derived waters. Gaillardet et al. (2019) shows that pCO\textsubscript{2} can increase by 2 times with T increase from 9°C to 17°C, which can elevate DIC and Ca concentrations over 50%. Macpherson et al. (2008) observed a 20% increase in groundwater pCO\textsubscript{2} in Konza over a 15-year period and suggested that increased soil respiration due to climate warming may have elevated soil and groundwater pCO\textsubscript{2}. Hasenmueller et al. (2015) demonstrated topographic controls on soil CO\textsubscript{2}. Variations of soil CO\textsubscript{2} and Ca and DIC concentrations therefore are an integrated outcome of climate, soil respiration, subsurface structures, and hydrological conditions.

5.2 Hydrological controls of root-enhanced carbonate weathering

Evidence from field data. Data in Konza show that although soil pCO\textsubscript{2} peaks in summer, these peaks do not occur right away in deeper groundwater until about 2 months later. Macpherson et al. (2008) and Tsypin and Macpherson (2012) contributed the delay to the water travel time from soil to groundwater aquifer. The calculation of travel time based on depth difference in soil and groundwater sampling location (214 cm) and average velocity (0.37 m/year) indicate that it will take 7-8 months for water to reach deeper groundwater. The 2 months delay, much shorter than the estimated 7-8 months, suggests that CO\textsubscript{2}-charged water may arrive deeper zones via preferential flow facilitated by roots or via large storm events with much faster flow.
The numerical experiments suggest that the root-relevant hydrology can play an essential role in enhancing chemical weathering (Figure 4 and 6). The enhanced weathering rates aligns with observations at Konza that woody-encroached watersheds exhibit higher Ca fluxes in stream and supports the hypothesis that deeper roots can enhance mineral-water interaction via deeper flow paths (Sullivan et al., 2019). Deepening roots can also enhance connectivity between shallow and deeper zones, therefore reducing concentration contrasts between soil water and groundwater. This can lead to more chemostatic C-Q relationships as shown in Woodr (b = -0.14 in $C = aQ^b$) compared to Grassr (b = -0.33) (Figure 4). These findings echo conclusions from Zhi et al. (2019) that chemistry differences in shallow water versus groundwater regulate C-Q patterns. The b values from the C-Q relationships coming out of the 1D modeling (Figure 4) suggest that if flow partitioning is the only difference between the grassland and woody watersheds, a C-Q relationship exhibiting dilution with negative b values is expected in the grassland. The Konza stream data in Sullivan et al. (2019) however showed that C-Q slopes in grasslands ($b = -0.003$) and in woody-encroached lands ($b = 0.013$) are both close to zero (Figure 7 and 8 in Sullivan et al. (2019)). The root influence on C-Q relationship therefore remains equivocal.

**Limitations of the model.** This discrepancy may suggest that other catchment features that are not represented in the simple 1D model can influence C-Q relationships. The model does not explicitly simulate how and to what degree root distribution at depth alters flow pathways. Instead we focus on the first-order principles of hydrological ramification of roots. The numerical experiments took general observations of rooting characteristics in grasslands and woodlands, and assumed that deepening roots in woodlands promote higher flow partitioning into deep subsurface (Canadell et al., 1996; Nardini et al., 2016; Pawlik et al., 2016). In natural systems, however, other factors can also influence flow partitioning. This includes, for example, contrasts in flow-conducting property (i.e., porosity and permeability) in shallow and deep zones, physical and chemical heterogeneity in carbonate distribution (Wen and Li, 2018), and connectivity between different areas of the catchment in dry and wet times (Wen et al., 2020).

Representing these dynamics require a large number of processes and parameters that we do not have data to constrain at this point.

**The need for root-relevant measurements.** The data-model discrepancy highlights the limitation of a simple model but also points to the need for measurements. In fact, because carbonate weathering is transport-limited and depends largely on water flow via carbonate-rich zones, co-located measurements of rooting characteristics, flow, and water chemistry at depth are essential. Root measurements however rarely go deeper than 30 cm (Richer and Billings, 2015). Existing work exploring root influence on weathering focused primarily on effects of soil CO$_2$ and root exudates (Drever, 1994; Lawrence et al., 2014; Gaillardet et al., 2019). Although it is well known that roots play a paramount role in modulating macropores and subsurface flow (Fan et al., 2017), the interactions between root characteristics, flow partitioning, and chemical weathering has remained poorly understood. Rooting characteristics depend on climate, plant species, topography, soil properties and geology (Canadell et al., 1996; Mazvimavi et al., 2004; Price, 2011; Nardini et al., 2016). Further studies are needed to characterize root distribution beyond 30 cm, how they vary with intrinsic plant species and external conditions, and how and to what extent they alter subsurface flow. The first step could link rooting characteristics, including density and depth, to soil properties and borrow insights from existing relationships between soil properties and subsurface structure. For example, images of roots and pore structures can be used to characterize the spatiotemporal heterogeneity of fluxes (Renard and Allard, 2013). Geostatistical indices such as permeability variance and correlation length can be used to quantify rooting structure, and relate them to flow partitioning and mineral weathering via numerical experiments (Wen and Li, 2017). The combination of numerical reactive transport experiments built on realistic rooting structure can help develop quantitative relationship between roots and flow partitioning, and could support models for estimating the influence of rooting dynamics on water and carbon cycles at the catchment scale.

5.3 Deepening roots enhance carbon fluxes into deep subsurface: a potential carbon sink?
Mounting evidence has shown that the terrestrial system has become a stronger carbon sink in recent decades (Heimann and Reichstein, 2008), potentially counting for the missing carbon sink as large as ~1 Pg C yr⁻¹ in the global carbon budget (Houghton, 2007; Cole et al., 2007). Although still much debated, recent studies have contributed the downward transport of soil-respired CO₂ and DIC into groundwater aquifers in deserts as a possible carbon sink in the global carbon cycle (Ma et al., 2014; Li et al., 2015). Considering the long residence time of DIC in groundwater (10⁵–10⁶ years) than in the atmosphere (~10⁴–10⁵ years; Archer and Brovkin, 2008), groundwater may act as a CO₂ storage sink. This work indicated that deepening roots can potentially reroute DIC fluxes to deeper groundwater storage. In particular, vegetation in dry places like deserts often have deep roots (Gupta et al., 2020). In fact, plants are known for growing deeper roots to tap groundwater during droughts (Brunner et al., 2015).

Deepening roots can enhance downward water drainage (i.e., high vertical connectivity) to the depth and potentially facilitate the transport of DIC fluxes into deep subsurface. As the pace of climate change accelerates, summer droughts are expected to intensify, which can potentially channel more CO₂ into the deeper subsurface via deepening roots.

With constraints from soil CO₂ data, the simulated CO₂ production rates in Grass and Wood are similarly at ~0.6 mol C/m²/yr under the infiltration rate of 0.37 m/yr (Figure S2). This is at the low end of the belowground net production (NPP) estimations at the Konza site (~2.0-30.0 mol C/m²/yr) assuming that belowground NPP accounts for 50% of the total NPP (Lett et al., 2004; Knapp and Ojima, 2014). The simulations showed that in woodlands, the DIC downward fluxes can be >2.0 times higher than those in grasslands (Figure 4). In other words, more soil-respired CO₂ can transport to groundwater and become stored there for centuries to millennium before entering a stream. At the short time scale, this enhanced downward transport will reduce CO₂ escape back into the atmosphere. This may explain the observations at Konza that woody encroachment increased NPP however soil CO₂ flux was significantly reduced compared to the open grassland (Lett et al., 2004). Changing land cover (e.g., woody encroachment and boreal forest creep) however is not the only mechanism for carbon sink (Stevens et al., 2017; Wang et al., 2020). Older aged forests also tend to have deepening roots and may act as the carbon sink (Luysaert et al., 2008), although this is not the case in Konza.

6 Conclusions

This work aims to understand thermodynamic and hydrological control of carbonate weathering driven by deepening roots. Field data and reactive transport simulation for a grassland in the Konza Prairie LTER site suggest that carbonate dissolution is thermodynamically controlled and seasonal changes in temperature and pCO₂ drives variations of Ca and DIC concentrations in soil water and groundwater. We derived equations based on reaction thermodynamics (Eq. 2-3) to estimate Ca and DIC as a function of pCO₂ and temperature, which has been shown to be applicable in other carbonate-dominated systems. The numerical experiments probed the potential effects of deepening roots on weathering by channeling a higher proportion of vertically downward flow (40% of the total) into deep subsurface with abundant calcite. The results show that deeper penetration of roots and higher recharge flow enhanced CO₂-carbonate contact. At an infiltration rate of 3.7 m/yr, calcite weathering flux in woodlands was 207% higher than that in grasslands. At 3.7×10⁻² m/yr, the weathering flux in woodland was 17% higher. The hydrological impacts on carbonate weathering were more than 10 times higher than the biogeochemical impacts via elevated soil CO₂ alone. The modeling demonstrates that the weathering rates depend on flow partitioning and relative magnitude of water contact time in the deep carbonate zone. At the century scale, with the assumed higher proportion of vertical flow, the deeper roots pushed the weathering fronts 2-times deeper, and resulted in a 10-times greater increase in porosity and permeability. Broadly, this deeper propagation of reaction fronts may accelerate rates of channel incision and hillslope erosion (Lebedeva and Brantley, 2013; Brantley et al., 2017b), and therefore speed up landscape evolution (Phillips, 2005). It alludes to the importance of considering changes in
subsurface hydrological flows associated with shifts in vegetation types and measuring rooting characteristics. This is particularly relevant as we assess the effects of climate change, land cover and elevated atmosphere CO$_2$ concentrations on chemical weathering and carbon cycles.

Data availability. All data used for model parameterization can be acquired from [http://lter.konza.ksu.edu/data](http://lter.konza.ksu.edu/data). The input files necessary to reproduce the results are available from the authors upon request (lili@engr.psu.edu).

Author contributions. H. Wen, P. Sullivan and L. Li initiated the idea and designed the numerical experiments. G.L. Macpherson and S. Billings provided the field data. H. Wen ran the simulations, analyzed simulation results, and wrote the first draft of the manuscript. All co-authors participated in editing the manuscript.

Competing interests. The authors report no conflicts of interest.

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