

# Global Biogeochemical Cycles®

## RESEARCH ARTICLE

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### Key Points:

- We develop models of stream CO<sub>2</sub> degassing that include carbonate buffering and apply them across a range of alkalinities and stream processes
- Carbonate buffering can support significant contributions to stream CO<sub>2</sub> fluxes but cannot support elevated downstream CO<sub>2</sub> concentrations
- Stable and radio- carbon isotopes are decoupled from CO<sub>2</sub> by carbonate buffering but can be leveraged to partition carbon sources

### Supporting Information:

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

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## Impacts of Carbonate Buffering on Atmospheric Equilibration of CO<sub>2</sub>, δ<sup>13</sup>C<sub>DIC</sub>, and Δ<sup>14</sup>C<sub>DIC</sub> in Rivers and Streams

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**Abstract** Rivers and streams play an important role within the global carbon cycle, in part through emissions of carbon dioxide (CO<sub>2</sub>) to the atmosphere. However, the sources of this CO<sub>2</sub> and their spatiotemporal variability are difficult to constrain. Recent work has highlighted the role of carbonate buffering reactions that may serve as a source of CO<sub>2</sub> in high alkalinity systems. In this study, we seek to develop a quantitative framework for the role of carbonate buffering in the fluxes and spatiotemporal patterns of CO<sub>2</sub> and the stable and radio- isotope composition of dissolved inorganic carbon (DIC). We incorporate DIC speciation calculations of carbon isotopologues into a stream network CO<sub>2</sub> model and perform a series of simulations, ranging from the degassing of a groundwater seep to a hydrologically-coupled 5th-order stream network. We find that carbonate buffering reactions contribute >60% of emissions in high-alkalinity, moderate groundwater-CO<sub>2</sub> environments. However, atmosphere equilibration timescales of CO<sub>2</sub> are minimally affected, which contradicts hypotheses that carbonate buffering maintains high CO<sub>2</sub> across Strahler orders in high alkalinity systems. In contrast, alkalinity dramatically increases isotope equilibration timescales, which acts to decouple CO<sub>2</sub> and DIC variations from the isotopic composition even under low alkalinity. This significantly complicates a common method for carbon source identification. Based on similar impacts on atmospheric equilibration for stable and radio- carbon isotopologues, we develop a quantitative method for partitioning groundwater and stream corridor carbon sources in carbonate-dominated watersheds. Together, these results provide a framework to guide fieldwork and interpretations of stream network CO<sub>2</sub> patterns across variable alkalinities.

**Plain Language Summary** Streams emit a lot of carbon dioxide (CO<sub>2</sub>) to the atmosphere, but it is difficult to figure out where the CO<sub>2</sub> originates. One source is a chemical reaction called carbonate buffering, which happens between different forms of dissolved inorganic carbon. This reaction may be important in streams with high alkalinity, but we lack knowledge about how it contributes across different alkalinities and scales. Some studies use isotopes of carbon to trace where CO<sub>2</sub> comes from and how it is released, but we lack knowledge about how carbonate buffering affects isotope patterns. Here, we create mathematical models of CO<sub>2</sub> production and release, including isotopes in streams. Our findings show that carbonate buffering can be a significant source of CO<sub>2</sub> in streams with high alkalinity. However, it doesn't keep CO<sub>2</sub> levels consistently high downstream, as studies previously suggested. Conversely, carbonate buffering has a big effect on the patterns of carbon isotopes. This means that common isotope methods for identifying stream CO<sub>2</sub> sources don't work well. Instead, we propose how to use stable and radioactive carbon isotopes together to determine the sources of carbon. Our study aims to guide future work and help understand how carbonate buffering impacts CO<sub>2</sub> patterns across stream environments.

## 1. Introduction

Rivers and streams are increasingly recognized as integral components of the terrestrial carbon cycle (Cole et al., 2007; Drake et al., 2018; Raymond et al., 2013), through which carbon dioxide (CO<sub>2</sub>) produced both in the terrestrial subsurface and stream corridor (including surface waters and hyporheic zone) environments are released into the atmosphere (e.g., Hotchkiss et al., 2015). Current estimates suggest global CO<sub>2</sub> emissions from inland waters are roughly half as large as anthropogenic emissions and comparable the net terrestrial carbon sink (DelSontro et al., 2018; Friedlingstein et al., 2022; Gómez-Gener et al., 2021; Lauerwald et al., 2023; Raymond et al., 2013; Sawakuchi et al., 2017); thus, the ability to quantify the magnitude and variability of these fluxes is necessary for gauging terrestrial climate feedbacks. Despite their importance in the terrestrial carbon cycle, the relative balance of CO<sub>2</sub> sources that support carbon fluxes to the atmosphere, which include groundwater sources such as soil respiration and subsurface chemical weathering reactions, or stream corridor sources

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including respiration of organic matter within the hyporheic zone and water-column as balanced by photosynthesis, remains uncertain. More recently, studies have shown the potential role of carbonate buffering reactions to contribute to evasing fluxes and spatial patterns of stream CO<sub>2</sub> partial pressure (*p*CO<sub>2</sub>) (Duvert et al., 2019; Kirk & Cohen, 2023; Stets et al., 2017; Wang et al., 2021). Crucially, these buffering dynamics are not typically included in freshwater system carbon budgets and may represent an overlooked aspect of terrestrial-aquatic carbon cycling.

Carbonate buffering reactions are historically well-described within the ocean carbon literature (Broecker et al., 1979; Revelle & Suess, 1957); however, relatively few studies have investigated these dynamics in terrestrial water systems where alkalinity and dissolved CO<sub>2</sub> concentrations vary by orders of magnitude. Briefly, dissolved CO<sub>2</sub> is subject to the reaction,



This reaction on its own does not alter alkalinity, and essentially acts to “store” dissolved CO<sub>2</sub> at levels above what would be predicted using gas solubility alone. Conceptually, the role of this CO<sub>2</sub> “storage” can be demonstrated through the application of Le Chatelier's principle, by which a reaction will occur to partially negate any changes to a system: (a) as dissolved CO<sub>2</sub> concentrations increase, for example, as rainfall equilibrates with elevated *p*CO<sub>2</sub> in the soil environment during infiltration, this causes Equation 1 to move from left to right, “storing” CO<sub>2</sub> in the form of HCO<sub>3</sub><sup>−</sup> + H<sup>+</sup>; (b) when CO<sub>2</sub> concentrations decrease, for example, as groundwater exits the subsurface at a seep and begins to equilibrate with the atmosphere, Equation 1 moves from right to left, acting to replenish dissolved CO<sub>2</sub> concentrations as degassing proceeds. Importantly, the amount of CO<sub>2</sub> that can be “stored” in this manner increases with increasing alkalinity (Broecker et al., 1979; Revelle & Suess, 1957). Notably, these carbonate buffering reactions may involve CO<sub>2</sub> of both terrestrial and aquatic origins.

These storage dynamics have been shown to operate within stream systems, and particularly in those with high alkalinity. In a compilation of US stream data, Stets et al. (2017) showed that diurnal changes in dissolved CO<sub>2</sub> reflecting stream metabolism are smaller than diurnal DIC changes, and that this difference increases with higher stream alkalinity. This effect leads to temporal hysteresis in CO<sub>2</sub>:O<sub>2</sub> ratios as DIC concentrations take longer to adjust than O<sub>2</sub> to changing metabolic rates. Further, Stets et al. (2017) suggest that this effect is responsible for the observations of high downstream *p*CO<sub>2</sub> in high alkalinity streams despite significant degassing during downstream transport. These buffering reactions may also contribute significantly to total stream emissions (e.g., Kirk & Cohen, 2023); for example, Duvert et al. (2019) found that up to 60% of emissions were supported by carbonate buffering at some locations within a high alkalinity, tropical Australian river system.

Carbonate buffering dynamics also impact the evolution of carbon isotopes in DIC (e.g., Venkiteswaran et al., 2014), both in terms of stable carbon ratios (δ<sup>13</sup>C) and radiocarbon ratios (Δ<sup>14</sup>C); however, these effects have not been explored in detail within stream systems. Stable carbon isotopes are frequently used to partition DIC sources, as respired organic carbon, DIC from carbonate mineral weathering, and atmospheric CO<sub>2</sub> have distinct isotope compositions (e.g., Campeau et al., 2017, 2018; Polsenae & Abril, 2012). Further, the evolution of δ<sup>13</sup>C values along stream reaches may provide information on degassing rates as <sup>12</sup>C is preferentially lost to the atmosphere, reflecting both kinetic fractionation of diffusion and equilibration with atmospheric CO<sub>2</sub>, which often has a higher δ<sup>13</sup>C<sub>CO<sub>2</sub></sub> value than stream waters. Measured Δ<sup>14</sup>C<sub>DIC</sub> values may also be used to partition DIC sources based on their age characteristics (Cole et al., 2022; Sveinbjörnsdóttir et al., 2020). For example, respiration of modern organic matter represents near-atmospheric Δ<sup>14</sup>C values, whereas the respiration of geogenic organic carbon and weathering of carbonate rock result in low Δ<sup>14</sup>C values. Previous work has shown that the radiocarbon composition of DIC equilibrates more slowly than CO<sub>2</sub>, with apparent <sup>14</sup>C gas exchange velocities roughly 5–500x lower than typical CO<sub>2</sub> velocities, which has been attributed to carbonate buffering dynamics (Bourke et al., 2014). However, the quantitative impacts of carbonate buffering on Δ<sup>14</sup>C equilibration has not been previously investigated to our knowledge.

Here, we develop a parsimonious model to investigate how carbonate buffering reactions impact atmospheric equilibration of river and stream DIC pools in terms of overall CO<sub>2</sub> fluxes and equilibration timescales. While this investigation is model-based, the thermodynamic principles that underlie these equations have been long-established. Rather than a direct model-observation comparison, these model experiments are used to develop a generalizable framework to better conceptualize the role of carbonate buffering in terrestrial-aquatic carbon cycling and guide sampling strategies and data interpretation schemes across a broad range of environments. The

**Table 1**  
Reaction Network and End-Member Source Values for Modeling Experiments

Reaction	log( $K^{12}$ ) @ 25°C	log( $K^{13}$ ) @ 25°C	log( $K^{14}$ ) @ 25°C
<b>Reaction Network</b>			
${}^i\text{CO}_{2(\text{aq})} \leftrightarrow \text{H}^+ + {}^i\text{CO}_3^{2-}$	−6.3447	−6.340835	−6.336995
$\text{H}^i\text{CO}_3^- \leftrightarrow \text{H}^+ + {}^i\text{CO}_3^{2-}$	−10.3288	−10.328986	−10.32914
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	−14 <sup>a</sup>	−	−
Source	$p\text{CO}_2$ (ppm)	$\delta^{13}\text{C}$ (‰ VPDB)	$\Delta^{14}\text{C}$ (‰)
<b>End-member Sources</b>			
Groundwater	20,000	−15	−500
Stream Corridor Respiration	−	−27	−66
Atmosphere	410	−9	−66
<sup>a</sup> log( $K$ ).			

goals of this study are to quantify the impacts of alkalinity on (a) stream  $\text{CO}_2$  concentration patterns and fluxes; and (b) the isotopic composition of DIC, including stable and radiogenic isotopes, and isotopic methods for partitioning stream DIC sources.

## 2. Methods

### 2.1. Carbonate System Geochemistry

To model the speciation of DIC in terrestrial streams and rivers, we incorporate reactions representing the dissolution of  $\text{CO}_2$  gas in water, the dissociation of  $\text{CO}_{2(\text{aq})}$  (defined here as equivalent carbonic acid,  $\text{H}_2\text{CO}_{3(\text{aq})}$ ), and the dissociation of the bicarbonate as applied separately to  $^{12}\text{C}$ ,  $^{13}\text{C}$ , and  $^{14}\text{C}$  DIC species. These reactions and their associated equilibrium constants at 25°C are shown in Table 1, and are based on the methodology of Druhan et al. (2021). Briefly, for a given reaction  $x$ , the ratio of equilibrium constants ( $K_x$ ) for DIC isotopologues sets the equilibrium fractionation factor as,

$$\alpha_x = \frac{K_x^i}{K_x^{12}}, \quad (2)$$

where  $i$  represents either  $^{13}\text{C}$  or  $^{14}\text{C}$  versions of reaction  $x$ . We use the equilibrium constants of Druhan et al. (2021) for  $^{13}\text{C}$  and  $^{14}\text{C}$ , assuming that fractionation factors are doubled for  $^{14}\text{C}$  relative to  $^{13}\text{C}$  based on their relative mass differences with  $^{12}\text{C}$ .

### 2.2. Evolution of the Carbonate System During Degassing

To model the evolution of stream DIC concentrations and isotopic composition during degassing, we simulate three distinct scenarios of increasing complexity:

- Scenario 1: Groundwater seep degassing with no additional  $\text{CO}_2$  inputs
- Scenario 2: Groundwater seep degassing with continuous inputs of  $\text{CO}_2$  from groundwater and stream corridor respiration
- Scenario 3: An 87 km<sup>2</sup> watershed river network in Gothic, CO for which we have previously developed and validated a reactive transport model incorporating groundwater inputs, water-column net respiration and hyporheic zone  $\text{CO}_2$  sources (Saccardi & Winnick, 2021).

These scenarios and the processes incorporated into each are diagrammed conceptually in Figure 1.

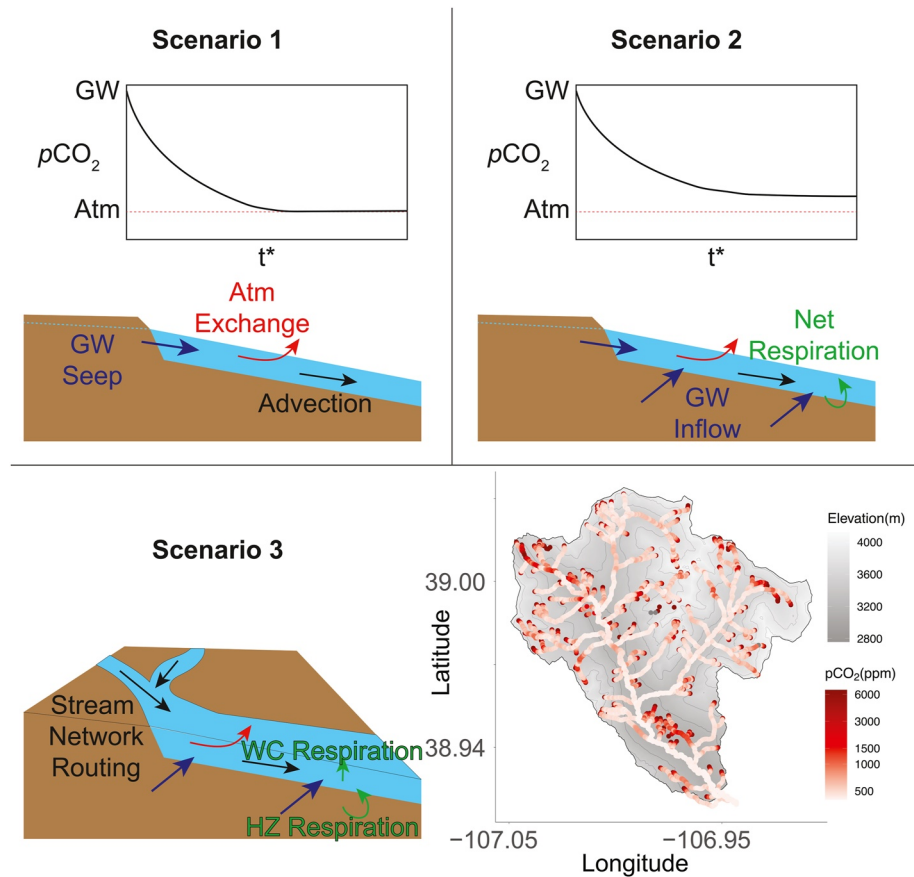
#### 2.2.1. Scenario 1: Groundwater Seep Degassing With No Additional Carbon Sources

In Scenario 1, we model a groundwater parcel degassing during stream transport with no additional carbon sources during transport (Figure 1a). This would correspond physically to a spring seep with no additional along-stream groundwater inputs or net respiration. In this scenario, the changes in DIC concentrations are modeled as,

$$\frac{\partial \text{DIC}}{\partial t} = -K_{\text{CO}_2} (\text{CO}_{2(\text{aq})} - \text{CO}_{2(\text{aq})\text{sat}}), \quad (3)$$

where  $K_{\text{CO}_2}$  is the reaeration coefficient of  $\text{CO}_2$ ,  $\text{CO}_{2(\text{aq})}$  is the dissolved  $\text{CO}_2$  concentration, and  $\text{CO}_{2(\text{aq})\text{sat}}$  is the theoretical concentration of  $\text{CO}_2$  in equilibrium with an atmospheric  $p\text{CO}_2$  of 410 ppm.

We assume an initial DIC value of groundwater ( $\text{DIC}_{\text{gw}}$ ) based on a specified groundwater  $p\text{CO}_2$  (20,000 ppm) (Jungkunst et al., 2008; Kessler & Harvey, 2001) and alkalinity, which ranges in our experiments from 0 to 6 meq/L based on the range of freshwater stream alkalinity values from a compilation of United States surface waters (Stets et al., 2017). The resulting  $\text{DIC}_{\text{GW}}$  was calculated as 0.179–6.15 mM depending on alkalinity using a temperature



**Figure 1.** Conceptual diagram of the modeling scenarios including characteristic patterns of pCO<sub>2</sub> and the incorporated processes. Scenario 1 is analogous to a degassing groundwater seep with no additional CO<sub>2</sub> inputs. Scenario 2 represents a groundwater seep degassing with simultaneous CO<sub>2</sub> inputs from groundwater and stream corridor respiration, analogous to a small headwater stream. Scenario 3 is the modeling of a full 87 km<sup>2</sup> 5th order watershed in the East River, CO, USA. It incorporates stream network water routing via advection, groundwater inputs, hyporheic exchange, net water column respiration, and atmospheric exchange. Simulated watershed pCO<sub>2</sub> values are from Saccardi and Winnick (2021) and represent a no-alkalinity simulation, which is compared to the updated model in Scenario 3. Note that symbol definitions translate between Scenarios, and groundwater Seep and Inflow end-member values are identical.

of 25°C. We additionally specify a  $K_{CO_2}$  value (0.0002 s<sup>-1</sup>); however, our analysis examines CO<sub>2</sub> evolution over non-dimensional timescale ( $t^*$ ) calculated as  $t^* = (t) (K_{CO_2})$  (unitless); thus, the results are scalable to any given  $K_{CO_2}$  value. The model is then solved using an explicit numerical approximation over discretized timesteps. At each timestep following the calculation of a new DIC value, the carbonate system is speciated using alkalinity and the updated DIC concentration, following the methods of Venkiteswaran et al. (2014). Briefly, we develop a system of equations based on the equilibrium constants in Table 1, along with equations for alkalinity (Alk) and DIC as,

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (4)$$

and

$$DIC = [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}], \quad (5)$$

respectively.

Model calculation scripts using R software are included in Supporting Information S1.

We solve Equation 3 and speciate the DIC pool separately for each isotopologue of carbon. For simplicity, we assume that the reaeration coefficients are the same for <sup>12</sup>CO<sub>2</sub>, <sup>13</sup>CO<sub>2</sub>, and <sup>14</sup>CO<sub>2</sub>. While degassing experiments

suggest mass-dependent kinetic fractionation of  $\sim 0.998$  for  $^{13}\text{CO}_2/^{12}\text{CO}_2$  (e.g., Zhang et al., 1995), fractionation associated with turbulent atmospheric exchange, which dominates in most river systems, has not been adequately characterized. We note that our equations are flexible to incorporate kinetic fractionation as,

$$\alpha_k = \frac{k^i}{k^{12}}, \quad (6)$$

where  $i$  denotes the reaeration coefficient  $k$  for either  $^{13}\text{CO}_2$  or  $^{14}\text{CO}_2$ , following the formulation of Zhang et al. (1995), though for the purposes of our model experiments, we assume  $\alpha_k = 1$ . We also note that within our model simulations,  $^{12}\text{C}$  degasses faster than  $^{13}\text{C}$  due to a larger proportional offset between atmospheric and stream  $^{12}\text{CO}_2$  concentrations. This causes apparent fractionation as the stream equilibrates with atmospheric boundary conditions; however, it does not physically represent kinetic fractionation. We note that these two processes that cause increasing  $\delta^{13}\text{C}$  values during degassing are not often discussed as separate processes and are typically referred to collectively as fractionation during degassing.

We calculate  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  values as,

$$\delta^{13}\text{C} = \left( \frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) * 1000\text{‰}, \quad (7)$$

and

$$\Delta^{14}\text{C} = \left( \frac{(^{14}\text{C}/^{12}\text{C})_{\text{corr}}}{(^{14}\text{C}/^{12}\text{C})_{\text{std}} * \exp\left(\frac{2023-1950}{8267}\right)} - 1 \right) * 1000\text{‰}, \quad (8)$$

where

$$(^{14}\text{C}/^{12}\text{C})_{\text{corr}} = (^{14}\text{C}/^{12}\text{C})_{\text{sample}} \left( \frac{1 + \delta^{13}\text{C}_{\text{std}}/1000}{1 + \delta^{13}\text{C}_{\text{sample}}/1000} \right)^2. \quad (9)$$

Within these equations,  $R_{\text{std}}$  represents the  $^{13}\text{C}/^{12}\text{C}$  ratio of the VPDB standard, and  $^{14}\text{C}/^{12}\text{C}_{\text{std}}$  is  $1.12\text{E}-12$ . Equation 9 essentially corrects for equilibrium fractionation effects within the  $^{14}\text{C}$  system. In this scenario and across the following sections, we assume an initial groundwater  $\delta^{13}\text{C}_{\text{DIC}}$  value of  $-15\text{‰}$  representing a balance of  $\text{C}_3$  soil respiration and carbonate from calcite weathering (Campeau et al., 2017) and  $\Delta^{14}\text{C}_{\text{DIC}}$  value of  $-500\text{‰}$  representing a mix of modern soil respiration and  $^{14}\text{C}$ -dead carbonate carbon based on the stoichiometry of calcite dissolution ( $\text{CaCO}_{3(\text{s})} + \text{H}_2\text{CO}_{3(\text{aq})} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$ ; Table 1). We also assume that on the timescales of stream transport, radioactive decay of  $^{14}\text{C}$  is negligible.

### 2.2.2. Scenario 2: Continuous Groundwater and Stream Corridor $\text{CO}_2$ Sources

In Scenario 2, we incorporate continuous inputs from groundwater inflows and stream corridor  $\text{CO}_2$  production via aerobic respiration (Figure 1b). In this scenario, we amend Equation 3 to incorporate these inputs as,

$$\frac{\partial \text{DIC}}{\partial t} = -k(\text{CO}_{2(\text{aq})} - \text{CO}_{2(\text{aq})\text{sat}}) + Q(\text{DIC}_{\text{gw}} - \text{DIC}) + F_{\text{prod}}, \quad (10)$$

where  $Q$  is the volume-normalized groundwater inflow rate ( $\text{s}^{-1}$ ), and  $F_{\text{prod}}$  is the net respiration ( $\text{mol/L/s}$ ) within both the water column and the hyporheic zone, which we define as stream corridor respiration here, though we split this term into the individual contributions from net water column respiration and hyporheic zone respiration in Scenario 3. This method assumes that alkalinity remains constant, ignoring potential variability in groundwater inflow alkalinities, anaerobic respiration that may contribute additional alkalinity, and carbonate precipitation which would decrease alkalinity. This situation is analogous to a homogenous stream reach with active groundwater inputs. Similar to Scenario 1, we solve this equation using an explicit numerical scheme across discretized timesteps. The same methods are applied, whereby at each timestep, a new DIC value is calculated and the DIC system is speciated based on the Venkiteswaran et al. (2014) scheme. As above, groundwater is specified with a  $p\text{CO}_2$  of 20,000 ppm;  $\delta^{13}\text{C}_{\text{DIC}}$  value of  $-15\text{‰}$  representing a balance of  $\text{C}_3$  soil respiration and carbonate from calcite weathering; and  $\Delta^{14}\text{C}_{\text{DIC}}$  of  $-500\text{‰}$  representing a mix of modern soil respiration and  $^{14}\text{C}$ -dead carbonate



carbon. Stream corridor respiration is assumed to have a  $\delta^{13}\text{C}_{\text{DIC}}$  value of  $-27\text{‰}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  of  $-66\text{‰}$  representing modern carbon. As in Scenario 1, we vary alkalinity across our simulations from 0 to 6 meq/L though for simplicity we include only 0.1, 1.0, and 4.0 meq/L simulations in the main text. We also vary input flux rates as  $10^{-7}$  (low),  $10^{-6}$  (med), and  $10^{-5.5}$  (high) mol/L/s (Izagirre et al., 2008) and the ratio of input fluxes from groundwater versus stream corridor respiration with ratio values of 0.001 (99.9% groundwater), 1 (equal contributions), and 1,000 (99.9% stream corridor respiration).

### 2.2.3. Scenario 3: Stream Network $\text{CO}_2$ Model

Finally, to explore the complexity of alkalinity controls on stream network-scale  $\text{CO}_2$  and isotope dynamics, we incorporate DIC speciation reactions into an existing stream network advection-reaction model of dissolved  $\text{CO}_2$  (Figure 1). This model was originally developed, applied, and validated for the East River watershed in Gothic, CO, USA (Saccardi & Winnick, 2021). Briefly, the East River watershed is an 87 km<sup>2</sup>, high elevation, mountainous watershed, with annual flow dominated by spring snowmelt (Winnick et al., 2017). In this model, we consider  $\text{CO}_2$  fluxes from (a) groundwater with a specified  $p\text{CO}_2$  and inflow fluxes that scale with changes in upstream accumulating area and specified runoff values reflecting flow conditions from August 2019; (b) hyporheic exchange parameterized using a surface renewal-theory mass-transfer model (Grant et al., 2018; Winnick, 2021) and assuming a constant offset between hyporheic zone and stream  $\text{CO}_2$  meant to reflect net respiration; (c) water column net respiration at a specified volume-normalized rate; and (d) atmospheric exchange in which gas exchange velocities ( $k_{600}$ ) are parameterized based on slope and discharge via empirical correlations between energy dissipation rates and  $k_{600}$  (Ulseth et al., 2019). The full details of model derivation and parameterization are presented in Saccardi and Winnick (2021), and the simulated map of stream  $p\text{CO}_2$  values is shown in Figure 1. Here, we update the model and simplify a number of model parameterizations as (a) we ignore wetland contributions and assume all groundwater sources have the same  $p\text{CO}_2$  across the watershed, as opposed to our original model which specified high  $p\text{CO}_2$  values from wetland areas; (b) we ignore snow-plugs which were introduced into the model as zones with no atmospheric gas exchange to match field observations. For simplification, we assume a single groundwater alkalinity value for the whole watershed, and that stream-corridor respiration does not alter alkalinity, ignoring, for example, alkalinity contributions from anaerobic respiration. Finally, we update the underlying model equations to incorporate DIC speciation as,

$$\frac{\partial \text{DIC}}{\partial t} = -v \frac{\partial \text{DIC}}{\partial x} - k(\text{CO}_{2(\text{aq})} - \text{CO}_{2(\text{aq})\text{sat}}) + Q(\text{DIC}_{\text{gw}} - \text{DIC}) + F_{\text{wc}} + k_{\text{hz}} * C_{\text{hz}}, \quad (11)$$

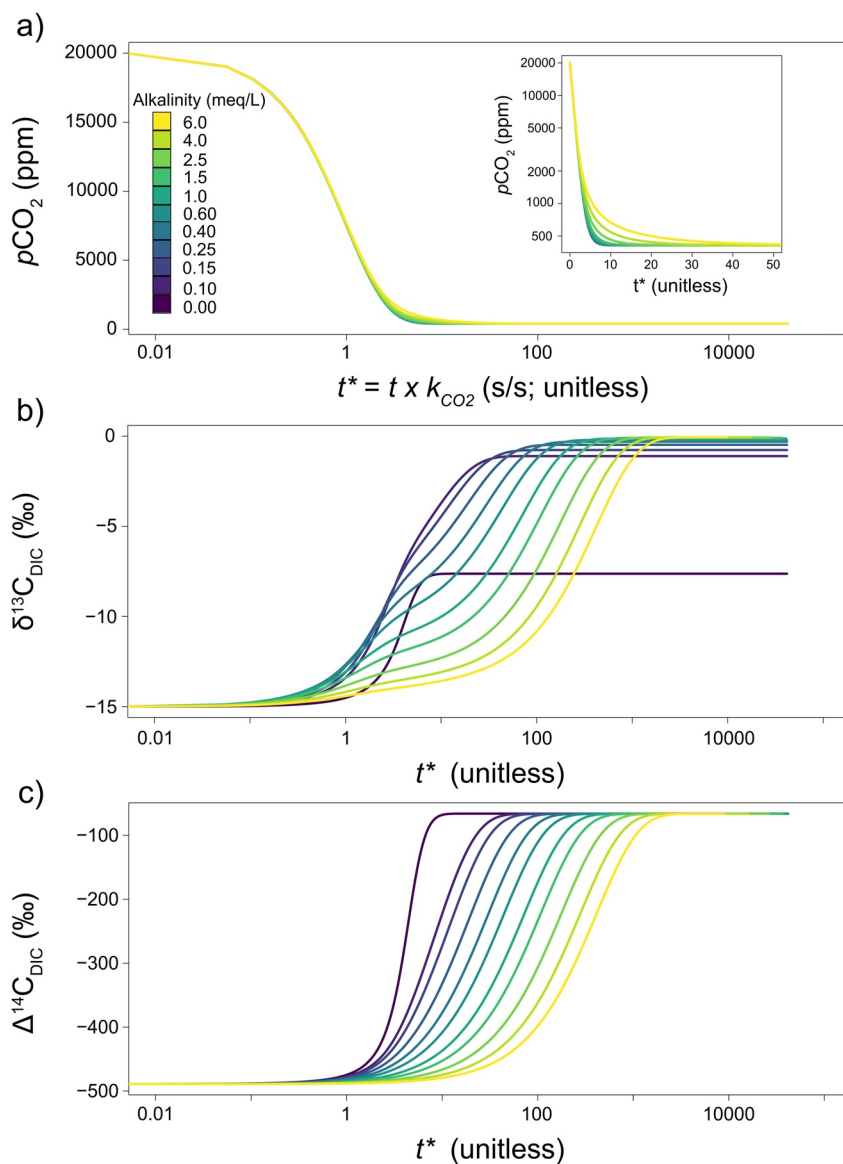
where  $v$  is advection velocity (m/s),  $x$  is distance along a stream (m),  $F_{\text{wc}}$  is the water column net respiration flux (ER—GPP; mol/L/s),  $k_{\text{hz}}$  is the rate of hyporheic exchange ( $\text{s}^{-1}$ ), and  $C_{\text{hz}}$  is the offset between stream and hyporheic zone DIC (mol/L). In relation to the previous scenario, we have here split net stream corridor respiration ( $F_{\text{prod}}$ ) into explicit water column ( $F_{\text{wc}}$ ) and hyporheic zone ( $k_{\text{hz}} * C_{\text{hz}}$ ) components. This model is applied to NHD HR streamlines at sub-reach scales. In this model exercise, we assume steady-state conditions (e.g.  $\partial \text{DIC} / \partial t = 0$ ), and use a backwards-difference method to solve for changes in DIC spatially across the stream network. At each new downstream spatial grid, we then use the updated DIC and the specified alkalinity value to speciate the DIC system. For modeled cells, we discretized NHD HR stream flowlines at a 0.5 m spacing.

We solve the model separately for three alkalinity values: 0.1, 1 (roughly the average measured site alkalinity), and 4 meq/L. We assume groundwater  $p\text{CO}_2$  of 20,000 ppm in the range of measured soil values (Winnick et al., 2020), an elevation of hyporheic zone  $p\text{CO}_2$  above stream values of 700 ppm, and an  $F_{\text{wc}}$  value of  $10^{-9}$  mol/L/s, roughly aligning with optimized values from the model validation of Saccardi and Winnick (2021). Crucially, our intent here is not to validate the model against previous field observations, but instead to interrogate how the carbonate buffering dynamics explored the idealized Scenario's 1 and 2 may be reflected in real-world systems. Given the previous studies which have shown the importance of carbonate weathering for generating alkalinity within the East River system (Carroll et al., 2018; Winnick et al., 2017), we assume end-member isotope compositions from Scenario 2, shown in Table 1.

## 3. Results

### 3.1. Scenario 1 Results

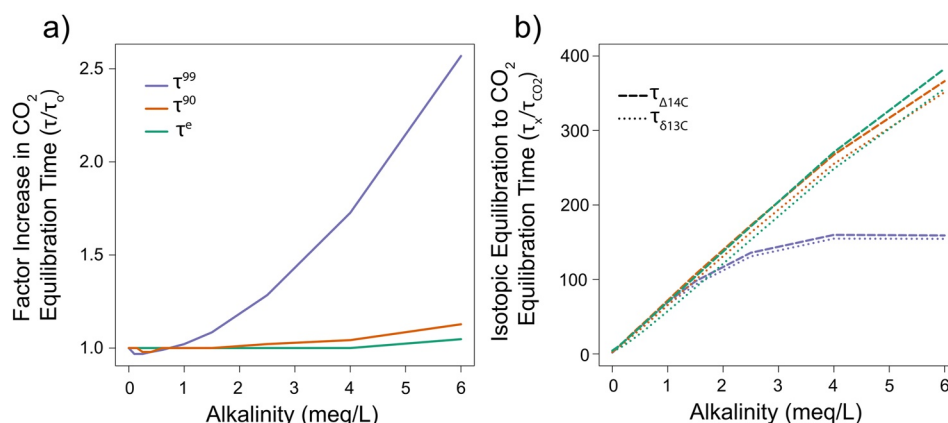
The temporal evolution of  $p\text{CO}_2$ ,  $\delta^{13}\text{C}_{\text{DIC}}$ , and  $\Delta^{14}\text{C}_{\text{DIC}}$  for our groundwater degassing simulations (scenario 1) are shown in Figure 2 across a range of alkalinities. Within these plots, the time axis ( $t^*$ ) is non-dimensional,



**Figure 2.** Temporal evolution of (a)  $p\text{CO}_2$ , (b)  $\delta^{13}\text{C}_{\text{DIC}}$ , and (c)  $\Delta^{14}\text{C}_{\text{DIC}}$  in Scenario 1 simulations. The  $x$ -axis in all plots represents nondimensional time, calculated by multiplying simulation time (s) at the specified reaeration rate ( $\text{s}^{-1}$ ). Line colors represent the specified groundwater alkalinity. Note that the large difference between the 0 and 0.1 meq/L alkalinity lines in plot (b) reflects the non-linear decrease in the fractional contribution of  $\text{CO}_{2(\text{aq})}$  to total DIC as alkalinity increases.

representing the simulation time (s) multiplied by the specified reaeration rate ( $\text{s}^{-1}$ ); these values are also equivalent to non-dimensional distance, and simulation time could be scaled to a dimensional distance by multiplying by an advective velocity. As shown in the top panel, high initial groundwater  $p\text{CO}_2$  values equilibrate with atmospheric values over  $t^*$  timescales of  $\sim 5$ – $40$  (unitless). Higher alkalinity values result in slightly longer  $p\text{CO}_2$  equilibration timescales, as highlighted by the inset in Figure 2a, though values eventually approach the same atmospheric  $p\text{CO}_2$  levels. This increase in the equilibration timescale is controlled by carbonate buffering reactions, which act to resupply  $\text{CO}_2$  as degassing progresses, as discussed in the Introduction (Equation 1). These changes in equilibration timescales due to carbonate buffering are relatively muted as compared to isotopic equilibration, which we discuss below.

In Figure 2b,  $\delta^{13}\text{C}_{\text{DIC}}$  starts at groundwater values of  $-15\text{‰}$  and approaches equilibrium with atmospheric  $\delta^{13}\text{C}_{\text{CO}_2}$  values of  $-9\text{‰}$  through time. Importantly, the final equilibrated  $\delta^{13}\text{C}_{\text{DIC}}$  values vary as a function of alkalinity. Under zero alkalinity conditions, equilibrated  $\delta^{13}\text{C}_{\text{DIC}}$  is slightly elevated ( $-7.6\text{‰}$ ) above atmospheric values as



**Figure 3.** Impacts of alkalinity on atmosphere equilibration timescales for Scenario 1 simulations of (a)  $pCO_2$ , and (b)  $\delta^{13}C_{DIC}$  and  $\Delta^{14}C_{DIC}$  relative to  $pCO_2$ . Line colors represent different metrics of equilibration timescales. Dashed and dotted lines in (b) represent  $\Delta^{14}C_{DIC}$  and  $\delta^{13}C_{DIC}$ , respectively.

$CO_2$  is only ~84% of total DIC. As alkalinity increases,  $CO_2$  quickly becomes a secondary component of DIC at atmosphere equilibration; for example,  $CO_2$  is only 12% of total atmosphere-equilibrated DIC at an alkalinity of 0.1 meq/L. As alkalinity increases, equilibrated  $\delta^{13}C_{DIC}$  values approach  $HCO_3^-$  and  $CO_3^{2-}$  values, which due to equilibrium fractionation are elevated ~9‰ above  $CO_{2(aq)}$  values. Thus, the DIC pool approaches ~0‰ when equilibrated with the atmosphere. In addition to these changes in the final equilibrated values, alkalinity also strongly impacts the timescales of equilibration. Under zero alkalinity conditions, isotopic equilibration timescales are comparable to those of  $pCO_2$ . As alkalinity increases, however,  $\delta^{13}C_{DIC}$  equilibration timescales increase significantly, with the high alkalinity (6 meq/L) scenario requiring non-dimensional timescales of >1,000 as compared to  $CO_2$  equilibration timescales of ~50.

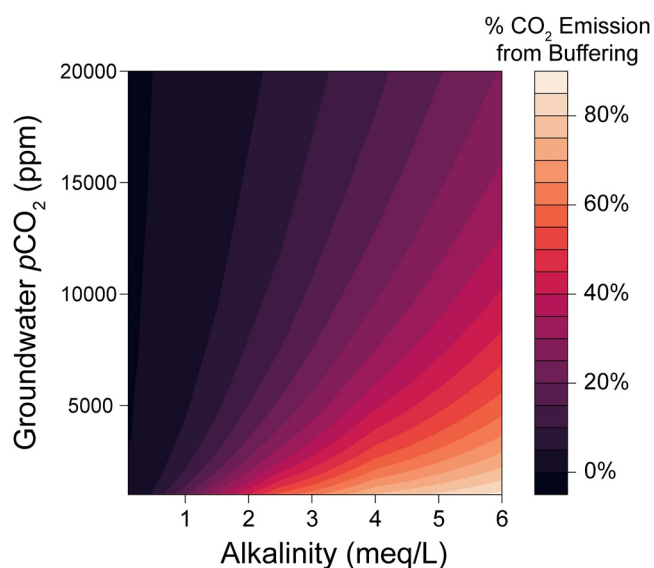
Values of  $\Delta^{14}C_{DIC}$  display similar patterns with a few important differences (Figure 2c). First, alkalinity has no impact on final  $\Delta^{14}C_{DIC}$  values, as the associated equilibrium fractionation is normalized for within Equation 9. However, as equilibrium fractionation is roughly twice as large for  $^{14}C$  as  $^{13}C$ , a larger initial proportion of  $^{14}C$  is buffered within the  $HCO_3^- + CO_3^{2-}$  DIC pool, thus timescales of equilibration are slightly larger.

In Figure 3a, we directly evaluate these timescales of equilibration through the calculation of folding-times of  $\tau^{99}$ ,  $\tau^{90}$ , and  $\tau^e$  representing the non-dimensional time required to degas 99%, 90%, and ~36% of groundwater  $CO_2$ , respectively. Figure 3a shows the factor increase in each of these timescales for a range of alkalinities compared to a simulation with no alkalinity. Alkalinity has relatively little impact on the  $\tau^{90}$  and  $\tau^e$  timescales, though it causes an increase of over 2.5x in  $\tau^{99}$  in the high alkalinity simulation. Given the nature of our non-dimensional analysis, this factor increase is a scalable result. In other words, for any given combination of reaeration rates, stream velocities, and initial  $pCO_2$  values, this would result in a 2.5x increase in the distance over which a groundwater seep degassed 99% of its  $CO_2$ . Physically, this sensitivity of  $\tau^{99}$  values demonstrates that the impact of carbonate buffering is highest at near-atmospheric  $pCO_2$ , resulting in longer timescales to lose the final 1% of  $pCO_2$ , and is visually evident in Figure 2a as the alkalinity curves diverge only as they approach atmospheric values.

The ratio of isotopic equilibration timescales to  $pCO_2$  equilibration is shown in Figure 3b. Increases in alkalinity result in roughly linear increases in the ratio of these equilibration timescales for  $\tau^{90}$  and  $\tau^e$ . In contrast,  $\tau^{99}$  values plateau above an alkalinity of ~4 meq/L and diverge from  $\tau^{90}$  and  $\tau^e$  at ~1.5 meq/L alkalinity. Importantly, the impacts on equilibration timescales are very similar between  $\delta^{13}C_{DIC}$  and  $\Delta^{14}C_{DIC}$ , to small variations due to differing equilibrium fractionation factors that result in slight differences in the proportion of  $^{13}C$  versus  $^{14}C$  buffered by the  $HCO_3^-$  and  $CO_3^{2-}$  pools.

Lastly, for Scenario 1, we calculate the proportion of  $CO_2$  emissions supported by carbonate buffering across a range of alkalinity and groundwater  $pCO_2$  values, as shown in Figure 4. This value is calculated by subtracting the total loss of  $CO_{2(aq)}$  during atmospheric equilibration from the total DIC loss during equilibration, normalized by the total DIC loss. Carbonate buffering plays a negligible role in  $CO_2$  emissions when alkalinity is low and groundwater  $pCO_2$  is high, as both of these conditions result in smaller proportional storage of  $CO_2$





**Figure 4.** Contour map of the % contributions of carbonate buffering reactions to total CO<sub>2</sub> emissions in Scenario 1 as a function of groundwater alkalinity and pCO<sub>2</sub>. Carbonate buffering reactions contribute proportionally more to overall emissions as groundwater alkalinity increases and groundwater pCO<sub>2</sub> decreases.

as  $\text{HCO}_3^- + \text{H}^+$ . However, under conditions of high alkalinity and low groundwater pCO<sub>2</sub>, carbonate buffering may account for up to 90% of emissions. While carbonate buffering dominates emissions, we note that the total amount of CO<sub>2</sub> degassed is low compared with high groundwater pCO<sub>2</sub>—low alkalinity conditions. We note that these estimates assume no calcite precipitation. This may become an important factor in high alkalinity systems with available Ca<sup>2+</sup>, whereby degassing raises the calcite saturation state leading to mineral precipitation and further buffering of CO<sub>2(aq)</sub> concentrations.

### 3.2. Scenario 2 Results

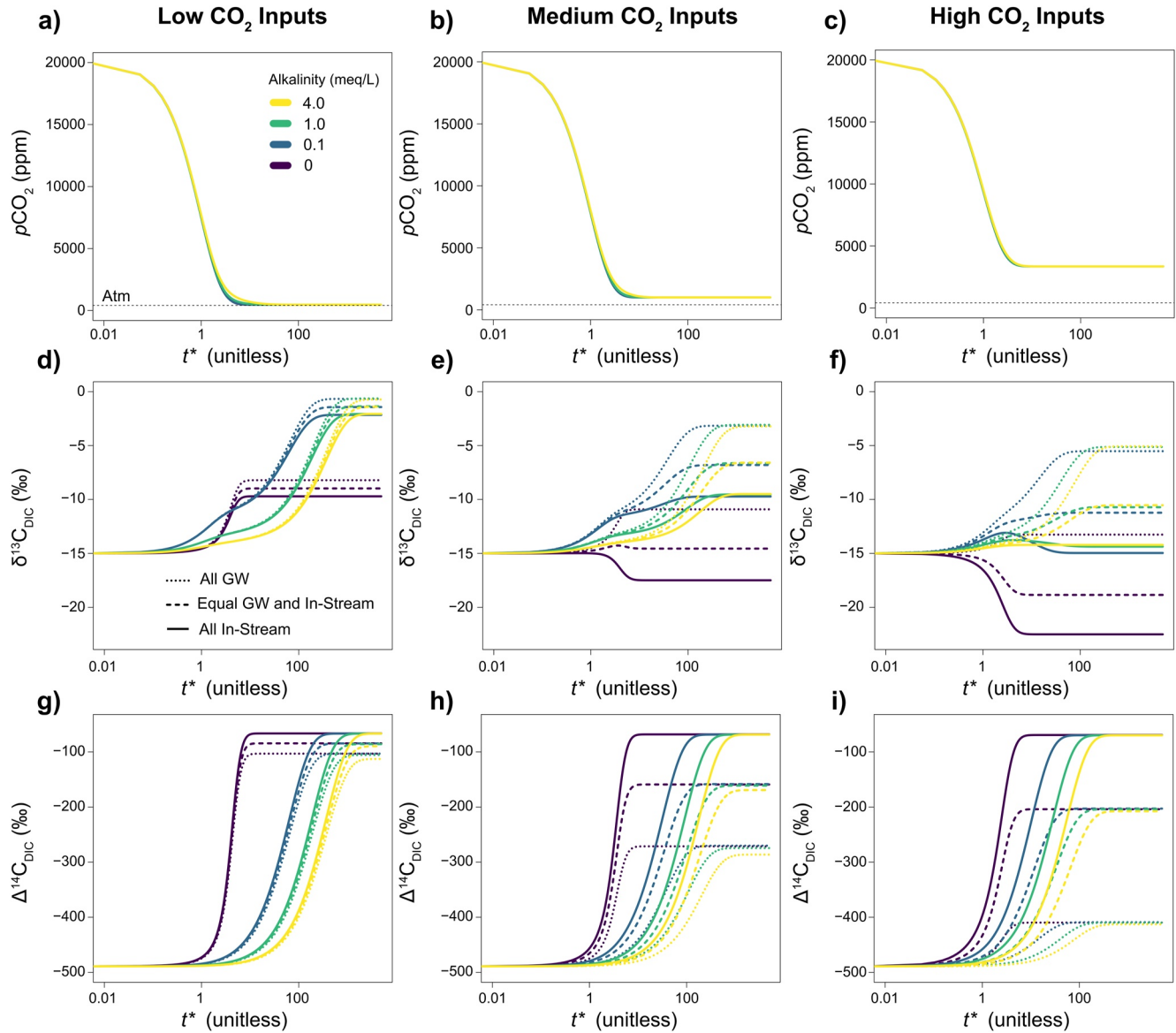
In Scenario 2, we incorporate continuous groundwater and net stream corridor respiration fluxes during seep degassing, reflecting more realistic scenarios in which evasion fluxes are partially supported by localized CO<sub>2</sub> sources. The temporal patterns of pCO<sub>2</sub>, δ<sup>13</sup>C<sub>DIC</sub>, and Δ<sup>14</sup>C<sub>DIC</sub> are shown in Figure 5 across a range of alkalinities, total CO<sub>2</sub> source fluxes, and ratios of groundwater to stream corridor sources. Across Figures 5a–5c, pCO<sub>2</sub> displays patterns similar to Figure 2. As total CO<sub>2</sub> sources increase, steady-state pCO<sub>2</sub> values increase to well above atmosphere-equilibrated values. These elevated pCO<sub>2</sub> values represent a stable balance between specific input fluxes and evasion rates, which can be calculated by assuming steady-state ( $dC/dt = 0$ ) and rearranging Equation 10 as,

$$\text{CO}_{2(\text{aq})\text{steady-state}} = \frac{Q(\text{DIC}_{\text{gw}} - \text{DIC}) + F_{\text{prod}}}{k} + \text{CO}_{2(\text{aq})\text{sat}} \quad (12)$$

As steady-state pCO<sub>2</sub> values increase, the effects of alkalinity on degassing patterns become more muted. For example, in Figure 5c, there is little visible difference between the high alkalinity simulation (4 meq/L) and the low alkalinity simulation (0.1 meq/L). This demonstrates similar patterns as in Figure 3a, which shows that the impacts of equilibration timescales are relatively insignificant when evaluated at pCO<sub>2</sub> levels above atmospheric (i.e.,  $\tau^0$  and  $\tau^e$ ). Patterns of pCO<sub>2</sub> are not impacted by the partitioning of fluxes between groundwater and stream corridor sources, assuming that the total fluxes are the same.

Carbon isotope patterns become more complicated when considering multiple sources of different compositions. This is most clear for δ<sup>13</sup>C<sub>DIC</sub> where atmospheric, groundwater, and stream corridor respiration all have different sources, versus Δ<sup>14</sup>C<sub>DIC</sub> where stream corridor and atmospheric sources are roughly the same. Broadly, increased alkalinity results in increasing steady-state timescales for both δ<sup>13</sup>C<sub>DIC</sub> and Δ<sup>14</sup>C<sub>DIC</sub>, with timescales of ~1 for no alkalinity to >100 for high alkalinity scenarios. These steady-state timescales are not significantly impacted by the magnitude of CO<sub>2</sub> source fluxes or their partitioning between groundwater and stream corridor respiration (i.e., comparing the yellow lines within and across the panels). Alkalinity also impacts the final steady-state value of δ<sup>13</sup>C<sub>DIC</sub> for a given CO<sub>2</sub> source flux and partitioning ratio (i.e., comparing the solid purple curve to the solid yellow curve within a panel), such that low alkalinity results in a lower δ<sup>13</sup>C<sub>DIC</sub> value for a given flux and partitioning ratio of carbon inputs.

Across these simulations, steady-state δ<sup>13</sup>C<sub>DIC</sub> and Δ<sup>14</sup>C<sub>DIC</sub> are also highly sensitive to both the magnitude of total source fluxes and their partitioning between groundwater and stream corridor sources. In the case of δ<sup>13</sup>C<sub>DIC</sub>, as both groundwater and stream corridor sources have lower-than-atmospheric values, increasing CO<sub>2</sub> input flux results in a decrease in steady-state values. Further, as δ<sup>13</sup>C<sub>DIC</sub> of stream corridor sources are lower than groundwater (−27‰ vs. −15‰ in these simulations), a higher proportion of stream corridor source results in lower steady-state δ<sup>13</sup>C<sub>DIC</sub> values. Comparing across Figures 5d–5f, we note a significant degree of equifinality in steady-state δ<sup>13</sup>C<sub>DIC</sub> values, whereby different combinations of alkalinity, total CO<sub>2</sub> sources, and source partitioning can result in similar steady-state δ<sup>13</sup>C<sub>DIC</sub> values. Even if alkalinity is constrained, different combinations of CO<sub>2</sub> sources with different δ<sup>13</sup>C<sub>DIC</sub> end-member values can result in the same steady-state δ<sup>13</sup>C<sub>DIC</sub>. For example, a low alkalinity stream with medium CO<sub>2</sub> inputs coming from stream corridor respiration (green solid line, Figure 5e) features similar steady-state δ<sup>13</sup>C<sub>DIC</sub> as a low alkalinity stream with high CO<sub>2</sub> inputs coming equally from groundwater and stream corridor respiration (green dashed line, Figure 5f).

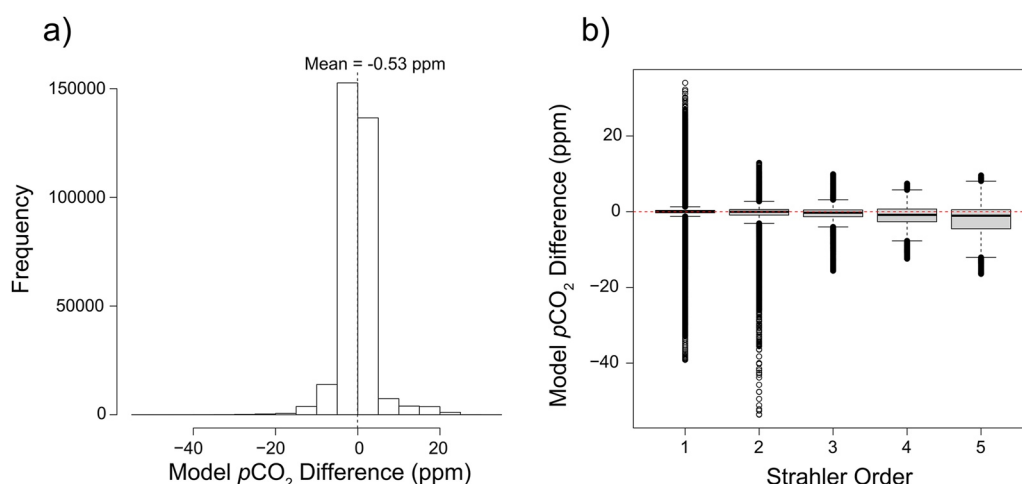


**Figure 5.** Temporal evolution of simulations in Scenario 2 showing  $p\text{CO}_2$ ,  $\delta^{13}\text{C}_{\text{DIC}}$ , and  $\Delta^{14}\text{C}_{\text{DIC}}$  (rows) for varying  $\text{CO}_2$  input fluxes (columns). X-axes represent non-dimensional time. The line color represents alkalinity, and line types represent the ratio of groundwater versus stream corridor respiration contributions to  $\text{CO}_2$  inputs.

The controls of sources on steady-state values are more easily discernible in the  $\Delta^{14}\text{C}_{\text{DIC}}$  data, where values are not sensitive to alkalinity. As we set  $\Delta^{14}\text{C}_{\text{DIC}}$  values of stream corridor respiration to near-atmospheric, stream corridor respiration does not have a significant impact on  $\Delta^{14}\text{C}_{\text{DIC}}$  steady-state values (i.e., comparing the solid lines across panels g–i). Instead, variability is controlled by the total magnitude of groundwater  $\text{CO}_2$  fluxes, which act as a source of low  $\Delta^{14}\text{C}_{\text{DIC}}$  and draw down steady-state values.

### 3.3. Scenario 3 Results

In this exercise, we compare the results of those simulations, which only represented the  $\text{CO}_2$  component of the DIC system (equivalent to a situation with an alkalinity of 0), with our updated model. Spatial patterns of  $\text{CO}_2$  are shown in Supporting Information S1 (Figures S1, S3, and S4) and do not result in significant visual differences in spatial patterns across the watershed, as depicted in the inset of Figure 1c. In contrast to our degassing experiments in Scenarios 1 and 2 in which  $p\text{CO}_2$  is always decreasing to approach atmospheric concentrations,



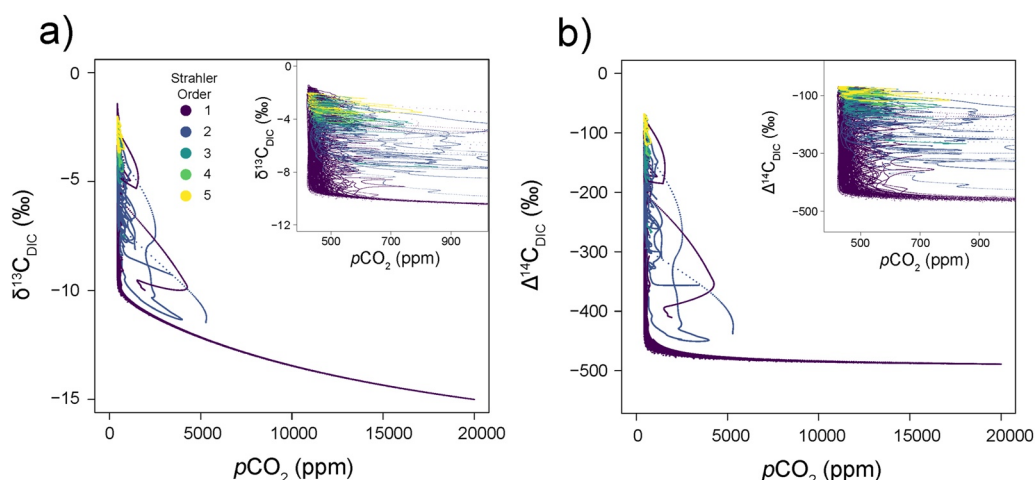
**Figure 6.** Comparisons of Scenario 3 simulations with 1 meq/L alkalinity and no alkalinity, showing (a) a histogram of the differences, and (b) a boxplot of differences binned by Strahler Order. The inclusion of alkalinity results in both increased and decreased simulated  $p\text{CO}_2$ , with decreased values occurring in areas with low gas exchange rates that allow for  $p\text{CO}_2$  to build up locally. Alkalinity does not result in increased downstream  $p\text{CO}_2$  at the stream network scale, as shown in (c).

the full watershed simulation features areas in which  $p\text{CO}_2$  increases due to inputs (groundwater and stream corridor respiration) that are locally higher than evasion fluxes. Under these conditions, the inclusion of alkalinity results in lower  $p\text{CO}_2$  estimates than simulations without alkalinity, as a proportion of the  $\text{CO}_2$  inputs is stored as  $\text{HCO}_3^- + \text{H}^+$ . At the watershed scale, there are a comparable number of model cells in which the inclusion of alkalinity results in lower versus higher  $p\text{CO}_2$  relative to no alkalinity (Figure 6a), with a difference range of  $-53$ – $34$  ppm in our 1 meq/L alkalinity simulation. This range increased with increasing alkalinity (Figures S2 and S5 in Supporting Information S1), but the overall pattern was unchanged.

Patterns in model differences are minimal when compared across stream scales, as defined by the Strahler Order in Figure 6b. Interestingly, the range of model differences decreases while standard deviations increase with the Strahler Order. There is also a slight trend toward lower  $p\text{CO}_2$  predictions from the alkalinity model at larger stream scales, and this likely reflects flatter topography and lower gas exchange velocities in the higher order streams. Averaged across the watershed, the alkalinity model predicts slightly lower  $p\text{CO}_2$  values by  $-0.054$  ppm. Counterintuitively, total watershed evasion fluxes from the alkalinity model are slightly higher, due to outsized flux contributions from areas with high gas exchange velocities (where the alkalinity model predicts slightly higher  $p\text{CO}_2$ ) on total fluxes. The difference in total watershed fluxes reflects the additional  $\text{CO}_2$  stored as  $\text{HCO}_3^- + \text{H}^+$  in infiltrating groundwater, as both simulations are given the same groundwater  $p\text{CO}_2$  and feature the same total stream corridor respiration fluxes.

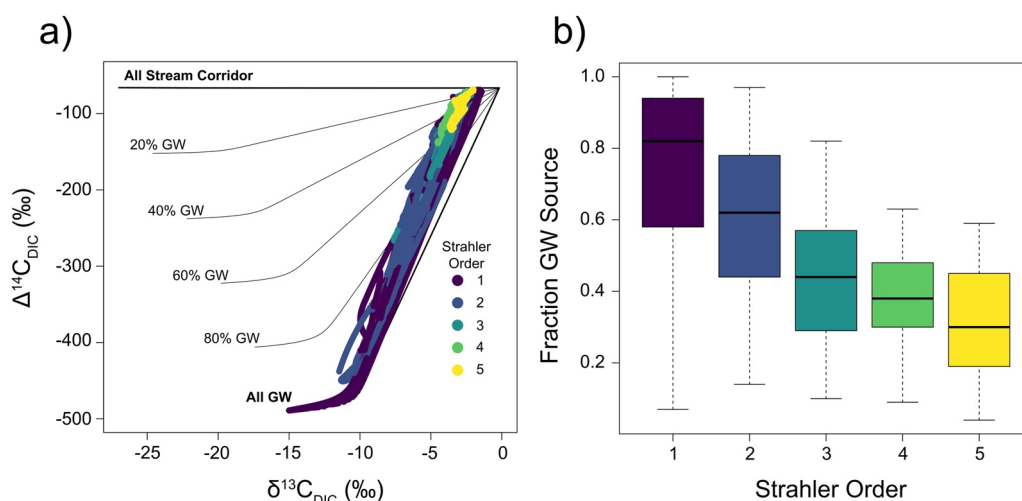
We also show how carbonate buffering reactions impact relationships between  $p\text{CO}_2$  and the isotopic composition of DIC in Figure 7 for the East River with an alkalinity of 1 meq/L, which expands on Figure 5 by incorporating scenarios with both increasing and decreasing  $p\text{CO}_2$ . During groundwater degassing in the headwaters, patterns resemble the degassing experiments from Scenario 1. However, in downstream reaches where  $p\text{CO}_2$  experiences local variability in response to changing balances between input fluxes and evasion rates, the model output deviates significantly from the degassing patterns. When local sources act to increase  $p\text{CO}_2$ , the total amount of DIC added is relatively small compared to the existing pool, which introduces hysteresis; thus,  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  are largely insensitive to changes in  $p\text{CO}_2$ . This behavior is highlighted in the insets in Figure 7, in which local changes in  $p\text{CO}_2$  result in minimal  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  changes, and overall patterns feature no large-scale co-variability. We note that in Figure 7a this decoupling occurs despite the fact that lower  $\delta^{13}\text{C}_{\text{DIC}}$  values of stream corridor respiration relative to groundwater should act to drive steeper, more sensitive correlations between  $p\text{CO}_2$  and  $\delta^{13}\text{C}_{\text{DIC}}$ . This decoupling of  $p\text{CO}_2$  and  $\delta^{13}\text{C}_{\text{DIC}}$  is similar under high alkalinity (Figure S6 in Supporting Information S1) and is also significant even in low alkalinity conditions of 0.1 meq/L (Figure S7 in Supporting Information S1). These results show that even under low alkalinity,  $p\text{CO}_2$  and the isotopic composition of DIC are not covary systematically across the watershed scale except during initial groundwater degassing.

To demonstrate the potential use of paired  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  in evaluating local partitioning between groundwater and stream corridor sources of DIC, we plot data from each model cell of the 1 meq/L simulation in  $\delta^{13}\text{C}_{\text{DIC}}$



**Figure 7.** Simulated relationships between (a)  $\delta^{13}\text{C}_{\text{DIC}}$  and  $p\text{CO}_2$  and (b)  $\Delta^{14}\text{C}_{\text{DIC}}$  and  $p\text{CO}_2$  in the Scenario 3 simulations with 1 meq/L alkalinity. Point colors represent the Strahler Order, and the insets highlight variability following groundwater degassing. Following groundwater seep degassing in 1st order streams,  $p\text{CO}_2$  and the isotopic composition of DIC are largely decoupled.

versus  $\Delta^{14}\text{C}_{\text{DIC}}$  space in Figure 8a. Contour lines represent degassing patterns for an initial DIC pool representing the isotopic end-member composition of varying mixtures of groundwater and stream corridor sources, generated using the same methods as in Scenario 1. We note that while this plot resembles an end-member mixing model, there is some curvature in the contour lines that reflect slight differences in the timescales of equilibration for  $^{14}\text{C}$  versus  $^{13}\text{C}$  discussed above. As shown, 1st order streams largely fall along All-groundwater degassing contour lines to start with a shift toward higher contributions from stream corridor respiration as values approach atmospheric equilibration. In general, there is a trend toward higher stream corridor respiration contributions at higher stream order, with a significant degree of variability within each order. We show this directly in Figure 8b, where the % groundwater contribution to DIC is calculated using a nearest-neighbor function to find which contour line passes through each model output point. Across all model cells, groundwater contributions vary from 100%



**Figure 8.** Carbon source partitioning using  $\delta^{13}\text{C}_{\text{DIC}} - \Delta^{14}\text{C}_{\text{DIC}}$ . (a) Simulated Scenario 3 (1 meq/L alkalinity) relationships between  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  represent contributions from stream corridor (combined water column and hyporheic zone sources), groundwater (GW), and atmospheric end-member sources. Contour lines represent degassing simulations from mixed groundwater-stream corridor end-member sources. Non-linearity of the contour curves represents slight offsets in  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  equilibration timescales (e.g., Figure 3b). (b) Fractional contributions of DIC from groundwater sources (versus stream corridor respiration) as a function of Strahler Order. Simulations show a shift in sources from groundwater in the headwaters to stream corridor respiration in higher order streams.

to 4%. We simulate a consistent transition from groundwater to stream corridor DIC sources at larger network scales, with the switch from groundwater to stream corridor dominance occurring between 2nd and 3rd order streams, consistent with our previous modeling results (Saccardi & Winnick, 2021). We note that output from the 4.0 meq/L simulation results in a shift toward higher groundwater contributions across the watershed, as groundwater has a significantly larger DIC concentration than the 1.0 meq/L simulation (Figure S8 in Supporting Information S1).

## 4. Discussion

### 4.1. Alkalinity Controls on CO<sub>2</sub> Concentrations and Fluxes

Across the simulated scenarios, we quantitatively demonstrate how alkalinity alters the equilibration of dissolved CO<sub>2</sub> with the atmosphere in rivers and streams. Increased alkalinity, as previously hypothesized, increases the role of carbonate buffering reactions in maintaining  $p\text{CO}_2$  along the stream reach. During active degassing, as shown in Scenarios 1–3, carbonate buffering reactions result in minimally increased atmosphere equilibration timescales, acting to maintain only slightly elevated  $p\text{CO}_2$ . Notably, however, these timescale increases are minimal and are only in evidence at near-atmospheric  $p\text{CO}_2$  values. Further, under conditions in which dissolved CO<sub>2</sub> is actively building up, for example, when local rates of stream corridor respiration or groundwater inputs are higher than degassing rates, carbonate buffering maintains lower  $p\text{CO}_2$  concentrations as it actively stores CO<sub>2</sub> as  $\text{HCO}_3^- + \text{H}^+$ . This effect is equivalent to the Revelle factor often discussed in the oceanography literature (Broecker et al., 1979; Revelle & Suess, 1957), and has been shown to impact stream CO<sub>2</sub> fluxes (Wang et al., 2021).

In a compilation of US stream data, Stets et al. (2017) showed that systems with high alkalinity tend to exhibit higher  $p\text{CO}_2$  at moderate stream scales (discharge of 0.1–6 m<sup>3</sup>/s) than systems with low alkalinity. This was hypothesized to reflect carbonate buffering reactions, through their role in maintaining high  $p\text{CO}_2$  during downstream degassing. In our modeling exercises, we show that carbonate buffering is unable to explain these observed patterns. In fact, when simulating at the stream network scale, we find that carbonate buffering reactions result in the opposite pattern as observed in the Stets et al. compilation:  $p\text{CO}_2$  is slightly elevated in first order streams but is typically lower in 3rd–5th order streams when alkalinity is included, reflecting the increasing importance of stream corridor respiration sources and lower gas exchange velocities that allow generated CO<sub>2</sub> to be stored as  $\text{HCO}_3^- + \text{H}^+$  (Figure 6b).

While beyond the scope of our study, we tentatively suggest that if the observational patterns presented in Stets et al. (2017) are robust, they likely reflect either systematically higher source fluxes (groundwater inputs and/or stream corridor respiration) or systematically lower gas exchange velocities potentially reflecting lower topographic relief (e.g., Rocher-Ros et al., 2019). Regarding elevated source fluxes, we note that Stets et al. (2017) demonstrated lower  $p\text{CO}_2$  in the smallest high alkalinity streams which would suggest lower groundwater  $p\text{CO}_2$  sources, and we are unaware of a mechanism that would link high alkalinity with higher stream corridor respiration rates. In terms of topography, as high alkalinity typically reflects increased chemical weathering rates often associated with soluble minerals such as carbonates, these landscapes may preferentially exhibit lower gas exchange velocities in higher order streams, resulting in elevated  $p\text{CO}_2$  at larger stream scales. To test this hypothesis would require local flow and topographic data, which are not included in the original compilation and may serve as the subject for future work. We also note that our stream network model simulations, in which the only altered variable is alkalinity, are not directly comparable to the US compilation data. For example, we hold groundwater  $p\text{CO}_2$  constant, whereas increased alkalinity may be expected to co-occur with reduced groundwater  $p\text{CO}_2$  based on chemical weathering reactions that convert CO<sub>2</sub> to alkalinity (e.g., Winnick & Maher, 2018).

We also demonstrate that increasing alkalinity and decreasing groundwater  $p\text{CO}_2$  values result in increasing relative contributions of carbonate buffering to total degassing fluxes (Figure 4). Under conditions where groundwater is the sole source of stream  $p\text{CO}_2$ , carbonate buffering may account for >60% of total degassing fluxes when groundwater has high alkalinity (>4 meq/L) and relatively moderate  $p\text{CO}_2$  (<5,000 ppm). These values are consistent with findings in Duvert et al. (2019), where carbonate buffering reactions were shown to support as much as ~60% of total fluxes in a high-alkalinity tropical stream system. While not included in our Figure 4 analysis, proportional carbonate buffering contributions to total fluxes would also decrease if total fluxes increased from stream corridor respiration. Taken together, these findings highlight the importance of accounting for



carbonate buffering reactions in budgeting stream network  $\text{CO}_2$  fluxes, particularly in high alkalinity ( $>1$  meq/L) systems.

Given these patterns that emerge from our modeling exercises, we expect stream  $\text{CO}_2$  spatial patterns and contributions of carbonate buffering to be most observable in stream systems with high alkalinity, relatively low  $p\text{CO}_2$  groundwater, and near-atmospheric stream  $p\text{CO}_2$ . High alkalinity environments generally correspond to the lithologic availability of soluble minerals such as carbonates or mafic silicates present in basalt for groundwater weathering reactions (e.g., Bluth & Kump, 1994; Ibarra et al., 2016). Low groundwater  $p\text{CO}_2$  may reflect either terrestrial environments with limited plant productivity or associated organic matter for subsurface respiration (e.g., Calmels et al., 2014), or weathering of soluble minerals that convert groundwater  $\text{CO}_2$  to alkalinity (e.g., Winnick & Maher, 2018). Lastly, local instances of near-atmospheric  $p\text{CO}_2$  values are observable across all watersheds reflecting high gas exchange velocities and/or low local  $\text{CO}_2$  inputs (Rocher-Ros et al., 2019), though stream values and total  $\text{CO}_2$  fluxes are generally lower at higher Strahler orders (Butman & Raymond, 2011; Hotchkiss et al., 2015). We also note that these patterns are also applicable to lentic freshwater environments, though beyond the scope of our modeling framework, and may contribute, for example, to observations of  $\text{CO}_2$ - $\text{O}_2$  relationships that deviate from respiration stoichiometry in high alkalinity lakes (Marcé et al., 2015), similar to the stream diel metabolic dynamics explored Stets et al. (2017).

#### 4.2. Alkalinity Impacts on Carbon Isotope Source Partitioning

In contrast to the effects on  $\text{CO}_2$  equilibration timescales, carbonate buffering reactions lead to much longer isotope equilibration timescales for both  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$ . Mechanistically, this is due to the fact that  $p\text{CO}_2$  is buffered only by the proportion of  $\text{HCO}_3^-$  that does not contribute to alkalinity ( $\text{CO}_2$  stored as  $\text{HCO}_3^- + \text{H}^+$ ). In contrast, the isotopic ratio of DIC is buffered by the entire  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  pools, which under high alkalinity are much larger than the  $\text{CO}_2$  pool that is actively degassed. As the equilibration timescales for both are regulated by the gas exchange velocity, these larger isotopic buffering results in a much longer equilibration timescale. For example, at an alkalinity of 1 meq/L and initial groundwater  $p\text{CO}_2$  of 20,000 ppm, the  $\text{CO}_2$  stored as  $\text{HCO}_3^- + \text{H}^+$  is 1.3% the size of the  $\text{CO}_{2(\text{aq})}$  pool, whereas the full buffering pool of  $^{12}\text{C}$ ,  $^{13}\text{C}$ , and  $^{14}\text{C}$  encapsulated in  $\text{HCO}_3^- + \text{CO}_3^{2-}$  is 150% the size of the  $\text{CO}_{2(\text{aq})}$  pool. Further, a higher proportion of total  $^{13}\text{C}$  and  $^{14}\text{C}$  are contained within  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  relative to  $^{12}\text{C}$  due to equilibrium fractionation within the DIC pool. Thus, high alkalinity is more effective at buffering the isotopic composition of DIC, which under high alkalinity conditions does not equilibrate until almost all of the net  $\text{CO}_2$  degassing has already occurred. At the stream network scale, this results in stream  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  that are much less sensitive to sub-reach changes in topography and source inputs that can dramatically alter  $p\text{CO}_2$  over small scales. While these results have been demonstrated indirectly through the application of similar models to groundwater degassing (e.g., Venkiteswaran et al., 2014) and have been noted observationally for  $^{14}\text{C}$  (Bourke et al., 2014), this study is the first to directly quantify these timescales for both  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$ .

These differences in the magnitude impacts of buffering dynamics on  $p\text{CO}_2$  versus carbon isotopes greatly complicate methods of  $\text{CO}_2$  source evaluation. The size of the isotope buffering pool along with degassing from the  $\text{CO}_2$  pool, which has a lower isotopic value than DIC effectively acts to decouple variations between carbon concentrations ( $p\text{CO}_2$  or DIC) and isotopic composition ( $\delta^{13}\text{C}_{\text{DIC}}$  or  $\Delta^{14}\text{C}_{\text{DIC}}$ ). During degassing, the bulk of the isotopic change occurs after  $p\text{CO}_2$  has equilibrated with the atmosphere, which makes measurements of covariation analytically difficult. More importantly, in situations where  $\text{CO}_2$  (and DIC) is building up rather than degassing,  $\delta^{13}\text{C}_{\text{DIC}}$  or  $\Delta^{14}\text{C}_{\text{DIC}}$  is largely insensitive to these new inputs via this hysteresis. This results in reach-scale patterns in which  $\delta^{13}\text{C}_{\text{DIC}}$  and  $p\text{CO}_2$  are largely decoupled and deviate significantly from the overall degassing pattern, as shown in Figure 7. Typical isotopic source evaluation methods either employ linear mixing models of  $p\text{CO}_2$  or DIC and  $\delta^{13}\text{C}_{\text{DIC}}$  (e.g., Campeau et al., 2017, 2018) or degassing models (Venkiteswaran et al., 2014). The assumptions underlying both of these methods are that  $p\text{CO}_2$  and  $\delta^{13}\text{C}_{\text{DIC}}$  co-vary systematically across a given study area. We show that this is not the case; carbonate buffering acts to decouple  $p\text{CO}_2$  and  $\delta^{13}\text{C}_{\text{DIC}}$  patterns in all but the 1st order headwaters that are dominated by groundwater seep degassing patterns. This decoupling occurs even at low and moderate alkalinity values (0.1 meq/L shown in Figure S7 of the Supporting Information S1; 1 meq/L shown in Figure 7). Therefore, studies that utilize  $p\text{CO}_2$ - or DIC-  $\delta^{13}\text{C}_{\text{DIC}}$  methods for evaluating carbon sources are only accurate under very low alkalinity conditions or in directly evaluating groundwater seep degassing trends in spring-fed headwaters.

Despite the factors that complicate the relationships between isotope composition and  $p\text{CO}_2$ , our modeling simulations suggest a useful path forward. Specifically,  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  both represent the full DIC pool and have equilibration timescales that are similarly impacted by alkalinity. Therefore, they may be used to partition DIC sources more directly through end-member mixing analyses. Furthermore, the increased equilibration timescales in high alkalinity systems mean that point measurements of  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  are more integrative of upstream conditions and may provide useful insight into broader spatial trends than  $p\text{CO}_2$ , which can often vary over scales of 10's of meters (e.g., Johnson et al., 2008). Paired  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  measurements may be particularly useful for DIC source partitioning in systems where groundwater DIC is controlled by carbonate mineral weathering reactions, such as watersheds with limestone or shale bedrock. Under these conditions and as parameterized across our simulations, groundwater, stream corridor respiration, and the atmosphere all represent unique end-members in  $\delta^{13}\text{C}_{\text{DIC}} - \Delta^{14}\text{C}_{\text{DIC}}$  space (e.g., Table 1). We note that Sveinbjörnsdóttir et al. (2020) have previously employed paired  $\delta^{13}\text{C}_{\text{DIC}} - \Delta^{14}\text{C}_{\text{DIC}}$  to evaluate DIC sources; however, they used a linear end-member mixing model, which our results show neglects non-linear variations between  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  degassing rates and may therefore only be accurate under low alkalinity conditions.

In our simulations, we calculated the contributions of groundwater versus stream corridor respiration to DIC using simulated  $\delta^{13}\text{C}_{\text{DIC}} - \Delta^{14}\text{C}_{\text{DIC}}$  relationships. At any given simulated stream point, measured values represent the integration of upstream processes at the spatial scale dependent on stream velocity, gas exchange velocity, and the alkalinity-dependent equilibration timescales of carbon isotope values. We propose that these methods may be employed within field systems, which requires the characterization of end-member source  $\delta^{13}\text{C}_{\text{DIC}} - \Delta^{14}\text{C}_{\text{DIC}}$  values, along with alkalinity measurements to calculate contour mixing lines (see Supporting Information S1 for example code). Currently, methods for estimating source contributions within a stream reach are intensive, and typically involve calculating stream corridor metabolic rates through DO sensor deployment and absolute  $\text{CO}_2$  fluxes through high resolution sampling (e.g., Hotchkiss et al., 2015). While  $\Delta^{14}\text{C}_{\text{DIC}}$  measurements are costly, this method has the advantage of allowing for rapid characterization of source partitioning across watershed scales, through sampling campaigns that target multiple streams. These may be particularly useful, for example, for targeting spatial variability and Strahler order scale dependencies in stream carbon sources at a point in time, such as during a storm event or peak snowmelt. Traditionally, source characterization across stream orders within a watershed would require the redeployment of DO sensors at each new stream reach, whereas this method would allow for a larger spatial characterization at a given timepoint by taking representative samples from a set of stream reaches assuming relatively consistent end-member sources across the watershed.

### 4.3. Model Limitations

While these models are meant to be broadly representative of the processes controlling atmospheric equilibration of river and stream waters, there are a number of assumptions we have made that must be validated on a site-by-site basis for direct data comparisons. First, our simulations parameterize stream corridor metabolism as net respiration rather than separately simulating photosynthesis and respiration. This parameterization assumes that organic matter derived from terrestrial materials is the same as that synthesized in the stream, such that stream corridor photosynthesis and respiration have equal and opposite impacts on the isotopic composition. This assumption may be violated, for example, in sites where terrestrially-derived DOC represents  $\text{C}_4$  plant matter, and at the field-scale, measurements of distinct isotopic end-members for different DOC sources are needed to evaluate this assumption. To simulate diel variations in the carbonate system, the model would likely need to be amended to parameterize photosynthesis and the associated fractionation independently, as opposed to our net respiration representation.

As stated throughout the manuscript, we also neglect processes that alter alkalinity concentrations, which may include anaerobic respiration, calcite precipitation, and spatiotemporal changes in groundwater chemistry. We similarly neglect  $\text{CO}_2$  generation from methane oxidation that may result in distinctly low  $\delta^{13}\text{C}_{\text{DIC}}$  values. We assume that there is no kinetic fractionation associated with  $\text{CO}_2$  degassing from turbulent exchange, and that apparent fractionation during degassing reflects only equilibration with the elevated atmospheric values of  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$ . We feel that this issue remains an open question that has not been directly addressed in stream environments, though our modeling framework is flexible to incorporate it as a specified kinetic fractionation factor when molecular diffusion is a significant factor in degassing rates (e.g., Zhang et al., 1995). Lastly, for simplicity, we have kept temperatures constant throughout this analysis. Temperature changes would impact

results via  $\text{CO}_{2(\text{aq})}$  solubility as well as equilibrium constants and associated equilibrium fractionation within the carbonate system presented in Table 1, which can be manually altered within the model.

## 5. Conclusions

Given the recent recognition of carbonate buffering reactions as an important control on spatial patterns of  $\text{CO}_2$  concentrations and fluxes in stream systems, we developed a non-dimensional reactive transport framework for evaluating their impacts on atmospheric equilibration of dissolved inorganic carbon. We find that while carbonate buffering does increase the timescales over which  $p\text{CO}_2$  approaches steady-state values, these changes are relatively small and cannot explain observations of elevated  $p\text{CO}_2$  at increasing spatial scales in high alkalinity versus low alkalinity systems. This increase in equilibration timescale, along with increased contributions of carbonate buffering reactions to total  $\text{CO}_2$  fluxes, depends on the size of the buffering reservoir (or amount of  $\text{CO}_2$  stored as  $\text{HCO}_3^- + \text{H}^+$ ) relative to  $\text{CO}_{2(\text{aq})}$ , such that carbonate buffering reactions contribute a larger proportion of  $\text{CO}_2$  fluxes as alkalinity increases and groundwater  $p\text{CO}_2$  decreases. In contrast to  $\text{CO}_2$ , the isotopic composition of DIC is buffered by the entire DIC pool as  $\text{CO}_2$  equilibrates with the atmosphere, which is much larger than the pool of  $\text{CO}_2$  stored as  $\text{HCO}_3^- + \text{H}^+$ . As a result, isotopic equilibration timescales are much more sensitive to stream alkalinity, with  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  increasing by  $\sim 2$  orders of magnitude relative to  $\text{CO}_2$  timescales. The result of this mismatch in timescales is that under moderate alkalinity conditions, isotope composition becomes largely decoupled from  $p\text{CO}_2$ , rendering typical methods for  $\text{CO}_2$  source tracing ineffective. We show, however, that due to similar impacts on equilibration timescales, paired  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  measurements may be effective tracers of groundwater versus stream corridor respiration sources of DIC in environments where groundwater DIC is controlled by carbonate weathering reactions, typical of moderate to high alkalinity systems. Taken together, we present a generalizable framework for quantifying and interpreting the role of carbonate buffering reactions in stream  $\text{CO}_2$  dynamics and develop a new potential method for utilizing the isotopic composition of DIC to trace stream carbon sources.

## Data Availability Statement

All code used in this work is available in Supporting Information S1. This code is also available publicly via the open-source Hydroshare platform in Winnick (2023), <https://www.hydroshare.org/resource/2a2132999fb84214aad0596783812db2/>.

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