Diffuse Groundwater Discharge Dominates Terrestrial Dissolved Inorganic Carbon Export and CO2 Evasion From a Semiarid Headwater Stream

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Abstract

Groundwater discharge to headwater streams and concomitant terrestrial dissolved inorganic carbon (DIC) export play a significant role in headwater stream CO2 evasion. However, previous studies rarely examined diffuse groundwater discharge and its impact on headwater stream CO2 evasion, thereby lacking the understanding of the role of diffuse groundwater discharge in terrestrial DIC export and stream CO2 evasion. This study quantified diffuse groundwater discharge along a 43 km semiarid headwater stream by combining hydraulic, isotopic (radon-222) and chemical (electrical conductivity) approaches, and estimated the reach-level CO2 budgets of the stream. Reach-scale water and mass balance modeling yielded highly variable diffuse groundwater discharge rates (n = 16, range: 1.08-7.80 m2/d, mean ± 1 sd: 4.57 ± 1.81 m2/d). Groundwater was supersaturated with CO2 at all sites, with strongly variable CO2 partial pressure (pCO2) and DIC concentrations at 1,223-27,349 μatm and 30-119 mg/L, respectively. Diffuse groundwater discharge dominated terrestrial DIC export to the stream (12-111 g C m-2 d-1, normalized to water surface area). A portion of groundwater dissolved CO2 transported to the stream was emitted to the atmosphere with evasion rates varying at 0.62-3.18 g C m-2 d-1. However, most dissolved CO2 was transformed into HCO3- through carbonate buffering because of the regulation of carbonate equilibrium. Overall, the stream CO2 evasion was driven by carbon transfer but limited by carbon supply. This study provides a bottom-up perspective to understand terrestrial DIC export and stream CO2 evasion in arid and semiarid areas.

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Key Points:

- Diffuse groundwater discharge controlled terrestrial dissolved inorganic carbon export to the stream.
- A large portion of dissolved CO_2 was transformed into HCO_3^- immediately after entering the stream.
- Semiarid headwater stream CO_2 evasion was driven by carbon transfer, but limited by carbon supply.

Abstract

Groundwater discharge to headwater streams and concomitant terrestrial dissolved inorganic carbon (DIC) export play a significant role in headwater stream CO_2 evasion. However, previous studies rarely examined diffuse groundwater discharge and its impact on headwater stream CO_2 evasion, thereby lacking the understanding of the role of diffuse groundwater discharge in terrestrial DIC export and stream CO_2 evasion. This study quantified diffuse groundwater discharge along a 43 km semiarid headwater stream by combining hydraulic, isotopic (radon-222) and chemical (electrical conductivity) approaches, and estimated the reach-level CO_2 budgets of the stream. Reach-scale water and mass balance modeling yielded highly variable diffuse groundwater discharge rates (n = 16, range: 1.08-7.80 m^2/d, mean ± 1 sd: 4.57 ± 1.81 m^2/d). Groundwater was supersaturated with CO_2 at all sites, with strongly variable CO_2 partial pressure (pCO_2) and DIC concentrations at 1,223-27,349 μatm and 30-119 mg/L, respectively. Diffuse groundwater discharge dominated terrestrial DIC export to the stream (12-111 g C m^{-2} d^{-1}, normalized to water surface area). A portion of groundwater dissolved CO_2 transported to the stream was emitted to the atmosphere with evasion rates varying at 0.62-3.18 g C m^{-2} d^{-1}. However, most dissolved CO_2 was transformed into HCO_3^- through carbonate buffering because of the regulation of carbonate equilibrium. Overall, the stream CO_2 evasion was driven by carbon transfer but limited by carbon supply. This study provides a bottom-up perspective to understand terrestrial DIC export and stream CO_2 evasion in arid and semiarid areas.

45 # 1. Introduction

46 CO_2 evasion from streams and rivers to the atmosphere is a significant process in the global
47 carbon cycle (Battin et al., 2009; Butman and Raymond, 2011; Duvert et al., 2018; Marx et al.,
48 2017; Raymond et al., 2013; Wehrli, 2013). The average partial pressure of carbon dioxide
49 (pCO_2) of global streams and rivers is estimated at 3,100 μatm compared with the atmospheric
50 pCO_2 of approximately 390 μatm. This large difference in pCO_2 results in the common
51 phenomenon of CO_2 supersaturation in the rivers and streams (Marx et al., 2017; Raymond et al.,
52 2013). Consequently, global streams and rivers emit a considerable amount of CO_2 to the
53 atmosphere with the rate estimated at approximately 2.58 petagrams of carbon (Pg C) per year
54 (Marx et al., 2017; Raymond et al., 2013; Sawakuchi et al., 2017). Among all streams and rivers,
55 headwater streams are hotspots, contributing 36% (i.e. 0.93 Pg C yr^{-1}) of the total CO_2 evasion,
56 which is disproportional to their catchment sizes (Marx et al., 2017; Raymond et al., 2013). This
57 significant contribution from the headwater streams is attributed to several factors including a
58 large number of the headwater streams (Marx et al., 2017), high CO_2 concentrations (Butman
59 and Raymond, 2011; Duvert et al., 2018; Horgby et al., 2019; Johnson et al., 2008; Leith et al.,
60 2015; Lupon et al., 2019; Öquist et al., 2009; Winterdahl et al., 2016), and high gas transfer
61 velocities (Liu and Raymond, 2018; Raymond et al., 2013).

62 Continuous CO_2 evasion from streams and rivers is usually derived from two carbon
63 sources, including internal production by microbial mineralization of dissolved organic carbon
64 (DOC), and external input of terrestrial CO_2 (Hotchkiss et al., 2015; Marx et al., 2017). The
65 internal production plays an important role in larger rivers, whereas the external input is essential
66 to continuously sustain CO_2 evasion from small streams, particularly in headwater streams

(Hotchkiss et al., 2015). As reported by several studies in the headwater streams, groundwater pCO_2 is typically 1-2 orders of magnitude higher than stream pCO_2 (Deirmendjian and Abril, 2018; Hope et al., 2004; Johnson et al., 2008; Rasilo et al., 2017). After CO_2-rich groundwater discharges to streams, most dissolved CO_2 (CO_2^*, similarly hereinafter) is emitted to the atmosphere over a short distance downstream (Duvert et al., 2018; Johnson et al., 2008; Öquist et al., 2009). Although these studies have improved our understanding of groundwater contribution to terrestrial carbon export and stream CO_2 evasion, it is hardly possible to upscale their results from local scales to regional scales because of the unknown spatial variability of groundwater carbon input. Some studies have attempted to quantify CO_2 evasion at the regional scale, but utilized only a limited number of groundwater measurements to represent groundwater contribution with an inherent assumption of relatively weak spatial variability of groundwater carbon input (Duvert et al., 2018; Duvert et al., 2019; Leith et al., 2015; Lupon et al., 2019; Öquist et al., 2009). However, the degree of the spatial variability of the groundwater carbon input is still unclear. This knowledge gap undermines our ability to upscale headwater stream CO_2 evasion to larger spatial scales.

Groundwater discharge plays a crucial role in transporting terrestrial carbon to streams and sustaining stream CO_2 evasion (Duvert et al., 2018; Horgby et al., 2019; Lupon et al., 2019; Marx et al., 2017; Winterdahl et al., 2016). Previous stream CO_2 evasion studies have largely concentrated on springs (focused groundwater discharge) where flow rates and CO_2 concentrations are measurable (Duvert et al., 2018; Johnson et al., 2008; Lupon et al., 2019). However, in many systems, groundwater discharge is known to occur through an entire stream diffusively and at rates that are difficult to be measured directly. This diffuse groundwater discharge has been frequently examined in many streams and rivers at varying length scales and

has been found to be strongly variable due to variable hydraulic gradients and riverbed permeability (Cook et al., 2006; Xie et al., 2016). Therefore, accurate quantitative analysis of CO_2 evasion from headwater streams at large scales requires reliable estimation of diffuse groundwater discharge rates.

Here, we longitudinally surveyed a 43 km semiarid headwater stream (Hailiutu River) where stream flow was mostly maintained by groundwater discharge throughout a year (Yang et al., 2012; 2014). We quantified the groundwater discharge by combining hydraulic, isotopic and chemical methods, and then estimated the stream carbon budget at the corresponding resolution. Through the constrained water and mass balances, we attempted to explore (i) the main driver of terrestrial carbon export in a semiarid headwater stream; (ii) the main driver of stream CO_2 evasion; and (iii) the role of diffuse groundwater discharge in terrestrial carbon export and release.

2. Data and Methods

2.1. Site description

Our study was conducted in the Hailiutu River catchment, located in Yulin City, Shanxi Province, semiarid northern China. The total area of this catchment is around 2,645 km^2, and the surface elevation of this catchment ranges from 1,486 m above sea level (m.a.s.l.) in the northwest to 1,009 m in the southeast (Figure 1). The land surface is mainly covered by undulating sand dunes and xeric shrubland (Yang et al., 2012). The regional aquifer is composed of the Holocene Maowusu sand dunes (thickness: 0-30 m) underlain by the upper Pleistocene Shalawusu sandstone (thickness: 5-90 m) (Yang et al., 2014). This catchment is controlled by

111 semiarid continental climate with low precipitation (340 mm yr^{-1}) and high potential
112 evapotranspiration (2,184 mm yr^{-1}) (Yang et al., 2012). The majority of the precipitation occurs
113 from June to September every year.

114 The Hailiutu River and its tributary, the Bulang River, are the two major streams in this
115 catchment (Figure 1). The Hailiutu River is formed by two small streams in the northwest of our
116 study area and extends all the way to the Hanjiamao Village (4 km above the confluence with the
117 Wuding River, Figure 1). It is a perennial second-order stream with the annual mean stream flow
118 rate of 2.41 m^3/s at the gauging station close to the catchment exit (2001-2007) (Yang et al.,
119 2012). The Hailiutu River water eventually flows into the Wuding River, a major tributary along
120 the middle reach of the Yellow River (Yang et al., 2012). The studied section of the Hailiutu
121 River is approximately 43 km in length.

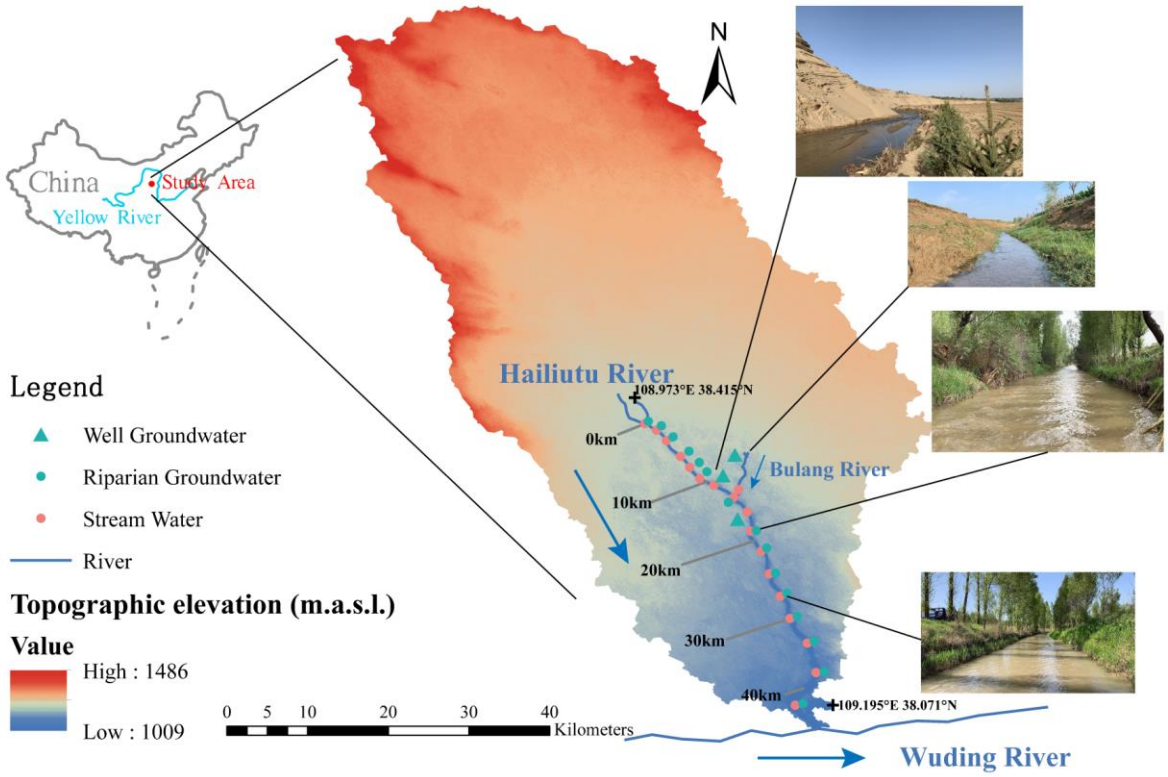

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Figure 1. Geographic location of the study area and sampling sites along the Hailiutu River.

2.2. Field survey and laboratory analyses

Our field survey was conducted between 9 and 14 May 2019 (dry season) when the stream was mainly sustained by groundwater discharge. We longitudinally surveyed the stream water and its adjacent groundwater at an average interval of 2.6 km (Figure 1). For groundwater sampling, we excavated holes (approximately 0.5 m wide and 0.4-0.6 m deep) at the riverbank and sampled the fresh groundwater within a short period of excavation (15 samples). Samples were also collected from domestic wells located within 1 km of the stream (2 samples, Figure 1). These wells were screened in the sand aquifer to depths between 15 and 135 m below ground level.

We quantified groundwater discharge to the Hailiutu River by combining differential flow gauging and the mass balance modeling of radon-222 (^{222}Rn) and electrical conductivity (EC). Flow gauging was undertaken at each sampling location by dividing the stream transect into intervals of approximately 0.5 m. The flow velocity of each 0.5 m section was measured using a flow meter (accuracy: ±1.5%, Jiangsu Nanshui Water Technology Company, China) with the one-point method. The total stream flow rate was obtained by summing the flow rate of all the sections (flow velocity multiplied by the cross-sectional area). ^{222}Rn activities in both the stream and the groundwater were obtained via the RAD7 detector coupled with the RAD H_2O Accessory (Durridge Company, USA). The stream and the groundwater excavations were sampled by submerging and sealing a 250 mL glass vial underwater. Domestic groundwater wells were purged with a minimum of three bore volumes removed and sampled after groundwater temperature, pH and EC had stabilized. EC in both the stream and the groundwater

was measured with the HACH HQ40d multiparameter probe (accuracy: ±0.5%, HACH Company, USA).

Both the stream water and groundwater were also measured for dissolved oxygen, pH and temperature in the field through the HACH HQ40d multiparameter probe. Their alkalinity was titrated through HACH Digital Titrator (accuracy: ±1%). pCO_2 and DIC concentrations were calculated by field measured pH, temperature and alkalinity (Supplementary information, SI, Text S1). In addition to the field direct measurements, water samples were also collected for analyzing cations, anions, DOC and $\delta^{13}C_{DIC}$ in the laboratory. All the water samples were filtered through 0.45 μm membrane filters and acidified by adding HCl if used for cation analysis. The cations and anions were analyzed through ICP-OES and ion chromatography, respectively, at the Key Laboratory of Surficial Geochemistry of the Ministry of Education, Nanjing University. DOC was analyzed through a TOC analyzer (SHIMADZU TOC-L, Japan) at the School of the Environment, Nanjing University. The $\delta^{13}C_{DIC}$ was measured through the Gasbench and MAT252 (Thermo Fisher Scientific, USA) at the State Key Laboratory for Mineral Deposits Research, Nanjing University.

2.3. Reach-scale water and mass balance modeling

Reach-scale groundwater discharge to the Hailiutu River was estimated by modeling the stream water balance and the mass balances of ^{222}Rn and EC simultaneously (Cook, 2013; Cook et al., 2006). The stream water balance is given by

$$\frac{\partial Q}{\partial x} = I + Tri - Ew \quad (1)$$

where Q is the stream flow rate (m^3/d), x is the distance in the direction of flow (m), I is the groundwater discharge per unit length (m^2/d), Tri is the tributary inflow rate per unit length (m^2/d), E is the evaporation rate (m/d) , and w is the stream width (m). Tri is equal to the tributary flux (positive, i.e. Bulang River flux) or irrigation diversion flux (negative, we found three irrigation diversion points) divided by the length between two adjacent stream measurement points.

The environmental tracer ^{222}Rn has been used frequently to quantify groundwater discharge to surface water (Cook, 2013; Cook et al., 2003; Cook et al., 2006; Hofmann et al., 2011; Xie et al., 2016). ^{222}Rn is a radioactive noble gas with a half-life of 3.8 days. It is a decay product of uranium series isotopes. Given the extensive existence of uranium in aquifer sediment, ^{222}Rn is produced continuously in groundwater. Once groundwater discharges to the stream, ^{222}Rn activity is affected by several factors including gas exchange with the atmosphere, radioactive decay and dispersive mixing. The mass balance of ^{222}Rn is given by the following equation (Cook, 2013; Cook et al., 2003; Cook et al., 2006)

$$\frac{\partial(QC)}{\partial x} = IC_{gw} + Tri \cdot C_{Tri} - kwC - \lambda dwC + F_{hypor} \quad (2)$$

where C, C_{gw}, and C_{Tri} are the ^{222}Rn activities (Bq/L) of the stream, the adjacent groundwater, and the tributary, respectively. C_{Tri} equals C for irrigation diversion. k is the ^{222}Rn gas transfer velocity (m/d), λ is the radioactive constant of ^{222}Rn (0.18 d^{-1}), d is the stream depth (m), and F_{hypor} is the net flux of ^{222}Rn from hyporheic zone into stream. The first two terms on the right side of the equation represent mass fluxes due to groundwater discharge and tributary inflow,

185 respectively. The third and fourth terms on the right side represent ^{222}Rn loss rates due to gas
186 exchange with the atmosphere and radioactive decay, respectively. The last term is hyporheic
187 flow related mass flux. Cook et al. (2006) derived the expression of the net flux of ^{222}Rn from
188 hyporheic zone into stream (F_{hypor})

189 $$F_{hypor} = \frac{wh\theta(\gamma - \lambda C)}{1 + \lambda t_h} \quad (3)$$

190 where h (m), θ (dimensionless), γ (Bq/L/day), and t_h (d) are the mean depth, the porosity, the
191 ^{222}Rn production rate, and the mean water residence time within the hyporheic zone, respectively.
192 Noting that $\frac{\partial(QC)}{\partial x} = C\frac{\partial Q}{\partial x} + Q\frac{\partial C}{\partial x}$, and substituting this together with Equation (1) and (3) into
193 (2) results in the following equation

194 $$Q\frac{\partial C}{\partial x} = I\left(C_{gw} - C\right) + Tri\left(C_{Tri} - C\right) + EwC - kwC - \lambda dwC + \frac{wh\theta(\gamma - \lambda C)}{1 + \lambda t_h} \quad (4)$$

195 For EC, the k, λ and F_{hypor} are zero as they are only related to ^{222}Rn production and losses.
196 Equation (4) then becomes

197 $$Q\frac{\partial C}{\partial x} = I\left(C_{gw} - C\right) + Tri\left(C_{Tri} - C\right) + EwC \quad (5)$$

198 Groundwater discharge was quantified by solving Equation (1), (4) and (5) simultaneously,
199 with an explicit finite difference method. A grid size of 10 m was used, resulting in a total of
200 4,298 cells given the modeled stream length of 42.98 km. We utilized the DiffeRential Evolution
201 Adaptive Metropolis scheme (“DREAM” algorithm) (Vrugt et al., 2009), which is based on an

evolutionary Markov chain Monte-Carlo (MCMC) approach to calibrate the groundwater discharge and other model parameters (i.e., k, h, γ and t_h). The DREAM algorithm runs multiple Markov chains simultaneously for multi-modal search problems and improves the efficiency of MCMC simulation significantly (Vrugt et al., 2009). This method has been effectively used to model stream tracer tests (Knapp and Cirpka, 2017; McCallum et al., 2020; Roche et al., 2019). The DREAM algorithm works by generating multiple Markov chains to sample the parameter space by selecting combinations of parameters that produce a better fit to the observed values (also known as the likelihood). The likelihood function used in this study was defined as

$$Likelihood = -\left(\sum_{i=1}^{17} \left(\frac{Q_{modeled} - Q_{measured}}{Q_{error}} \right)^2 + \sum_{i=1}^{17} \left(\frac{Rn_{modeled} - Rn_{measured}}{Rn_{error}} \right)^2 + \sum_{i=1}^{17} \left(\frac{EC_{modeled} - EC_{measured}}{EC_{error}} \right)^2 \right) \quad (6)$$

where $Q_{modeled}$, $Rn_{modeled}$, and $EC_{modeled}$ are the modeled stream flow rate, ^{222}Rn activity, and EC derived from the MCMC simulation, respectively. $Q_{measured}$, $Rn_{measured}$, and $EC_{measured}$ are the field measured stream flow rate, ^{222}Rn activity, and EC, respectively. Q_{error}, Rn_{error}, and EC_{error} are the errors of stream flow rate, ^{222}Rn activity, and EC, respectively.

In the DREAM algorithm, new proposals are generated first using combinations of other chains. If these proposals produce a higher likelihood, the proposal is accepted. If the new likelihood is lower, the chains accept the proposal conditional on a transition probability (a transition to a slightly worse likelihood is more probable than a transition to a much lower likelihood). At each level, either the proposed values (if transition conditions are met) or the

current values form a set of samples. Each of these samples is treated equally, and the resulting statistics of all the sampled parameters sets encapsulate the range of plausible values or uncertainty.

2.4. Reach-scale carbon budgeting

Based on the reach-scale water balance, we established a reach-scale CO_2 budget to explore the contributions of external input, internal production and carbonate buffering process to the stream CO_2 evasion. For a representative stream reach, we assumed that the stream was in steady state (i.e., the inputs and outputs are equal)

$$F_{up}^{CO_2} + F_{gw}^{CO_2} + F_{Tri}^{CO_2} + F_{m}^{CO_2} = F_{down}^{CO_2} + F_{air}^{CO_2} + F_{b}^{CO_2} \quad (7)$$

where $F_{up}^{CO_2}$, $F_{gw}^{CO_2}$, $F_{Tri}^{CO_2}$, and $F_{m}^{CO_2}$ are the upstream CO_2 input, the groundwater CO_2 input, the tributary CO_2 input, the net internal CO_2 production (DOC mineralization minus photosynthesis), respectively. $F_{down}^{CO_2}$, $F_{air}^{CO_2}$, and $F_{b}^{CO_2}$ are the downstream CO_2 output, the stream CO_2 evasion rate, and the CO_2 loss through carbonate buffering (positive value means CO_2^* transformed into HCO_3^-, and negative value means HCO_3^- transformed into CO_2^*), respectively. Note that all the mass fluxes in Equation (7) are normalized to the water surface area of the given stream reach and expressed in g C m^{-2} d^{-1}. $F_{up}^{CO_2}$, $F_{gw}^{CO_2}$, $F_{Tri}^{CO_2}$, and $F_{down}^{CO_2}$ are determined by multiplying the CO_2 concentrations and the water fluxes derived from the water balance. $F_{m}^{CO_2}$ is derived from the reach-scale mass balance of DOC. $F_{air}^{CO_2}$ is estimated by Fick's Law. Finally, $F_{b}^{CO_2}$ can be calculated from Equation (7).

241 In the water column, DOC can be degraded to CO_2^*, sustaining the stream CO_2
242 oversaturation and CO_2 evasion to the atmosphere. CO_2^* can also be conversely consumed by
243 photosynthesis. Here, we utilized a reach-scale DOC mass balance to estimate $F_m^{CO_2}$

244 $$F_m^{CO_2} = F_{up}^{DOC} + F_{gw}^{DOC} + F_{Tri}^{DOC} - F_{down}^{DOC} \quad (8)$$

245 where F_{up}^{DOC}, F_{gw}^{DOC}, F_{Tri}^{DOC}, and F_{down}^{DOC} are the upstream DOC input, the groundwater DOC
246 input, the tributary DOC input, and the downstream DOC output, respectively. Likewise, these
247 carbon fluxes are also quantified by multiplying the corresponding DOC concentrations and the
248 water fluxes derived from the water balance.

249 $F_{air}^{CO_2}$ is estimated by Fick's Law and given below

250 $$F_{air}^{CO_2} = \left(pCO_{2\,aq} - pCO_{2\,air} \right) \times K_H \times K_{CO_2} \times 12 \div 1000 \quad (9)$$

251 where $pCO_{2\,aq}$ and $pCO_{2\,air}$ are the CO_2 partial pressure in the stream and the air (μatm),
252 respectively. We assumed that the atmospheric pCO_2 was 390 μatm. K_H and K_{CO_2} are the
253 temperature-dependent Henry's Law constant (mol/L/atm) and the CO_2 gas transfer velocity
254 (m/d).

255 K_H is determined according to the empirical equation from Clark and Fritz (1997)

256 $$-\log_{10}\left(K_H\right) = -7 \times 10^{-5} T^2 + 0.016T + 1.11 \quad (10)$$

257 where T is the temperature of stream water (°C).

258 K_{CO_2} can be determined from the calibrated ^{222}Rn gas transfer velocity (k, m/d) derived
259 from the reach-scale water and mass balance modeling (Raymond et al., 2012)

260 $$K_{CO_2} = k\left(\frac{Sc_{CO_2}}{Sc_{Rn}}\right)^{-0.5} \quad (11)$$

261 where Sc_{CO_2} and Sc_{Rn} are the Schmidt number of CO_2 and ^{222}Rn, respectively. Both Sc_{CO_2} and
262 Sc_{Rn} can be calculated from stream temperature (℃) (Raymond et al., 2012)

263 $$Sc_{CO_2} = 1742 - 91.24T + 2.208T^2 - 0.0219T^3 \quad (12)$$

264 $$Sc_{Rn} = 2939 - 173.87T + 4.532T^2 - 0.0468T^3 \quad (13)$$

265 Previous studies found that carbonate buffering can significantly impact stream CO_2
266 evasion by shifting carbonate equilibrium, particularly in high alkalinity streams and rivers
267 (Duvert et al., 2019; Stets et al., 2017). Oversaturated CO_2 in the stream can be either emitted to
268 the atmosphere or transformed into HCO_3^-. Relevant chemical reactions are given below

269 $$CO_2(g) = CO_2(aq) \quad (14)$$

270 $$CO_2(aq) + H_2O = H_2CO_3 = H^+ + HCO_3^- = 2H^+ + CO_3^{2-} \quad (15)$$

271 $$Ca^{2+} + 2HCO_3^- = CaCO_3\downarrow + CO_2^* + H_2O \quad (16)$$

272 Equation (7) can be rearranged to examine the impact of the carbon buffering process to the
273 stream CO_2 pool as follows

$$F_b^{CO_2} = F_{up}^{CO_2} + F_{gw}^{CO_2} + F_{Tri}^{CO_2} + F_m^{CO_2} - F_{down}^{CO_2} - F_{air}^{CO_2} \quad (17)$$

2.5. Hydrogeochemical modeling

We modeled carbonate buffering process after groundwater discharged to the stream through the PHREEQC simulation program (Parkhurst and Appelo, 2013). The mean water temperature, pH, Ca^{2+}, Mg^{2+} and alkalinity of our groundwater samples were assigned as the initial model parameters, then we modeled the re-equilibrium processes between the groundwater and the air for different pCO_2 values and calculated the corresponding calcite saturation (Ion Activity Product / Solubility Product Constant of calcite, IAP/K calcite, similarly hereinafter). Through the change of calcite saturation, we can explore the shift in carbonate equilibriums.

2.6. Uncertainty and statistical analysis

Uncertainty analysis was based on the results of the MCMC simulation. For the variables estimated in the MCMC simulation (i.e., I, k, h, γ and t_h), we treated the 16th-84th percentiles of the model outputted ranges as their uncertainty bounds. For the other variables including $F_{gw}^{CO_2}$, $F_m^{CO_2}$ and $F_b^{CO_2}$, their uncertainty bounds were determined according to the uncertainty bounds of I. The uncertainty of $F_{air}^{CO_2}$ were based on the k uncertainty.

Furthermore, we used one-way analysis of variance (ANOVA test) to compare the carbon concentration differences between the stream and the groundwater, and different carbon budget components at the significance level of $p < 0.05$.

3. Results

3.1. Longitudinal patterns of stream flow and groundwater discharge

Field measured values for reach-scale water and mass balance modeling are listed in SI Table S1, and the spatial variations in Q, ^{222}Rn activities and EC are depicted in Figure 2a-c, respectively. Differential flow gauging shows that stream velocity ranged between 0.190 and 1.156 m/s and Q increased continuously from 0.283 m^3/s at the upstream end of the studied reach to 2.093 m^3/s at the downstream end, with some fluctuations between 15 and 25 km (Figure 2a). Stream width varies between 3.8 and 11 m, with the mean value of 6.34 m. The stream is relatively shallow (range: 0.11–0.49 m) with a mean depth of 0.25 m.

The stream ^{222}Rn activities were significantly lower than those from the adjacent groundwater (ANOVA, $n = 34$, $F = 481$, $p < 0.0001$). The mean ± 1 standard deviation (similarly hereinafter) of the stream and groundwater ^{222}Rn activities are 0.889 ± 0.236 and 5.082 ± 0.752 Bq/L, respectively. The ^{222}Rn activity along the stream was fluctuating but relatively stable at 0-27 km (0.832-1.150 Bq/L) and decreased from 1.046 at 27 km to 0.322 Bq/L at 43 km (Figure 2b).

The stream EC shows a decreasing trend along the stream (Figure 2c), with the maximum of 994 μs/cm at the upstream end and the minimum of 456 μs/cm at 34 km. The groundwater EC was significantly lower than the stream EC (ANOVA, $n = 34$, $F = 4.58$, $p < 0.05$) and varied between 241 and 679 μs/cm.

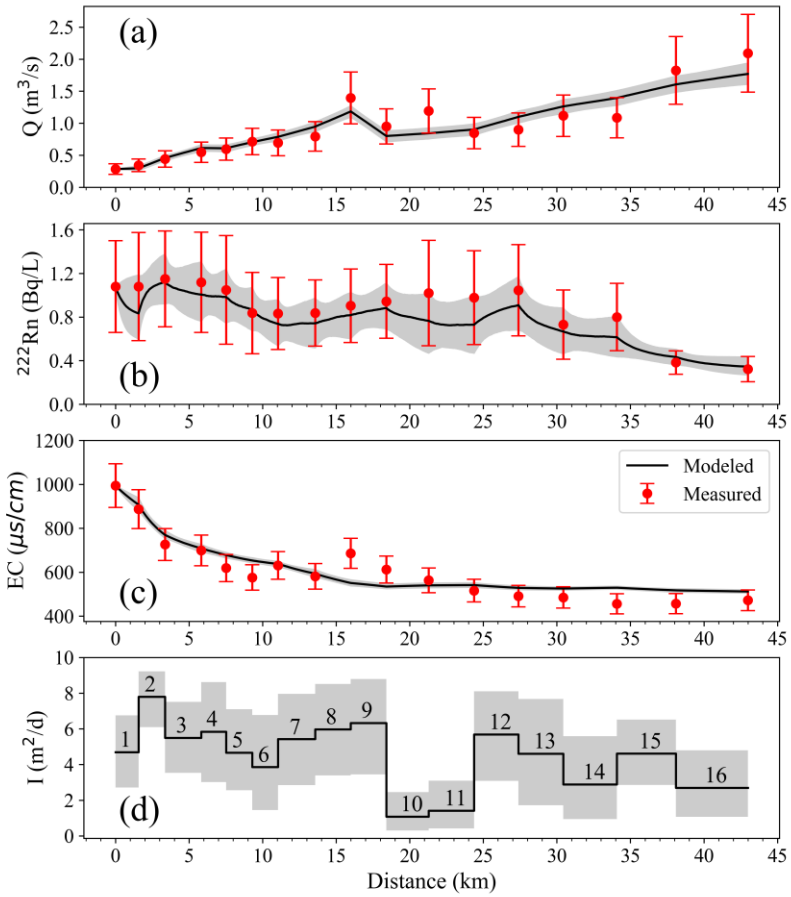


Figure 2. Reach-scale water and mass balance modeling results of (a) stream flow rates (*Q*), (b) ^{222}Rn activities, (c) EC, and the resultant variation in (d) groundwater discharge rates (*I*). The black lines and shaded areas show optimal modeling results (50th percentile) and uncertainty bounds (16th-84th percentile) derived from the MCMC simulation, respectively. The red dots are the field measured values and the error bars show the relevant uncertainties. The stream reach numbers are annotated above the line segments in (d).

Model parameters are defined in SI Table S2. Parameters E, θ and λ were assumed to be constant. For each stream reach, the upstream and downstream sampling sites were used to calculate w, d, and C_{gw}. There are three small irrigation canals along the Hailiutu River where we did not measure the ^{222}Rn activities and EC. We assumed that the ^{222}Rn activities and EC in the irrigation canals were the same as those of the nearest stream sampling site ($C_{Tri}=C$). This assumption is reasonable as these values were only used to account for water and mass losses

from the study stream. Q_0, C_0 at the first sampling site (Hailiutu-01 in SI Table S1) were utilized as the boundary conditions of the longitudinal water and mass balance model.

Errors are required in the likelihood function for the MCMC simulation. We measured the Hailiutu-01, Hailiutu-02, Hailiutu-03 and Hailiutu-09 stream flow rates twice. The average relative error at these four sites were utilized as the potential error for all stream flow rates (29%). The error of the ^{222}Rn activities were the 2-sigma uncertainty derived from the CAPTURE software (https://durridge.com/). An error of 10% was assumed for EC to cover potential measurement and analytical errors as used by McCallum et al. (2012).

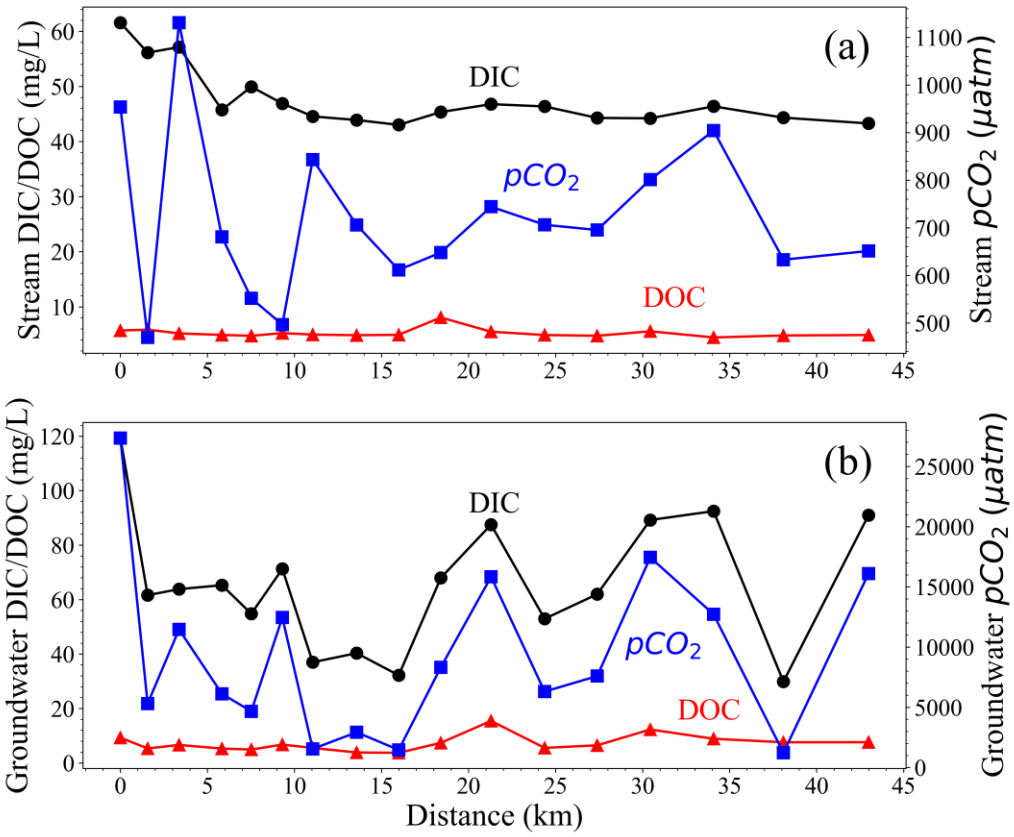
Modeled groundwater discharge rates (I) are shown in Figure 2d, while other calibrated parameters (k, h, γ and t_h) are depicted in SI Figure S1. The reach-scale water and mass balance modeling results (black lines in Figure 2a-c) agree with the field measurements reasonably well (for the most optimal case, the likelihood is -21.56, the root mean square errors are 0.18 m^3/s, 0.126 Bq/L and 55 μs/cm for Q, ^{222}Rn activities and EC, respectively). The modeling results indicate that the groundwater discharge occurred along the entire stream other than concentrating on some local areas, and I varied between 1.08 and 7.80 m^2/d with the mean ± 1 standard deviation at 4.57 ± 1.81 m^2/d. The highest and lowest I occurred at Reach 2 and Reach 10, respectively. The uncertainty of I is approximately 2 m^2/d (shaded area in Figure 2d).

3.2. Longitudinal patterns of carbon concentrations in stream and groundwater

Stream DIC concentrations show a slightly decreasing trend from 62 mg/L at the upstream end to 43 mg/L at the downstream end (Figure 3a). In comparison, groundwater DIC concentrations (66 ± 24 mg/L) fluctuated more strongly than those of stream water (48 ± 5 mg/L)

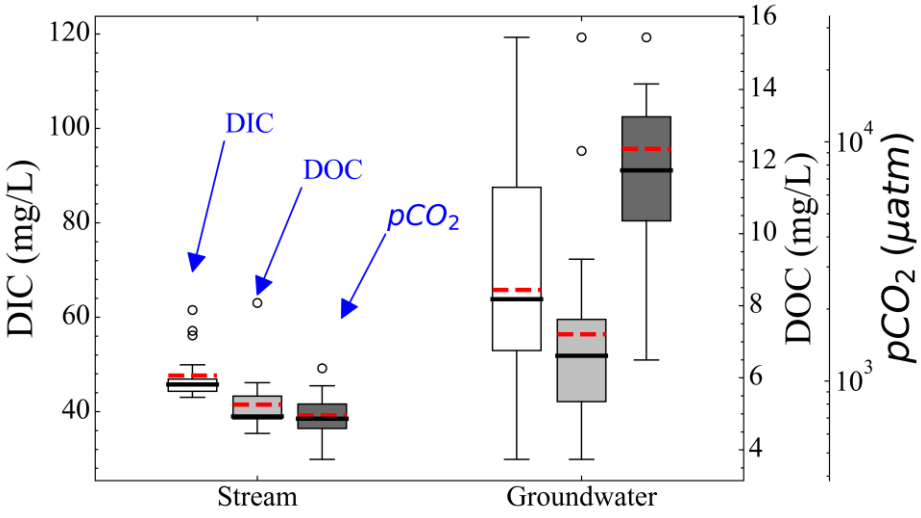
(Figure 3). Notably, DIC was the main carbon species in both the stream and the adjacent groundwater, because the DIC concentrations were approximately nine times higher than DOC concentrations in both the stream and groundwater (ANOVA, n = 34, F = 1012 and 97, respectively, both p values < 0.0001). Stream and groundwater DOC concentrations were relatively constant along the stream with the values at 5 ± 1 and 7 ± 3 mg/L, respectively. Both the stream and the adjacent groundwater were supersaturated with CO_2 with pCO_2 at 719 ± 168 μatm and 9,343 ± 7,050 μatm, respectively, when compared with the average atmospheric pCO_2 of 390 μatm. Furthermore, groundwater pCO_2 correlates well with groundwater DIC (Figure 3b, $R^2 = 0.91$, $p < 0.0001$).

Overall, the DIC, DOC and CO_2 concentrations in the groundwater were significantly higher than those in the stream (Figure 4, ANOVA, n = 34, F = 9.01, 6.70 and 25.42, respectively, all p values < 0.05). Particularly, pCO_2 in the groundwater was an order of magnitude higher than that in the stream with the mean values at 9,343 and 719 μatm, respectively. We also found that DIC concentrations and pCO_2 in the riparian groundwater were higher than those in the groundwater from the wells (SI Table S3).



359

360 **Figure 3.** Spatial variations in DIC, DOC and pCO_2 along (a) the Hailiutu River and (b) the adjacent
361 groundwater.



362

Figure 4. The comparison of DIC, DOC and pCO_2 in the Hailiutu River (n = 17) to those in the adjacent groundwater (n = 17). Boxes indicate median and interquartile range, whiskers show the maximum and minimum values, dots are outliers from the whiskers, and red dashed lines represent mean values.

3.3. Hydrogeochemical processes after groundwater discharges to stream

pCO_2 and IAP/K (calcite) in the groundwater are higher and lower than the corresponding values in the stream, respectively (Figure 5, ANOVA, n = 34, F = 25.42 and 60.46, respectively, both p values < 0.001). The stream was generally supersaturated with calcite with the IAP/K (calcite) of 11.45 ± 4.99 (Range: 6.31~27.54). The modeled results (blue dashed curve in Figure 5) indicate that the calcite saturation (IAP/K) increased significantly after the CO_2-rich groundwater discharged to the stream.

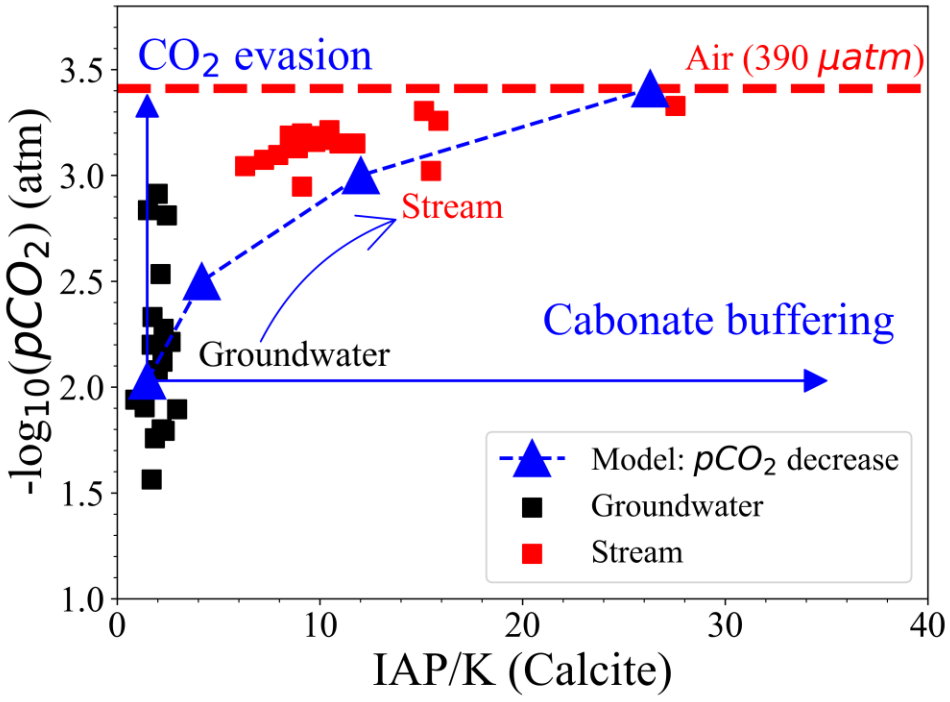


Figure 5. The hydrogeochemical processes after the groundwater (black squares) discharged to the stream (red squares). IAP/K(Calcite) was derived from the PHREEQC modeling. The upward arrow indicates the CO_2 evasion process, while the rightward arrow shows the carbonate buffering process (i.e., CO_2^* was transformed

into HCO_3^-), thereby causing the supersaturation of calcite. The blue triangles are the modeled results when groundwater re-equilibrates with the air of $-\log_{10}(pCO_2)$ (atm) at 2.03 (i.e., 9,343 μatm, the average pCO_2 of the 17 groundwater samples in our study), 2.5, 3.0, 3.41 (i.e., 390 μatm, the atmospheric pCO_2), respectively. The model parameters used in the PHREEQC simulation are defined in SI Table S4.

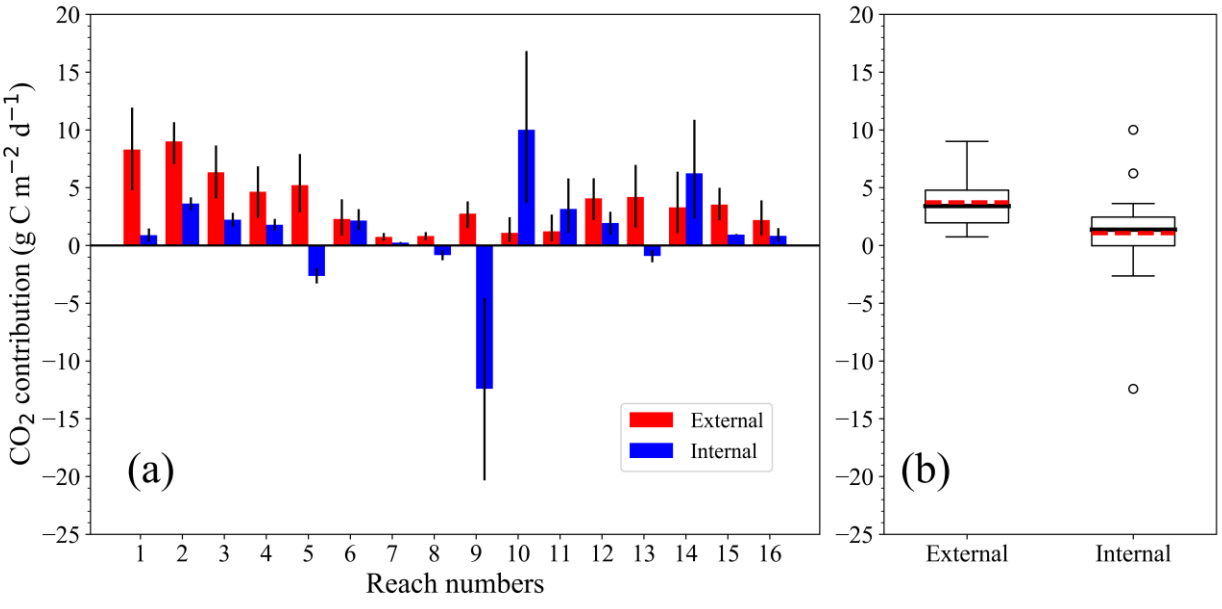
3.4. Terrestrial carbon export and stream CO_2 evasion

The measured data for quantifying the reach-scale carbon budget are listed in SI Table S3, and these results are depicted in Figure 6-8. The comparison between external and internal CO_2 contributions indicates that the external CO_2 input was higher than the net internal CO_2 production ($F_{gw}^{CO_2}$: 3.73 ± 2.52 g C m^{-2} d^{-1}, $F_m^{CO_2}$: 1.08 ± 4.66 g C m^{-2} d^{-1}, Figure 6). It should be noted that the net internal CO_2 production at all the stream sections except Reaches 5, 8, 9 and 13 made positive contribution to the stream CO_2 balance (Figure 6a). Since DIC is the main carbon species in both the groundwater and the stream as discussed above, the terrestrial carbon export is primarily in the form of DIC. The reach-scale terrestrial DIC export (F_{gw}^{DIC}, the product of the groundwater DIC concentrations and *I*) was 48.78 ± 28.78 g C m^{-2} d^{-1}, and varied between 12.20 and 111.13 g C m^{-2} d^{-1} (Figure 7a). *I* at Reach 2 was the highest (Figure 2d), and F_{gw}^{DIC} was also the highest (Figure 7a). Conversely, where *I* was limited (e.g., Reaches 10 and 11), F_{gw}^{DIC} was also constrained (Figure 7a).

Notably, both the stream and the groundwater were high in pH (8.50 ± 0.10 and 7.60 ± 0.25, SI Table S3) and alkalinity (3.98 ± 0.46 and 5.04 ± 1.71 meq/L, SI Table S3). Thus, carbonate buffering plays a significant role in regulating the stream CO_2 pool in our study (Duvert et al., 2019; Stets et al., 2017). The CO_2 mass balance results show that most reaches (except Reaches 8 and 9) had positive $F_b^{CO_2}$ values (Figure 7b). This indicates that most CO_2^* was transformed

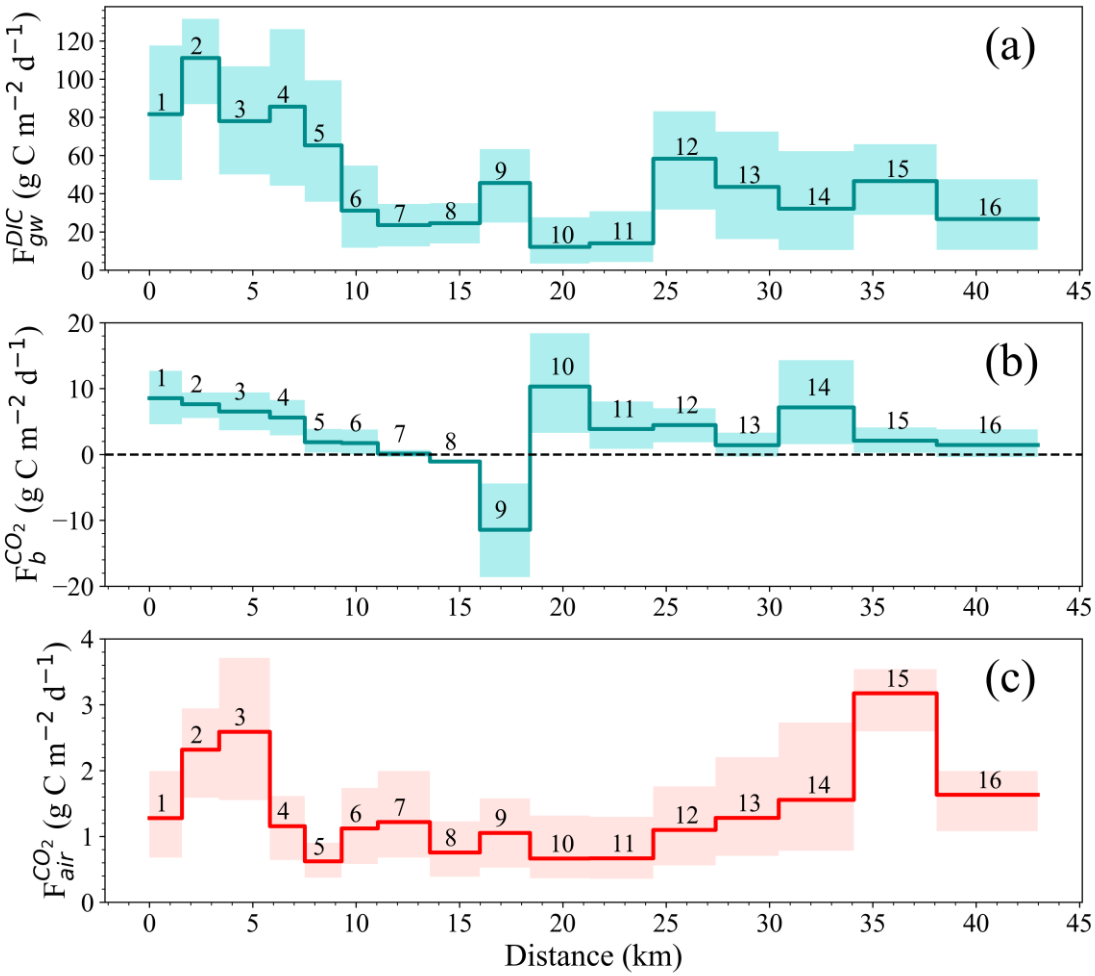
399 into HCO_3^- after the CO_2-rich groundwater discharged to the stream and the carbonate buffering
400 inhibited the stream CO2 evasion. Furthermore, we found $F_b^{CO_2}$ was positively correlated with
401 $F_m^{CO_2}$ (SI Figure S2), and $F_b^{CO_2}$ is generally higher than $F_{air}^{CO_2}$ with the average values of 3.15 and
402 1.39 g C m^{-2} d^{-1} (Figure 7b and 7c), respectively.

403 Our model calculation based on Equation (9) shows that $F_{air}^{CO_2}$ varied strongly along the
404 stream (1.39 ± 0.73 g C m^{-2} d^{-1}, range: 0.62~3.18 g C m^{-2} d^{-1}, model B in Figure 8). $F_{air}^{CO_2}$ was
405 also derived from an empirical model (model A in Figure 8, SI Text S2) with the values at 1.79 ±
406 1.25 g C m^{-2} d^{-1} (range: 0.36~4.16 g C m^{-2} d^{-1}). This comparison indicates that our model for
407 calculating $F_{air}^{CO_2}$ performed reasonably well (Figure 8b). Since our K_{CO_2} values were calibrated
408 through the water and mass balance modeling, our $F_{air}^{CO_2}$ values are likely to be better than those
409 empirically derived values.



410

411 **Figure 6.** (a) The reach-scale comparison and (b) the corresponding boxplot comparison of external CO_2 input
412 ($F_{gw}^{CO_2}$)to net internal CO_2 production ($F_m^{CO_2}$). Error bars in (a) represent the uncertainties caused by
413 groundwater discharge. Boxes in (b) indicate median and interquartile range, whiskers show the maximum and
414 minimum values, dots are outliers from the whiskers, and red dashed lines represent mean values.



415

416 **Figure 7.** The spatial variation in (a) terrestrial DIC export via diffuse groundwater discharge (F_{gw}^{DIC}), (b)
417 carbonate buffering transformation within the stream ($F_b^{CO_2}$) (positive values mean that CO_2^* is transformed
418 into HCO_3^-, and vice versa), and (c) stream CO_2 evasion rate ($F_{air}^{CO_2}$) along the stream. The shaded areas
419 around each line represent the uncertainty bounds. Numbers above line segments are stream reach numbers.

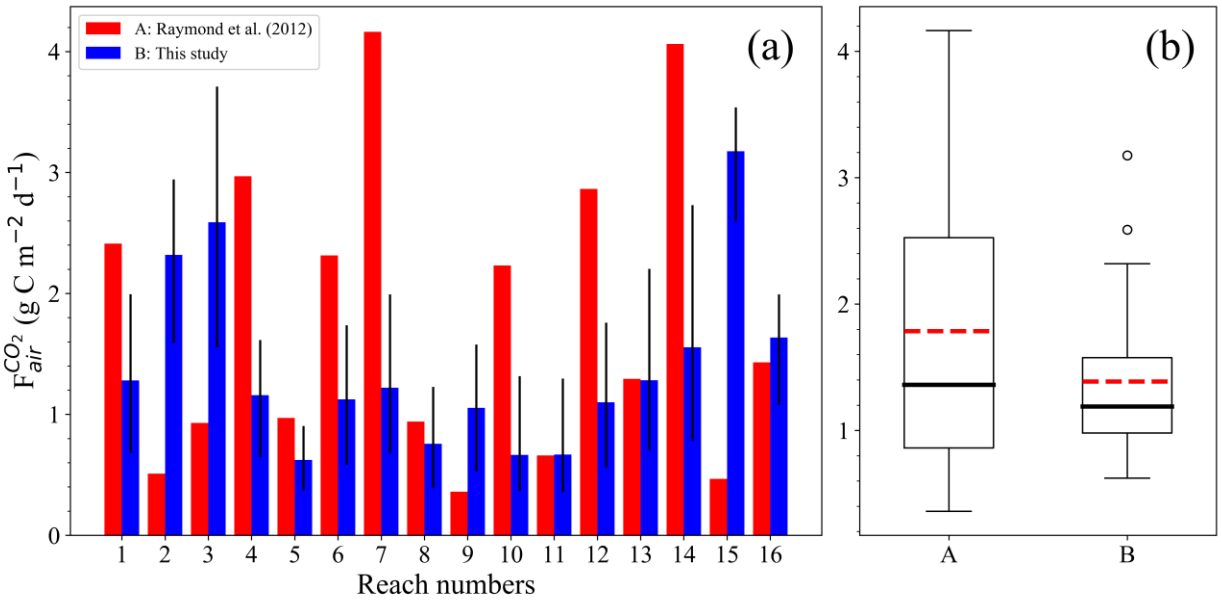


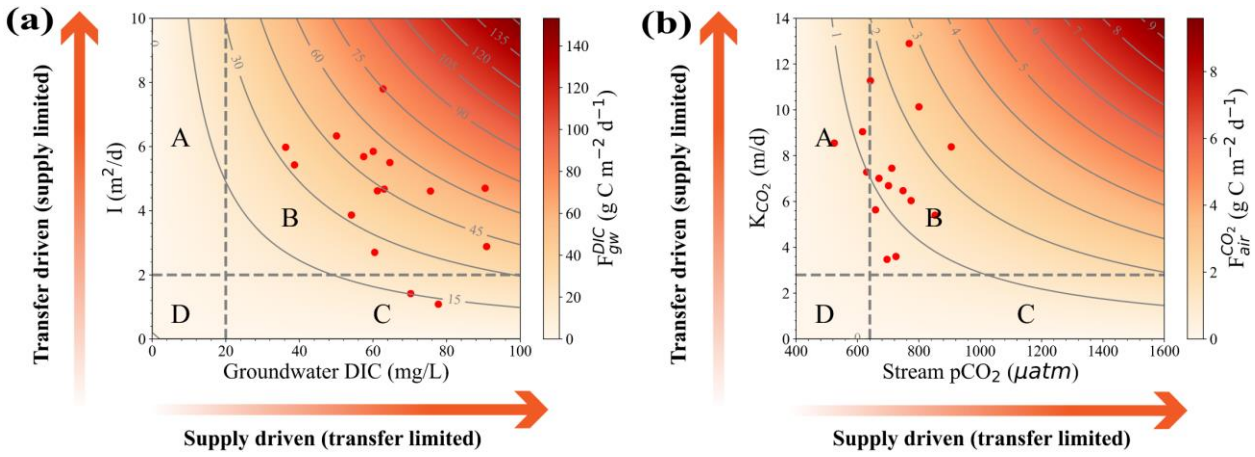
Figure 8. (a) Comparison of reach-scale stream CO_2 evasion rates between an empirical model (model A, Equation (7) in Raymond et al. (2012), SI Text S2) and our study (model B). (b) The statistical comparison between model A and model B. Error bars in (a) represent the uncertainty caused by the uncertainty of ^{222}Rn gas transfer velocity. Boxes in (b) indicate the medians and interquartile ranges, whiskers show the maximum and minimum values, dots are outliers from the whiskers, and the red dashed lines represent the mean values.

3.5. Potential drivers for terrestrial carbon export and release

Both the terrestrial DIC export and the stream CO_2 evasion can be controlled by either carbon transfer (i.e., groundwater discharge rate and CO_2 gas transfer velocity, Zone A in Figure 9) or carbon supply (i.e., groundwater DIC concentration and stream pCO_2, Zone C in Figure 9). The reaches located at Zone B in Figure 9 are hotspots for carbon fluxes and driven by both the transfer and the supply, whereas the reaches located in Zone D are limited by both the transfer and the supply and so are not important for carbon fluxes. In our study, most reaches are hotspots (located at Zone B in Figure 9a) for terrestrial DIC export except Reaches 10 and 11 (limited by groundwater discharge, Figure 2d). Stream CO_2 evasion rates are mainly located close to the

435 threshold for dividing Zone A and Zone B in Figure 9b, indicating that the carbon fluxes are
436 driven by the transfer but limited by the supply.

437 Terrestrial DIC export to headwater streams is mainly controlled by groundwater discharge
438 and groundwater DIC concentrations (Horgby et al., 2019; Leith et al., 2015; Lupon et al., 2019;
439 Öquist et al., 2009; Öquist et al., 2014). In our study, we found that the terrestrial DIC export is
440 positively correlated with the groundwater discharge, but no significant correlation between the
441 terrestrial DIC export and the groundwater DIC concentration (Figure 10a and 10c). In
442 comparison, the stream CO_2 evasion is positively correlated with both the CO_2 gas transfer
443 velocity and stream pCO_2, with the former more significant than the latter (Figure 10b and 10d).



444

445 **Figure 9.** The main control factors on (a) terrestrial DIC export (F_{gw}^{DIC}) and (b) stream CO_2 evasion ($F_{air}^{CO_2}$).
446 We utilized the mean reach distance (2.69 km), surface area (17,571 m^2), and stream water temperature
447 (14.4 ℃) in our study to estimate the isolines (grey solid lines) for terrestrial DIC export and stream CO_2
448 evasion. The red dots represent the 16 stream reaches. The carbon fluxes can be driven by either carbon
449 transfer (A), carbon supply (C), or both (B). Hotspots of carbon fluxes (B) can then occur when the supply is
450 sufficient and the transfer is fast. Conversely, both the supply and the transfer limited zones (D) are less
451 significant for carbon fluxes. The threshold values (grey dashed lines) for dividing these zones (A-D) are
452 somewhat subjective and based on plausible minimum values of carbon fluxes at hotspots identified through

the literature review (Butman and Raymond, 2011; Liu and Raymond, 2018; Marx et al., 2017; McCallum et al., 2012; Raymond et al., 2013).

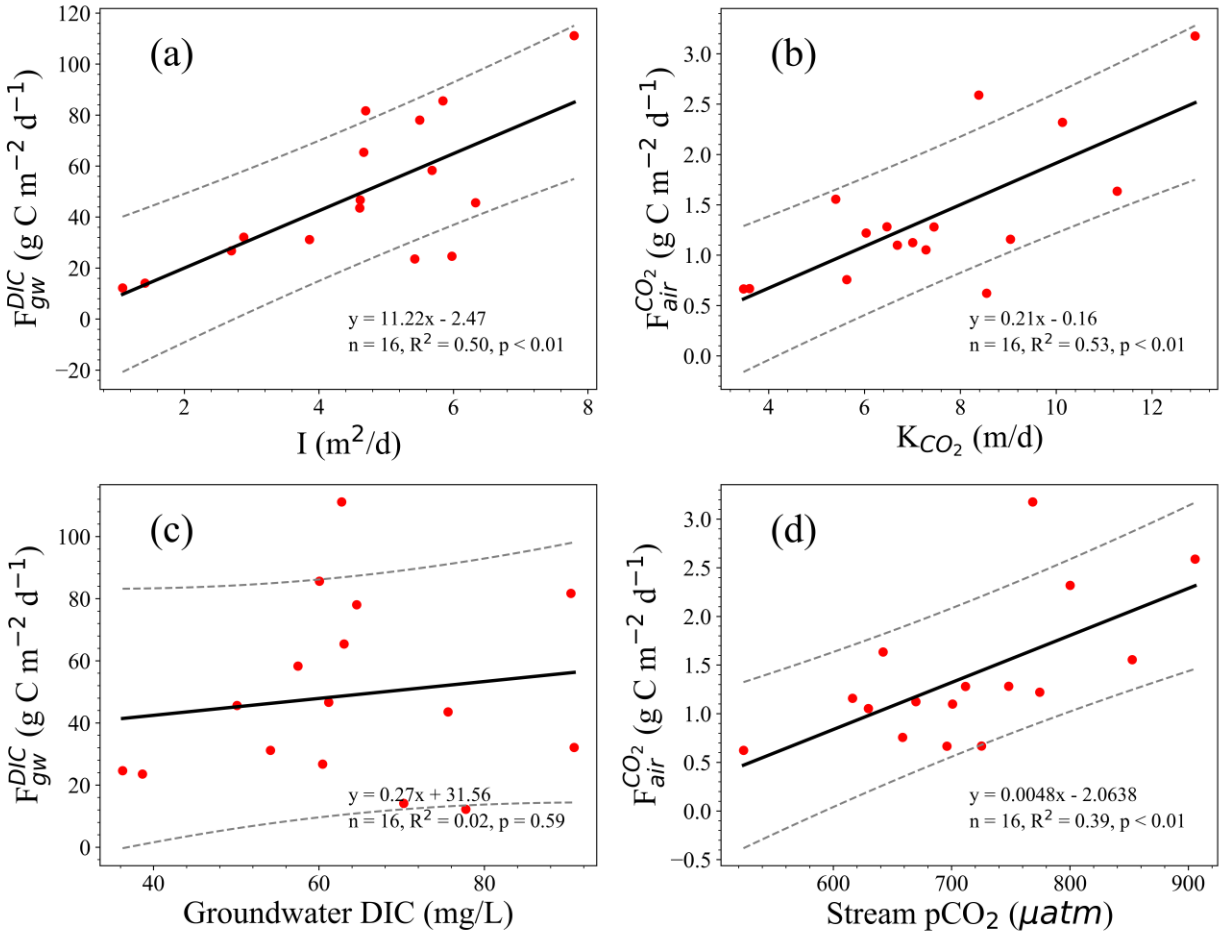


Figure 10. Correlations between (a) terrestrial DIC export (F_{gw}^{DIC}) and groundwater discharge (*I*), (b) stream CO_2 evasion ($F_{air}^{CO_2}$) and CO_2 gas transfer velocity (K_{CO_2}), (c) terrestrial DIC export and groundwater DIC concentration, and (d) stream CO_2 evasion and stream pCO_2. Black lines are the linear regression results, while the grey dashed lines are the 10% and 90% confidence intervals.

4. Discussion

4.1. Diffuse groundwater discharge as a significant driver for terrestrial DIC export

Since our field survey was conducted in the dry season, the steady increase in the stream flow rate was largely attributed to the diffuse groundwater discharge other than the precipitation nor the surface water inflow. This has been supported by the presence of the relatively high stream ^{222}Rn activities and the gradual decline in the stream EC along the stream. In our studied catchment, the stream bank and streambed were composed of highly conductive and homogeneous sand (Yang et al., 2012; 2014). Focused groundwater discharge via preferential flow paths is unlikely to occur in such an environment. Rather, the groundwater discharge is more likely to occur in a diffusive pattern along the stream (Duvert et al., 2018; Lupon et al., 2019).

Previous studies highlighted the control of focused groundwater discharge on stream CO_2 evasion, but failed to demonstrate the contribution from diffuse groundwater discharge (Duvert et al., 2018; Johnson et al., 2008; Lupon et al., 2019). In this study, we found that the diffuse groundwater discharge not only maintained the streamflow, but also continuously exported a considerable amount of terrestrial carbon to the stream, in particular the terrestrial DIC. As the diffuse groundwater discharge is widely existent (Cook et al., 2003; Cook et al., 2006; McCallum et al., 2012; Xie et al., 2016), it is expected to be the main driver for the terrestrial DIC export in not only our headwater stream but also many other headwater streams.

4.2. Terrestrial DIC export as the major carbon source for streams

As demonstrated by previous studies, supersaturated CO_2^* in streams and rivers is mainly derived from external input (i.e., terrestrial DIC export) or internal metabolism (Hotchkiss et al., 2015). Here, we found that the terrestrial DIC export via the diffuse groundwater discharge played a more significant role in contributing CO_2^* to the studied headwater stream compared

with the internal metabolism, which is consistent with existing studies (Duvert et al., 2018; Hotchkiss et al., 2015; Öquist et al., 2009; Winterdahl et al., 2016). More importantly, our study indicates that the riparian zone had a stronger impact on the terrestrial DIC export and stream CO_2 evasion because of the higher DIC and CO_2 concentrations in the riparian groundwater than those in the groundwater from the domestic wells (Hope et al., 2004; Leith et al., 2015; Lupon et al., 2019; Vidon et al., 2010). In semiarid headwater streams, the riparian zone allows for better vegetation growth than areas that are relatively far from the streams. Therefore, soil respiration is more active in the riparian zone than in the rest of the catchment, causing the higher CO_2 concentrations (Hope et al., 2004; Leith et al., 2015).

This finding was also supported by groundwater $\delta^{13}C_{DIC}$ values (-11.90 ± 1.98 ‰, see SI Table S5), which fall in the potential $\delta^{13}C_{DIC}$ range for C4 plants (corn in our case) grown in the riparian zone (Clark and Fritz, 1997). Furthermore, our $\delta^{13}C_{DIC}$ data also suggest that terrestrial DIC export is the main carbon source of stream DIC pool. After terrestrial DIC was exported to the stream, the CO_2 gas exchange between the stream and atmosphere and the internal metabolism resulted in more positive $\delta^{13}C_{DIC}$ values in stream than in groundwater (ANOVA, $n = 34$, $F = 8.64$, $p < 0.01$) (Deirmendjian and Abril, 2018).

4.3. Stream CO_2 evasion was driven by carbon transfer but limited by carbon supply

The terrestrial CO_2 export via the diffuse groundwater discharge directly sustained the stream CO_2 evasion. However, considering the high pH and high alkalinity setting in our study area, most of the terrestrial DIC exported to the stream were in the form of HCO_3^-. Thus, the transformation between CO_2^* and HCO_3^- (carbonate buffering) can also indirectly enhance or limit the stream CO_2 evasion by regulating stream CO_2 pool (conceptual model in Figure 11),

506 especially in high alkalinity streams (Duvert et al., 2019; Stets et al., 2017). Our CO_2 mass
507 balance results indicate that the carbonate buffering caused most CO_2^* to be transformed into
508 HCO_3^- after the CO_2-rich groundwater discharged to the stream, thereby increasing the calcite
509 saturation of the stream water (Figure 5) (Jacobson and Usdowski, 1975; Lorah and Herman,
510 1988; Lu et al., 2000). Although most reaches are the hotspots for the terrestrial DIC export
511 (Figure 9a), most CO_2^* loss occurred through the carbonate buffering, causing the limited carbon
512 supply for the stream CO_2 evasion. The limited CO2 evasion was supported by very close mean
513 $\delta^{13}C_{DIC}$ values of stream water and groundwater (-10.46 ‰ and -11.90 ‰, respectively, SI Table
514 S5). This CO_2 loss mechanism is attributed to the high alkalinity and pH setting in groundwater
515 and stream. This diffuse groundwater discharge pattern is different from previous studies where
516 most CO2 was emitted to the atmosphere due to focused groundwater discharge (Duvert et al.,
517 2018; Johnson et al., 2008). Thus, the stream CO_2 evasion in our study catchment was driven by
518 the carbon transfer but limited by the carbon supply (most reaches have high CO_2 gas transfer
519 velocity but relatively low stream pCO_2).

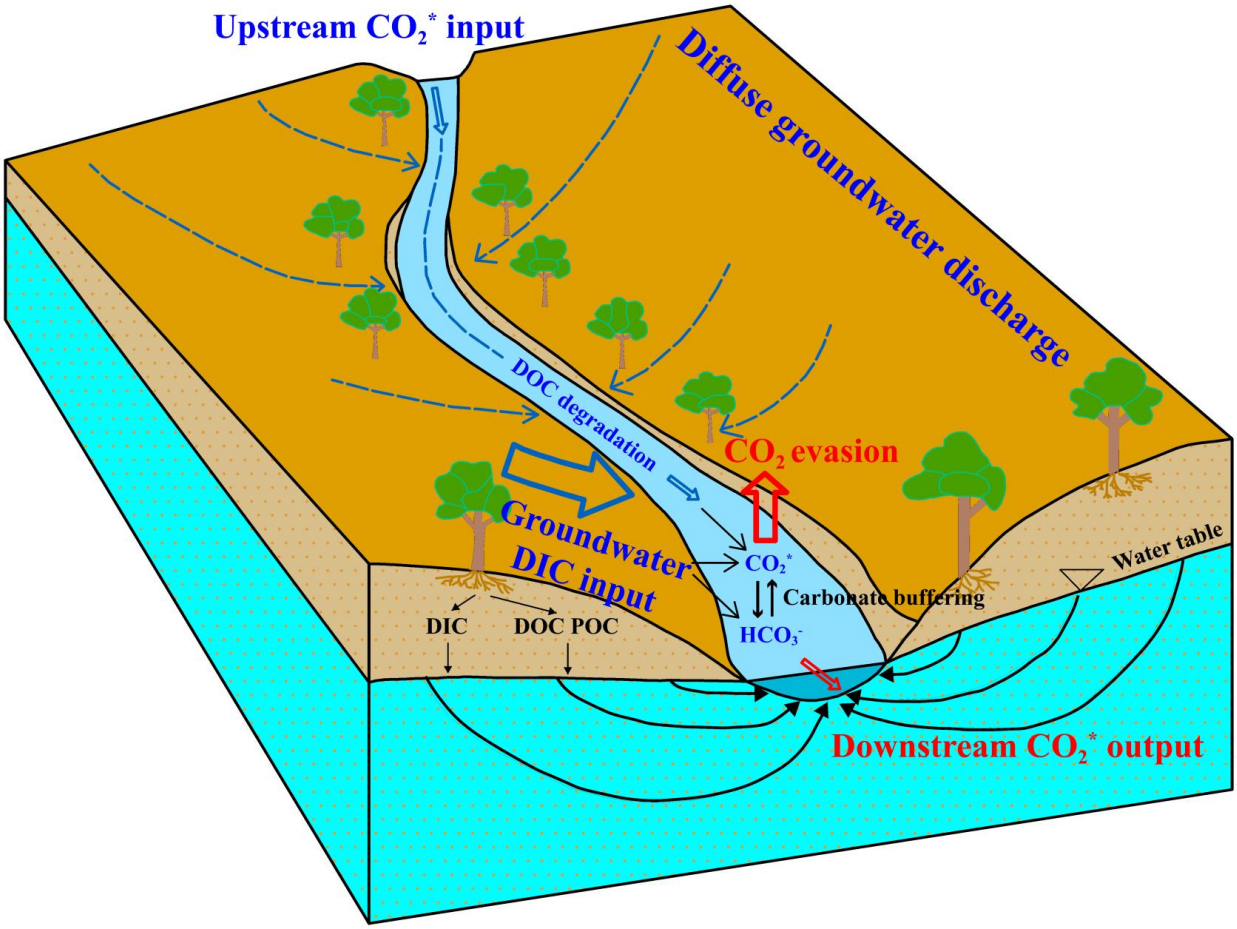


Figure 11. The conceptual model demonstrates that diffuse groundwater discharge dominates terrestrial DIC export, and carbonate buffering process regulates stream CO_2 pool through transformation between CO_2^* and HCO_3^-. This carbonate buffering process can either enhance (i.e., HCO_3^- transformed into CO_2) or limit (i.e., CO_2 transformed into HCO_3^-) stream CO_2 evasion. In our study stream, the carbonate buffering largely limited the stream CO_2 evasion.

4.4. Implication for CO_2 evasion from semiarid headwater streams

Previous studies quantifying headwater stream CO_2 evasion focused mostly on peatland streams (Billett and Harvey, 2013; Hope et al., 2001; Long et al., 2015) and forested streams (Aho and Raymond, 2019; Jones and Mulholland, 1998; Marx et al., 2018; Öquist et al., 2009; Wallin et al., 2013) due to high internal production in these environments. However, headwater

streams in arid and semiarid regions are likely to be a significant "transfer station" for terrestrial carbon export and release to the atmosphere because of their close connection with terrestrial ecosystem through diffuse groundwater discharge. Our reach-scale carbon budget results indicate that stream CO_2 evasion rates (0.62-3.18 g C m^{-2} d^{-1} in our study) could be comparable to the average CO_2 efflux of conterminous US streams (2.42-10.98 g C m^{-2} d^{-1}) (Butman and Raymond, 2011). Comparison in headwater stream CO_2 evasion rates between our study, peatland and forested headwater streams suggests that headwater stream CO_2 evasion from arid and semiarid regions may be as important as that from humid regions (SI Table S6).

Former studies pointed out semiarid headwater streams may also be hotspots for CO_2 evasion (Gómez-Gener et al., 2015; Schiller et al., 2014). Our CO_2 evasion rates are higher than those reported in these studies (Mediterranean rivers, 0.20-2.63 and 0.49-1.15 g C m^{-2} d^{-1}, respectively). We attributed the higher stream CO_2 evasion rates in our study to the greater diffuse groundwater discharge rates and higher CO_2 gas transfer velocities (transfer driven). As our survey was conducted during the dry season, our results may represent the lower bound of the Hailiutu River CO_2 evasion rates. Larger CO_2 evasion rates are expected to occur when groundwater discharge is higher during the wet season.

5. Conclusions

In this study, we discovered that headwater streams in arid and semiarid areas are significant sources of CO_2 to the atmosphere. These understudied streams received a considerable amount of dissolved CO_2 from terrestrial ecosystems via diffuse groundwater discharge. Interestingly, a large portion of dissolved CO_2 was not directly and quickly emitted to the atmosphere, but transformed into HCO_3^- through carbonate buffering. The stream CO_2

553 evasion was driven by fast carbon transfer processes between terrestrial ecosystems, stream and
554 atmosphere, but limited by relatively small carbon supply in stream due to the inhibition of
555 carbonate buffering. To the best of our knowledge, previous studies seldom integrated the vital
556 contribution of terrestrial carbon export via diffuse groundwater discharge to headwater stream
557 carbon budget, which may underestimate headwater stream CO_2 evasion rates (Duvert et al.,
558 2018; Hotchkiss et al., 2015; Johnson et al., 2008; Lupon et al., 2019; Marx et al., 2017; Öquist
559 et al., 2009). Our analysis highlights the importance of the diffuse groundwater discharge on
560 terrestrial DIC export and stream CO_2 evasion at the regional scale.

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562 The authors confirm that there is no conflict of interest. Additional supporting information
563 can be found in the supporting information (SI). All research data used in this study are available
564 and can be found at figshare repository (https://doi.org/10.6084/m9.figshare.12295769.v1). This
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[Water Resources Research]

Supporting Information for

Diffuse Groundwater Discharge Dominates Terrestrial Dissolved Inorganic Carbon Export and CO_2 Evasion From a Semiarid Headwater Stream

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Contents of this file

Additional Supporting Information (Files uploaded separately)

Introduction

Text S1 demonstrates the calculation of pCO_2 and DIC in our study. Text S2 shows how we derived the empirical stream CO_2 evasion rate. Figure S1 shows the calibrated water and mass

balance parameters derived from MCMC modeling. Figure S2 depicts the relationship between carbonate buffering transformation and net internal CO_2 production. Table S1-S3 are the measured data and parameters for water and carbon balance calculation. Table S4 shows the initial parameters used for PHREEQC simulation. Table S5 is the measured carbon isotopic data. Table S6 is the comparison of different headwater stream CO_2 evasion rates. All measurements were obtained between 9 and 14 May 2019 (dry season), and according to the methods described in the manuscript. Table S7 is all the related data used in this study, and uploaded separately as excel file.

Text S1. pCO_2 and DIC calculation

Dissolved inorganic carbon (DIC) is defined as the sum of CO_2^* (i.e., $CO_{2(aq)}$ + H_2CO_3), HCO_3^- and CO_3^{2-}. The relative proportion of the three inorganic carbon species (partition coefficient) depends on pH and temperature in water

$$\alpha_0 = \left(1 + \frac{K_1}{\left[H^+\right]} + \frac{K_1 K_2}{\left[H^+\right]^2}\right)^{-1} \quad \text{(S1)}$$

$$\alpha_1 = \left(1 + \frac{\left[H^+\right]}{K_1} + \frac{K_2}{\left[H^+\right]}\right)^{-1} \quad \text{(S2)}$$

$$\alpha_2 = \left(1 + \frac{\left[H^+\right]^2}{K_1 K_2} + \frac{\left[H^+\right]}{K_2}\right)^{-1} \quad \text{(S3)}$$

where α_0, α_1, and α_2 are the partition coefficient of CO_2^*, HCO_3^- and CO_3^{2-}, respectively. $\left[H^+\right]$ is the activity of H^+ (mol/L), which equals 10^{-pH}. K_1 and K_2 are the temperature-dependent first and second dissociation constant for the dissociation of H_2CO_3, respectively. K_1 and K_2 are determined according to empirical equations from Clark and Fritz (1997)

$$-\log_{10}(K_1) = 1.1\times10^{-4}T^2 - 0.012T + 6.58 \quad \text{(S4)}$$

$$-\log_{10}(K_2) = 9\times10^{-5}T^2 - 0.0137T + 10.62 \quad \text{(S5)}$$

where T is the temperature in water (°C).

Alkalinity is defined as

$$\begin{aligned} Alkalinity &= \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[OH^-\right] - \left[H^+\right] \\ &= \alpha_1 DIC + 2\alpha_2 DIC + \left[OH^-\right] - \left[H^+\right] \end{aligned} \quad \text{(S6)}$$

Rearranging Equation (S6) leads to the expression of DIC

$$DIC = \frac{1}{\alpha_1 + 2\alpha_2}\left(Alkalinity + \left[H^+\right] - \left[OH^-\right]\right) \quad \text{(S7)}$$

when pH is 5~9 and $Alkalinity$ > 1 meq/L, $\left[H^+\right] - \left[OH^-\right]$ can be neglected and the expression of DIC can be simplified into

$$DIC = \frac{1}{\alpha_1 + 2\alpha_2} Alkalinity \quad \text{(S8)}$$

where the unit of $Alkalinity$ is meq/L, α_1 and α_2 can be derived from Equation (S2) and (S3), respectively, and the unit of DIC is mmol/L.

According to Plummer and Busenberg (1982), the partial pressure of CO_2 (pCO_2, atm) can be calculated by (all the variables are in mol/L)

$$pCO_2 = \frac{HCO_3^- \times H^+}{K_H \times K_1} \quad \text{(S9)}$$

where HCO_3^- is the activity of bicarbonate and can be determined by multiplying the DIC (mol/L) and the partition coefficient α_1, H^+ equals 10^{-pH}, and K_1 can be derived through Equation (S4). K_H is the Henry's law constant (mol/L/atm), and can be derived from Clark and Fritz (1997)

$$-\log_{10}\left(K_H\right) = -7\times10^{-5}T^2 + 0.016T + 1.11 \quad \text{(S10)}$$

where T is the temperature in water (℃).

Text S2. Empirical stream CO_2 evasion model

We utilized Equation (7) in Raymond et al. (2012) to estimate the normalized K_{CO_2} with a Schmidt number of 600 (k_{600})

$$k_{600} = 4725 \times (VS)^{0.86} \times Q^{-0.14} \times D^{0.66} \quad \text{(S11)}$$

where V, S, Q, and D are the stream velocity (m/s), slope (dimensionless), stream flow rate (m^3/s), and stream depth (m). S is derived from Digital Elevation Model in our study area, and the other variables (V, Q, and D) are field measured values.

Empirical K_{CO_2} can be calculated by

$$K_{CO_2} = k_{600} \times \left(\frac{Sc_{CO_2}}{600} \right)^{-0.5} \quad \text{(S12)}$$

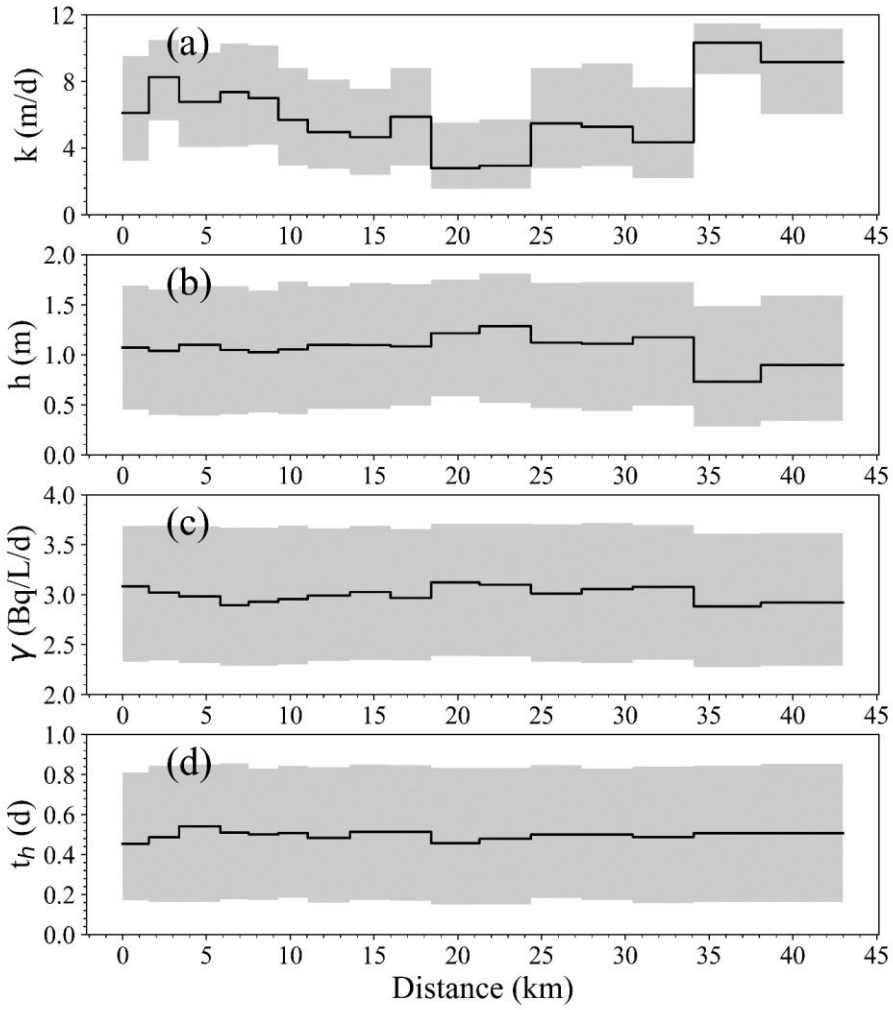
where Sc_{CO_2} is the Schmidt number of the field measured stream temperature (°C) and derived from Raymond et al. (2012)

$$Sc_{CO_2} = 1742 - 91.24T + 2.208T^2 - 0.0219T^3 \quad \text{(S13)}$$

The stream CO_2 evasion rate ($F_{air}^{CO_2}$, g C m^{-2} d^{-1}) of the empirical model was calculated by

$$F_{air}^{CO_2} = \left(pCO_{2\,aq} - pCO_{2\,air} \right) \times K_H \times K_{CO_2} \times 12 \div 1000 \quad \text{(S14)}$$

where $pCO_{2\ aq}$ and $pCO_{2\ air}$ are the CO_2 partial pressure in the stream and the air (μatm), respectively. We assumed that the atmospheric pCO_2 was 390 μatm. K_H and K_{CO_2} are the temperature-dependent Henry's Law constant (mol/L/atm) derived from Equation (S10) and the CO_2 gas transfer velocity (m/d) derived from Equation (S12).



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93 **Figure S1.** Longitudinal spatial variability of the optimal model parameters and
94 corresponding uncertainty bounds (16th-84th percentiles) including (a) ^{222}Rn gas transfer
95 velocity (*k*), (b) hyporheic zone thickness (*h*), (c) ^{222}Rn production rate in the hyporheic zone (γ
96), and (d) hyporheic zone residence time (t_h) derived from the evolutionary Markov chain
97 Monte-Carlo simulation.

98

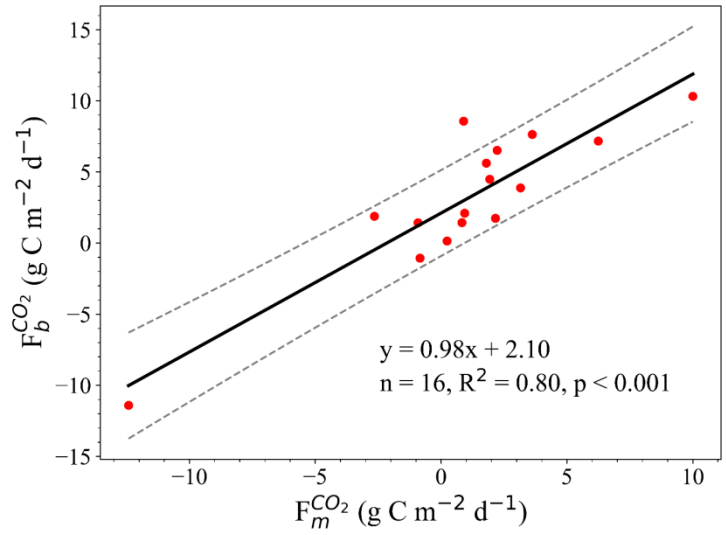

Figure S2. The positive relationship between carbonate buffering transformation ($F_b^{CO_2}$) and net internal CO_2 production ($F_m^{CO_2}$). The black line is the linear regression result, while the grey dashed lines are the 10% and 90% confidence intervals.

	Distance	Flow rate Q	Width w	Depth[a] d	Velocity[b] v	Stream		Groundwater	
-	km	m^3/s	m	m	m/s	EC(μS/cm)	^{222}Rn(Bq/L)	EC(μS/cm)	^{222}Rn(Bq/L)
Hailiutu-01	0	0.283	6.3	0.19	0.234	994	1.080	659	4.830
Hailiutu-02	1.57	0.343	4.1	0.24	0.347	887	1.080	640	5.340
Hailiutu-03	3.37	0.440	4.7	0.49	0.190	726	1.150	396	6.442
Hailiutu-04	5.83	0.547	4.4	0.42	0.294	699	1.119	648	4.922
Hailiutu-05	7.52	0.596	3.8	0.33	0.477	619	1.049	396	5.337
Hailiutu-06	9.30	0.713	5.2	0.41	0.338	576	0.837	609	5.077
Hailiutu-07	11.05	0.693	8.2	0.15	0.578	631	0.832	376	5.470
Hailiutu-08	13.57	0.793	9.6	0.11	0.735	581	0.837	375	4.797
Hailiutu-09	15.99	1.394	8.0	0.19	0.930	686	0.904	338	5.707
Hailiutu-10	18.41	0.949	5.9	0.22	0.727	612	0.944	558	5.707
Hailiutu-11	21.29	1.191	7.9	0.21	0.705	563	1.020	679	4.020
Hailiutu-12	24.37	0.845	6.2	0.17	0.808	516	0.978	420	6.636
Hailiutu-13	27.39	0.898	5.0	0.19	0.956	491	1.046	517	4.070
Hailiutu-14	30.44	1.116	11.0	0.13	0.786	485	0.731	488	4.350
Hailiutu-15	34.08	1.085	5.3	0.21	0.958	456	0.800	628	4.755
Hailiutu-16	38.09	1.824	6.8	0.31	0.869	457	0.383	241	4.482
Hailiutu-17	42.98	2.093	5.4	0.34	1.156	472	0.322	674	4.447

Table S1. Field measured values for reach-scale water and mass balance modeling. [a] *d* equals the cross-section area divided by the stream width. [b] *v* equals the stream flow rate divided by the cross-section area. The Bulang River (Q, EC and ^{222}Rn activity are 0.076 m^3/s, 433 μS/cm and 0.767 Bq/L, respectively) flows into the Hailiutu River at the distance of 14 km. Three irrigation diversion points exist between Hailiutu-01~Hailiutu-02, Hailiutu-04~Hailiutu-05, and Hailiutu-09~Hailiutu-10, and their outgoing fluxes are 0.071, 0.116, and 0.557 m^3/s, respectively.

Type	Symbol	Description	Values
Fixed[a]	E	Evaporation rate	0.005 m/d
	θ	Hyporheic zone porosity	0.38
	λ	Radioactive constant of ^{222}Rn	0.18 d^{-1}
	w	Stream width	Measured values
	d	Stream depth	Measured values
	C_{gw}	Groundwater ^{222}Rn activity (or EC)	Measured values
	C_{Tri}	Tributary ^{222}Rn activity (or EC)	Measured values
	Q_0	Incoming stream flow rate	0.283 m^3/s
	C_0	Incoming stream ^{222}Rn activity (or EC)	1.08 Bq/L (or 994 μS/cm)
Calibrated[b]	I	Groundwater discharge	0-10 m^2/d
	k	^{222}Rn gas transfer velocity	1-12 m/d
	h	Hyporheic zone thickness	0.1-2 m
	γ	^{222}Rn production rate in hyporheic zone	2-4 Bq/L/d
	t_h	Hyporheic zone residence time	0.01-1 d
Modeled	Q	Stream flow rate	-
	C	Stream ^{222}Rn activity (or EC)	-

Table S2. Model parameters for reach-scale water and mass balance modeling. [a] E usually varies in 10^{-3}-10^{-2} m/d and is negligible (Cook et al., 2003; Cook et al., 2006). θ was taken from (Ma et al., 2017). λ is a constant value of 0.18 d^{-1}. For a given stream reach, w, d, C_{gw}, and C_{Tri} are the mean values between two measurement points. [b] The calibrated parameter ranges were chosen according to literature review (Cook, 2013; Cook et al., 2006; McCallum et al., 2012; Raymond et al., 2012; Xie et al., 2016)

Measured	Temperature	pH	DO	Alkalinity	DIC	DOC	pCO_2	Ca^{2+}	Mg^{2+}	IAP/K(calcite)
	℃	-	mg/L	meq/L	mg/L	mg/L	μatm	mg/L	mg/L	-
Stream										
Hailiutu-01	14.8	8.48	10.30	5.14	61.55	5.71	954	76.50	34.38	15.49
Hailiutu-02	17.7	8.76	9.40	4.76	56.12	5.86	470	75.13	32.15	27.54
Hailiutu-03	12.1	8.36	8.71	4.74	57.13	5.18	1131	65.59	28.53	9.12
Hailiutu-04	13.3	8.49	9.17	3.82	45.75	4.91	681	67.33	27.33	10.47
Hailiutu-05	15.6	8.63	9.34	4.20	49.92	4.75	552	63.52	24.50	15.85
Hailiutu-06	15.9	8.65	9.15	3.95	46.90	5.25	497	60.84	23.12	15.14
Hailiutu-07	12.2	8.38	9.48	3.70	44.56	4.97	843	59.54	19.66	7.24
Hailiutu-08	21.5	8.50	7.67	3.68	43.90	4.86	706	57.13	18.10	11.75
Hailiutu-09	15.3	8.52	8.25	3.60	43.02	4.93	611	60.36	19.62	10.47
Hailiutu-10	9.7	8.49	9.74	3.78	45.35	8.08	648	58.74	19.16	8.51
Hailiutu-11	13.1	8.46	8.72	3.90	46.78	5.49	744	57.49	18.10	8.91
Hailiutu-12	17.2	8.50	8.40	3.88	46.37	4.89	706	57.41	17.68	10.96
Hailiutu-13	15.9	8.48	8.04	3.70	44.28	4.75	695	57.61	16.59	9.77
Hailiutu-14	14.4	8.41	8.26	3.68	44.21	5.57	801	56.96	16.86	7.94
Hailiutu-15	8.7	8.35	9.56	3.84	46.38	4.46	904	60.20	16.56	6.31
Hailiutu-16	11.7	8.50	9.37	3.70	44.33	4.81	633	59.16	17.10	9.12
Hailiutu-17	16.2	8.50	8.47	3.62	43.28	4.89	651	57.56	16.20	10.00
Groundwater										
Hailiutu-01-G	15.0	7.26	1.59	8.68	119.29	9.29	27349	80.36	46.53	1.70
Hailiutu-02-G	12.8	7.71	1.63	4.88	61.62	5.34	5304	65.99	26.45	2.29
Hailiutu-03-G	12.1	7.36	0.26	4.74	63.84	6.61	11465	57.67	13.03	0.89
Hailiutu-04-G	14.3	7.68	2.09	5.16	65.29	5.29	6117	73.69	24.88	2.63
Hailiutu-05-G	10.2	7.70	0.90	4.32	54.79	4.93	4667	60.85	17.18	1.74
Hailiutu-06-G	14.6	7.39	0.73	5.36	71.27	6.75	12454	68.75	24.36	1.35
Hailiutu-07-W	13.7	8.04	2.08	3.02	37.00	5.51	1545	46.96	12.66	2.45
Hailiutu-08-G	16.7	7.81	4.94	3.24	40.33	3.85	2927	60.02	11.92	2.14
Hailiutu-09-W	13.1	8.00	4.75	2.62	32.19	3.73	1461	36.50	12.77	1.51
Hailiutu-10-G	11.6	7.54	1.13	5.24	67.97	7.39	8320	82.99	23.21	2.00
Hailiutu-11-G	15.6	7.38	2.15	6.58	87.52	15.45	15834	95.85	27.79	2.19
Hailiutu-12-G	14.4	7.57	1.00	4.12	52.95	5.53	6304	71.96	12.20	1.70
Hailiutu-13-G	13.3	7.55	2.77	4.80	61.99	6.49	7593	96.69	27.81	2.24
Hailiutu-14-G	13.8	7.33	0.25	6.60	89.22	12.30	17446	96.37	28.07	1.86
Hailiutu-15-G	9.2	7.47	0.20	7.00	92.48	8.89	12720	128.50	29.78	2.95
Hailiutu-16-G	13.9	8.05	7.37	2.44	29.87	7.61	1223	44.54	7.91	2.00
Hailiutu-17-G	14.0	7.38	1.76	6.82	91.01	7.62	16102	108.40	31.87	2.34

Table S3. Measured values for quantifying the reach-scale CO_2 budget. The Hailiutu-07-W and Hailiutu-09-W are groundwater collected from wells, while others are the riparian groundwater.

Parameters	Values
temperature	13.43 ℃
pH	7.6
pe	4
Ca^{2+}	75.06 mg/L
Mg^{2+}	22.26 mg/L
Alkalinity	5.04 meq/L

122 **Table S4.** Initial model parameters for modeling IAP/K calcite value change after the CO_2-rich
123 groundwater discharged to the stream.
124

River points	Distance	Stream		Groundwater	
		$\delta^{13}C_{DIC}$	SD	$\delta^{13}C_{DIC}$	SD
-	km	‰	‰	‰	‰
Hailiutu-01	0	-10.29	0.03	-6.15	0.09
Hailiutu-02	1.57	-9.42	0.02	-12.01	0.02
Hailiutu-03	3.37	-10.66	0.03	-12.41	0.03
Hailiutu-04	5.83	-10.52	0.04	-12.49	0.02
Hailiutu-05	7.52	-10.21	0.03	-10.91	0.05
Hailiutu-06	9.30	-10.13	0.03	-13.86	0.02
Hailiutu-07	11.05	-10.74	0.03	-11.45	0.03
Hailiutu-08	13.57	-10.70	0.05	-11.17	0.06
Hailiutu-09	15.99	-10.69	0.04	-10.01	0.06
Hailiutu-10	18.41	-10.24	0.05	-12.79	0.03
Hailiutu-11	21.29	-10.31	0.06	-13.87	0.04
Hailiutu-12	24.37	-10.49	0.07	-12.18	0.03
Hailiutu-13	27.39	-10.71	0.05	-12.47	0.03
Hailiutu-14	30.44	-10.88	0.03	-13.74	0.03
Hailiutu-15	34.08	-10.68	0.04	-12.35	0.02
Hailiutu-16	38.09	-10.76	0.03	-9.81	0.08
Hailiutu-17	42.98	-10.41	0.03	-14.56	0.03

Table S5. $\delta^{13}C_{DIC}$ values of the Hailiutu River and its adjacent groundwater. All $\delta^{13}C_{DIC}$ are reported as per mil deviation (‰) from the standard Vienna Pee Dee Belemnite (VPDB). SD represents the standard deviation. The Hailiutu-07 and Hailiutu-09 groundwater samples are groundwater collected from wells, and others are riparian groundwater.

Location	Stream type	pCO_2 (µatm)[a]	Stream CO_2 evasion (g C m^{-2} d^{-1})[a]	Reference
Scotland, UK	peatland	174-2678 (1136)	0.07-110.94 (9.33)	Long et al. (2015)
Scotland, UK	peatland	420-4500 (-)	0.26-45.88 (-)	Hope et al. (2001)
UK[b]	peatland	671-10271 (-)	0-43.2 (-)	Billett and Harvey (2013)
Connecticut, USA	forest	667-11104 (3534)	0.75-66.23 (7.40)	Aho and Raymond (2019)
Northern Sweden	forest	722-24167 (-)	3.99-17.56 (-)	Wallin et al. (2013)
Northern Sweden	forest	2015-7838 (-)	- (6.45)	Öquist et al. (2009)
Tennessee, USA	forest	360-6228 (-)	1.88-4.48 (-)	Jones and Mulholland (1998)
Northern Czech Republic	forest	450-3749 (-)	0.02-59.5 (5.90)	Marx et al. (2018)
Alps, Swiss	Alpine	309-1305 (634)	18.66-44.69 (31.20)	Horgby et al. (2019)
Northern China	Semiarid	470-1131 (719)	0.62-3.18 (1.40)	This study

Table S6. Comparison of CO_2 evasion rates from different headwater streams. [a] pCO_2 and stream CO_2 evasion rates are expressed as minimum-maximum (mean). [b] This research surveyed headwater streams in six UK peatland catchments.

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