Sensitivity of the global carbonate weathering carbon-sink flux to climate and land-use changes

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The response of carbonate weathering carbon-sink flux (CCSF) to its environmental drivers is still not well understood on the global scale. This hinders understanding of the terrestrial carbon cycle. Here, we show that there is likely to be a widespread and consistent increase in the global CCSF (ranging from +9.8% (RCP4.5) to +17.1% (RCP8.5)) over the period 1950–2100. In the coming years the increasing temperature might be expected to have a negative impact on carbonate weathering. However, the increasing rainfall and anticipated land-use changes will counteract this, leading to a greater CCSF. This finding has been obtained by using long-term historical (1950–2005) and modeled future (2006–2100) data for two scenarios (RCP4.5 and RCP8.5) for climate and land-use change in our CCSF equilibrium model. This study stresses the potential role that carbonate weathering may play in the evolution of the global carbon cycle over this century.

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Here are huge uncertainties in the response of the terrestrial carbon cycle to changing environmental conditions, such as global warming and human intervention. A growing body of evidence indicates that contemporary continental weathering processes are sensitively responding to climate change and human activities. The carbonate weathering carbon sink, about 0.2–0.7 Gt C yr⁻¹, is an important component of the global carbon budget, accounting for ~7–25% of the estimated terrestrial carbon sink. The rapid kinetics driving carbonate weathering (reaching equilibrium in three hours under experimental conditions) results in dissolution rates nearly 15 times faster than those of silicate rocks, thereby responding quickly to environmental fluctuations. The chemical weathering of carbonate rocks is a complex terrestrial process that is controlled by numerous natural and anthropogenic drivers. To summarize and simplify the mixed impacts of all drivers, a generic equation for the carbon-sink flux produced by carbonate weathering can be expressed as:

\[
\text{CCSF} = 0.5 \times 12 \times R \times \text{DIC}
\]

where CCSF (t C km⁻² yr⁻¹) is the carbonate weathering carbon-sink flux, R is runoff in m yr⁻¹, and DIC (mmol L⁻¹) is the concentration of dissolved inorganic carbon produced by carbonate weathering; 12 is the molar atomic weight of carbon, and the ratio 0.5 indicates that only one half of the HCO₃⁻ generated by carbonate weathering is of atmospheric origin.

Previous work has highlighted the diverse geochemical, climatic and ecological factors that influence both R and DIC, and thus the CCSF variations, including (amongst others) surface temperature, precipitation and runoff, net primary production of ecosystem and soil CO₂, carbonate lithologies, atmospheric CO₂ concentration, soil water content, and land-use patterns, and practices. In natural environments, these factors are tightly interwoven and controlled by climate and land cover. Recently, studies on different spatial scales have reported that climate perturbations and human interventions have dramatically changed CCSF over the past few decades. For example, in the Mississippi River basin the increased rainfall, high proportion of cultivated area, water management, and use of lime for fertilization have remarkably increased the HCO₃⁻ export flux, with a nearly 50% increase in the recent decades. In addition, the N-fertilizer uses for agricultural lands have altered the CCSF by changing the runoff patterns and affecting the soil pCO₂ through changing, amongst others, the productivity and soil properties.

Here, we explore the spatiotemporal CCSF variations on global carbonate rock outcrops by constructing a mixed-effect model that considers the interrelated impacts of climate and land-use dynamics. We provide a comprehensive interpretation of environmental impacts on CCSF fluctuations by analyzing the spatial-temporal relationship over a lengthy historical period, 1950–2005. We further predict the response of CCSF to the changes in temperature, precipitation, and land use that are presented in the Coupled Model Intercomparison Project Phase 5 (CMIP5) climate projection, adopting two of its representative scenarios, RCP4.5 and RCP8.5. CMIP5 is trying to predict future climate by estimating the amounts of atmospheric carbon dioxide that will be produced in the future. Different RCPs predicting the radiative forcing achieved by the year 2100 AD range from 2.6 to 8.5 (RCP2.6–RCP8.5) watts per square meter (Wm⁻²). Here, RCP4.5 is selected to be representative of the moderate-stabilized emission scenarios (medium CO₂ increase), whereas RCP8.5 represents the more aggressive scenarios (large CO₂ increases). Based on these choices, we attempt to predict the coupled effects of current major shifts in climate and land use on the CCSF fluctuations in the future. We reveal the sensitivity of the CCSF response to the above-mentioned drivers in different latitudinal regions and estimate the role played by carbonate rock weathering in the global carbon cycle over the remainder of this century.

Results

General overview. In this section, we show the results of our CCSF model first at a global scale and then focus on drivers that will vary at broad regional scales. As a first step, soil CO₂ pressure (pCO₂soil) is derived from (3) and ET (evapotranspiration) is based on Eq. (6) (see Methods). Accordingly, we can calculate the calcium equilibrium concentration [Ca²⁺]eq from Eq. (2) (see Methods), and the R from the difference between precipitation (P) and ET. Next, we extract the [HCO₃⁻]eq and P-ET for each grid cell located on a carbonate outcrop to obtain the CCSF by Eqs. (1) or (7) (see Methods), then sum to obtain the total carbon sink (TCS) budget using Eq. (8) (see Methods). We consider that these results can help us to estimate the feedback of CCSF response to climate and land-use change under the different future scenarios envisioned by CMIP5, thereby evaluating the role that carbonate weathering will play in the global carbon cycle in the future.

Overall fluctuation in [HCO₃⁻]eq, R, and CCSF. In Fig. 1a, b, we present the overall changes of the two fundamental CCSF drivers, [HCO₃⁻]eq and runoff (R), over the full model period. The [HCO₃⁻]eq displays steadily increasing trends of +2.1–+2.6% from 1950 to 2100. The larger [HCO₃⁻]eq increase is found in scenario RCP8.5, with about +0.0006 mmol L⁻¹ yr⁻¹ (Fig. 1a). The amplitude of global runoff variations, by contrast, is 5.7–8.0 times larger than the [HCO₃⁻]eq in the same period (Fig. 1b), with runoff increasing at around +0.18 mm yr⁻² for the historical period, a finding that is close to other published results. For the full period, runoff from carbonate rocks increases around +12.0% (RCP4.5) or +20.9% (RCP8.5). After summing these two drivers by using Eq. (8) (see Methods), we found a widespread and consistent increase in global CCSF, with values around +9.8% (RCP4.5) or +17.1% (RCP8.5) at the end of this century (Fig. 1c). As with runoff, the CCSF increase under RCP8.5 (0.0068 t C km⁻² yr⁻²) is higher than under RCP4.5 (0.0043 t C km⁻² yr⁻²).

Spatial differences in CCSF and its long-term trend. To determine which areas have experienced significant CCSF changes, particularly the areas that are mainly responsible for the calculated increases, we now consider the different geographical regions. Figure 2a summarizes the spatial annual mean CCSF at the global scale for the historic period. Mean annual CCSF ranges from 0.06 t C km⁻² yr⁻¹ in the arctic regions to...
46.42 t C km\textsuperscript{-2} yr\textsuperscript{-1} in and near the equatorial regions. We observe prominent spatial differences, with the highest CCSF occurring in tropical areas and temperate to subtropical humid areas, such as Southwest China, North America, and West Europe, whereas the lowest CCSF occurs mostly in the arctic regions and arid areas, e.g., Central Asia and Saharan Africa. We use spatial linear regression analysis to extend the spatial-temporal CCSF trends of 1950–2005 to 2006–2100. The two RCP scenarios show similar spatial CCSF trends. The strongest CCSF increases occur in most tropical regions and also in North America, West Europe, and Tibet (Fig. 2b, c). The CCSF under RCP8.5 displays similar but stronger increases in most of the areas than does RCP4.5. There are negative effects in the Middle East and North Africa, as these regions experience CCSF decrease due to a drier climate.

**Latitudinal change of CCSF, R, and [HCO\textsubscript{3}\textsuperscript{-}]\textsubscript{eq} trends.** Next, we consider spatial CCSF changes by summarizing the latitudinal variation trends of soil pCO\textsubscript{2}, CCSF, R, and [HCO\textsubscript{3}\textsuperscript{-}]\textsubscript{eq} (Fig. 3). This approach can help us to get a better understanding of how the regional CCSF responses to climate and land-use change may differ during the two periods (historical, and future under RCP4.5 and RCP8.5). As shown in Fig. 3a, the soil pCO\textsubscript{2} increasing trends in high latitudes are generally higher than those in the low latitudes. RCP8.5 scenarios show a larger pCO\textsubscript{2} increase. Figure 3b demonstrates the modelled [HCO\textsubscript{3}\textsuperscript{-}]\textsubscript{eq} which shows consistent increasing trends in cool and humid regions, such as the mid and high latitudes, but decreasing trends in lower latitudes. The more dramatic climate and land-use change scenario of the future (RCP8.5) results in a stronger negative [HCO\textsubscript{3}\textsuperscript{-}]\textsubscript{eq} trend in low latitudes, and a more positive trend in high latitudes (+0.0005 mmol L\textsuperscript{-1} yr\textsuperscript{-1} versus 0.0025 mmol L\textsuperscript{-1} yr\textsuperscript{-1}). In contrast, runoff shows rising trends generally, especially at low latitudes under the two RCP scenarios (Fig. 3c), where there is a high proportion of land-use change from forest to crop. The latitudinal CCSF variation as shown in Fig. 3d behaves like the runoff changes, showing an increase in low latitudes and being 2.85–6.25 times greater than in high latitudes. Although [HCO\textsubscript{3}\textsuperscript{-}]\textsubscript{eq} concentrations in high latitudes will experience dramatic increases, the CCSF variations in these regions are less significant when compared to their values in low latitudes. The southern mid latitudes are interesting regions, as here the changes are considerable. However, due to the small proportion of carbonate rock outcrops there (1.6%), those changes are less important for the global carbon-sink budget.

**Discussion**

From the Results section above, we have found that the coupling between natural and anthropogenic factors in different latitudinal zones results in large differences in the regional CCSF response. Thus, a better understanding of the sensitivity of carbonate weathering carbon flux to its different environmental drivers is crucial for estimating the role of CCSF in the global carbon cycle in the future. Therefore, the causes of CCSF variations under the climate and land-use change in different areas will be explored next.

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**Fig. 1 Interannual changes in relevant variables.** a [HCO\textsubscript{3}\textsuperscript{-}]\textsubscript{eq}, b R (runoff), and c CCSF (carbonate weathering carbon-sink flux) on global carbonate rock outcrops during the historical period (1950–2005) and the two future (2006–2100) scenarios (RCP4.5 and RCP8.5). All the variables display increasing trends. The historical period (black line) has the lowest CCSF variation and RCP8.5 (purple line) has the highest, indicating the substantial response of CCSF to dramatic climate change and land-use conversion.
First, we made a comparison of modelled CCSFs with observed global data. The aim here is to test the accuracy of our model estimates of CCSF changes in the different climatic and land-use patterns around the world. Table 1 compares our results to other studies to check reliability. Our modelled CCSF variations are in good agreement with a variety of independent carbonate weathering carbon-flux estimates around the world, including those from the full range of latitudinal zones and with distinct climate and land-use conditions: the difference (error) is generally <10%. Accordingly, we judge that our model reliably predicts spatial CCSF differences and can be used for future estimation.

If our global mean CCSF (4.3 t C km$^{-2}$ yr$^{-1}$) is applied to the global carbonate area (i.e., ~50% of the continent surface$^5$), we obtain a total annual global carbon sink of 0.32 Gt C yr$^{-1}$.

Temperature is a fundamental controlling factor in carbonate weathering as demonstrated by many studies$^6,9,15$. Generally, it is found that [HCO$_3^-$] variation is highly sensitive to temperature, reaching maximum values in the temperature range (10–15 °C), i.e., both very low and high temperatures will limit carbonate weathering$^6,15$. This behavior is a result of competition between thermodynamic control of the weathering and the variability of soil CO$_2$ production by soil biota$^6,15$. [HCO$_3^-$]$_{eq}$ will be positively correlated to temperature below 15 °C (Fig. 4a). In the intertropical zone, the warm temperatures may considerably decrease the [HCO$_3^-$]$_{eq}$. This is confirmed by inspecting the latitudinal trends of [HCO$_3^-$]$_{eq}$. For instance, the strongest warming trends (+0.015 °C yr$^{-1}$ to +0.023 °C yr$^{-1}$) in high latitudes will significantly increase the [HCO$_3^-$]$_{eq}$ there. In contrast, rising temperatures in low latitudes will limit the carbonate dissolution, which results in a negative [HCO$_3^-$]$_{eq}$ trend (Fig. 3b). However, according to our results, latitudinal [HCO$_3^-$]$_{eq}$ variations do not always follow temperature variations alone. The impacts of

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**Fig. 2 Spatial distribution of CCSF and its changes.**

a. Annual average CCSF (carbonate weathering carbon-sink flux) in carbonate rock outcrops for the historical period (1950–2005) and its changes for the two differing climate and land-use change scenarios, b. RCP4.5, and c. RCP8.5. Note: nearly 72% of carbonate rock outcrop is distributed in the mid and high latitudes (30°–90°) and less in the low latitudes (0°–30°).
changing precipitation and land use control soil $pCO_2$ distribution (Fig. 4d). Discussed together with temperature, these factors are also equally significant and therefore control the actual global $[\text{HCO}_3^-]_{eq}$ distribution (Fig. 4b, c). For example, we observe three $[\text{HCO}_3^-]_{eq}$ peaks on the global graph (Fig. 4a). Two of them are not located in the theoretical region of maximum dissolution ($10$–$15^\circ C$), a feature that has not received much attention. We argue that the higher $[\text{HCO}_3^-]_{eq}$ in these regions is mainly caused by changes in land-use patterns (Fig. 4c), soil $pCO_2$ (Fig. 4d), and increased precipitation (Fig. 4b).

According to our analysis, the CCSF fluctuations are strongly depending on the runoff, rather than on $[\text{HCO}_3^-]_{eq}$ or temperature (Figs. 1–3) alone. Precipitation, temperature, and vegetation cover are key factors that control runoff in many models (Fig. 4) and thus also CCSF variations.

We employ long-term spatial regression analysis to detect relationships between CCSF and the variables, runoff, and equilibrium $\text{HCO}_3^-$ concentration. Figure 5 compares the individual impacts of $[\text{HCO}_3^-]_{eq}$ and $R$ on the annual CCSF fluctuations. The results show that the regional variations of CCSF were...
typically driven by trends in runoff (global mean R² > 0.95, P < 0.001) but not [HCO₃]ₑq. The substantial variability of CCSF is responding to differing runoff, as noted also in other studies. The reason why CCSF is more sensitive to runoff than to [HCO₃⁻] has been attributed chiefly to the chemostatic behavior of the latter.

To better explain the dominant control of this behavior, we divide global CCSF values into three latitudinal zones (0°–30°, 30°–60°, and 60°–90°) with different mean temperatures, as shown in Fig. 6. [HCO₃⁻] shows a significant positive relationship with CCSF only for the high latitudes (60°–90°), while the correlation declines towards the equator (Fig. 6a). Runoff, however, shows a significant (R² > 0.96, P < 0.001) positive relationship with CCSF across all latitudinal zones (Fig. 6b). More importantly, it is noticed that when the [HCO₃⁻]ₑq decreases in low latitudes due to global warming, the accompanying increase in runoff overwhelms the temperature effect, leading to net increases in CCSF. Therefore, based on the results of our model, we suggest that global CCSF variations are highly dynamic and mainly determined by the hydrological cycle (runoff).

For a long time human activities were not considered in global carbonate weathering models. However, recent studies have found that land use does play a significant role in CCSF control and should be considered in carbon-sink models. On the one hand, consideration of land use can help us to explain why similar [HCO₃⁻]ₑq but different [HCO₃⁻]ₑq curves should show similarities to temperature and/or precipitation trends if climatic factors are considered alone. However, we found that the three [HCO₃⁻]ₑq peaks occur in three latitudinal zones (50°–70°N, 0–10°S, and 40°–50°S) that have a high proportion of forest cover. Globally, as the proportion of forested areas increase, soil pCO₂ and [HCO₃⁻]ₑq increases. In contrast, when grass and crop cover increase, soil pCO₂ and [HCO₃⁻]ₑq decreases (Fig. 4c, d). Land-use change can also dramatically alter water balances. In northern high latitudes where precipitation is low and forest cover is high, runoff (R) decreases sharply (Fig. 4e–g). In contrast, the increasing cropland area in low latitudes drastically increases net runoff. Based on our simulation, the role of land-use change will be even more important in the future. From 2006 to 2100, cropland proportion in low latitudes will drastically increases net runoff. Based on our simulation, the role of land-use change will be even more important in the future.

| Location  | Latitudinal zone (low/mid/high) | T (°C) | P (mm yr⁻¹) | Main land-use type | CCSF (t C km⁻² yr⁻¹) in other study | This study |
|-----------|---------------------------------|-------|-------------|-------------------|-------------------------------------|------------|
| Guizhou   | Low                             | 15    | 1225-1425   | Forest/crop/grass | 7.86-10.90 (1)                     | 7.63-11.16 |
| Xijiang   | Low                             | 14-22 | 800-1200    | Forest/crop/grass | 7.31 (2)                           | 7.30       |
| Kikori    | Low                             | 21    | 4330        | Forest            | 29.36 (3)                          | 29.19      |
| Thailand  | Low                             | 26    | 3168        | Forest/grass/crop | 42.30 (4)                          | 40.60      |
| Puerto Rico | Low                         | 24    | 2100        | Forest/grass/crop | 19.77 (5)                          | 28.24      |
| Florida   | Low                             | 21.1  | 1336        | Forest            | 9.49-10.05 (6)                     | 11.04      |
| Slovenia  | Mid                             | 6-11  | 800-3000    | Forest            | 15.16-32.89 (7)                    | 16.49-26.76 |
| Southern Alps | Mid                          | 9     | 1300        | Forest            | 11.91 (8)                          | 11.58      |
| Siberia   | High                            | –7 to –14 | 250-400 | Forest/non forest | 1.52-2.15 (9)                      | 1.49-3.30  |
| Mackenzie | High                            | –1    | 250-1500    | Forest/non forest | 4.94 (10)                          | 3.44       |

References: (1) Zeng et al. (2012); (2) Xu and Liu (2018); (3) Ferguson et al. (2015); (4) Pitman (2016); (5) Giusti (2017); (6) Moore et al. (2018); (7) Sarazin & Ciabrini (2019); (8) Huh et al. (2020); and (9) Millot et al. (2021).

Note: the higher CCSF cited for the Mackenzie River basin in northern Canada may be due to oxidative weathering contributing to the carbonate weathering, which does not contribute to the carbon sink but is possibly a CO₂ source.
coal combustion\textsuperscript{25} have become additional drivers of carbonate weathering. The carbonate dissolution produced by nitrate or sulfuric acids will lead to increased $[\text{HCO}_3^-]_{\text{eq}}$ as a CO$_2$ source. For example, Perrin et al.\textsuperscript{19} found this CO$_2$ source by nitric acid due to agricultural contribution is not negligible, since it could reach 6–15% of CO$_2$ uptake by natural silicate weathering and could consequently partly counterbalance this natural CO$_2$ sink. However, to give an estimate of this flux in the future may be difficult, which is out of the focus of this contribution.

In this study, we have assembled a new model to explore spatial-temporal global CCSF fluctuations over the historical period, 1950–2005, and extended it to the end of this century 2100 AD. Besides natural fluctuations in temperature and carbon dioxide concentration, anthropogenic land-use changes have been considered. The results show that there will be widespread and consistent increases in global CCSF, ranging from +9.8% (RCP4.5) to +17.1% (RCP8.5), that are chiefly due to increasing runoff (+12% to +20.9%) and $[\text{HCO}_3^-]_{\text{eq}}$ (+2.1% to +2.6%). For the full period, 1950–2100, due to the increased runoff caused by both land-use transition and increasing rainfall, CCSF variations in low latitudes are expected to become the largest. Although the low latitudes contain only 28% of terrestrial

Fig. 4 Latitudinal variations of relevant variables. $[\text{HCO}_3^-]_{\text{eq}}$ (dark-shaded area in a–d) and $R$ (runoff, light-shaded area in e–g) in relation with mean temperature (black line in a and e), mean precipitation (blue line in b and f), land-use type (multicolor lines in c and g), and soil pCO$_2$ (purple lines in d) in the historical period (1950–2005). Three $[\text{HCO}_3^-]_{\text{eq}}$ peaks occur in three latitudinal zones (50–70° N, 0–10° S, and 40–50° S). The dashed line in a is the upper temperature limit (15°C) for maximum carbonate dissolution. The highest runoff ($R$) can be found in the tropical zone and the area close to 40° S.
carbonate rock outcrops, the CCSF increase here accounts for 61–68% of the TCS in the future. The warming trend in mid and high latitudes will accelerate the carbonate dissolution but the total impact is less important. In future, the increase of runoff will dominate CCSF increases, due to the chemostatic behavior of \( \text{HCO}_3^- \). Global warming, by contrast, will lead to lower \( \text{HCO}_3^- \) in tropical regions due to the warmer temperatures. However, land-use changes and the accompanying rise in water flux could well counteract this impact, leading a higher net CCSF. Our study highlights the significant role of land-use change in global CCSF variation, which needs to be considered in future global CCSF models.

**Methods**

**Selection of database.** To simulate the CCSF fluctuations from the historical period to the end of this century, we use a long-term statistical climate dataset from the NASA Earth Exchange Global Daily Downscaled Projections (NEX-GDDP) CMIP5 archive (Coupled Model Intercomparison Project Phase 5). This dataset spans spatial and temporal variations in climate change, including a global dataset of reconstructed (1950–2005) historical precipitation, maximum and minimum near-surface temperatures, and future predictions (along the concentration pathways, RCP4.5 and RCP8.5, from 2006 to 2100). We calculate the mean temperature by using the average value of daily maximum and minimum temperatures. From the NEX-GDDP model suite, we select the Earth System Model of the Geophysical Fluid Dynamics Laboratory (GFDL-ESM2M), National Oceanic and Atmospheric Administration (NOAA), which is one of the most robust models considering interactions between each sphere. Land-use harmonization products provided by the IPCC Fifth Assessment Report give opportunities for estimating the impacts of a wide range of land-use trends on long-term terrestrial ecosystem processes. The land-use harmonization dataset (LUH; [http://hub.umd.edu/data.shtml](http://hub.umd.edu/data.shtml)) provides the annual land-use grid dataset from a long-term historical period and also provides the future land-use predictions under the different RCP scenarios (CMIP5). The fraction of each land-use type is described on a 0.25° grid in the LUH report, with the historical reconstruction period and four land-use change scenarios for future predictions. We use the two representative concentration pathways, RCP4.5 and RCP8.5, which correspond to the NEX-GDDP climate data. LUH provides seven land-use types (primary forest, secondary forest, pasture, crop, primary non forest, secondary non forest, and urban) and we reclassified each LUH land-use report into five different broad land cover types (forest, grass, non forest, crop, and urban) in each pixel.

For the spatial distribution of global carbonate rock, we use the v3.0 version world map of carbonate rock outcrops provided by the Geography and Environmental Science Department, University of Auckland ([http://www.sges.auckland.ac.nz/sges_research/karst.shtm](http://www.sges.auckland.ac.nz/sges_research/karst.shtm)). This map only displays the outcrop of karstic solid rocks. It does not include carbonate rock types that are covered by later consolidated strata. The carbonate rock types in the natural environment consist chiefly of limestone (CaCO_3) and dolostone (Ca(Mg)CO_3). Due to the uncertainties of precisely distinguishing limestone from globally less common dolostone in the geological maps, we calculated CCSF by assuming that all carbonate outcrops are calcite in this study.

Atmospheric CO_2 (CO_2 atm) is also an important factor in the air–water–rock system. We added CO_2 atm as an additional parameter for both historical and future emissions following the two pathways (RCP4.5 and RCP8.5). The historical CO_2 atm trends and different future emission prediction data (til 2100) were obtained from Potsdam Institute for climate impact research ([http://www.pik-potsdam.de/~mmalte/rcps/index](http://www.pik-potsdam.de/~mmalte/rcps/index)).
Calculating equilibrium [Ca\(^{2+}\)] in a karst system. The calcium equilibrium concentration [Ca\(^{2+}\)]\(_{eq}\) (mol m\(^{-3}\)) for a solution saturated with respect to calcite can be derived to very high accuracy from the analytical expression:

\[
[Ca^{2+}]_{eq} = \frac{K_c K_w K_{GEC}}{4K_r T} \cdot \rho CO_2
\]

where \(K_c\), \(K_w\), \(K_{GEC}\), and \(K_r\) are the temperature-dependent equilibrium constants for the chemical reactions, \(\gamma CO_2\) and \(\gamma\) are the activity coefficients for calcium and bicarbonate, respectively, and \(\rho CO_2\) (atm) is the carbondioxide partial pressure.

Calculation of \(pCO_2\) for carbonate weathering. \(CO_2\) is a key driving factor for carbonate dissolution. It is present in the atmosphere and will be enhanced by soil respiration. The \(pCO_2\) along the soil–rock or atmosphere–rock interface controls the saturation state of carbonate chemistry for ground water, thereby determining the amount of carbonate that can be dissolved in karst aquifers. In this study, soil \(pCO_2\) is calculated by the method given by the Gwiazda and Broecker and more recently modified by Gaillardet et al., who conclude that \(CO_2\) production by respiration in the root zone (CO\(_2\) \(\delta\) in g m\(^{-2}\) yr\(^{-1}\)) can be assumed to be 75% of the ecosystem net primary production (NPP). Meanwhile, a power function is used to define the \(pCO_2\) profile by solving the complete CO2 diffusion equation in soil. It is assumed at the basis of the root production zone, the soil \(CO_2\) reaches maximum and becomes constant below this horizon: soil \(CO_2\) can thus be expressed as a function of atmospheric \(CO_2\) concentration, temperature, and NPP, as shown below:

\[
pCO_2(t, z) = pCO_2(t, z) + \frac{A + 0.75 \mu CO_2}{T^2}
\]

where \(A = 1.03 \times 10^9\) is a conversion unit constant, \(pCO_2(z)\) is the atmospheric \(CO_2\) pressure in ppmv. NPP is net primary productivity in grams of dry matter per meter square per year (g m\(^{-2}\) yr\(^{-1}\)). \(T\) is the surface temperature expressed in K and \(pCO_2(z)\) is the \(CO_2\) pressure reached in a karst aquifer. In this study, soil \(pCO_2\) is calculated by the method given by the Gwiazda and Broecker and more recently modified by Gaillardet et al., who conclude that \(CO_2\) production by respiration in the root zone (CO\(_2\) \(\delta\) in g m\(^{-2}\) yr\(^{-1}\)) can be assumed to be 75% of the ecosystem net primary production (NPP). Meanwhile, a power function is used to define the \(pCO_2\) profile by solving the complete CO2 diffusion equation in soil. It is assumed at the basis of the root production zone, the soil \(CO_2\) reaches maximum and becomes constant below this horizon: soil \(CO_2\) can thus be expressed as a function of atmospheric \(CO_2\) concentration, temperature, and NPP, as shown below:

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where \(A = 1.03 \times 10^9\) is a conversion unit constant, \(pCO_2(z)\) is the atmospheric \(CO_2\) pressure in ppmv. NPP is net primary productivity in grams of dry matter per meter square per year (g m\(^{-2}\) yr\(^{-1}\)). \(T\) is the surface temperature expressed in K and \(pCO_2(z)\) is the \(CO_2\) pressure reached in a karst aquifer. In this study, soil \(pCO_2\) is calculated by the method given by the Gwiazda and Broecker and more recently modified by Gaillardet et al., who conclude that \(CO_2\) production by respiration in the root zone (CO\(_2\) \(\delta\) in g m\(^{-2}\) yr\(^{-1}\)) can be assumed to be 75% of the ecosystem net primary production (NPP). Meanwhile, a power function is used to define the \(pCO_2\) profile by solving the complete CO2 diffusion equation in soil. It is assumed at the basis of the root production zone, the soil \(CO_2\) reaches maximum and becomes constant below this horizon: soil \(CO_2\) can thus be expressed as a function of atmospheric \(CO_2\) concentration, temperature, and NPP, as shown below:

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Author contributions

Z.L. was the leader of the project financially supported by NSFC. G.K. and Z.L. designed the modelling. S.Z. ran the model and wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

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