

Carbon uptake by karsts in the Houzhai Basin, southwest China

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[1] Using an estimated bicarbonate concentration ($[\text{HCO}_3^-]$) in water and discharge rates of surface water and underground water from the Houzhai Basin, southwest China, from 1986 to 2007, we estimate that the mean carbon uptake rate was $20.7 \text{ g C m}^{-2} \text{ yr}^{-1}$. The surface water and underground water contribute about equally to the total carbon uptake from 1986 to 2007. About 97% of the interannual variation of annual carbon uptake can be explained by the discharge rate. Within a year, the net carbon uptake rate by karst during the wet season (May–October) was found to be about 2.4 times that during the dry season (November–April). If the seasonal variations of discharge rate and bicarbonate concentrations are not accounted for, estimates of annual net carbon uptake by karst can be biased by >25%, but that bias becomes very small (<5%) when averaged from 1986 to 2007 for the Houzhai Basin. We also found that one of the empirical models as used in global modeling overestimated the net carbon uptake by karst at Houzhai Basin by 29%. Carbon uptake from chemical weathering of all karsts in China is estimated to be about 12 Tg C yr^{-1} at present ($1 \text{ Tg} = 10^{12} \text{ g}$), or about 57% of the rate of net carbon accumulated in the forest biomass from 1981 to 1998 in China; we therefore recommend the inclusion of carbon uptake from chemical weathering in the regional carbon budget of China.

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1. Introduction

[2] Karst is a distinctive landscape that is largely shaped by the dissolving action of water on carbonate bedrock (usually limestone, dolomite, or marble), it occupies about 11.2% of the Earth's surface, or about 15 millions km^2 in the world [Dürr *et al.*, 2005]. About 0.4 million km^2 of karst is located in southwest China [Yuan, 1997]. Karst water is enriched with calcium carbonate and can potentially take up a significant amount of carbon dioxide (CO_2) from the atmosphere. CO_2 can dissolve in water and forms an equilibrium mixture as carbonic acid, bicarbonate and carbonate ions. The equilibrium concentration of the dissolved inorganic carbon (DIC) in a system water of $\text{C}_a\text{CO}_3\text{--CO}_2\text{--H}_2\text{O}$ can reach $1231 \mu\text{mol/L}$ in the water with calcium carbonate at a temperature of 15°C and atmospheric $[\text{CO}_2]$ of 380 ppmv, about 66 times higher than that in a system water of $\text{CO}_2\text{--H}_2\text{O}$ under the same conditions [Dreybrodt, 1988]. Dissolution of calcium carbonate in karst results in carbon uptake from atmosphere and the rate of carbon uptake increases with the partial pressure of atmospheric CO_2 [Troester and White, 1984], and decreases with an increase in water temperature in the laboratory, as a result of lower

solubility of calcite and CO_2 in water at higher temperature [Weyl, 1959; White, 1988]. Carbonate dissolution is usually accompanied by deposition of dissolved carbonate minerals and the release of CO_2 elsewhere [White, 1997]. Because the deposition flux usually is much smaller than that of corrosion, karst regions are often a net carbon sink [Jiang and Yuan, 1999; James *et al.*, 2006].

[3] Quantifying the net carbon uptake by karst water is important, because carbon uptake from chemical weathering can significantly influence evolution of atmospheric $[\text{CO}_2]$ and the Earth's climate over periods of thousands to millions of years [Bernier *et al.*, 1983], and that the magnitude of carbon exported from land to rivers has become quite uncertain. A recent study showed that the only about 33% of the carbon entered rivers from land has reached ocean [Aufdenkampe *et al.*, 2011]. About 40% of the carbon exported from land to ocean, or $0.24 \text{ Gt C yr}^{-1}$ ($1 \text{ Gt} = 10^{15} \text{ g}$), is from chemical weathering globally [Kempe, 1979a, 1979b]. Two methods have been used to estimate the carbon uptake from chemical weathering: the inverse methodology that estimates the carbon uptake rate of chemical weathering using observations of river chemistry [Meybeck, 1987] and the forward method that calculates the carbon uptake rate of chemical weathering by summing up the carbon uptake of different lithological classes and their areas [Hartmann *et al.*, 2009]. The inverse method is only applicable for catchments where measurements of river chemistry are available, is therefore rarely applied at a global scale. The second method has been used to estimate global carbon uptake rate from chemical weathering using the empirical relationship between carbon uptake rate and control factors [Amiotte Suchet and

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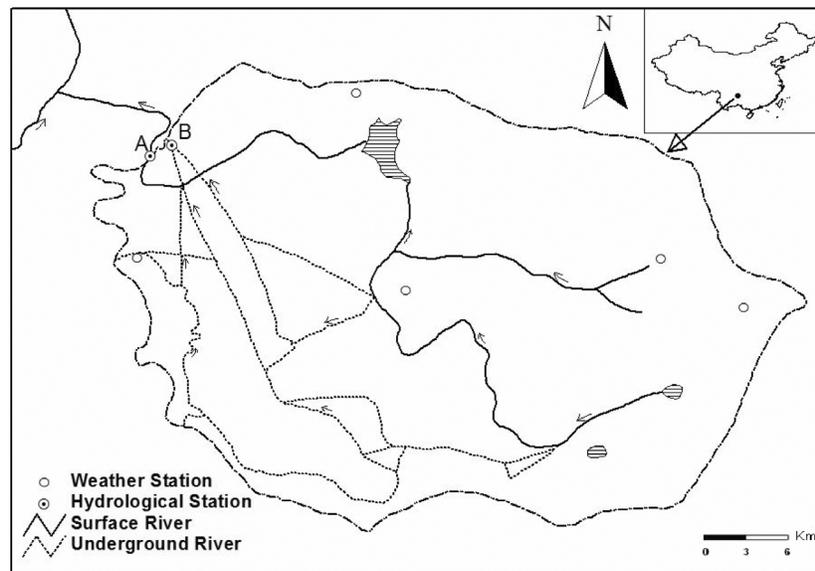


Figure 1. Map of the Houzhai Basin and locations of surface (solid lines) and underground rivers (dashed lines). Sites A and B indicate discharge measurement sites for surface river and underground river, respectively. Circles show the locations of weather stations. Arrows indicate flow directions. All water samples were collected at site A for surface water and site B for underground water.

Probst, 1995; Ludwig *et al.*, 1998; Hartmann *et al.*, 2009]. The most significant control factors are runoff and lithological class at a regional scale [Amiotte Suchet and Probst, 1993a; Bluth and Kump, 1994]. Most estimates of global carbon uptake by chemical weathering do not account for the seasonal variation of runoff. The empirical relationships between carbon uptake and runoff for each lithological class as used in global modeling are largely based on measurements in Europe [Amiotte Suchet *et al.*, 2003], North America [Gibbs and Kump, 1994] and Japan [Hartmann, 2009], these empirical relationship may not be applicable in China.

[4] Current estimates of carbon uptake by karsts in China are quite uncertain, varying from 5 Tg C yr^{-1} [Jiang and Yuan, 1999] to about 18 Tg C yr^{-1} [Liu and Zhao, 2000]. For southern China where about half of the karsts in China are located, the estimated rate of carbon uptake can be quite variable using different methods. For example, Jiang and Yuan [1999] compared two estimates of carbon uptake rate by karsts in southern China. On the basis of the rate of limestone corrosion and the theoretical equilibrium concentration of HCO_3^- for the $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system, Jiang and Yuan [1999] estimated that the rate of carbon uptake by karst in southern China is 2.6 Tg C yr^{-1} , which is 32% lower than the estimate of 3.8 Tg C yr^{-1} from the mean concentration of HCO_3^- and mean rate of water discharge in southern China. Many previous studies have not take account of the seasonal and interannual variation of carbon uptake, and the contribution of underground water to total carbon uptake by karsts in China [Liu *et al.*, 2010].

[5] In this study, we calculated the net carbon uptake using estimated bicarbonate concentration and discharge rate of water from the Houzhai Basin in Guizhou Province, southwest China from 1986 to 2007. The objectives of this study are to (1) estimate the seasonal and interannual variations of carbon uptake in karsts in the Houzhai Basin and to identify the major drivers of seasonal and interannual

variations in carbon uptake; (2) identify the potential biases in estimating total carbon uptake by karst without accounting for the seasonal variation of runoff, and the contribution by underground river transport; (3) compare the derived relationship between total carbon uptake and water discharge rate from this study with those used in the global modeling; and (4) compare the potential rate of carbon uptake by karsts with other carbon sinks, such as forest growth in China.

2. Description of Field Sites

[6] Houzhai drainage region is located in Guizhou Province, southwest China (latitude $26^\circ 13'\text{--}26^\circ 15'\text{N}$, longitude $105^\circ 41'\text{--}105^\circ 43'\text{E}$). The total area of the drainage is 80.65 km^2 . Its topography is high in southeast, and low in northwest where surface water and underground water exit (Figure 1). The basin has a humid subtropical monsoon climate, with an annual mean temperature of 15.2°C . The annual average rainfall is 1314.6 mm , with 85% of rains falling during the wet season (May–October) and 15% during the dry seasons (November–April). The bedrock type in the drainage area is the primarily carbonate rocks formed through sedimentation during the Triassic. The Houzhai River is the only surface river with only one exit (solid line for the surface river with exit A in Figure 1). An extensive survey was carried in 1970s by the provincial geological department to map out the underground river system (the dashed line and exit B in Figure 1). A hydrological station was built at both exits for measuring the water discharge rate and taking water samples regularly.

3. Methods

[7] A permanent station was set up in 1976 for monitoring water discharge rate through runoff and for providing

chemical analyses of water samples collected at the exits (Figure 1) in the Houzhai drainage area. Five weather stations were installed in 1980s. At each weather station, measurements of incoming solar radiation, rainfall, wind speed and direction, relative humidity and air temperature were made at 2 m height. The height of water tables, H , for the surface and underground rivers have been measured daily since 1986. Six water samples were collected from the surface or underground rivers each at a water depth of 0.6 m at exit weekly, and were measured for pH using a portable meter, water temperature and the concentration of bicarbonate ($[\text{HCO}_3^-]$) by titration with standard hydrochloric acid (HCl) immediately after samples were taken at the sampling site.

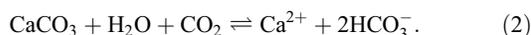
[8] Bicarbonate concentration was measured as follows: add 100 cm³ of water sample to a 250 mL flask, and 4 drops of phenol red indicator and shake the sample until the indicator is well mixed. Titrate with standard hydrochloric acid (0.025 mol L⁻¹) until the red color disappears at a pH of 8.4. Record the amount of standard hydrochloric acid used (V_1). Then add 3 drops of methyl orange indicator, the shake the water sample well. Continue titrating using standard hydrochloric acid until the water sample becomes orange at pH of 4.4. Record the amount of hydrochloric acid used (V_2). The concentration of bicarbonate, ρ , can then be estimated as

$$\rho = \frac{(V_2 - V_1) \times c \times 61.017 \times 1000}{V}, \quad (1)$$

where ρ is the bicarbonate concentration of water sample (mg L⁻¹), V is the volume of water sample in (cm³), c is the concentration of hydrochloride (mol L⁻¹), and 61.017 is the molecular mass of bicarbonate in g mol⁻¹.

[9] All water samples were stored in the dark and then taken to the laboratory in the permanent station for measuring the concentration of calcium (Ca²⁺), magnesium (Mg²⁺) (determined with the Jarrell Ash model 975 inductively coupled argon plasma spectrometer) and sulfate (SO₄²⁻) (determined turbidimetrically as barium sulfate (BaSO₄)). In response to financial difficulties, all measurements were temporarily suspended in 2003 and 2004, and then resumed in 2005. All data are provided in the auxiliary material (Data Set S1).¹

[10] When coming in contact with water (H₂O) and carbon dioxide (CO₂), calcium carbonate (CaCO₃) dissolves into ions of calcium (Ca²⁺) and hydrogen carbonate (HCO₃⁻); that is,



At steady state, the uptake of dissolved CO₂ in water during dissolution is equal to flux of CO₂ from atmosphere. That flux in g C m⁻² time step⁻¹ can be calculated following *Amiotte Suchet and Probst* [1993a]:

$$F = \frac{1}{2} c q \frac{M_C}{M_{\text{HCO}_3}}, \quad (3)$$

where 1/2 means that 1 mol of bicarbonate needs only half a mole of CO₂ from atmospheric or soil, c is concentration in

karst water (g/m³), q is rate of water discharge (m/time step). M_C and M_{HCO_3} are molecular weights of C and HCO₃⁻, respectively. Because pH of karst water varied between 7.3 and 8.2, we estimated that CO₃⁻-C accounted for less than 3% of total dissolved inorganic C in karst water [*Gelbrecht et al.*, 1998], and is therefore ignored in calculating F .

[11] Concentration of HCO₃⁻ in grams per meter cubed, c , was measured from the water samples collected from surface water or underground water at each exit. The rate of water discharge, q (m s⁻¹) is calculated as Q/A , where A is the total catchment area (=8.065 × 10⁷ m²), and Q in meters cubed per second is estimated from the following empirical relationship: Surface water discharge (Q_s)

$$Q_s = \begin{cases} 4.79 \times 10^{-5} \times \exp(12.17 \times H_s) + 0.27 & (H_s < 0.85) \\ 0.51 \times \ln(H_s - 0.75) + 2.99 & (H_s \geq 0.85) \end{cases} \quad (4)$$

Underground water discharge (Q_u)

$$Q_u = \begin{cases} 1.14 \times \exp(2.16 \times H_u) - 1.31 & (H_u < 0.40) \\ 8.20 \times H_u - 1.98 & (H_u \geq 0.40) \end{cases}, \quad (5)$$

where H_s and H_u are the heights of water table of the surface water and underground water in meters, respectively. Estimates of all coefficients in equations (4) and (5) are obtained from calibration as used routinely in hydrological studies. When the water table ($H_s < 0.85$ m or $H_u < 0.4$ m) is low, water flows through the V weir only, and we use empirical equations for the V weir to estimate discharge rate; otherwise water passes through the V weir and square weir together, and we use the other empirical equations for estimating surface or underground water discharge rate. Correlations of these empirical relationships are all significant ($r^2 > 0.90$; see Figure S1 in the auxiliary material), and the relative error of the estimated discharge rate using equation (4) or (5) is estimated to be <5%. Seepage of water through soil or rock was minimized by concreting the surface at exits for both surface and underground water discharge.

[12] In this study, we compared three different methods for estimating the net carbon uptake by karst. Method 1 calculates the net flux of carbon dissolution in karst water using the estimates of monthly mean $[\text{HCO}_3^-]$ and water discharge for surface and underground flows, separately; that is,

$$F_1 = \frac{1}{2} \frac{M_C}{M_{\text{HCO}_3}} \sum_{n=1}^{12} (q_{s,n} c_{s,n} + q_{u,n} c_{u,n}), \quad (6)$$

where the second subscript of q or c represents month of year (n), varying from 1 to 12. Method 2 calculates the net flux of carbon dissolution in karst water using the estimates of annual means of $[\text{HCO}_3^-]$ and discharge rate for surface and underground water separately; that is,

$$F_2 = \frac{1}{2} \frac{M_C}{M_{\text{HCO}_3}} \left(\bar{c}_s \sum_{n=1}^{12} q_{s,n} + \bar{c}_u \sum_{n=1}^{12} q_{u,n} \right), \quad (7)$$

where \bar{c}_s and \bar{c}_u and represent the annual mean concentrations of bicarbonate in surface and underground water, respectively.

¹Auxiliary material data sets are available at <ftp://ftp.agu.org/apend/jg/2011jg001686>. Other auxiliary material files are in the HTML. doi:10.1029/2011JG001686.

[13] Method 3 calculates the net carbon flux of carbonate dissolution in karst water from runoff; that is,

$$F_3 = a \sum_{n=1}^{12} (q_{s,n} + q_{u,n}), \quad (8)$$

where a is an empirical constant that depends on rock type, and is estimated to be $0.0294 \text{ (g C mm}^{-1}\text{)}$ [Bluth and Kump, 1994] or $0.0383 \text{ (g C mm}^{-1}\text{)}$ [Amiotte Suchet and Probst, 1995] for carbonate rocks. We named the empirical model by Bluth and Kump [1994] as method 3a and the empirical model by Amiotte Suchet and Probst [1995] as method 3b. Both models have been used in globally modeling studies [Hartmann et al., 2009].

[14] Differences among the three different methods depend how variable the concentration of bicarbonate is within a year. If concentration of bicarbonate is constant, the calculated fluxes using methods 1 and 2 are equal. To understand the difference in the calculated fluxes using different method, we partition F_1 into two components; that is,

$$F_1 = \frac{1}{2} \frac{M_C}{M_{\text{HCO}_3}} \left(\bar{c}_s \sum_{n=1}^{12} q_{s,n} + \bar{c}_u \sum_{n=1}^{12} q_{u,n} \right) + \frac{1}{2} \frac{M_C}{M_{\text{HCO}_3}} \sum_{n=1}^{12} (q'_{s,n} c'_{s,n} + q'_{u,n} c'_{u,n}), \quad (9)$$

where

$$q'_{s,n} = q_{s,n} - \bar{q}_s,$$

$$q'_{u,n} = q_{u,n} - \bar{q}_u,$$

$$c'_{s,n} = c_{s,n} - \bar{c}_s,$$

$$c'_{u,n} = c_{u,n} - \bar{c}_u.$$

The first term on the right-hand side of equation (9) is the contribution to F_1 from the mean discharge rate (\bar{q}) and mean concentration (\bar{c}), and is equal to F_2 , and the second term is the contribution to F_1 from the covariation of monthly discharge rate and bicarbonate concentration (cq). $F_1 = F_2$ only if the second component is zero.

[15] Method 1 is used for estimating the net carbon uptake by karst in this study unless specified otherwise. It is the most accurate method in theory, as it accounts for the seasonal variations of both q and c . Method 2 has been used to estimate regional carbon uptake by karst when measurements of bicarbonate or total dissolved inorganic carbon concentration are available [see Liu and Zhao, 2000]. Method 3 is often used for estimating regional- or global-scale carbon uptake from chemical weathering in the past or at present [Amiotte Suchet and Probst, 1995; Berner et al., 1983; Bluth and Kump, 1994; Hartmann et al., 2009]. Both methods 2 and 3 used the estimates of mean annual runoff from other studies, and often do not account for its seasonal and interannual variations. It often is unclear if underground water discharge is included when methods 2 and 3 are used in some previous studies [Hartmann et al., 2009; Liu and Zhao, 2000]. We will discuss the differences in the estimated carbon uptake rate, F using these

three methods and contribution of underground water discharge to F in sections 4 and 5.

[16] To estimate the total carbon uptake by karst in China, we divided the karst area into two regions, north region and south region, following the methodology of Liu and Zhao [2000]. The total area of karst is $4.46 \times 10^{11} \text{ m}^2$ in south China (A_{south}) and $4.61 \times 10^{11} \text{ m}^2$ in north China (A_{north}). The mean carbon uptake by karst in south China (\bar{F}_{south}) is based on the results of this study, as the most karst area in south China experiences similar rainfall as the Houzhai Basin. The mean carbon uptake rate of karst in north China (\bar{F}_{north}) is assumed to be one fourth of the rate by karst in south China (see Liu and Zhao [2000] for justification), therefore the total carbon uptake by all karst in China, F_T , is calculated as

$$F_T = A_{\text{south}} \bar{F}_{\text{south}} + 0.25 A_{\text{north}} \bar{F}_{\text{south}}, \quad (10)$$

where A_{south} and A_{north} are the total area of karst in south China and north China in meters squared, and \bar{F}_{south} is the mean annual carbon uptake by karst in south China in grams of carbon per meters squared per year, as estimated from this study.

4. Results

4.1. Seasonal and Interannual Variations of Water Discharge Rate

[17] The rate of carbon uptake by karsts depends on water discharge rate estimated from the measured height of water table using equations (4) and (5). Our results show that discharge rate varies seasonally and interannually for both surface water and underground water between 1986 and 2007 (see Figure 2). The mean seasonal trend of surface water discharge rate is quite similar to that for underground water. Within each year, the maximal rate of water discharge occurs in July, and is about 4 times as much as the minimal rate of water discharge in February or March for both surface water and underground water discharge on average. The maximal discharge rate lags the maximal rainfall in June by one month on average.

[18] From 1986 to 2007, we estimated that the mean annual surface runoff was very close to the mean annual underground runoff, or about 381 mm yr^{-1} . The total runoff (both surface and underground runoff) was estimated to account for 56% of annual rainfall on average. Over the same period, about 72% runoff occurred in the wet season (May–October) and 28% in the dry season (November–April) in the Houzhai Basin. The annual discharge rate varies from the lowest in 1990 (182 mm yr^{-1}) to the highest in 1999 (531 mm yr^{-1}) for surface water, and from the lowest in 1990 (229 mm yr^{-1}) to the highest in 1991 (506 mm yr^{-1}) for the underground water.

4.2. Variation of Bicarbonate Concentration in Karst

[19] The second factor affecting the carbon uptake in karst is the concentration of bicarbonate or $[\text{HCO}_3^-]$. The errors for individual measurements of $[\text{HCO}_3^-]$ in the surface water generally are larger than those for the underground water (Figures 3a and 3b), and the interannual variation of monthly mean $[\text{HCO}_3^-]$ for the surface water is less than that for the underground water (Figures 3c and 3d). On average,

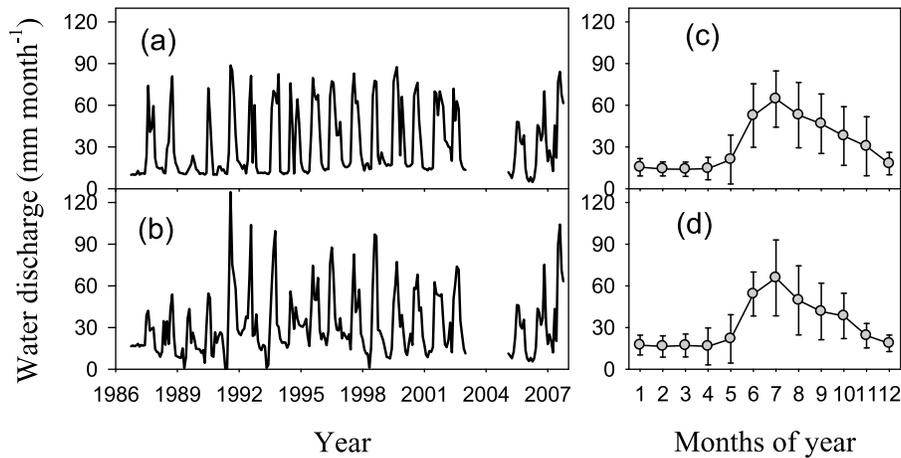


Figure 2. Discharge rate (mm month^{-1}) from (a) the surface river and (b) underground water in the Houzhai Basin, Guizhou, China. (c, d) Mean monthly water discharge rates for the surface water and underground water, respectively. The 1 standard error of the estimated discharge rate is generally less than 1% of the estimate for the water discharge rate shown in Figures 2a and 2b and is therefore not shown in those two plots. The error bar in Figures 2c and 2d represent the 1 standard error of the interannual variation of the monthly discharge rate from 1986 to 2008.

the mean $[\text{HCO}_3^-]$ for the surface water was about 10% higher than that for the underground water. From 1986 to 2007, the annual mean $[\text{HCO}_3^-]$ significantly increased over time for surface water, with a trend of $1.7 \text{ g m}^{-3} \text{ yr}^{-1}$, possibly as a result of land use and management (see Figure 3a). This will be discussed later.

[20] The mean monthly concentration of bicarbonate in the wet season (May–October) was lower than that in the dry season (November–April) for both surface water and underground water. This possibly resulted from dilution by a larger influx of water during the wet season. However, the

relative difference between the highest and lowest mean monthly $[\text{HCO}_3^-]$ was about 8% for surface water and about 21% for underground water (Figures 3c and 3d), these relative differences were much smaller than that for mean monthly discharge rate of surface water or underground water.

4.3. Variations of Carbon Uptake by Karst Topography

[21] Using the weekly measured $[\text{HCO}_3^-]$ and the estimated discharge rate (q), we calculated weekly, then the mean monthly carbon uptake rate according to equation (3)

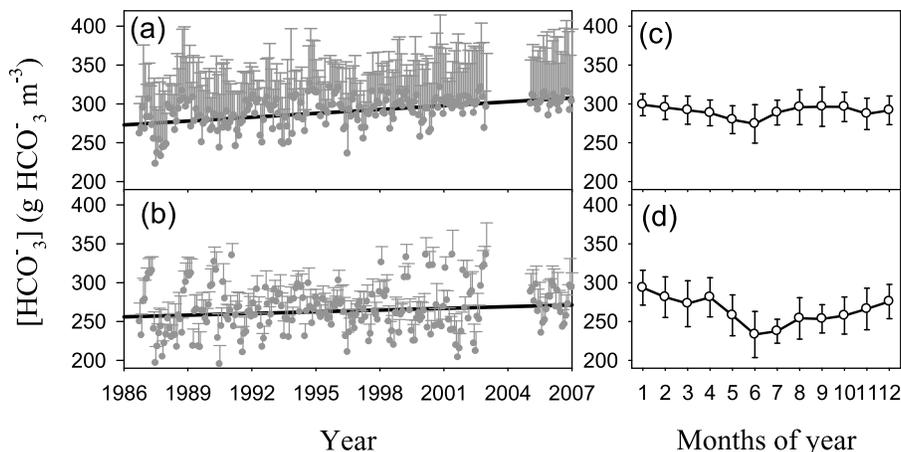


Figure 3. Mean and standard deviation (1σ) of the concentration of bicarbonate ($[\text{HCO}_3^-]$, $\text{g HCO}_3^- \text{ m}^{-3}$) of six water samples taken weekly from (a) the discharged surface water and (b) underground water and the mean and standard deviation (1σ) of the monthly concentration of bicarbonate in (c) the surface water and (d) underground water in the Houzhai Basin. The error bars in Figures 3c and 3d represent the 1 standard error of interannual variation of monthly mean concentrations. For clarity, we only plot the upper error bars in Figures 3a and 3b. The linear trend of the annual mean concentration of bicarbonate as shown by the black line in Figures 3a and 3b is $1.7 \text{ g HCO}_3^- \text{ m}^{-3} \text{ yr}^{-1}$ for the surface water and $0.8 \text{ g HCO}_3^- \text{ m}^{-3} \text{ yr}^{-1}$ for underground water. The linear trend is significantly different from zero for surface water only.

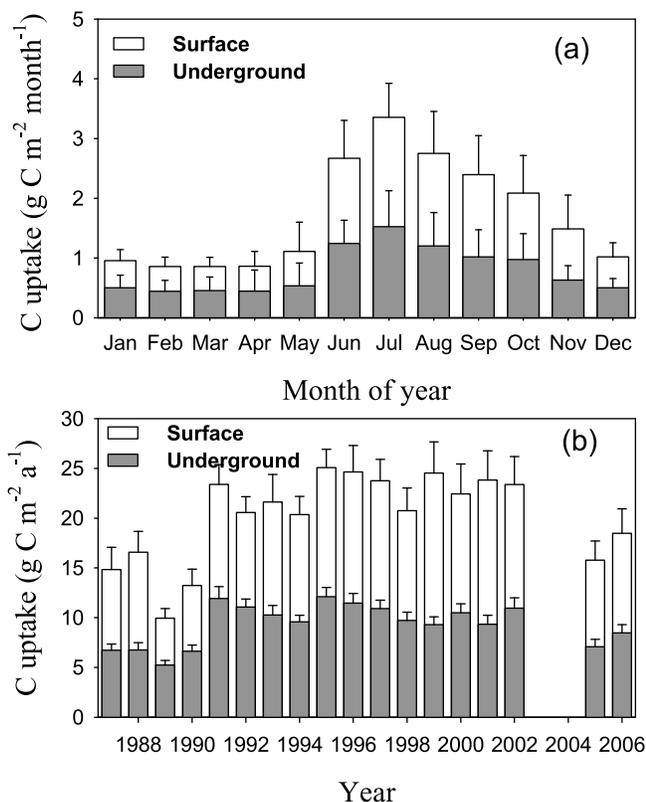


Figure 4. (a) Mean and standard deviation (1σ) of the estimated monthly carbon uptake rate ($\text{g C m}^{-2} \text{ month}^{-1}$) in the surface water (open bars) or underground water (shaded bars) in the Houzhai Basin between 1986 and 2007. (b) Mean and standard deviation (1σ) of the estimated annual carbon uptake ($\text{g C m}^{-2} \text{ yr}^{-1}$) in the surface water (open bars) or underground water (shaded bars) in the Houzhai Basin from 1987 to 2006. For clarity, we only show the upper error bars for both plots.

for surface water or underground water from 1986 to 2007 (Figure 4). Variability of the mean monthly carbon uptake was largely driven by variations in discharge rate for either surface water or underground water, as the mean monthly Q was relatively more variable than $[\text{HCO}_3^-]$ within a year (see Figures 2 and 3). In wet season (May–October), the mean monthly carbon uptake rate was about 150% and 120% higher than that in the dry season (November–April) for surface water and underground water from 1986 to 2007, respectively (see Figure 4a). On average the carbon uptake during the wet season accounted for about 70% of annual carbon uptake for either surface water or underground water. The interannual variation monthly carbon uptake from the surface water discharge is larger than that for the underground discharge as shown by the relatively larger error bars for surface water discharge (see Figure 4a).

[22] The mean annual estimated carbon uptake was 10.9 ± 2.6 and 9.8 ± 2.1 $\text{g C m}^{-2} \text{ yr}^{-1}$ for surface water and underground water, respectively. The annual carbon uptake was lowest in 1989 (5.1 $\text{g C m}^{-2} \text{ yr}^{-1}$) and highest in 1996 (15.4 $\text{g C m}^{-2} \text{ yr}^{-1}$) for the surface water, and was lowest in 1989 (5.8 $\text{g C m}^{-2} \text{ yr}^{-1}$) and highest in 1991 (12.7 $\text{g C m}^{-2} \text{ yr}^{-1}$) for the underground water (Figure 4b). Seasonal variation of carbon uptake from surface water

discharge is larger than that for the underground water discharge (see Figure 4b), as a result of greater seasonal variation of surface water discharge than that for the underground water discharge (see Figures 2c and 2d).

[23] As shown in Figure 5, the interannual variation of yearly water discharge rate drives the interannual variations of the net carbon uptake by surface and underground water discharge (see Figures 5a and 5c), as the mean annual concentration of bicarbonate is relatively constant for both the surface and underground water (see Figure 5b). Surface water and underground water contributed about equally to the total annual carbon uptake by karsts in the Houzhai Basin from 1986 to 2007.

[24] The net carbon uptake increased from 1987 to 1996, and remained quite steady from 1996 to 2002, and then declined in 2005 and 2006, largely as a result of changes in discharge rate (see Figures 5a and 5c). Increase in bicarbonate concentration in the surface water over time (see Figure 5b) only had a small effect on the interannual variation of net carbon uptake from chemical weathering by karst in Houzhai Basin from 1987 to 2006.

4.4. Comparison of Three Methods for Estimating Carbon Uptake Rates

[25] Figure 6a shows that method 3b consistently overestimates the net annual carbon uptake by karst in the

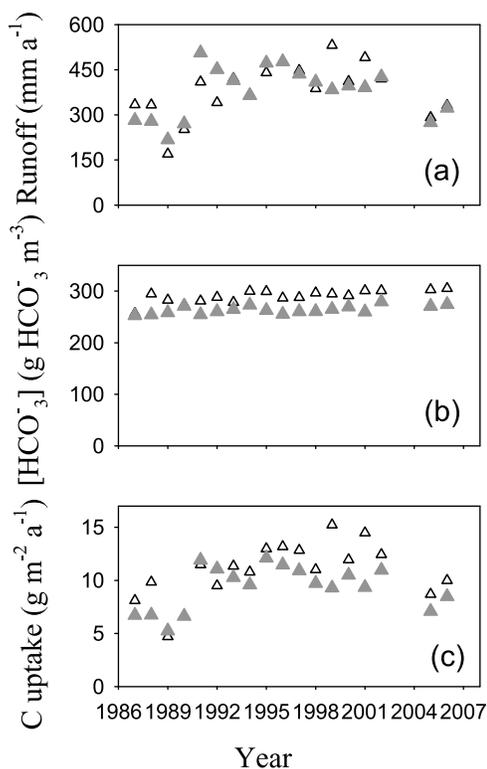


Figure 5. (a) Annual discharge (mm yr^{-1}) from surface runoff or underground runoff. (b) Annual mean concentration of bicarbonate ($[\text{HCO}_3^-]$, $\text{g HCO}_3^- \text{ m}^{-3} \text{ yr}^{-1}$) in the surface or underground water and (c) net carbon uptake rate ($\text{g C m}^{-2} \text{ yr}^{-1}$) from surface runoff or underground runoff in the Houzhai Basin from 1987 to 2006. The open triangles are for surface water, and shaded triangles are for underground water.

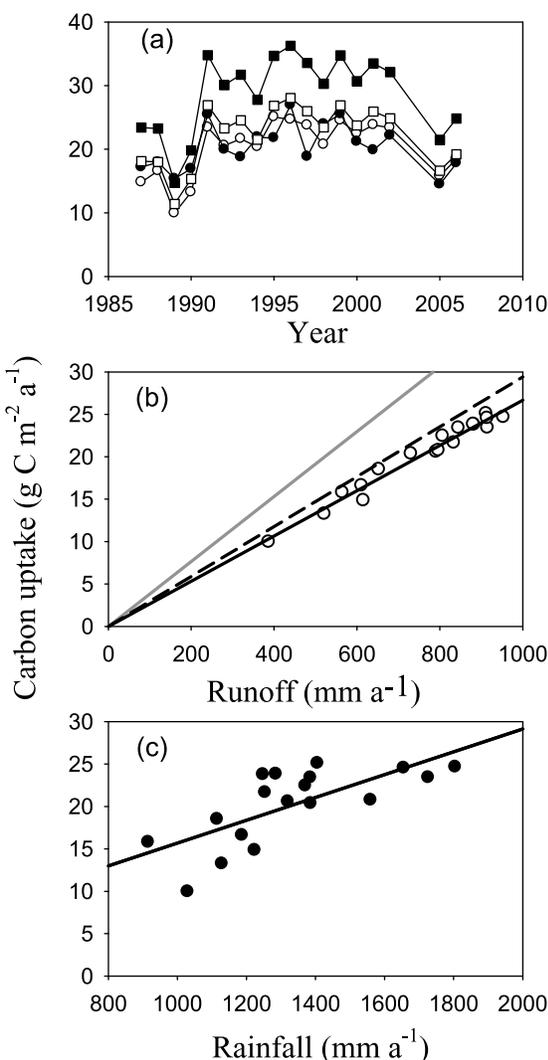


Figure 6. (a) Annual net carbon uptake as estimated using method 1 (open circles), method 2 (solid circles), method 3a (open squares) or method 3b (solid squares) for the Houzhai Basin from 1987 to 2006. (b) Comparison of the relationship between net annual carbon uptake and annual runoff derived from this study (solid line, $r^2 = 0.97$) with previous studies (dashed line [Bluth and Kump, 1994] or shaded line [Amiotte Suchet and Probst, 1995]) as used in global modeling. The open circles represent annual runoff and estimated net carbon uptake by karst in Houzhai Basin using method 1 from 1987 to 2006. (c) Correlation between annual rainfall (R) and carbon uptake (F) by karst as estimated using method 1 ($F = 2.25 + 0.013R$, $r^2 = 0.51$, where R is the annual rainfall in mm yr⁻¹).

Houzhai Basin by 34% to 58%, as compared with the estimates using method 1 from 1986 to 2006. The estimated annual net carbon uptake rate by methods 1, 2 and 3a generally are within 20%. The bias in the estimated mean net carbon uptake over the whole period from 1986 to 2006 is quite small if seasonal variations of runoff or bicarbonate concentrations are not considered as in methods 2 and 3a, but the estimate of net carbon uptake for individual years can differ by as much as 36% for the Houzhai Basin.

[26] The mean net carbon uptake by karst in Houzhai Basin from 1986 to 2006 is estimated to be 20.7 g C m⁻² yr⁻¹ using method 1, 20.8 g C m⁻² yr⁻¹ using method 2 or 22.3 g C m⁻² yr⁻¹ using method 3a and 29.0 g C m⁻² yr⁻¹ using method 3b. The correlation between annual net carbon uptake estimated using method 1 and runoff is statistically significant (see Figure 6b) with a slope of 0.027 g C m⁻² mm⁻¹, about 29% lower than the slope (0.038 g C m⁻² mm⁻¹) to the value of parameter a in method 3b [Amiotte Suchet and Probst, 1995; Hartmann et al., 2009].

[27] About 97% of the variance of interannual variation of carbon uptake by karst can be explained by runoff. Because of the nonlinear relationship between rainfall and runoff, only 51% of the variance of interannual variation of carbon uptake can be explained by rainfall.

5. Discussion

5.1. Major Drivers of Carbon Uptake in Karst Water in the Houzhai Basin

[28] The rate of carbon uptake depends on [HCO₃⁻] and q , both of which may also be affected by rainfall, water temperature and other factors [Back and Hanshaw, 1970; Gaillardet et al., 1999; Oh and Raymond, 2006; Ushie et al., 2010; Åberg et al., 2010]. In the following section we will discuss how [HCO₃⁻] or q vary with rainfall and water temperature using field observations and our estimates in this study.

[29] Increases in rainfall significantly increase water discharge rate of both surface and underground runoff and lower [HCO₃⁻] in the underground water only (Figure 7). The correlation between rainfall and discharge rate is positive and statistically significant for both surface water (The Pearson correlation, $r^2 = 0.54$, $n = 229$) and underground water ($r^2 = 0.63$, $n = 229$), whereas the correlation between rainfall and [HCO₃⁻] is not statistically different from zero for surface water, and is significantly different from zero (being negative) for the underground water ($r^2 = 0.29$, $n = 229$). The correlation between rainfall and discharge rate was not significantly different if discharge rate was lagged by one month, and became significantly weaker with >1 month lag for both surface discharge and underground discharge. Similarly the correlation between rainfall and [HCO₃⁻] lagged by 1 month was not significantly different from that without any lag, and became weaker for [HCO₃⁻] lagging rainfall by >1 month. As the relative sensitivity of water discharge rate to rainfall is much higher than that of [HCO₃⁻], therefore mean monthly rate of carbon uptake increases with rainfall for both surface water and underground water. Our result is quite similar to the findings by Raymond and Oh [2007] on carbon export from three major watersheds in the United States.

[30] The second factor is water temperature. Because solubility of CO₂ in water decreases with an increase temperature, [HCO₃⁻] should be lower at higher water temperature [Weyl, 1959; White, 1988]. Figure 8 shows that the monthly mean [HCO₃⁻] decreases with water temperature for both surface water and underground, but the decrease is statistically significant only for underground water ($r^2 = 0.17$, $n = 229$). The lack of significant correlation between [HCO₃⁻] and water temperature for the surface water may result from other factors, such as evaporation and refreshing.

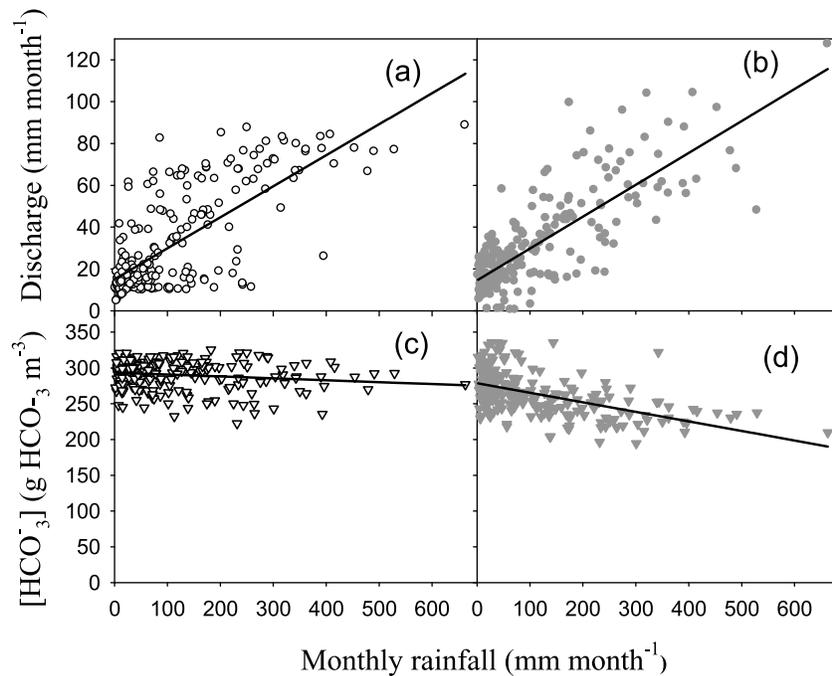


Figure 7. Variation of mean monthly discharge rate (mm month^{-1}) from (a) surface water or (b) underground water with monthly rainfall (mm) and the mean monthly concentration of bicarbonate ($[\text{HCO}_3^-]$, $\text{g HCO}_3^- \text{m}^{-3}$) in (c) the surface water or (d) underground water with monthly rainfall (mm) in the Houzhai Basin from 1986 to 2007.

This is also consistent with the results from other studies [Wallin *et al.*, 2010].

[31] Overall, rainfall has the most important influences on carbon uptake by karst water in the regions, an increase in water temperature can reduce solubility of CO_2 in water and therefore carbon uptake, but its effect is much smaller than that of rainfall in the Houzhai Basin.

5.2. Comparison of Carbon Uptake With Other Studies

[32] In this study, we also showed that the 19 years' mean carbon uptake from 1987 to 2006 can be accurately estimated without accounting for the seasonal variation of discharge rate or bicarbonate concentrations. However, the

monthly covariation of discharge rate and bicarbonate concentration in water within a year can account for more 25% of the total annual net carbon uptake for individual years, and methods that do not account for that variation can have significant errors for estimating net carbon uptake for individual years at our site.

[33] Our results also show that 97% of the variation in the annual net carbon uptake by karst in Houzhai Basin from 1987 to 2006 can be explained by runoff (see Figure 6b). But one of the empirical relationships between net carbon uptake and runoff as used in global modeling for sedimentary carbonate rocks will overestimate the net carbon uptake by karst in Houzhai Basin by about 29% (see Figure 6b).

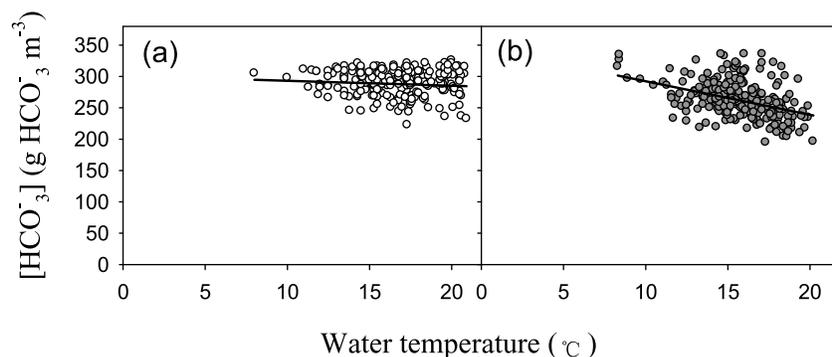


Figure 8. Variation of the monthly mean bicarbonate concentration ($[\text{HCO}_3^-]$, $\text{g HCO}_3^- \text{m}^{-3}$) with monthly mean water temperature ($^{\circ}\text{C}$) in (a) the surface water or (b) underground water in the Houzhai Basin between 1986 and 2007.

Therefore it is important to calibrate or verify the empirical model in global modeling using regional observations.

[34] Why is the net carbon uptake per unit of water discharge by karst in Houzhai Basin lower than that found from other studies [Amiotte Suchet and Probst, 1993b; Hartmann, 2009]? A recent study by Han *et al.* [2010] found that sulfuric acid can reduce the net carbon uptake by chemical weathering of carbonate in the nearby karst region in China by about 36%, similar to the difference in the net carbon uptake per unit water discharged between our study and other studies for carbonate rocks. This may be the major cause, but requires further investigation.

[35] In this study, we estimated that the mean annual carbon uptake rate by karsts in the Houzhai region is $20.7 \text{ g C m}^{-2} \text{ yr}^{-1}$ from 1987 to 2006. Our estimate is significantly higher than the estimate of $8.6 \text{ g C m}^{-2} \text{ yr}^{-1}$ by Jiang and Yuan [1999] who estimated the carbon uptake from chemical weathering using the estimated (not measured) bicarbonate concentration and discharge rate from hydroecological map of China. Difference between these two estimates can be largely explained by the difference in the estimated rate of water discharge. The rate of water discharge (both surface and underground water) we estimated varies from 412 mm in 1989 to 954 mm in 1996 for the site in this study, which is much higher than the estimated discharge rate of 368 mm used by Jiang and Yuan [1999] which was probably for surface water discharge only.

[36] The karst topography in Houzhai region is representative of many other karsts in southern China. As their rate of carbon uptake is much higher than karsts in northern China [Jiang and Yuan, 1999], karsts in southern China may be a significant carbon sink. Using our estimate of carbon uptake rate by karsts and total area of karsts in southern China of $44.6 \times 10^{10} \text{ m}^2$ [Li, 1992], we estimated that the mean carbon uptake rate of karst in southern China is 9.2 Tg C yr^{-1} . If we further assumed that the carbon uptake rate of karst in southern China is about 4 times the rate of karst in northern China [Jiang and Yuan, 1999; Liu and Zhao, 2000], the total carbon uptake by karsts in China will be 12 Tg C yr^{-1} , much higher than 5 Tg C yr^{-1} reported by Jiang and Yuan [1999] and lower than 18 Tg C yr^{-1} reported by Liu and Zhao [2000]. This is comparable to the estimated rate of net carbon accumulation in forest biomass (21 Tg C yr^{-1}) in China from 1981 to 1998 by Fang *et al.* [2001], or about 3% of the total fossil fuel emissions from China over the same period [see Boden *et al.*, 2010]. Therefore it is clearly important to include the carbon uptake by karsts in studying regional or national carbon budget in China.

[37] More importantly the carbon uptake by karsts is likely to increase in the future, as land use change will result in more CO_2 dissolved in the water, and consequently the carbon uptake [Raymond *et al.*, 2008]. From 1986 to 2007, the mean $[\text{HCO}_3^-]$ in the surface water in the Houzhai Basin increased significantly over time at a rate of $1.7 \text{ g m}^{-3} \text{ yr}^{-1}$. A study by Macpherson *et al.* [2008] also found that limestone weathering rate in Konza Prairie, USA increased steadily by about 20% increase from 1991 to 2005. The carbon uptake rate by karsts in China may become greater than the rate of carbon accumulation in forest biomass. More studies should be carried in the future to quantify the spatial

and temporal variations of carbon uptake in different karsts in China and globally.

6. Conclusions

[38] On the basis of field measurements, we estimated that carbon uptake by karsts in the Houzhai Basin, southwest China, from 1986 to 2007. We found the following.

[39] (1) The mean carbon uptake rate was $20.7 \text{ g C m}^{-2} \text{ yr}^{-1}$, and the surface water and underground water contribute about equally to the total uptake from 1986 to 2007; contribution from underground water discharge to net carbon uptake by karst in Houzhai Basin can explain much of the difference between our estimate and estimates from other studies.

[40] (2) Our results also suggest that the empirical model by Bluth and Kump [1994] is more accurate than the model by Amiotte Suchet and Probst [1995] for estimating net carbon uptake by chemical weathering of carbonate rocks by karst in Houzhai Basin. The latter overestimates the net annual carbon uptake by about 29%.

[41] (3) We divided the annual net carbon uptake by karst as two components, one is the contribution from mean bicarbonate concentration (\bar{c}) and mean discharge rate (\bar{q}), and other is the covariation of monthly bicarbonate concentration and discharge rate (cq). Our results suggest that the second component is close to zero when it is averaged over the period 1987 to 2006, can account for as much as 25% of annual net carbon uptake for individual years.

[42] (4) Rainfall is the most important driver of seasonal and interannual variation of carbon uptake by karsts in the region. Within a year, the carbon uptake was highest in July and lowest in December or January on average. The rate of water discharge during the wet season is 150% higher than that during the dry season, whereas $[\text{HCO}_3^-]$ during the wet season is only 6% lower than that during the dry season, therefore carbon uptake rate during the wet season is about 2.4 times as much as that during the dry season. Between years, 64% of the estimated interannual variation of carbon uptake can be explained by annual rainfall from 1986 to 2007.

[43] (5) Carbon uptake by karsts is a significant component of net carbon budget in China. We estimate that karsts in China together take up about 12 Tg C yr^{-1} at present or about 57% the rate of carbon accumulated in the forest biomass from 1981 to 1998 in China. It is likely that carbon uptake by karsts will be as large as the net carbon accumulation in forest biomass in China by 2050.

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