



Carbon export and HCO_3^- fate in carbonate catchments: A case study in the karst plateau of southwestern China

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ABSTRACT

The consumption of CO_2 due to carbonate weathering is thought to be an important terrestrial sink for atmospheric CO_2 . However, the reaction and fate of weathering products may significantly affect the magnitude of the sink. Carbon mass balances were determined in Hongfeng Lake, a small artificial lake located in the carbonate plateau of SW China. This was accomplished by measuring the concentrations of DIC (dissolved inorganic C), DOC (dissolved organic C), POC (particulate organic C), and CO_2 partial pressure in lake waters, inflows and outflows, and in surrounding spring waters. Results show that maximum DIC (mainly HCO_3^- derived from carbonate weathering by CO_2) to DOC ratios in the catchment export load reach ~ 21 , implying that as much as $\sim 80\%$ of the exported primary production is in the form of HCO_3^- , and, therefore, the CO_2 consumed by carbonate weathering and subsequent DIC export is a critical component of the C balance in this ecosystem. This exported HCO_3^- subsidizes C cycling of aquatic ecosystems in the catchment, and 32% (excluding carbonate-derived C) returns to the atmosphere as CO_2 evasion through the fluvial and lacustrine water–air interface and 10% is stored in lake sediment. This lake has a small CO_2 emission rate ($13.2 \pm 3.9 \text{ mmol m}^{-2} \text{ d}^{-1}$, or $0.097 \text{ mol m}^{-2} \text{ a}^{-1}$ relative to catchment area) compared to mean values for many reservoirs found in temperate and tropical climatic zones. This is likely due in part to low organic C loads supplied by the karst-dominated catchment, and low lake water DOC concentrations. The estimate indicates that more C (39%) returns to the atmosphere and much less (13%) is stored in sediments, implying that the C sink of carbonate weathering may not be as significant as once thought.

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1. Introduction

The consumption of CO_2 due to rock weathering, particularly in temperate and tropical climatic zones, its transformation to HCO_3^- in water, and assimilation of CO_2 in photosynthesis to form organic C, are two primary global sinks of atmospheric CO_2 (e.g., Raymond and Cole, 2003; Sabine et al., 2004; Zeebe and Caldeira, 2008; Gao et al., 2009). Continued increases in global atmospheric CO_2 concentrations (Solomon et al., 2007, 2009) combined with the recognition that natural oceanic and terrestrial CO_2 sinks can only provide partial CO_2 removal with considerable lag times ($\sim 50\%$ over several decades, $\sim 80\%$ over several centuries) (e.g., Prentice et al., 2001; Archer, 2005) has resulted in increased research focused on the more variable and accessible terrestrial CO_2 sinks (e.g., Piao et al., 2009; Beilman et al., 2009; Lewis et al., 2009). Inter-annual variations in the atmospheric CO_2 concentration growth rate are primarily controlled by exchanges of CO_2 between the atmosphere and the terrestrial biosphere, with a smaller but significant fraction due to variability in ocean fluxes.

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As terrestrial organic C is transported by rivers from land to sea, some is consumed and metabolized, releasing CO_2 to the atmosphere (e.g., Kling et al., 1991; del Giorgio and Peter, 1994; Dillon and Molot, 1997; Jones et al., 2001; Cole and Caraco, 2001). Some organic C is retained in sediments of rivers, floodplains, lakes, and reservoirs (Dean and Gorham, 1998; Stallard, 1998; Galy et al., 2007), which affects regional and global C balances (Cole et al., 2007; Kosten et al., 2010) and plays a significant role in the support of aquatic metabolism (Battin et al., 2008; Dubois et al., 2009).

Exchanges of inorganic C are as important to C cycling as exchanges of organic C. The chemical weathering of rocks is the primary regulator of atmospheric CO_2 concentrations over geologic time. The HCO_3^- exported from river catchments is a primary source of oceanic alkalinity, and is important in regulating the CaCO_3 saturation state of the oceans (Raymond and Cole, 2003). The HCO_3^- in river catchments originates from the mineralization of organic matter as well as chemical weathering of silicates and carbonates. With high solubility and a high rate of dissolution, carbonates can consume more atmospheric and pedologic CO_2 than silicates as weathering proceeds (Liu and Zhao, 2000; Gombert, 2002; Liu et al., 2010). Even where carbonates comprise as little as 5% of exposed bedrock,

carbonate weathering still has an important influence on water chemistry (Barth et al., 2003). Global consumption of CO₂ by carbonate dissolution has been estimated to be between 0.3 and 0.4 Gt C a⁻¹ (Liu and Zhao, 2000; Gombert, 2002), which represents 23% of the unknown C sink. Liu et al. (2010) indicated that there is a net CO₂ sink of up to 0.7 Gt C a⁻¹ as DIC in water, resulting from enhanced consumption of CO₂ by carbonate dissolution.

However, carbonate weathering products (HCO₃⁻, from carbonate dissolution and atmospheric CO₂) continue to react within the C cycle during transport from land to sea. First, the C may re-precipitate to form carbonates, and as a result an equal amount of C is released into the atmosphere, offsetting CO₂ uptake (examples include oceans and closed lake basins in arid and semiarid climates, Einsele et al., 2001). Secondly, the C may be assimilated into organic matter (Liu et al., 2010) and preserved for long periods of time in sediments. Thirdly, the C may return to the atmosphere from waters acting as a net source of CO₂, especially where carbonate rock is eroded by H₂SO₄ or organic acids (Yoshimura et al., 2001; Han and Liu, 2004; Xu and Liu, 2010).

Therefore, determining whether carbonate weathering is a net source or sink, and at what magnitudes, can only be resolved by considering the importance of different processes (Gaillardet and Galy, 2008). These processes include the consumption of CO₂ by rock weathering, organic matter burial and oxidation, re-precipitation of inorganic C, and release of CO₂. The partial pressures of CO₂ and concentrations of each C component were compared in lake, river, and spring waters of the Hongfeng Lake catchment, and CO₂ evasion and C burial in the lake estimated. The objectives were (1) to characterize C export from the carbonate catchment, (2) to clarify reaction and fate of the exported HCO₃⁻ using a C mass balance approach, and (3) to contribute to a broader understanding of how carbonate weathering affects C cycling through catchment-scale integration of atmospheric CO₂ uptake, aquatic CO₂ return, and organic and inorganic C burial in sediments.

2. Materials and methods

The Guizhou karst plateau in southwestern China is located in the center of the SE Asian Karst Region where karstification is most developed. This karst area is the largest in the world (Han and Liu, 2004). The Hongfeng Lake catchment, located in the center of this plateau (Fig. 1), is approximately 65 km long from north to south and 17 km wide from east to west, with an area of 1596 km², at an elevation of between 750 and 1765 m above mean sea level. The bedrock here is comprised primarily of Permian and Triassic limestones and dolomites, mixed with minor exposures of clastic rocks (Fig. 1b). Karst landforms are well-developed and characterized by steep-sloped valleys and gorges, caves, poljes, towers, and dolines. Land use is varied throughout the catchment and includes agricultural, urban, and forested areas. The catchment is generally sparsely vegetated, and the vegetation includes mainly shrubs and limited broadleaf and coniferous forests in some regions. This region has a subtropical, monsoon climate, with a mean annual precipitation of 1195 mm, and a mean annual temperature of 14 °C.

Hongfeng Lake is located in the region of the upper-, middle-reaches of the Maotiao River, a tributary of the Wujiang River, located in the upper reaches of the Yangtze River catchment (Fig. 1). It was constructed in 1960 and is the largest artificial lake in Guizhou Province, with headwaters consisting of several springs (Fig. 1c). The surface area of the lake is 32.2 km², and its limnological parameters are listed in Table 1. It is a warm, monomictic lake, in which thermal stratification is gradually established each year from April to May, and then dissipates from September to October. Due to anthropogenic effects, the total N (TN) and total P (TP)

concentrations in the lake are high (Table 1), and the lake is eutrophic (e.g., He et al., 2008; Zhang et al., 2008).

Lake water samples were collected with a Niskin Water Sampler (Model 1010, General Oceanics, USA) at sampling sites L1 and L2 (Fig. 1) in January, April, July, October, and November 2001, and January and August 2002. Lake water samples were collected at different depths in the water column with 2–3 m vertical spacing, and 5 m vertical spacing was used during for the well-mixed winter and spring samples (see Appendix 1). Surface water samples were also collected from rivers draining into and out of the lake (R1–R6 in Fig. 1c) in January, April, July and October 2001, and from surrounding springs (G1–G12 in Fig. 1c) in December 2001 (see Appendix 1). Short (35 cm) sediment cores were collected at site L1 with a gravity sampler in January and August 2002, and were sectioned with 1 cm vertical spacing.

After water samples were collected, the temperature, electrical conductivity, pH, and dissolved O₂ (DO) were measured in the field using a pIONner 65 multi-parameter instrument. Concentrations of HCO₃⁻ were determined on site using HCl titration. Major anions including Cl⁻, SO₄²⁻, NO₃⁻, and NO₂⁻ were determined using an HPLC-1100 liquid chromatograph, and K⁺, Na⁺, Ca²⁺ and Mg²⁺ were determined using an Atomic Absorption Spectrophotometer (Perkin Elmer 51002, PC-50) after samples were filtered (GF/F) on site and returned to the laboratory. Filtered water aliquots were treated with 100% phosphoric acid to produce CO₂, which was then analyzed by mass spectrometry (Thermo Scientific MAT 252) to determine the stable C isotope composition of dissolved inorganic C (δ¹³C_{DIC}). Particulate matter retained on GF/F filters was used to determine POC concentrations after being processed with HCl vapor to remove inorganic C (Harris et al., 2001). Dissolved organic C (DOC) concentrations were measured using a total organic C analyzer (ELEMENTAR, high TOC II) with a detection limit of 0.2 mg L⁻¹. The DIC and CO₃²⁻ concentrations and CO₂ partial pressures were calculated from HCO₃⁻, pH, the reaction constants, and Henry's law constant for CO₂. For the analysis of sediment, samples were freeze-dried and then milled to a 200-mesh size (0.07 mm). Inorganic C concentrations were determined by titration and organic C concentrations were determined with an elemental analyzer (Perkin Elmer 2400 Series II) after the samples were rinsed with dilute HCl.

Detailed, monthly hydrological data was available for Hongfeng Lake (Zhang, 1999); in a hydrological year, the inflow was approximately 8.50 × 10¹¹ L, and the outflow was 8.49 × 10¹¹ L. Using discharges in every season and the C concentrations in every component, the annual total C inputs and outputs in Hongfeng Lake were estimated (Appendix 2). The exchange flux (*F*) of CO₂ through the water–air interface was estimated by a molecular diffusion model:

$$F = k \times \Delta C$$

where *k* represents the gas exchange rate, and Δ*C* represents the difference of gas concentration across the interface (Cole et al., 1994; Galy-Lacaux et al., 1997; Jones et al., 2001). The gas exchange rate (*k*) is a function of the film thickness (*z*) (*k* = *D*/*z*, where *D* is the diffusion coefficient of gas in water and *z* is the boundary layer thickness). For CO₂, the gas exchange rate has been determined to be 0.5 m d⁻¹ in most lakes (Cole et al., 1994), and the corresponding boundary layer thickness was equivalent to 300 μm (in summer) and 200 μm (in winter). Galy-Lacaux et al. (1997) adopted a boundary layer thickness of 100 μm in a reservoir in French Guiana. Schmidt and Conrad (1993) used 200 μm for summer and 100 μm for winter and spring in Lake Constance, Germany. Jones et al. (2001) adopted a unified boundary layer thickness of 200 μm for estimating CO₂ exchange fluxes over the water–air interface of Loch Ness, Scotland. Hongfeng Lake is a small lake in a mountainous area, with low, perennial wind speeds, so a unified boundary layer thickness of 200 μm was used for this research. The diffusion coefficients

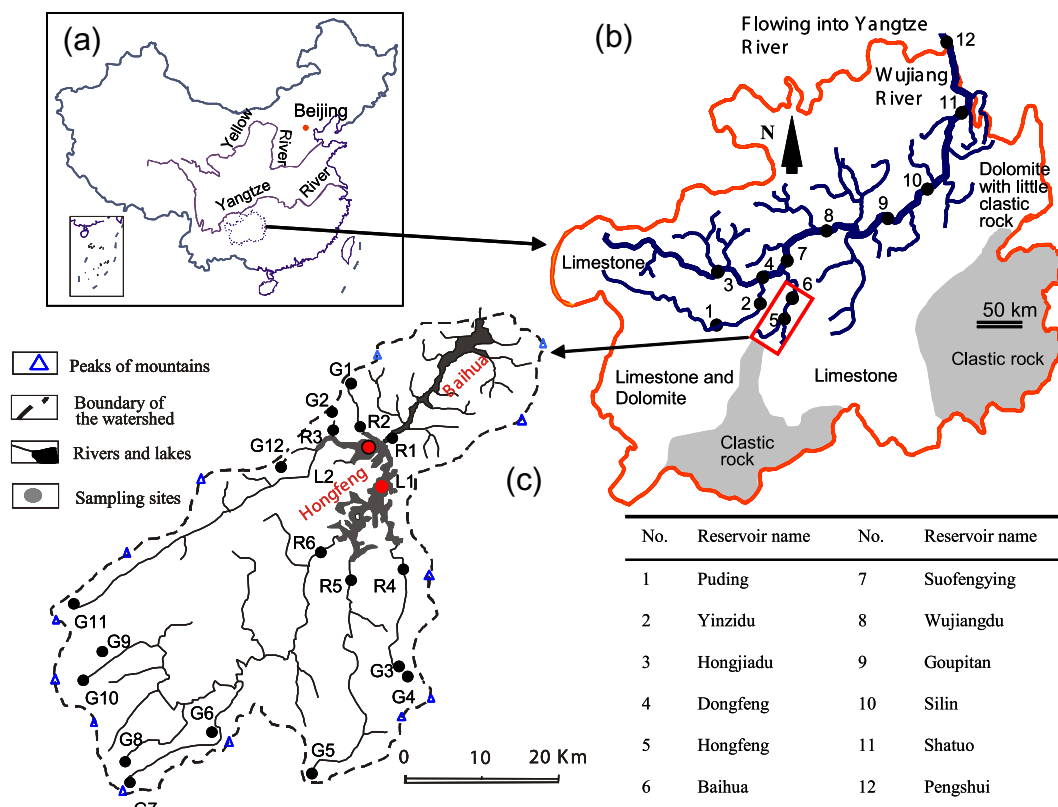


Fig. 1. China (a), Guizhou Province (b) and the Hongfeng Lake catchment (c). Constructed and planned reservoirs (solid circles) and exposed rock types in the Wujiang River catchment are shown in panel b. Sampling sites (solid circles) in the Hongfeng Lake catchment are shown in panel c.

Table 1
Physical, chemical and biological parameters of Hongfeng Lake.

Parameters	
Impounding date	May, 1960
Mean level of water	1233.3 m
Lake surface area	32.2 km ²
Catchment area	1596 km ²
Mean depth	9.2 m
Maximum depth	45 m
Volume	0.298 × 10 ⁹ m ³
Discharge of streams	0.85 × 10 ⁹ m ³
Water residence time	0.35 a
Transparency	1.79 m
NO ₃ ⁻	0.111 mmol N/L
TN	0.204 mmol N/L
TP	1.516 μmol P/L
Chl-a	6.2–10.9 (mg/m ³)
DOC	159 ± 26 μmol C/L

of CO₂ in water were $1.26 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (winter, water temperature of 10 °C) and $1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (summer, water temperature of 25 °C), and the corresponding exchange coefficient of CO₂ was within 0.5–0.8 m d⁻¹.

3. Results

3.1. DIC export and atmospheric CO₂ consumption

The calculated annual DIC input to the lake was $253 \times 10^7 \text{ mol}$, which consisted of $240 \times 10^7 \text{ mol}$ of HCO₃⁻, $2.1 \times 10^7 \text{ mol}$ of CO₃²⁻, and $11.2 \times 10^7 \text{ mol}$ of free CO₂ (Table 2, Appendix 2). Han and Liu (2004) calculated atmospheric CO₂ consumption rates due to chemical weathering of rock throughout the entire Wujiang River catchment (Fig. 1b) as $98 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$ (silicates) and

$581 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$ (carbonates). Applying these rates to the Hongfeng Lake catchment (a part of the Wujiang River catchment, Fig. 1) yields approximately $108 \times 10^7 \text{ mol}$ of CO₂ consumed annually due to rock weathering. Considering erosion of carbonates by H₂SO₄ (Han and Liu, 2004), the HCO₃⁻ generated from rock weathering in the Hongfeng Lake catchment would reach $233 \times 10^7 \text{ mol/a}$, which is within 3% of that observed (Table 2).

The total export load of DIC was $1.58 \text{ mol m}^{-2} \text{ a}^{-1}$ (Table 2), which is about 2 times higher than that in Lake Qinghai, China ($0.725 \text{ mol m}^{-2} \text{ a}^{-1}$) and about 3.5 times higher than that in Lake Turkana, Kenya ($0.475 \text{ mol m}^{-2} \text{ a}^{-1}$), as reported by Einsele et al. (2001). Based on DIC concentrations measured in the lake outflow, the total DIC passing annually through the reservoir outlet is approximately $216 \times 10^7 \text{ mol}$ (Appendix 2). Therefore, the DIC annually retained in the reservoir was approximately $37.2 \times 10^7 \text{ mol}$, and retention was 0.15 (Table 2). Dillon and Molot (1997) documented a range of DIC retention (–0.1 to 0.66, mean = 0.26) in seven lakes studied in central Ontario, Canada. Low DIC retention in Hongfeng Lake is likely due to a combination of short water residence times (Table 1), and lake outflow water being drawn from the bottom of the lake, where DIC concentrations are high.

3.2. Lacustrine organic carbon sources

The primary source of POC in Hongfeng Lake is autochthonous. Lake water POC concentrations ranged from 25 to 120 μmol C L⁻¹ with an average of $56 \pm 23 \text{ μmol C L}^{-1}$ (Table 3). According to Zhang (1999), total lake primary productivity reached $109 \times 10^7 \text{ mol C a}^{-1}$. The total POC annually supplied to the lake by rivers was only $2.8 \times 10^7 \text{ mol}$ (Table 2). Less than 3% of the lake's POC is derived from allochthonous inputs, which is consistent with the lake's high level of productivity and overall level of eutrophication.

Table 2
Comparison of catchment export and lake retention of C species.

	Export from catchment ($\times 10^7 \text{ mol a}^{-1}$)	Export load ($\text{mol m}^{-2} \text{ a}^{-1}$)	Loss in lake ^a ($\times 10^7 \text{ mol a}^{-1}$)	Retention ^b
DOC	12.2	0.076	−4.30	−0.36
POC	2.80	0.018	0.860	0.31
HCO ₃ [−]	240 (110.3 – CO ₂ ; 129.7 – carbonate) ^c	1.50 (0.69 – CO ₂ ; 0.81 – carbonate) ^c	32.6	0.14
CO ₃ ^{2−}	2.1	0.013	1.47	0.72
CO ₂	11.2	0.070	3.10	0.28
Inorganic sub-total	253	1.58	37.2	0.15

^a Loss in lake = input – output.

^b Retention = loss in lake/input (export from catchment).

^c The ratio of HCO₃[−] sources from CO₂ and from carbonate was given by Han and Liu (2004): 46% from atmospheric CO₂ and 54% from the dissolution of carbonate rocks.

Table 3
Organic C concentrations in Hongfeng Lake, rivers and springs (mean \pm sd) ($\mu\text{mol C L}^{-1}$).

Sampling site	January of 2002		August of 2002	
	DOC	POC	DOC	POC
Lake inlet	162 \pm 11	78 \pm 17	170 \pm 13	64 \pm 25
Lake center	190 \pm 25	71 \pm 32	158 \pm 12	46 \pm 16
Dam front	135 \pm 9	58 \pm 20	147 \pm 29	41 \pm 12
Lake average	163 \pm 28	68 \pm 25	157 \pm 43	49 \pm 20
Rivers flowing into lake	141 \pm 39	96 \pm 78	nd	25 \pm 13
Lake outflow	191	41	nd	18
Spring water average	27 \pm 6	17 \pm 11	nd	nd

The average DOC concentration in Hongfeng Lake water was $159 \pm 26 \mu\text{mol C L}^{-1}$ (Table 3) in January and August of 2002, which is within the range (133–256 $\mu\text{mol C L}^{-1}$) of monthly observation values from 2003 as reported by Li et al. (2006). DOC is the main component of organic C in the lake (Table 3). When compared with DOC concentrations documented from lakes and reservoirs throughout the world, which range from 83 to 2500 $\mu\text{mol C L}^{-1}$ (median value = 476 $\mu\text{mol C L}^{-1}$) (Sobek et al., 2007), concentrations in Hongfeng Lake are at the lower end of this range, and are far less than the median value.

Concentrations of DOC in streams flowing into the lake were all lower than 200 $\mu\text{mol C L}^{-1}$, with an average of $141 \pm 39 \mu\text{mol C L}^{-1}$. Concentrations of DOC in the main stem of the Wujiang River (Fig. 1) were much lower, ranging from 32 to 78 $\mu\text{mol C L}^{-1}$ (mean of 54 $\mu\text{mol C L}^{-1}$) during dry seasons, and ranging from 54 to 248 $\mu\text{mol C L}^{-1}$ (mean of 85 $\mu\text{mol C L}^{-1}$) during wet seasons (Liu, 2007). Riverine DOC concentrations in the Hongfeng Lake catchment and in the Wujiang River are much lower than average DOC concentrations in other documented river systems (e.g., 416.7 $\mu\text{mol C L}^{-1}$, Meybeck, 1982).

The DOC export load from the Hongfeng Lake catchment ($0.076 \text{ mol m}^{-2} \text{ a}^{-1}$, Table 2) is equivalent to 15% of the average value ($0.522 \text{ mol m}^{-2} \text{ a}^{-1}$) of the seven lakes in central Ontario, Canada, investigated by Dillon and Molot (1997). The low DOC export via surface or sub-surface waters, as evidenced by the much lower DOC concentration in spring waters (Table 3), is likely due to low vegetation coverage in the catchment and adsorption and mineralization of dissolved organic matter in soil vadose zones and aquifers (Kroeger et al., 2006). This scenario is also supported by the steep landscape and rapid downward infiltration of surface waters, which are key factors in reducing catchment DOC export (Sobek et al., 2007).

From the January data, the retention of DOC in the lake is approximately −0.36 (Table 2), indicating that some DOC sources were not recognized. According to documented DOC concentrations in precipitation from this area (Liu, 2007), it is estimated that the total DOC annually provided to the lake by precipitation is $0.1 \times 10^8 \text{ mol}$. Runoff is likely to be a measurable DOC source to

the lake, but quantitative data are not available. Algal photosynthesis is an important DOC source to the lake as reflected by higher DOC concentrations in the lake as compared to rivers flowing into it (Table 3), in surface lake water as compared to bottom lake water, and in river waters flowing out of the lake as compared to river waters flowing into the lake. Diffusion of DOC from bottom sediments to the overlying water is another source, which can account for 20–80% of the total DOC pool (Warnken and Santschi, 2004). In the other reservoirs in this area (Fig. 1), the contribution of DOC released from sediments to overlying waters has been shown to reach 16–30% (Liu, 2007). Hongfeng Lake seems to be a net source of DOC, similar to the results of Hood et al. (2005), which suggested that DOC production in alpine lakes is an important contributor to stream water DOC loads.

3.3. DIC variation and CO₂ evasion

Overall, DIC concentrations were much lower in summer (July) than in other seasons (Fig. 2), due to assimilation by phytoplankton photosynthesis and the dilution effect of precipitation. In winter and spring, when the lake was well mixed, DIC concentrations differed little in surface and bottom waters. $\delta^{13}\text{C}$ of DIC is significantly and positively correlated with the reciprocals of DIC concentrations (Fig. 3), implying that stratification and mixing of lake water are the primary processes controlling variation patterns of DIC concentrations in the lake. The intercepts of regression lines (−15.528‰ and −18.319‰, Fig. 3) demonstrate that the DIC added was mainly derived from organic matter mineralization, indicating that biological activities in the water column are also important factors influencing DIC variation.

The surface lake water had an average CO₂ partial pressure of $1013.5 \pm 302.5 \mu\text{atm}$, and as a whole was over-saturated with respect to atmospheric CO₂ (2001–2002; Fig. 4). From supplementary, bimonthly data (February, 2004 to January, 2005), it was observed that surface lake waters were under-saturated during summer (June–August), and over-saturated during other seasons. In general, surface lake waters were over-saturated with respect to atmospheric CO₂, with an annual average CO₂ partial pressure of $780.3 \pm 235.1 \mu\text{atm}$ (2004–2005; Fig. 4). The average emission flux of CO₂ over the water–air interface was estimated to be $13.2 \pm 3.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 4), meaning that approximately $1.55 \times 10^8 \text{ mol}$ of CO₂ was emitted annually from the lake.

By comparison, CO₂ partial pressures were highest in spring waters, with an average of $10,207 \pm 7749 \mu\text{atm}$ in December of 2001 (Appendix 1). The mean value for river waters was $3443 \mu\text{atm}$ (Appendix 1), which is in good agreement with the average value of world rivers (3230 μatm , Cole and Caraco, 2001). With the emission rate of riverine CO₂ given by Cole and Caraco (2001), it was estimated that approximately $2.7 \times 10^8 \text{ mol}$ of CO₂ was emitted annually from the rivers in the Hongfeng Lake catchment.

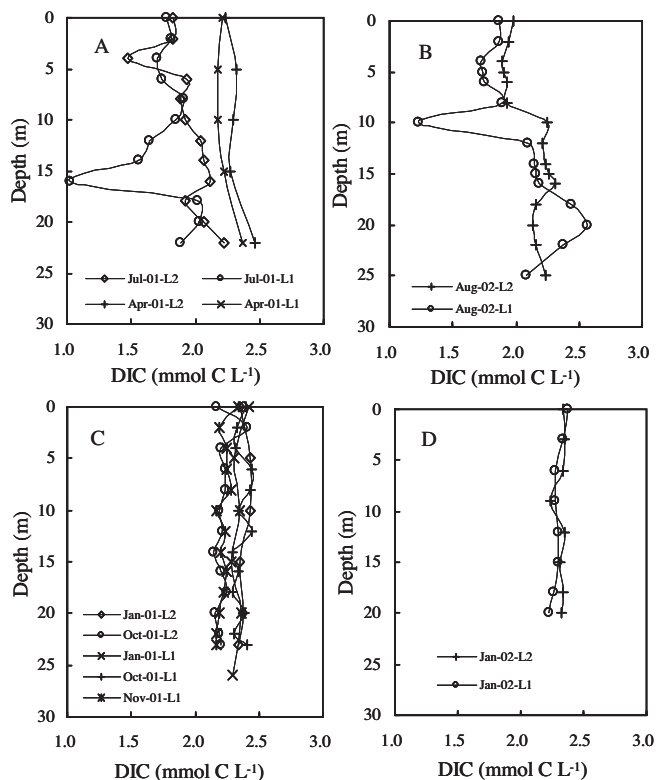


Fig. 2. DIC versus water depth during the thermally stratified summer (upper) and well-mixed winter (bottom) in Hongfeng Lake (A and C: 2001, B and D: 2002).

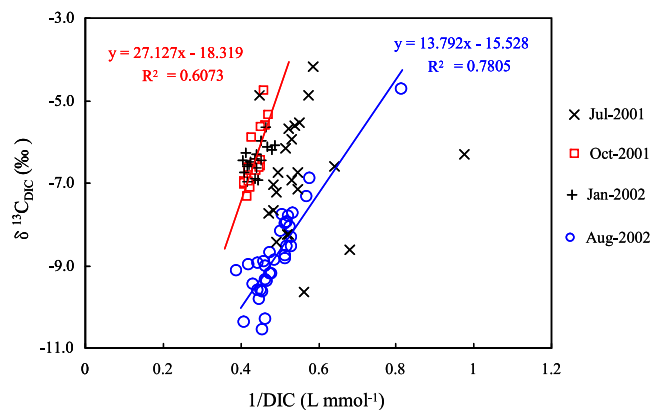


Fig. 3. Carbon isotopic compositions of DIC versus the reciprocals of DIC concentrations in Hongfeng Lake.

3.4. Carbon exchange at the sediment–water interface

Using ^{210}Pb and ^{137}Cs dating methods, linear sedimentation and sediment mass accumulation rates in the lake have been estimated to be $9.3 \pm 0.7 \text{ mm a}^{-1}$ and $0.17 \pm 0.01 \text{ g cm}^{-2} \text{ a}^{-1}$, respectively (Wan et al., 1990, 1991). The sediment mass accumulation rate is consistent with the apparent sediment accumulation rate ($0.18 \text{ g cm}^{-2} \text{ a}^{-1}$) determined based on the total volume of sediment stored and the age of the reservoir. This mass accumulation rate is 2.6–2.8 times higher than those documented in natural lakes in this area (Erhai Lake: $0.047 \pm 0.002 \text{ g cm}^{-2} \text{ a}^{-1}$; Lugu Lake: $0.045 \pm 0.004 \text{ g cm}^{-2} \text{ a}^{-1}$; Xu et al., 1999).

In Hongfeng Lake sediments, the organic C (OC) content decreases gradually from 7.4–11.6% in the upper 2 cm to ~2–3% at a depth of 17 cm (Table 4). Assuming that OC loading to lake

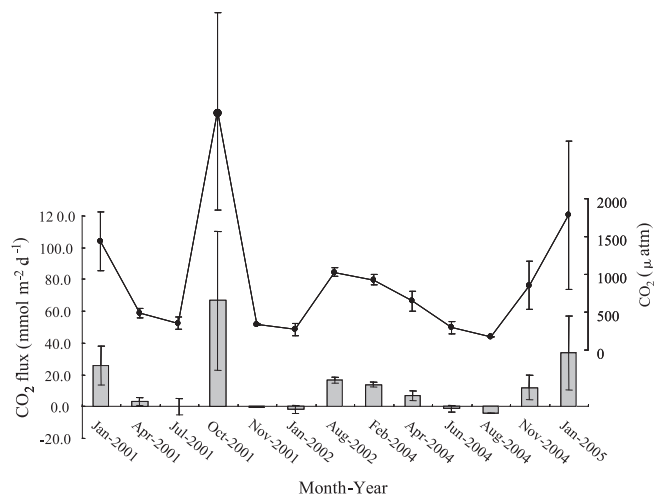


Fig. 4. CO_2 partial pressure of surface water (line) and CO_2 evasion flux across the atmosphere–water interface in Hongfeng Lake (bars).

Table 4

Contents of inorganic and organic C in the lake sediments (%).

Sediment depth (cm)	January of 2002		August of 2002	
	Inorganic C	Organic C	Inorganic C	Organic C
1	12.1	11.6	10.5	7.4
2	4.3	10.5	11.3	6.3
3	2.9	7.7	1.2	5.8
4	4.2	5.9	2.3	5.6
5	5.0	6.7	1.5	4.7
6	1.6	3.1	1.0	4.8
7	1.5	4.5	0.7	5.5
8	1.8	4.5	0.7	3.9
9	1.6	4.2	0.8	5.3
10	1.5	4.1	1.7	4.6
11	1.6	3.4	1.5	4.8
12	1.4	3.2	1.4	3.1
13	1.8	3.1	1.4	3.6
14	1.4	3.0	1.4	3.6
15	1.3	2.8	1.4	3.3
16	1.3	3.1	1.4	2.6
17	2.1	3.0	1.4	3.0
18	1.5	2.9	1.4	3.2
19	1.5	2.8	1.4	2.5

sediments is in the steady state, it can be estimated that the OC is delivered to the sediment–water interface at a rate of approximately $16.17 \text{ mg C cm}^{-2} \text{ a}^{-1}$, of which ~70% is remineralized within approximately 12 a, leaving $5.05 \text{ mg C cm}^{-2} \text{ a}^{-1}$ to be buried in the sediment (Liu, 2007). This ratio is close to the experimental results of Stephenson et al. (1995), who showed that ~18% of the original OC remains in a refractory C pool after 11 a. This rate is much lower than the often-cited organic C burial rate in reservoirs ($40 \text{ mg C cm}^{-2} \text{ a}^{-1}$, Dean and Gorham, 1998). However, it is consistent with the study of Kortelainen et al. (2004), suggesting that while variability is expected, the overall magnitude of the organic C sink in lacustrine sediments may not be as large as that suggested by Dean and Gorham (1998).

The upper 2 cm of Hongfeng Lake sediments contain high inorganic C concentrations (10.5–12.1%), which rapidly decline below this depth, averaging only 1.4% by 6 cm (Table 4). This inorganic C mainly originates from CaCO_3 precipitation stimulated by photosynthesis in the lake (Wang et al., in preparation), and is supplied to surface sediments at a rate of $19.55 \text{ mg C cm}^{-2} \text{ a}^{-1}$, with $2.38 \text{ mg C cm}^{-2} \text{ a}^{-1}$ stored in the sediment. Approximately 88% of the carbonate deposited is dissolved due to organic matter decomposition, similar to the results of Jahnke et al. (1997), which showed a value of 90%.

High concentrations of HCO_3^- in sediment pore waters result in its diffusion upwards to the overlying water (Wu et al., 1997). Wu et al. (1997) estimated that in Hongfeng Lake, the diffusion flux of HCO_3^- from sediments to overlying water was $17.76\text{--}29.16 \text{ mg C cm}^{-2} \text{ a}^{-1}$, which would account for approximately 27% of that supplied from the catchment. If it is assumed that the C exchanges at the sediment–water interface reach equilibrium, it can be calculated that an additional $0.9 \times 10^8 \text{ mol of C}$ is released from the sediment back into the water in other forms (DOC, CH_4 , CO_2 , CO_3^{2-} , etc.).

4. Discussion

4.1. Sources of error

As there are detailed water influx and efflux data available for this reservoir, estimations of fluxes through inflowing rivers and the reservoir outlet are thought to be reliable. Uncertainties are likely derived mainly from the difficulty associated with accurately estimating groundwater inputs. Here, a total water volume balancing method was used to estimate groundwater discharge:

$$\Delta V = \text{Input}_{\text{-river}} + \text{Input}_{\text{-groundwater}} - \text{Output}_{\text{-outlet}} - \text{Output}_{\text{-other}} + \Delta p$$

where ΔV = annual change of water volume in the reservoir, and Δp = the difference between precipitation and evaporation. The annual precipitation was 1199.7 mm (Mei and Xiong, 2003), and the annual pan evaporation was 1177.3 mm in 2001 (Qin et al., 2009). Annual lake level fluctuations are very small due to human regulation. Water supplied to the reservoir by direct groundwater input was estimated to be as low as $1.99 \times 10^{10} \text{ L a}^{-1}$, which accounts for a small fraction (3%) of the total water volume, limiting its influence on the final results.

4.2. Importance of inorganic carbon export

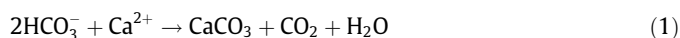
Weathering of rock into HCO_3^- by soil CO_2 is a major abiotic production pathway, but is small compared to biotic production pathways (Cole et al., 2007). Organic C, especially DOC, generally composes the majority of terrestrial C exported from catchments (e.g., Brunet et al., 2009; Raymond and Oh, 2007; McDowell and Asbury, 1994). Dillon and Molot (1997) found that the DIC to DOC ratio ranged from 0.13 to 0.32 in seven oligotrophic lakes in central Ontario, Canada, indicating that exported DIC was approximately one quarter of the total dissolved C exported from these catchments.

The calculations show that approximately 95% of the C exported from this catchment is in the form of DIC, which is mainly derived from the weathering reactions of carbonates by soil CO_2 (Table 2). The DIC to DOC ratio in the export load from the catchment is correspondingly high (up to 21). If C originating from carbonates is excluded, approximately 80% of the exported primary production (hypothetically consisting of exported and consumed CO_2 , DOC, and POC) via rivers from the catchment is in the form of HCO_3^- . The total amount of CO_2 consumption in the catchment ($0.703 \text{ mol m}^{-2} \text{ a}^{-1}$) and CO_2 export from the catchment ($0.07 \text{ mol m}^{-2} \text{ a}^{-1}$, Table 2) is approximately 2.2–3.5% of the catchment's net primary production (NPP), which presumably ranges from $417 \text{ g C m}^{-2} \text{ a}^{-1}$ (1981–2000 mean in southwestern China, Gu et al., 2007) to $262 \text{ g C m}^{-2} \text{ a}^{-1}$ (1982–1999 mean in the Yangtze River catchment, Ke et al., 2003), and at $9.3 \text{ g C m}^{-2} \text{ a}^{-1}$, falls within the range of net ecosystem production (NEP) ($0\text{--}15 \text{ g C m}^{-2} \text{ a}^{-1}$) as documented by Cao et al. (2003). This comparison indicates that the CO_2 consumed by carbonate dissolution and subsequent DIC export are a critical component, and should be

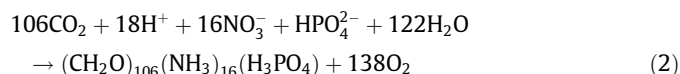
taken into account in C balance in terrestrial ecosystems or the inventory of soil C may be overestimated by at least 60%.

4.3. Fate of exported HCO_3^-

The catchment's spring waters were at or near to the equilibrium of calcite dissolution due to the rapid dissolution kinetics of calcite (Fig. 5), similar to most of the world's karst areas (Liu et al., 2010). However, most of the river water was supersaturated with calcite (Fig. 5). Carbon dioxide was produced by the reaction of CaCO_3 precipitation (1) as follows:

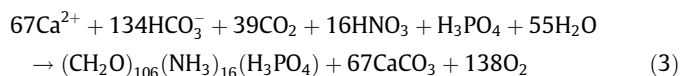


which is evidenced by the decrease of Ca^{2+} concentrations from 1.40 mmol L^{-1} in spring waters to 1.21 mmol L^{-1} in river waters (Appendix 2). The pronounced decreases in HCO_3^- concentration and CO_2 partial pressure and increase in pH from spring waters to river waters (Fig. 5) indicate that the reaction might be enhanced partly by photosynthesis (2).



This idea is also supported by the fact that pCO_2 was positively correlated with DO in river waters (Wang et al., in preparation).

The processes of how the imported HCO_3^- took part in the lake's C cycling can be described on the basis of its seasonal variations. As the lake was thermally stratified during the summer, photosynthesis kept CO_2 in an under-saturated state, pH elevated, and CaCO_3 in an over-saturated state in the epilimnion (II in Fig. 5). It has been estimated that the ratio of organic C production to calcite deposition during a period of strong photosynthesis was 1.58, and the overall reaction is as follows (Wang et al., in preparation):



In the hypolimnion, remineralization of organic matter led to decreased pH, increased CO_2 , and under-saturation of CaCO_3 . The biological cycling, in which DIC was utilized by algal photosynthesis and then replenished by organic matter mineralization, might be fast relative to water retention time, so C isotopes (-15.528‰ and -18.319‰ in Fig. 3) of the DIC added in the lake just falls in the range of organic matter decay (-15‰ to -20‰). As the lake waters mixed from late autumn to early spring (I in Fig. 5), decomposition of organic matter produced both CO_2 and NH_4^+ , and oxidation of the NH_4^+ to NO_3^- produced H^+ causing pH to decrease so that CO_2 was not converted into HCO_3^- , resulting in high partial pressures. This is in agreement with the facts that CO_2 concentrations were highest (Fig. 5) and CO_2 emissions from the lake were greatest in October 2001 (Fig. 4), when stratified lake water turned over. It is estimated that approximately 42% of the retained DIC ($37.2 \times 10^7 \text{ mol a}^{-1}$, Table 2) in the lake returns to the atmosphere by CO_2 evasion ($15.5 \times 10^7 \text{ mol a}^{-1}$), and 38% and 19% is stored in sediment as organic and inorganic C ($14.0 \times 10^7 \text{ mol a}^{-1}$ and $7.0 \times 10^7 \text{ mol a}^{-1}$, respectively) (Fig. 6). Theoretically, inorganic C stored in sediment can be regarded as being transferred from the catchment, and organic C in sediment and CO_2 emitted from the lake as originating from the consumed CO_2 in the catchment.

4.4. Carbon balance in relation to CO_2 evasion

The CO_2 evasion rate in Hongfeng Lake ($13.2 \pm 3.9 \text{ mmol m}^{-2} \text{ d}^{-1}$) is much less than average evasion rates documented from reservoirs in temperate and tropical climatic zones ($31.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $79.5 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively, St. Louis

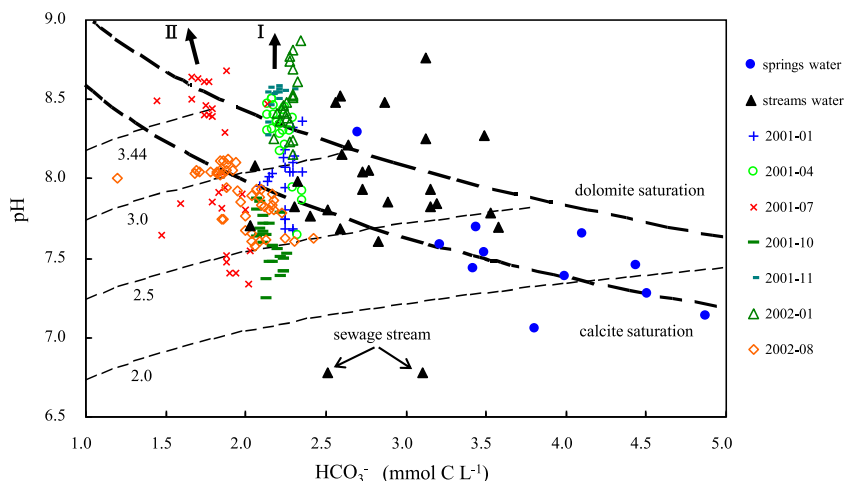


Fig. 5. pH versus lake, spring and stream HCO_3^- concentrations. Dolomite and calcite saturation lines are also shown, and CO_2 equilibrium lines (dashed) are marked with values of $-\log p\text{CO}_2$. Arrows I and II discriminate the trends of pH – HCO_3^- co-variation of lake waters in the winter/spring (blue/green) and summer (red/orange), respectively.

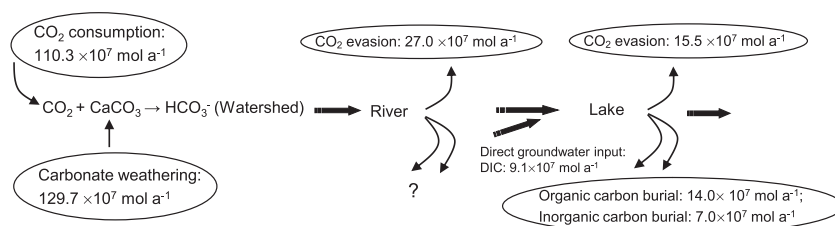


Fig. 6. The C mass balance of the Hongfeng Lake watershed.

et al., 2000), and is slightly lower than the mean value of the world's lakes ($\sim 16.2 \text{ mmol m}^{-2} \text{ d}^{-1}$, Cole et al., 1994). Hongfeng Lake is similar to the oligotrophic Loch Ness, Scotland ($12.3 \text{ mmol m}^{-2} \text{ d}^{-1}$, Jones et al., 2001) despite the fact that the latter is an oligotrophic, unproductive lake with low-alkalinity. Similarly, Yu et al. (2007) reported a relatively low CO_2 evasion flux ($4.87\text{--}7.7 \text{ mmol m}^{-2} \text{ d}^{-1}$) in the nearby Hongjiadu Reservoir (Fig. 1b). In general, the mean CO_2 evasion flux from natural lakes in this area ($10.8 \text{ mmol m}^{-2} \text{ d}^{-1}$, Wang et al., 2003) is lower than the mean value from the world's lakes (Cole et al., 1994).

Low DOC export from the catchment to Hongfeng Lake is likely one important factor in the lake's low CO_2 evasion rate. Usually, lake CO_2 originates mainly from allochthonous DOC input from catchments (Sobek et al., 2003; Roehm et al., 2009). Low DOC concentrations, short water residence time, and a large Ac/As ratio (Ac: catchment area; As: lake surface area) (Table 1) are all unfavorable to the remineralization and metabolism of DOC in the lake. The total amount of POC and DOC annually supplied to the lake by rivers (Table 2) is less than the total CO_2 evasion from the lake. Results here and from Hongjiadu Reservoir (Yu et al., 2007), in combination with the above-mentioned low DOC exports, lead to a hypothesis that reservoirs in karst areas (such as the ones in Fig. 1b) are likely to be insignificant sources of atmospheric CO_2 .

The CO_2 evasion from the lake as a function of catchment area was $0.097 \text{ mol m}^{-2} \text{ a}^{-1}$. This value is within the range (-0.017 to $0.225 \text{ mol m}^{-2} \text{ a}^{-1}$) reported by Dillon and Molot (1997) for seven small, shallow, oligotrophic lakes in central Ontario, Canada. However, it is slightly less than the mean value for these lakes ($0.123 \text{ mol m}^{-2} \text{ a}^{-1}$, Dillon and Molot, 1997) and that for the oligotrophic Loch Ness, Scotland ($0.144 \text{ mol m}^{-2} \text{ a}^{-1}$, Jones et al., 2001). It can be estimated that approximately 20% of the exported primary production from the catchment returns to the atmosphere

as CO_2 evasion through the fluvial water–air interface, and 12% through the lake water–air interface, with 10% stored as organic C in lake sediment (Fig. 6). These proportions are comparable to those for the global C balance proposed recently by Cole et al. (2007), who suggested that as terrestrially-derived C is transported to the sea, 12% is stored in sediments (mainly as organic C), and 40% is lost as CO_2 to the atmosphere. This coincidence indicates that the inorganic C exported from carbonate catchments shares a similar fate with organic C exported from most terrestrial environments.

Almost all CO_2 released from the lake is derived from the HCO_3^- imported from the catchment, similar to the scenario in Loch Ness, Scotland where approximately 3/4 of the CO_2 evasion is derived from inorganic C input (Jones et al., 2001). It can be estimated that approximately 25% of the CO_2 consumed by carbonate dissolution in the catchment returns to the atmosphere as CO_2 evasion through the fluvial water–air interface, and 14% through the lake water–air interface (Fig. 6). The estimate here means a much larger return flux (39%), with far less C (13%) stored in sediments (Fig. 6), as the consumed CO_2 is conveyed from land to sea than expected (20% and 39%, respectively, Liu et al., 2010), implying that the C sink of carbonate weathering in terrestrial environments may not be as significant as once thought and thus needs a material modification in estimating its magnitude.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.apgeochem.2011.09.003](https://doi.org/10.1016/j.apgeochem.2011.09.003).

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