ORIGINAL ARTICLE

Dynamics of CO_2 in a karst catchment in the southwestern plateau, China

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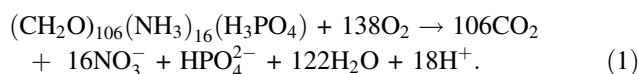Cong-Qiang Liu · Fang Liu · Yingchun Lü

Abstract Inland waters, including rivers and lakes, are increasingly recognized as playing significant roles in the transport, mineralization and burial of organic carbon exported from land. However, in many areas, dissolved inorganic carbon (DIC) dominates the carbon export from catchments. Owing to different production processes and turnover times of organic versus inorganic carbon, CO_2 emitted from rivers and lakes may have different impacts on global carbon cycling depending on its origin. Here, pCO_2 and dissolved oxygen concentrations were determined, and the ratios of excess CO_2 to O_2 depletion ($\Delta CO_2/\Delta O_2$) were compared in spring water, river water and lake water in a carbonate catchment located in the southwestern plateau region of China. Results show that groundwater CO_2 evasion, at 2.0 g C m^{-2}year^{-1}, is insignificant in terms of terrestrial carbon loss compared with soil CO_2 emission. In the rivers, calcite precipitation due to oversaturation is an important mechanism for CO_2 production in some seasons. In the lake, HCO_3^- contributed approximately 75 % of the total carbon supply to organic matter production and calcite deposition during seasons favoring photosynthesis. The seasons which had high $\Delta CO_2/\Delta O_2$ are the main periods of CO_2 emission from the lake, and the extra CO_2 may be produced from HCO_3^- titration by H^+. Thus, lake CO_2 evasion was controlled primarily by pH, not respiration. The spring, river, and lake waters mainly process DIC exported from the catchment, of which HCO_3^- is primarily derived from carbonate weathering by soil CO_2 that, with extraordinarily high $\Delta CO_2/\Delta O_2$, may originate from sources including organic matter decomposition, root respiration (autotrophic), and acid dissolution. Therefore, freshwater CO_2 emission is a return pathway of catchment soil CO_2 to the atmosphere more than that of net primary production and net ecosystem production.

Keywords CO_2 dynamics · Ratio of excess CO_2 to O_2 depletion · Spring-river–lake system · Carbonate catchment · Southwestern China

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Introduction

Primary production in terrestrial ecosystems significantly influences atmospheric CO_2 concentrations, and constitutes a complex feedback mechanism within the global climatic system, therefore much attention has been paid to the terrestrial carbon cycle (Heimann and Reichstein 2008; Lewis et al. 2009; Piao et al. 2009; Regnier et al. 2013). As organic carbon generated on land is exported from river catchments, some of it is decomposed by microorganisms in aquatic environments during transport (Cole and Caraco 2001). Thus, the world's rivers, lakes and estuaries are generally over-saturated and act as sources of atmospheric CO_2 (Kling et al. 1991; Cole et al. 1994; Cai and Wang 1998; Richey et al. 2002; Roehm et al. 2009; Tranvik et al. 2009; Butman and Raymond 2011). In these environments, CO_2 production via organic matter decomposition links to O_2 consumption with the stoichiometric relationship (1):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \rightarrow 106CO_2 \\ + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+. \tag{1}$$

Thus, the ratio of CO_2 production to O_2 consumption is 0.77 (106/138, traditional Redfield ratio). Taking into account that lipids consume approximately 36 % more oxygen than carbohydrates during their oxidation, the ratio theoretically varies around 0.71 (Fraga et al. 1998), which is in excellent agreement with experimental results (0.70, Lee et al. 2003). Respiration quotients ($CO_{2\ released}/O_{2\ consumed}$) of marine algae have been shown to fall in the range of 0.62–0.79 (Chen et al. 1996). Freshwater phytoplankton has a different stoichiometry from marine algae, with C:N:P ratios of 300:30:1 (Elser et al. 2000). If differences in biochemistry are ignored and the stoichiometry for freshwater phytoplankon is applied in Eq. (1), the ratio of CO_2 production to O_2 consumption would be 0.83 (300/360).

The H^+ produced in Eq. (1) can lead HCO_3^- to be transformed into CO_2:

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O. \tag{2}$$
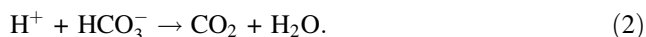
From Eqs. (1) and (2), the following stoichiometry was obtained (Zhai et al. 2005):

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 + 18HCO_3^-$$
$$\rightarrow 124CO_2 + 140H_2O + 16NO_3^- + HPO_4^{2-}. \tag{3}$$
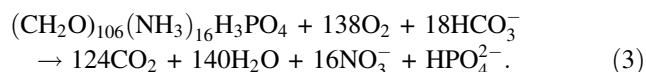
The ratio of CO_2 production to O_2 consumption for this equation is equal to 0.90 (124/138), which is the planktonic respiration quotient plus the contribution of HCO_3^- titration. Therefore, the normal range of the ratio in high-DIC systems could be defined to be from 0.62 to 0.90 (similarly hereafter). Although different air–water gas exchange rates of DO and CO_2 with the atmosphere could in part explain the concentration of excess CO_2 that could not be explained by depletion of DO (Salomão et al. 2008), the stoichiometric relationship between carbon and oxygen is still an important tool to understand the dynamics of CO_2 and O_2 in aquatic environments (Zhai et al. 2005; Dai et al. 2006).

Most of these studies focus on the export and degradation of organic carbon (Richey et al. 2002; Roehm et al. 2009), with comparatively little attention paid to inorganic carbon species or its export. In fact, the DIC conveyed by rivers from the land to the sea is as important in understanding both regional and global carbon cycling as organic carbon is (Barth et al. 2003; Raymond and Cole 2003; Raymond et al. 2008; Öquist et al. 2009; Liu et al. 2010), especially in carbonate catchments, where as much as ~90 % of exported carbon (excluding the carbon from carbonate) is in the form of DIC (Wang et al. 2012). Other examples where DIC dominates the carbon export from catchments have been documented (e.g., Tranvik et al. 2009; Finlay et al. 2010; Sand-Jensen and Staehr 2012). DIC (HCO_3^-, CO_3^{2-}, and dissolved CO_2) is related to gaseous carbon ($CO_{2(g)}$) via carbonate equilibria (Bulter 1982). When CO_2 dissolves in water ($CO_{2(aq)}$), it hydrates to yield H_2CO_3. Generally, it is convenient to abbreviate all dissolved CO_2 ($H_2CO_3 + CO_{2(aq)}$) simply as $[CO_2]$. Hydrated CO_2 ionizes to give hydrogen (H^+), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}), ions (Stumm and Morgan 1970; Bulter 1982). The relative proportions of inorganic forms of carbon are dependent on pH and to a lesser extent temperature (Rantakari and Kortelainen 2008).

However, the origins, transport and fate of DIC exported from terrestrial ecosystems are not completely understood (Richey et al. 2002; Maberly et al. 2013). The chemical weathering of carbonate and silicate minerals produces HCO_3^- and consumes soil CO_2 (Barth et al. 2003; Rantakari and Kortelainen 2008; Liu et al. 2010). Macpherson et al. (2008) found that pCO_2 and alkalinity in groundwater from a limestone-dominated area in the USA increased over the previous decade, which is in accord with the increase in carbonate alkalinity export documented in US rivers over the last 50 years (Raymond and Cole 2003). The reasons for these increases are not yet well known. In comparison, concentrations of CO_2 and H^+ in US rivers decreased instead of increase in the 22 years preceding the research of Jones et al. (2003). Inland waters contribute substantially to global carbon fluxes, despite only occupying a small fraction of the Earth's surface (Cole 2013), so that traditional models of global carbon cycling need to integrate these fresh water systems (Battin et al. 2009; Regnier et al. 2013). The CO_2 produced in inland waters is generally thought to be derived from the mineralization of organic carbon supplied by inland catchments. However, if the CO_2 in inland waters is derived primarily from inorganic carbon exported from catchments, its impacts on global carbon cycling may be different due to different production processes and turnover times. The CO_2 from autotrophic respiration may have little global impact due to very short residence time (Kuzyakov 2006) compared to the CO_2 from heterotrophic respiration, and the DIC derived from strong acids dissolution has a potential to act as a net source of atmospheric CO_2. In this study, the relative variations of pCO_2 and dissolved oxygen (DO) were quantified and compared, coupled with inorganic carbon concentrations and $\delta^{13}C$, in groundwater, river water and lake water in a carbonate catchment in the southwestern plateau, China, with the objective of clarifying the dynamic processes of CO_2 production during the export of DIC from land, to river and lake.

Materials and methods

Background of study area

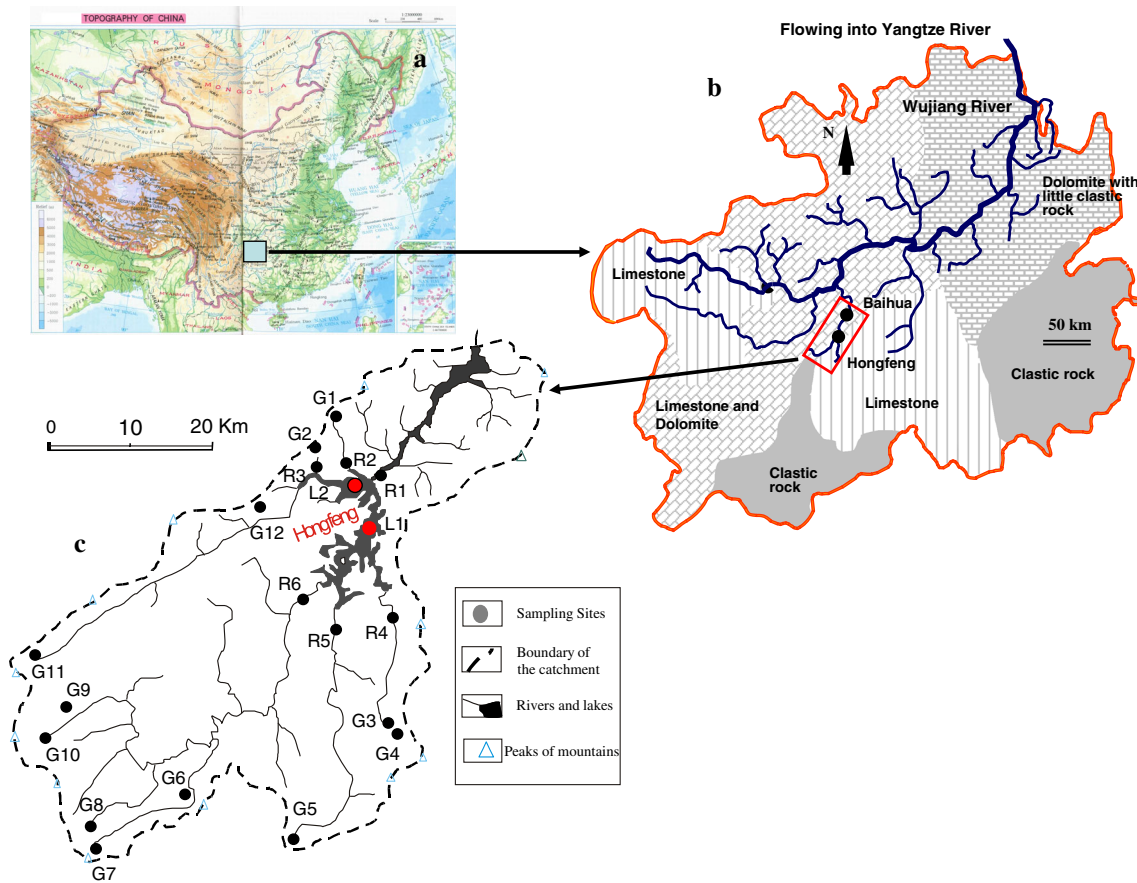The Hongfeng Lake catchment is located on the Guizhou, karst plateau in southwestern China (Fig. 1a). The lake is

Fig. 1 Maps of China (**a**), Guzhou province (**b**) and the Hongfeng Lake catchment (**c**). The Wujiang River and the exposed rocktypes are shown in panel **b**. The sampling sites (*solid circles*) in the catchment are also shown in panel **c**

located in the upper-, middle-reaches region of the Maotiao River, a tributary of the Wujiang River, located in the upper reaches of the Yangtze River catchment (Fig. 1b). The Hongfeng Lake catchment is approximately 65-km long from south to north and 17-km wide from east to west, with an area of 1,596 km², at an elevation of between 750 and 1,765 m above mean sea level. The bedrock here is comprised primarily of Permian and Triassic age limestones and dolomites, mixed with minor exposures of siliciclastic 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; vegetation includes mainly shrubs and limited broadleaf and coniferous forests in some areas. This region has a subtropical, monsoon climate, with a mean annual precipitation of 1,195 mm, and mean annual temperature of 14 °C.

Water chemistry in the catchment has been well studied (Han and Liu 2004; Wang et al. 2012). In brief, carbonate dissolution controls the chemical compositions of water. Calcium and HCO_3^-, followed by Mg^{2+} and SO_4^{2-},

dominate the chemical composition of major ions in the waters (Han and Liu 2004). Total cation concentrations in the spring waters, river waters, and lake waters ranged from 2.5 to 6.5 meq l⁻¹, of which Ca^{2+} and Mg^{2+} account for more than 95 %. The proportion of bicarbonate in total anion concentrations ranged 50–80 %, and SO_4^{2-} from 5 to 30 %. This comparison shows that carbonate is dissolved not only by CO_2, but also by sulfuric acid, though there is no evidence of SO_4^{2-} supplied from the dissolution of evaporites in the catchment (Han and Liu 2004; Li et al. 2008). The linear correlation of SO_4^{2-} to NO_3^- and Cl^-, and isotopic evidence of S and N indicate that SO_4^{2-} and NO_3^- are most likely of anthropogenic origin (Han and Liu 2004; Liu et al. 2006). Nitrogenous fertilizer, wastewater input, and atmospheric deposition are all possible sources.

Hongfeng Lake was constructed in 1960 and is the largest artificial lake in the Guizhou Province, with headwaters consisting of several springs (Fig. 1c). With a surface area of 32.2 km², a mean depth of 9.2 m and a water residence time of 0.35 year, 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 excessive use of fertilizer, and

discharge of raw waste water in the catchment, the total nitrogen (TN) and total phosphorus (TP) concentrations in the lake are high, and the lake is eutrophifed (e.g., He et al. 2008; Zhang et al. 2008).

Sampling and analysis

Lake water samples were collected with a Niskin Water Sampler (Model 1010, General Oceanics, USA) at sampling sites L1 and L2 (Fig. 1c) in January, April, July, October and November of 2001, and January and August of 2002. Lake water samples were collected at different depths in the water column with a 2–3 m vertical spacing, a 5-m vertical spacing was used during the well-mixed winter and spring. 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 of 2001, and from surrounding springs (G1–G12 in Fig. 1c) in December of 2001.

After water samples were collected, temperature, electrical conductivity, pH and DO were measured in the field using a PIONneer 65 multi-parameter instrument. Alkalinity was determined using HCl titration with a TitraLab 840 Titration Workstation (Radiometer-Analytical). Filtered water aliquots were treated with 100 % phosphoric acid to produce CO_2, which was then analyzed by mass spectrometry (Thermo Scientific MAT 252) to determine the stable carbon isotope composition of DIC ($\delta^{13}C_{DIC}$). The precision was better than 0.3 ‰. The carbon isotope of free CO_2 ($\delta^{13}C_{CO2}$) was calculated with the measured $\delta^{13}C_{DIC}$ and the isotope fractionation factors on the basis of mass and isotope balances (Herczeg and Fairbanks 1987).

Calculation

HCO_3^- concentrations were estimated with the amounts of HCl added in alkalinity titration from the HCO_3^- equivalence point (pH = 8.3) to the CO_2 equivalence point (pH = 4.5) (Bulter 1982). This kind of estimation is acceptable for freshwater carbonate systems because the influences of other weak acids and bases, such as borate, ammonia, and organic acid, on alkalinity, are negligible. DOC concentrations in waters in this area are very low (Wang et al. 2012), therefore its influence on alkalinity is rather small and correction for this is unnecessary. Experimental results show that the difference in DIC concentrations from titration and from phosphoric acid treatment (see DIC isotope analysis) is within 2 %, suggesting that the estimation is acceptable.

DIC and CO_3^{2-} concentrations and CO_2 partial pressure (pCO$_2$) could be calculated from HCO_3^-, pH, the reaction constants (K_{a1} and K_{a2}), and Henry's law constant (K_H) for CO_2 (Eqs. 4, 5, 6, and 7). These constants (K_{a1}, K_{a2}, and K_H) could be estimated with sample temperature (Wallin et al. 2010).

$$[CO_2] = [H^+][HCO_3^-]/K_{a1} \tag{4}$$

$$[CO_3^-] = K_{a2}[HCO_3^-]/[H^+] \tag{5}$$

$$[DIC] = [HCO_3^-] + [CO_3^{2-}] + [CO_2] \tag{6}$$

$$pCO_2 = [CO_2]/K_H = \frac{[H^+][HCO_3^-]}{K_H K_{a1}} \tag{7}$$

The departure of freely dissolved CO_2 from atmospheric equilibrium is defined as excess CO_2 (ΔCO_2) (Eq. 8), and the departure of oxygen as oxygen depletion (ΔO_2) (Zhai et al. 2005) as Eq. (9):

$$\Delta CO_2 = [CO_2] - K_H \times pCO_2(\text{in air}) \tag{8}$$

$$\Delta O_2 = [O_2]_{eq} - [O_2]. \tag{9}$$

Here, $[CO_2]$ and $[O_2]$ are the in situ dissolved CO_2 and O_2 concentrations, respectively. pCO$_2$ (in air) is the atmospheric CO_2 partial pressure, 360 μatm. And $[O_2]_{eq}$ denotes the DO concentration at equilibrium with atmospheric O_2.

Results

Seasonal variations in pCO$_2$, HCO_3^-, pH, and DO

Temperature, pCO$_2$, pH, DO, HCO_3^-, CO_3^{2-}, and DIC in the lake's water column all varied coherently between site L1 and site L2 (Fig. 2). Comparatively, these data showed less variability at site L2 than at site L1, which is attributed to the location of L2 within the reservoir area (little effect from river import).

At L2, pH varied between 7.5 and 8.5, with water column pH profiles varying with the sampling season. In summer, with stable thermal stratification (July 2001; August 2002), pH values in surface waters were much higher than in deep waters. In January and October of 2001, while pH in these months differed, both exhibited slightly lower pH values in surface waters than in deep waters. In April and November of 2001, and January of 2002, pH differed little, and values in surface waters were slightly higher than in deep waters.

pCO$_2$ profiles exhibit a clear, inverse relationship with pH values (Fig. 2), indicating that pH has a significant influence on pCO$_2$ values in Hongfeng Lake, like in other hard-water lakes (Finlay et al. 2009). Lake water was under-saturated with respect to atmospheric CO_2 as the pH rose over 8.5–8.6 (depending on DIC concentration), and therefore served as an atmospheric CO_2 sink. As a whole, pCO$_2$ ranged between 300 and
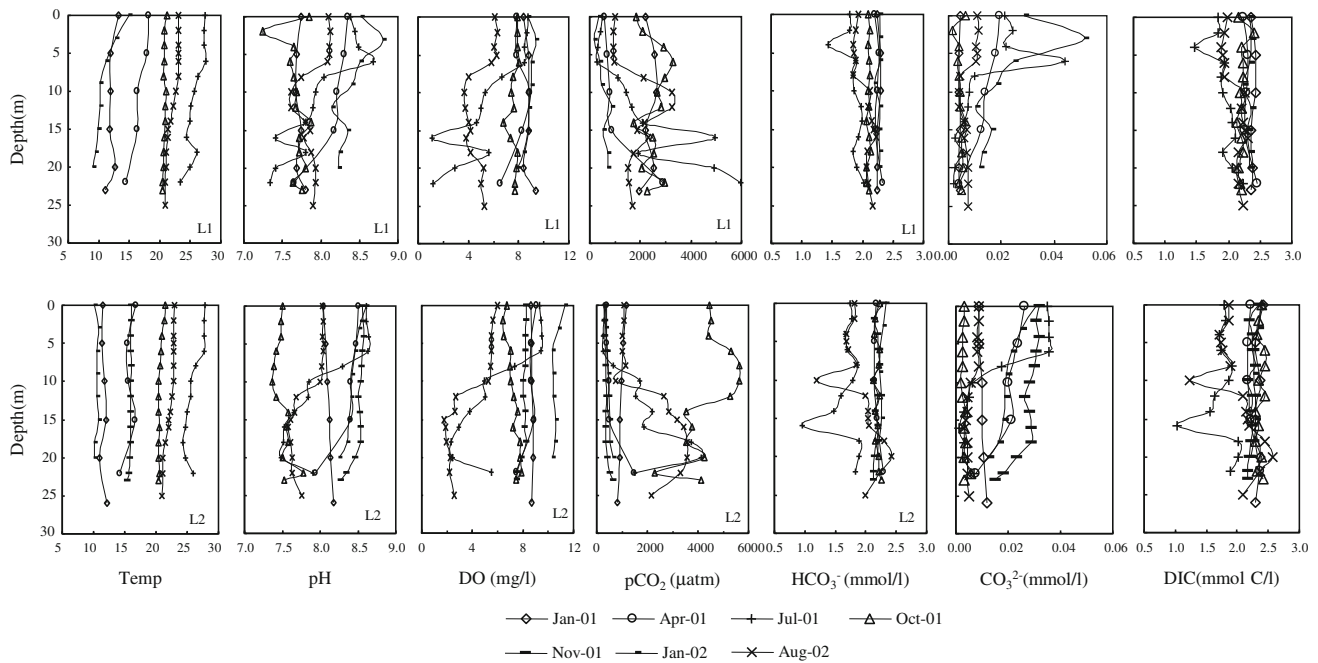
Fig. 2 Seasonal variations in temperature (Temp), pH, DO, pCO_2, HCO_3^-, CO_3^{2-}, and DIC versus water depth at sampling sites L1 and L2 in Hongfeng Lake

500 μatm in surface waters, and between 1,000 and 6,000 μatm in bottom waters during the period of thermal stratification. During the period from winter to early spring, pCO_2 ranged 1,000–2,000 μatm, with little difference between surface and deep water values due to vertical mixing. An exceptionally high pCO_2 of up to 5,000 μatm appeared in October, 2001. During the period from November, 2001 to January, 2002, pCO_2 decreased to between 200–400 μatm in surface waters and 400–700 μatm in bottom waters, likely due to the climate, which favors photosynthesis.

DO concentrations in surface and bottom waters were nearly equivalent during winter and spring, while in summer, with thermal stratification, DO concentrations increased in surface waters due to photosynthesis and decreased in bottom waters due to consumption via organic matter decomposition (Fig. 2).

HCO_3^- had completely different variations in the lake as compared to pH. The HCO_3^- concentrations were significantly lower in July, 2001 and August, 2002 than in other seasons. Variations in HCO_3^- concentrations versus water depth were similar in those months other than July and August (Fig. 2), despite there being large differences in pH. pH varying between 7.5 and 8.5 has little influence on HCO_3^- concentrations (Bulter 1982). CO_3^{2-} concentrations varied in the same way as pH, and DIC appeared strongly coupled to HCO_3^-, which is expected as HCO_3^-, on average, comprised 96 % of DIC.

Excess CO_2 versus O_2 depletion ($\Delta CO_2/\Delta O_2$) in lake water

Compared with the normal range of $\Delta CO_2/\Delta O_2$ (0.62–0.90), the $\Delta CO_2/\Delta O_2$ in the lake can be divided into three categories (Fig. 3):

C1. Lower ratio than the lower limit of the normal range: In July, 2001 and November, 2001 to January, 2002, the ratio values ranged 0.41–0.57 with an average of 0.46.

C2. Normal ratio: In August, 2002, the ratio was 0.6261, which is consistent with Zhai et al. (2005)'s result (0.63). In April, 2001, the ratio was 0.8705.

C3. Higher ratio: Most of the samples taken in January and October, 2001 fell above the 1:1 line (Fig. 3a), except for few samples whose values fell within the normal range (Fig. 3b). The regression line of the data from October, 2001 had a slope of 1.8912, which is far larger than the upper limit of the normal range. The data obtained in January, 2001 did not have a significant correlation due to stronger mixing of lake water, but many of them were consistent with those from October (Fig. 3a).

Variations in $\delta^{13}C$ of CO_2 in lake water

The Keeling plot of $\delta^{13}C$ is a powerful tool to trace carbon sources (Karlsson et al. 2007). On the basis of the
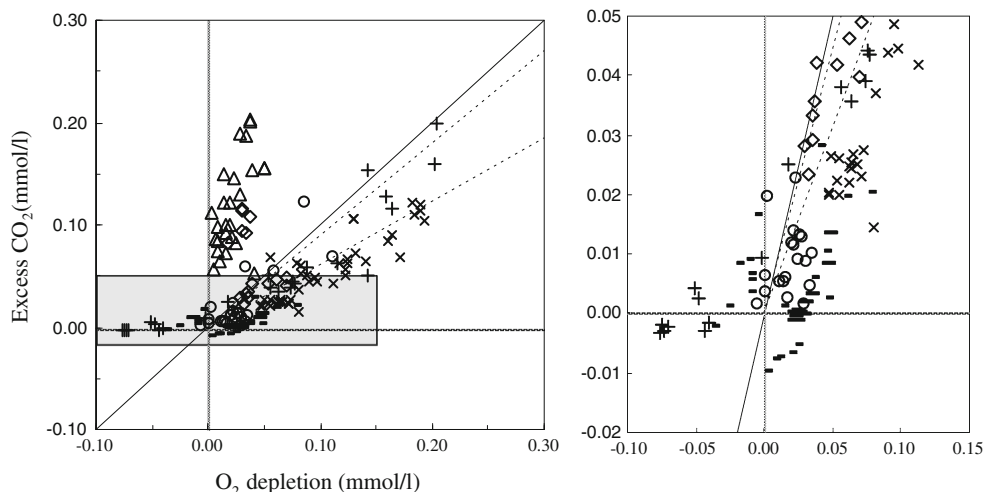
Fig. 3 Excess CO_2 versus O_2 depletion in the lake waters (the *right* panel is magnified from part of the *left* one, the *dotted lines* have a slope of 0.62 and 0.9, respectively, the legends are the same as those in Fig. 2). These data can be divided into three groups: C1: The slope is smaller than the lower limit value of the normal range: $y = 0.5705x + 0.0227$ $r = 0.907$, $p \ll 0.0001$ (July 2001); $y = 0.453x - 0.0114$ $r = 0.943$, $p \ll 0.0001$ (November 2001);

$y = 0.4185x + 0.0131$ $r = 0.787$, $p = 0.02$ (January 2002, **a**); $y = 0.4062x - 0.0055$ $r = 0.7798$, $p = 0.023$ (January 2002, **b**); C2: The slope is within the normal range: $y = 0.6261x - 0.0102$ $r = 0.891$, $p \ll 0.0001$ (August 2002); $y = 0.8705x - 0.0045$ $r = 0.797$, $p \ll 0.0001$ (April 2001); C3: The slope is greater than the upper limit value of the normal range: $y = 1.8912x + 0.0757$ $r = 0.5837$, $p = 0.002$ (October 2001)

Fig. 4 $\delta^{13}C_{CO2aq}$ versus $(1/CO_{2aq})$ in the lake waters at sampling site L2 (**a** July 2001; **b** August 2002; **c** October 2001; **d** January 2002)
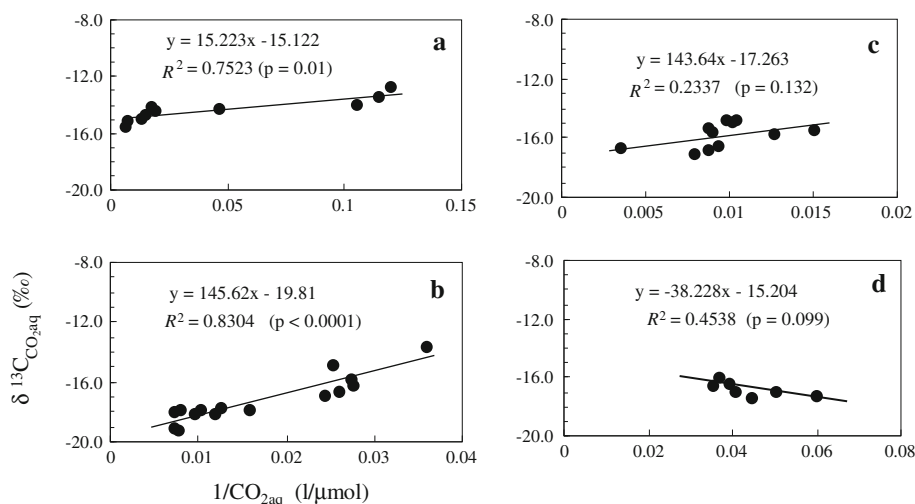
intercepts of regression lines, the Keeling plots of $\delta^{13}C$ of CO_2 in the lake water (Fig. 4) can be divided into three groups, which correspond to variations in $\Delta CO_2/\Delta O_2$.

In July, 2001 and January, 2002 (Fig. 4a, d), the $\delta^{13}C$ (intercept) in the added CO_2 was at its highest, −15.122 and −15.204 ‰, respectively, which corresponds to the low $\Delta CO_2/\Delta O_2$ range of values (C1). In August, 2002 (Fig. 4b), the $\delta^{13}C$ in the added CO_2 was at its lowest (−19.81 ‰), which corresponds to the normal $\Delta CO_2/\Delta O_2$ range of values (C2). In October, 2001 (Fig. 4c), the $\delta^{13}C$ in the added CO_2 (−17.263 ‰), corresponds to the high $\Delta CO_2/\Delta O_2$ range of values (C3).

Variations in CO_2 versus DO in river water

The average value of pCO_2 in river water was 3,443 µatm, which is consistent with that in river waters from other regions of the world (3,230 µatm, Cole and Caraco 2001), indicating that rivers are a significant source of atmospheric CO_2. River pCO_2 increased exponentially with rising DO in January and July, 2001 (Fig. 5a). Production of CO_2 was not correlated with O_2 consumption in the rivers. The data points were scattered in the diagram of excess CO_2 against O_2 depletion; however, most of them fell above the 1:1 line (Fig. 5b) (similar to the results of
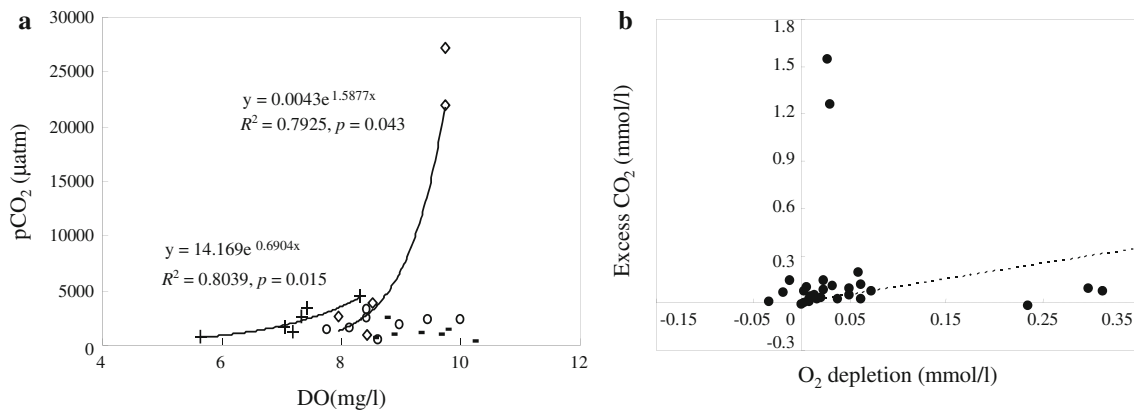
Fig. 5 pCO_2 versus DO (**a**), and excess CO_2 versus O_2 depletion (**b**) in the river waters. The dotted line represents the ratio of 1:1, (the legend in panel **a** is the same as that in Fig. 2)
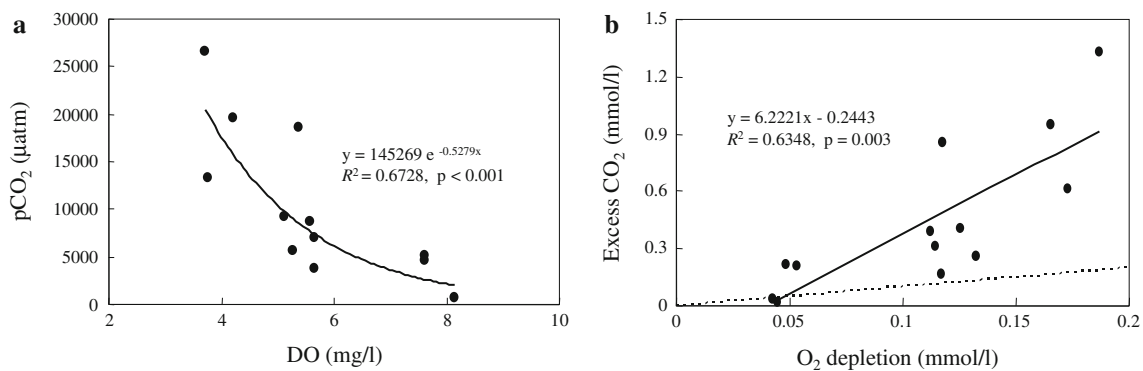

Fig. 6 pCO_2 versus DO (**a**), and excess CO_2 versus O_2 depletion (**b**) in the spring waters. The *dotted line* represents the ratio of 1:1

Salomão et al. (2008)). River pCO_2 was not correlated to DO concentrations in April, 2001 or January, 2002 (Fig. 5a), indicating that the dynamics of CO_2 production in the river water may vary in different months.

Variations in CO_2 versus DO in spring waters

The spring water is a primary source of the river and lake water in the catchment. pCO_2 in the spring waters ranged between 800 and 26,600 µatm, with an average of $10,207 \pm 7,749$ µatm. It was significantly and negative correlated with DO (Fig. 6a). The excess CO_2 was positively and linearly correlated with O_2 depletion (Fig. 6b) with a high slope of 6.2221.

Discussion

Sources of CO_2 in spring water

CO_2 in the spring water is a mixture of CO_2 derived from the soil over a range of depths. The curve of pCO_2 versus

DO concentrations (Fig. 6a) could be explained as a mixing curve (hyperbola), reflecting the different CO_2 sources. The CO_2 and 1/DO are linearly correlated and described by the following regression equation (Eq. 10):

$$pCO_2 = 127,368(1/DO) - 13,802 \, (r = 0.802, \\ p = 0.002).$$
(10)

When DO was equal to 8.89 mg l^{-1}, at equilibrium with atmospheric O_2 (at 16.5 °C), the corresponding pCO_2 was 523 µatm according to the above equation, which is in good agreement with the measured pCO_2 in the surface soil (Li et al. 2002). Also, the maximum pCO_2 in the groundwater (26,612 µatm) was close to the observed maxima of pCO_2 in the soils of this area (28,408 µatm, Li et al. 2002; 25,000–30,000 µatm, Liu et al. 2012).

CO_2 in soils is produced via a combination of processes that includes microbial decomposition of organic matter (heterotrophic respiration), root respiration (autotrophic respiration) and dissolution of carbonate by acids. It is very difficult to differentiate the contributions of each of these processes (Kuzyakov 2006). The extraordinarily high value (6.2221) of $\Delta CO_2/\Delta O_2$ has not been reported before, and

cannot yet be explained quantitatively in relation to CO_2 production in this study. If the $\Delta CO_2/\Delta O_2$ for aerobic degradation of organic matter in soil and groundwater is assumed to be an average value of 0.71 (Lee et al. 2003), the maximum pCO_2 would be approximately 4,300 µatm when the DO at equilibrium with atmospheric O_2 is exhausted, which only accounts for 42 % of the total CO_2. Root respiration is likely an important factor. In general, root respiration contributes 30–70 % of the total soil CO_2 efflux (Baggs 2006) with a maximum of 90 % (Hanson et al. 2000) depending on vegetation type and season. A high soil CO_2 efflux of 1,553 g C m^{-2} year^{-1} was reported in this karst area (Liu et al. 2012), in comparison with the relatively low net primary production (NPP: 262–417 g C m^{-2} year^{-1}) and net ecosystem production (NEP: 0 to -15 g C m^{-2} year^{-1}) (Cao et al. 2003). It could be speculated that a portion of the soil CO_2 is produced by autotrophic respiration, which is utilized in situ to dissolve carbonate to produce HCO_3^-. Additionally, as groundwater is often depleted in oxygen, anaerobic decomposition of organic matter, and nitrate and sulphate reduction may occur there, producing CO_2 without O_2 consumption (Salomão et al. 2008). Abiologically, sulfuric acid from some natural and human processes (Li et al. 2008) and nitric acid from oxidation of NH_4^+ (nitrification) (Semhi et al. 2000; Liu et al. 2006; Perrin et al. 2008; Guo et al. 2010) can enhance carbonate weathering by approximately 11–20 % (Li et al. 2008; Xu and Liu 2010), and 6–15 % (Perrin et al. 2008), respectively, thus increasing alkalinity (Eq. (11)).

$$H^+ + CaCO_3 \leftrightarrow Ca^{2+} + HCO_3^- \qquad (11)$$

A wide range (15–35 %) for the abiological contribution could be given according to the above documented values. Considering the geological and environmental setting of the study area, which is located in the most serious acid rain region in China, and includes many exposed coal seams, the estimate for the abiological contribution made here may well be conservative. The added acids would lead to a decrease in pH (Guo et al. 2010) and an increase in soil CO_2 concentration as soil carbonate is exhausted, and thus the added H^+ could not be effectively neutralized. In fact, pH values ≤4 have been observed, and carbonate minerals were frequently absent in some soils in the carbonate area of this catchment (Liu et al. 2007). Therefore, it could be concluded that soil CO_2 in this catchment is derived from sources including microbial decomposition of organic matter, autotrophic respiration, and acid dissolution.

Terrestrial C loss via groundwater

Groundwater with high CO_2 concentrations may release CO_2 directly to the atmosphere within 200 m to a few kilometers of its entry into streams or rivers (Öquist et al. 2009; Davidson et al. 2010). Based on the assumption that all of the CO_2 in groundwater is eventually released to the atmosphere, Davidson et al. (2010) used the approach of multiplying mean headwater CO_2 concentrations by mean annual discharge to estimate groundwater CO_2 evasion. Here we used the CO_2 concentration difference between spring water and river water instead of mean headwater CO_2 concentration in estimating groundwater CO_2 evasion. The amount of terrestrial C lost via groundwater CO_2 to stream evasion of CO_2 is approximately 2.0 g C m^{-2} year^{-1}, which is in good agreement with the result (2.14 g C m^{-2} year^{-1}, ranging 1.43–2.91) in the Thames River catchment (Worrall and Lancaster 2005), and just within the lower limit (2.0–4.0 g C m^{-2} year^{-1}) documented by Davidson et al. (2010), but much lower than the reported value (40 g C m^{-2} year^{-1}) for a small forested catchment in Brazil (Johnson et al. 2008). The value is approximately 0.15 %, and 0.6–0.8 % of the measured soil CO_2 emission, and NPP of this area, respectively, therefore supporting the idea that groundwater CO_2 outgassing is a minor pathway of C return into the atmosphere from terrestrial ecosystems (Davidson et al. 2010). However, the amount of groundwater CO_2 outgassing (2.68×10^8 mol year^{-1}) is comparable to the CO_2 evasion from the rivers and lakes within the study catchment (Wang et al. 2012).

CO_2 production in river water

Exchange of CO_2 at the river water–air interface is very rapid (Salomão et al. 2008), thus, spring water CO_2 (in headwaters) is unlikely to influence river water CO_2 variations. In small streams, groundwater input may influence CO_2 concentrations, while in larger streams variations in CO_2 concentrations are mainly controlled by CO_2 production processes. The mechanisms for river CO_2 production include aerobic and anaerobic respiration and $CaCO_3$ precipitation.
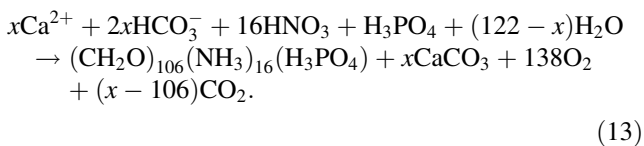
In general, CO_2 in rivers is produced primarily by decomposition of allochthonous organic matter imported from catchment soils or anthropogenic sources (Salomão et al. 2008; Teodoru et al. 2009). However, the positive correlation between pCO_2 and DO shown in Fig. 5a is inconsistent with the generally-accepted idea. The decomposition of organic matter cannot be the only source of CO_2 in these rivers, which is in congruence with the low export flux of allochthonous organic matter from the karst watershed (Wang et al. 2012).

Unlike spring waters, river waters were over-saturated with calcite. As a result, the calcium ion concentration decreased from 1.40 mmol l^{-1} in the spring waters to 1.21 mmol l^{-1} in river waters due to $CaCO_3$ precipitation (Eq. (12)):

$$2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + H_2O. \qquad (12)$$
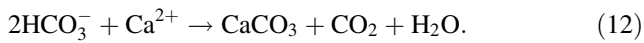
Carbonate precipitation is an important source of CO_2 in the ocean (Frankignoulle et al. 1994; Gattuso et al. 1999) and in water bodies without considerable biological activities, such as the Dead Sea (Barkan et al. 2001). Further, it is assumed to be one of the sources of CO_2 in the rivers in this carbonate catchment.

The pH increase from 7.48 in spring waters to 7.98 in river waters is an important factor in regulating pCO_2. The ratio of ΔpH to $\Delta \log pCO_2$ equals -1.07, close to -0.95 in the ocean (Chen et al. 2006). CO_2 emission can increase pH, and $CaCO_3$ precipitation can decrease pH (Soetaert et al. 2007), as a result, Eq. (12) can slightly increase pH. In comparison, photosynthesis is an important process leading to pH increases due to consumption of H^+ and CO_2 (move left in Eq. (1)). The following equation is derived by adding Eq. (12) and the photosynthesis reaction:

$$\begin{aligned} x\mathrm{Ca}^{2+} &+ 2x\mathrm{HCO}_3^- + 16\mathrm{HNO}_3 + \mathrm{H}_3\mathrm{PO}_4 + (122-x)\mathrm{H}_2\mathrm{O} \\ &\rightarrow (\mathrm{CH}_2\mathrm{O})_{106}(\mathrm{NH}_3)_{16}(\mathrm{H}_3\mathrm{PO}_4) + x\mathrm{CaCO}_3 + 138\mathrm{O}_2 \\ &\quad + (x-106)\mathrm{CO}_2. \end{aligned}$$
$$(13)$$

When the $CaCO_3$ precipitation rate exceeds the rate of photosynthesis in the rivers $(x > 106)$, pCO_2 would increase with DO (Eq. (13)). Photosynthesis could stimulate CO_2 production via calcite precipitation (Eq. (13)), leading to the unusual positive correlation between pCO_2 and DO (Fig. 5). Generally, it is unlikely that microbial activity in river sediments can sustain a very high production rate of CO_2 (Öquist et al. 2009). It is postulated that this reaction (Eq. (13)) might play an important role in the persistence of high pCO_2 (3,443 µatm) in the rivers, as the export of organic carbon from the carbonate catchment was low.

CO_2 production in the lake

Metabolism is an important factor driving CO_2 variations in the lake, and metabolism is very strongly influenced by climatic conditions. Photosynthesis in such a lake, in the subtropical climate zone, seems to be influenced more significantly by radiation than by temperature, while respiration is mainly regulated by temperature, according to seasonal variations of temperature, DO, pH, pCO_2, and HCO_3^- concentrations (Fig. 2). In August, 2002, photosynthesis in the lake decreased due to weakened radiation in the successive overcast days before sampling, but respiration was maintained at a high level under high temperatures. Therefore, the pH values in the surface water decreased to about 8.0, the pCO_2 was high, and the DO was almost at its minimum. On the contrary, from November, 2001 to January, 2002, radiation was in favor of

photosynthesis, although temperatures were low, which limited respiration. Thus, pH and DO concentrations during this period were at their highest and pCO_2 was at its lowest, and the lake water was under-saturated with respect to atmospheric CO_2. This assertion is in good agreement with the results of previous studies. For example, Karlsson (2009) argued that light is an important limiting factor in lake ecosystems, Gudasz et al. (2010) and Kosten (2010) confirmed that organic carbon mineralization in lake sediments and CO_2 emission from lakes is mainly controlled by temperature.

The carbon mass balance in Hongfeng Lake was sustained by DIC (mainly HCO_3^-) imported from the catchment (Fig. 7). The important biological, microbial, and chemical processes in relation to CO_2 and HCO_3^- in the lake includes: organic matter decomposition producing CO_2 (① in Fig. 7) that could be directly utilized for photosynthesis (van Breugel et al. 2005); HCO_3^- conversion into CO_2 (② in Fig. 7) for photosynthesis under the catalysis of carbonic anhydrase (Tortell et al. 2006; Kranz et al. 2009); and organic matter degradation to release CO_2 that reacted with carbonate to produce HCO_3^- at the sediment–water interface (③ in Fig. 7) (Jahnke et al. 1997). The significance of the CO_2 produced by the different pathways varies in different seasons:

Firstly, when photosynthesis in the lake weakened below respiration, CO_2 was mainly released from organic matter remineralization, with a normal ratio of CO_2 production to O_2 consumption (C2 in Fig. 3), and the most negative carbon isotopic composition (-19.81 ‰ in Fig. 4b) in the added CO_2. This scenario (①, Fig. 7) primarily occurred in the beginning of autumn (August 2002) and in April 2001, when thermal stratification was beginning or ending.

Secondly, as photosynthesis in the lake increased, and CO_2 concentrations decreased, HCO_3^- could then be utilized as a carbon source for algal photosynthesis. McConnaughey and Whelan (1997) proposed a model wherein the protons generated by calcification caused HCO_3^- to generate CO_2 for photosynthesis. Allemand et al. (1998) argued that hydration of HCO_3^- provided CO_2 for photosynthesis. Recently, Kranz et al. (2009) experimentally confirmed that the cyanobacterium *Trichodesmium* preferred to utilize HCO_3^- (more than 90 %), instead of CO_2, as a carbon source for photosynthesis. Study focused on the mechanisms of HCO_3^- utilization for photosynthesis is beyond the scope of this paper. During the period of strong photosynthesis in excess of respiration (July 2001, and November 2001–January 2002), the ratios of $\Delta CO_2/\Delta O_2$ were, 0.4621 on average, much lower than the traditional Redfield ratio (Fig. 3). Assuming that the photosynthetic quotient ($PQ = \Delta O_2/\Delta \Sigma C$) of algae was constant (~ 1.05) (Gattuso et al. 1999) and that HCO_3^-
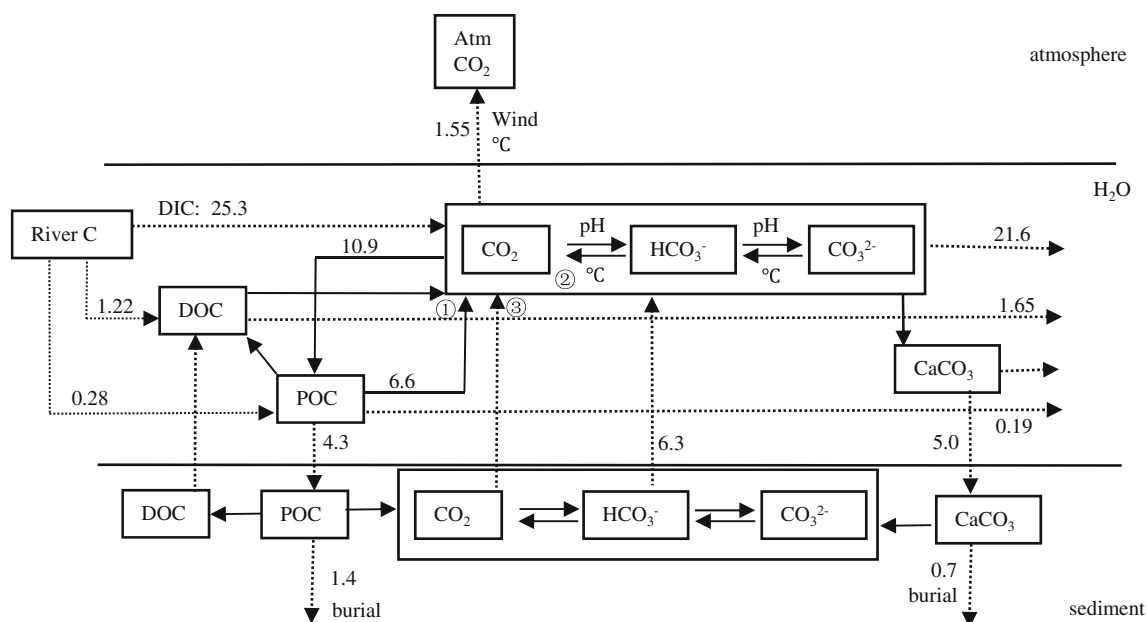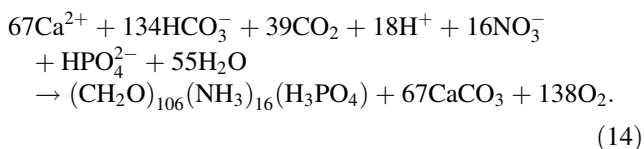
Fig. 7 A sketch showing how carbon cycling in Hongfeng Lake is supported and balanced by inputted DIC. ①, ② and ③ denote the different pathways of CO_2 production (see text). The fluxes of C was utilized due to the insufficiency of CO_2 for photosynthetic demand for carbon, the x in Eq. (13) can be calculated to equal 67, corresponding to the difference in the ratios of $\Delta CO_2/\Delta O_2$, thus, the overall reaction should be:

conversion (*solid arrows*) and C transportation (*dashed arrows*) are shown with a unit of $\times 10^8$ mol C year^{-1} (reference to Finlay et al. 2009, data from Wang et al. 2012)

$$67Ca^{2+} + 134HCO_3^- + 39CO_2 + 18H^+ + 16NO_3^-$$
$$+ HPO_4^{2-} + 55H_2O$$
$$\rightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 67CaCO_3 + 138O_2.$$
$$(14)$$

According to Eq. (14), the ratio of organic carbon production to calcite precipitation is 1.58 (106/67), which is in good agreement with Allemand et al.'s (1998) experimental results, suggesting that the ratio of photosynthesis/calcification was 1.6, and close to the TOC/PIC production ratio (1.35–1.37) given by Delille et al. (2005). The HCO_3^- uptake accounts for 77 % (134/173) of the total carbon supply, which coincides with Tortell et al.'s (2006) results showing that the HCO_3^- contribution ranged 60–90 % with an average of 78.6 % in subarctic Pacific phytoplankton assemblages. The more positive intercepts (−15.122 and −15.204 ‰, Fig. 4a, d) corroborate the idea that the origin of the added CO_2 in those seasons is more closely related to HCO_3^-.

Thirdly, in the seasons (January and October 2001) with a high ratio of excess CO_2 to O_2 depletion, exceeding 1:1 (C3 in Fig. 3), a fraction of CO_2 was produced through mechanisms other than aerobic remineralization of organic matter. Salomão et al. (2008) attributed the CO_2 in rivers

with a high ratio of excess CO_2:O_2 depletion to anaerobic remineralization. This explanation does not apply here because the lake water was oxic in these seasons, and therefore most of the organic matter would be expected to aerobically decompose (Maerki et al. 2009). The CO_2 carbon isotope data also supports the idea that not all of the CO_2 was derived from respiration, otherwise the carbon isotope of the added CO_2 (−17.263 ‰ in Fig. 4c) would be at its most negative values instead of varying between those in the previous two kinds of CO_2 (−15.1 and −19.8 ‰), corresponding to the maxima of pCO_2. The input of groundwater with a high CO_2 concentration and high $\Delta CO_2/\Delta O_2$ ratio is not an option because of very little precipitation in those months. The CO_2 might be partially produced from HCO_3^- (in Fig. 7) titration by H^+. For example, in October 2001, the high pCO_2 in the surface water resulted directly from the low pH (Fig. 2). The low pH was likely due to the addition of H^+ from oxidation of NH_4^+ released from organic matter decomposition (Dai et al. 2006), and/or other H^+-generating biogeochemical processes (Rice and Herman 2012).

It is noteworthy that pCO_2 (Fig. 2) and the CO_2 evasion rate (Wang et al. 2012) in the lake were not at their greatest as CO_2 was primarily produced by organic matter remineralization (① in Fig. 7, and C2 in Fig. 3). In comparison, the maximum pCO_2 and CO_2 evasion rate occurred in January and October 2001 as the extra CO_2 produced by HCO_3^- titration by H^+ (③ in Fig. 7, and C3 in Fig. 3) was added. This result led to a hypothesis that CO_2 evasion in

carbonate lakes was controlled primarily not by balance between photosynthesis and respiration, but by pH. This conclusion could be supported by the results from previous studies. In hard-water lakes, metabolism is not the factor regulating the carbon flux (Finlay et al. 2010), and inter-annual variation in net CO_2 flux and pCO_2 is correlated strongly with pH (Finlay et al. 2009). Even in boreal lakes where inorganic carbon comprises a small percentage (10–30 %) of total carbon (DIC + DOC) export, HCO_3^- titration by H^+ is still an important CO_2 production mechanism (Rantakari and Kortelainen 2008; Wallin et al. 2010). The HCO_3^- was mainly derived from carbonate dissolution by organic matter remineralization at the sediment–water interface (Jahnke et al. 1997), which is in accord with Kortelainen et al.'s (2006) survey, suggesting that CO_2 emission in lakes had a close relationship with the sediments.

Conclusions

The CO_2 evaded from spring waters was derived from soil CO_2, which originated from sources including organic matter decomposition, root respiration, and acid dissolution. The CO_2 in stream waters was produced from HCO_3^- via calcite precipitation due to oversaturation, and the HCO_3^- was derived from the weathering of carbonate by soil CO_2 in the catchment, and then was conveyed into the streams. Further, DIC imported from the catchment dominated the carbon balance in the lake, and lacustrine CO_2 was produced from the imported HCO_3^- via two pathways. One is the addition of H^+, which led to HCO_3^- shifting towards more CO_2, and the other is the decomposition of organic matter that was formed within the lake through photosynthesis that consumed HCO_3^-. The former controls the net emission of CO_2 from the lake. For catchment-river–lake systems in carbonate areas, CO_2 evasion from rivers and lakes is a return pathway of soil CO_2 in the catchment to the atmosphere more than that of NPP.

In the Lake Hongfeng catchment, the lake, streams, and springs, as well as soil emitted CO_2 into the atmosphere at rates comparable with those of other areas. It is likely that in this catchment with low productivity and small export of organic carbon, CO_2 in soil and waters is strongly influenced by root respiration, and by strong acids dissolution. The CO_2 derived by these pathways is not an integral part of the catchment NEP and NPP. Direct comparison between these carbon fluxes and catchment NPP and NEP is not appropriate here. In particular, impacts of the CO_2 emitted from rivers and lakes on the global carbon cycle may be overestimated due to different turnover times, if the CO_2 derived from root respiration is assumed to originate from heterotrophic decomposition of terrestrial organic carbon.

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