

Daytime deposition and nighttime dissolution of calcium carbonate controlled by submerged plants in a karst spring-fed pool: insights from high time-resolution monitoring of physico-chemistry of water

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Abstract Water temperature, dissolved oxygen (DO), pH, and specific conductivity (spc) were measured in a time interval of 15 min in a karst spring and the spring-fed pool with flourishing submerged plants in Guilin, SW China under dry weather for periods of 2 days. Measurements allowed calculation of calcium and bicarbonate concentrations ($[Ca^{2+}]$ and $[HCO_3^-]$), and thus CO_2 partial pressure (P_{CO_2}) and saturation index of calcite (SIc). Results show that there were not any diurnal variations in the physico-chemical parameters of the water for the spring. However, during daytime periods, pool water P_{CO_2} decreased to far less than the spring water in a few hours, pH and SIc increased to greater than the spring, and $[Ca^{2+}]$ and $[HCO_3^-]$ decreased to less than the spring. During nighttime periods, pool water P_{CO_2} returned to or even increased to greater than the spring, pH and SIc decreased to less than the spring, and $[Ca^{2+}]$ and $[HCO_3^-]$ increased to greater than the spring. The decrease in $[Ca^{2+}]$ and $[HCO_3^-]$ to less than the spring during daytime periods implies daytime deposition of calcium carbonate, while the increase in $[Ca^{2+}]$ and $[HCO_3^-]$ to greater than the spring during nighttime periods implies nighttime dissolution of calcium carbonate. The direction of the observed changes depended essentially on the illumination, indicating that daytime photosynthetic and nighttime respiratory activities in the pool aquatic plant ecosystem, which were further

evidenced by the increase and decrease in DO during daytime and nighttime periods respectively, were the main processes involved. The large variations of the components of the carbonate system imply considerable changes of the capacities of CO_2 and O_2 in water. The finding has implications for water sampling strategy in slow-flowing karst streams and other similar environments with stagnant water bodies such as estuaries, lakes, reservoirs, and wetlands, where aquatic plant ecosystem may flourish.

Keywords Deposition and dissolution of calcium carbonate · Submerged plants · Diurnal · Physico-chemistry of water · Karst spring-fed pool · Guilin China

Introduction

Among the most important set of chemical reactions occurring under near Earth surface conditions are those involved in the dissolution and deposition of sedimentary carbonate minerals. These minerals comprise about 20% of Phanerozoic sedimentary rocks (Morse and Arvidson 2002). Calcite and, to a significantly lesser extent, dolomite are the major carbonate minerals in sedimentary rocks. In modern sediments, aragonite and high-magnesian calcites dominate in shallow water environments. However, calcite is by far the most abundant carbonate mineral in deep sea sediments. An understanding of the factors that control their dissolution and deposition is important for modeling of geochemical cycles and the impact of fossil fuel CO_2 on climate, diagenesis of sediments and formation of sedimentary rocks. It also has practical application for areas such as the behavior of carbonates in petroleum and natural gas reservoirs, and the preservation

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of buildings and monuments constructed from limestone and marble. Important findings from the hundreds of papers constituting the large literature on this topic that have steadily evolved over the last half century have been summarized and reviewed by Morse and Arvidson (2002). However, these findings focus mainly on the chemical kinetics controlling the rates of reaction between sedimentary carbonate minerals and solutions. There are very few papers that focus on the deposition or/and dissolution of calcium carbonate controlled by aquatic plants in karst spring-fed streams (Spiro and Pentecost 1991; Pentecost 1995, 1998; Liu et al. 2006), which may have implications for karst-related carbon cycles (Liu and Zhao 2000; Gombert 2002) and the paleoclimatic/paleoenvironmental reconstruction with such karst records as tufa and travertine (Liu et al. 2003; Andrews 2006). Here, it is shown, based on high time-resolution monitoring results, that aquatic plants exerted clear influence on the diurnal variations of the physico-chemistry of water in a karst spring-fed pool. From these variations, daytime deposition and nighttime dissolution of calcium carbonate and the underlying mechanisms were revealed. It was found that the daytime deposition of calcium carbonate was mainly related to the photosynthesis, while the nighttime dissolution of calcium carbonate was related to the respiration of the aquatic plants.

Study area and sites

The karst spring-fed pool (Fig. 1), where submerged plants (mainly *Spirogyra* sp. and *Chara Vaillant ex linn*) flourished, was formed in 1987 by the weir of the spring S31 in the Guilin Karst experimental site, which is near the village of Yaji, an eastern suburb of Guilin, about 8 km southeast of Guilin's downtown area. Geomorphologically, the site is on the boundary between adjacent peak cluster and peak forest karst systems (Fig. 2). The experimental site comprises a hydrological system with a recharge area of about 2 km², which was mainly determined by tracing tests of dye, ammonium molybdate and zinc chloride. Its recharge area is in a peak cluster region with nine dolines and numerous shallow epikarst springs. The springs flow out from the doline slopes or bottoms, and some of them (e.g., S25 and S26) are perennial. Others (e.g., S54 and S56) are intermittent. The output of the site is composed of one perennial spring (S31, focus of this study, Fig. 2) and three intermittent springs (S29, S291 and S32) at the eastern border of the Guilin peak forest plain (Fig. 2). The altitude of the plain surface is about 150 m above sea-level, whereas the highest peak in the recharge area reaches 652 m. Elevations of the doline bottoms range between 250 and 400 m.

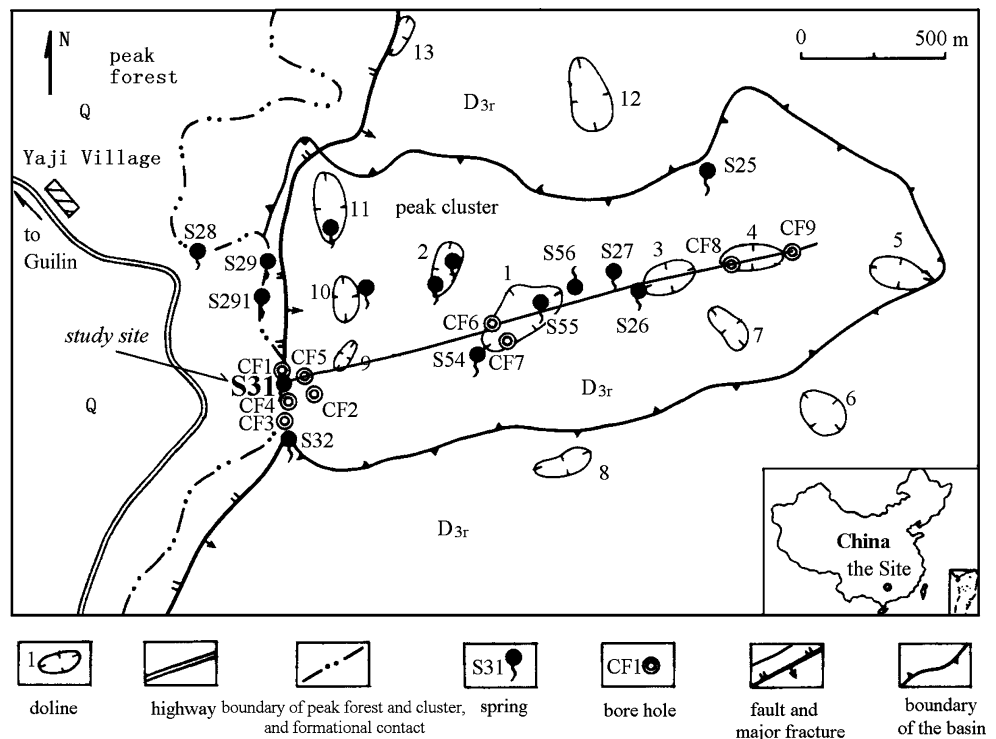


Fig. 1 The spring S31 and the pool with flourishing submerged plants (mainly *Spirogyra* sp. and *Chara Vaillant ex linn*), formed by the weir of the spring, where the data loggers of WTW 350i were located to monitor the variations in physico-chemistry of water. Note that the distance from the spring orifice to the weir is 8.5 m, and some tufa deposits can be found on the aquatic plants' leaves and pool bottom near the weir but not around the spring orifice)

The entire system is developed in massive pure Upper Devonian limestone (Rongxian Formation, D_{3r} in Fig. 2) with a bioclastic sparite to micrite texture. The limestones at the site dip about 5°–10° toward the south-east, and there is a major fault striking NNE on the western boundary of the peak cluster region. Based on the surface survey and aerial photograph interpretation, the major joints and fractures trend ENE, WNW and NNE and strongly influence development and orientation of dolines as well as flow directions of groundwater. Dolines 1, 3 and 4 are distributed along a major fracture zone (Fig. 2) that coincides with significant calcite veining in the ENE direction. Minor karst features such as karren, grikes and kameniza are well developed on doline slopes, concentrated in the near-surface (epikarst) zone, which is 3–10 m thick.

The karst hydrogeological conditions of the site are characterized by a very thick vadose zone, a heterogeneous interior structure, and highly variable input and output (Fig. 3). The thickness of the vadose zone ranges from 110 m (as estimated from the bottom of the lower doline) to 400 m (from the high peak slopes). The heterogeneity of the system's structure is expressed in an extreme range of hydraulic conductivities between the epikarst zone, large conduits and diffuse flow regions within microfractures beneath the epikarst. For example, two of the four boreholes in the recharge area (CF6 and CF9) hit significant conduits and show large water-table fluctuations during flood periods (as much as 30 m in CF6). An additional five boreholes (CF1–CF5 in Fig. 2) near Spring S31 show similar features of water table fluctuations, although CF1

Fig. 2 Sketch hydrogeological map of the Guilin Karst Experimental Site (after Liu et al. 2004)



and CF4 are in a fracture medium according to drilling data (Yuan et al. 1996).

The primary water input to the system is rainfall, and the long-term mean annual rainfall around Guilin is 1915.2 mm (Yuan et al. 1996). The mean temperature in Guilin is 18.8°C. About 70% of annual rainfall is concentrated in the 5 months of the rainy season from April to August. Moreover, according to data from five rainfall autologgers set up in different areas of the system, both the monthly rainfall and that of individual storm events vary remarkably from the plain to the dolines, and from the lower doline to the higher doline. Generally, the monthly rainfall in the doline is higher than that in the plain by 0–30%. From the lower doline to high doline, the rainfall decreases by 0–17%. The discharge from four springs (S29, S291, S31 and S32 in Fig. 2) at the output of the system fluctuated

remarkably (Yuan et al. 1996). For example, the discharge of S31 could be from 0.001 to 4 m³/s. This is reflection of not only the uneven input, but also the heterogeneity of the system's structure.

Methods

Continuous monitoring and analytical chemistry

The main field campaign was conducted on 21–23 September 2005, sunny days when the spring S31 was in its low flow (~1 l/s) in dry season. During this time two WTW (Wissenschaftlich- Technische- Werkstaetten) Technology MultiLine 350i multi-parameter data loggers were programmed and located at the spring S31 and at the weir respectively to collect continuous readings of specific conductivity (spc, as µs/cm at 25°C), pH, dissolved oxygen (DO) and temperature of the spring water and pool water at 15 min interval for periods of 2 days. The loggers were calibrated prior to deployment using pH (4, 7 and 10) and spc (1,412 µs/cm) standards. Hand-held water quality meter measurements were undertaken to check the reliability of data logger measurements. It was found that hand held meter and logger measurements are identical within 3% error (Liu et al. 2006).

In situ titrating was used to measure the [HCO₃⁻] and [Ca²⁺] of water with the Aquamerck Alkalinity test and Hardness test. The resolutions are 4 and 6 mg/l, respectively. Monthly

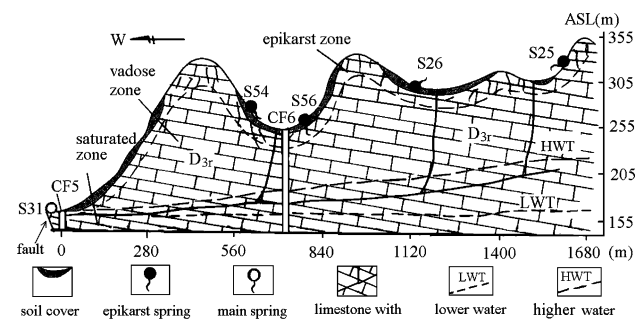


Fig. 3 Hydrogeological section of the Experimental Site (after Liu et al. 2004)

samples of water were collected for analysis of major hydrochemical components in laboratory. Analyses were made by standard titration for bicarbonate, Atomic Absorption Spectrophotometry for K^+ and Na^+ , titration with EDTA for Ca^{2+} , Mg^{2+} and SO_4^{2-} , and the Mohr titration for Cl^- (Liu et al. 2004).

Estimating CO_2 partial pressure and calcite saturation index from continuous records of temperature, pH and spc

On the days when no rainfall happens and evaporation could be ignored, as the case of this study, spc fluctuations in the spring-fed pool could be attributed solely to Ca^{2+} and HCO_3^- changes by deposition or dissolution of calcite. So, paired Ca^{2+} (or HCO_3^-) and spc values were correlated and, regression was used to establish a time-series of diurnal Ca^{2+} and HCO_3^- changes (Liu et al. 2004).

The full hydrochemical data sets, including recorded temperature and pH, calculated Ca^{2+} and HCO_3^- through the regression equation, mean monthly values of K^+ , Na^+ , Mg^{2+} , Cl^- and SO_4^{2-} , were processed through the modified program WATSPEC (Wigley 1977), which calculates CO_2 partial pressure (P_{CO_2}) and calcite saturation index (SIc) for each record. P_{CO_2} is calculated from:

$$P_{CO_2} = \frac{(HCO_3^-)(H^+)}{K_H K_1} \quad (1)$$

where K_H and K_1 are the temperature-dependent Henry's Law and first dissociation constants for CO_2 gas in water, respectively, and (*i*) denotes activity of *i*.

SIc is calculated from:

$$SIc = \log \left(\frac{(Ca^{2+})(CO_3^{2-})}{K_c} \right) \quad (2)$$

where activities are denoted by brackets, and K_c is the temperature dependent equilibrium constant for calcite dissociation. If $SIc > 0$, water is supersaturated with respect to calcite, and calcium carbonate could deposit; if $SIc < 0$,

water is aggressive to calcite, and calcium carbonate dissolution could happen; and if $SIc = 0$, the system reaches equilibrium.

Results and discussions

General hydrochemical compositions of the spring S31

Table 1 gives the general hydrochemical compositions of the spring S31 on 2 June (wet season) and 19 September (dry season) 2005. It shows that Ca^{2+} and HCO_3^- were the major cation and the major anion in the waters respectively, with molarity percentage of >90% for both ions. Thus, the hydrochemical type of the spring water is HCO_3^- -Ca, which reflects the control of the pure upper Devonian limestone bedrock at the site.

Diurnal variations of hydrochemistry

Calculation of SIc and P_{CO_2} from data-logger data

To calculate the SIc and P_{CO_2} of water by using the program WATSPEC (Wigley 1977), a minimum of nine parameters are required. They are water temperature, pH and concentrations of the seven major ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^-). Owing to the low concentrations of K^+ , Na^+ , Mg^{2+} , Cl^- and SO_4^{2-} (Table 1), which are used in the calculations to correct for ion-strength effects (Stumm and Morgan 1981), and no formation of mineral deposits related to these components, their variations with time were neglected when calculating the SIc and P_{CO_2} by using the data recorded by the data loggers. During the calculation, the concentration value on 21 September 2005 in Table 1 was adopted for the each of the five ions. In the next step, to obtain the time-series of SIc and P_{CO_2} , concentrations of Ca^{2+} and HCO_3^- must be determined. At the study site these concentrations are linearly related to spc by the relationships (Liu et al. 2004):

Table 1 Physico-chemical features of the spring S31

Sampling date	K^+ (mg/l)	Na^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Cl^- (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)
21 September 2005	0.01	0.05	90.50	0.29	3.48	259.95	13.84
2 June 2005	0.00	0.02	81.27	1.61	3.48	244.08	6.35
Sampling date	Water temperature (°C)	pH	spc (µs/cm, 25°C)	SIc ^a	P_{CO_2} ^b (ppmv)	Hydro-chemical type	
21 September 2005	19.8	7.08	420	-0.08	19634	HCO_3^- -Ca	
2 June 2005	19.9	7.29	395	0.07	11402	HCO_3^- -Ca	

^a Calcite saturation index in water ($SIc = \log IAP/K$, where IAP is ionic activity product and K is the calcite equilibrium constant). If $SI > 0$, supersaturation occurs and calcium carbonate may deposit; if $SI < 0$, water is aggressive to calcite; and if $SI = 0$, the system reaches equilibrium

^b Calculated CO_2 partial pressure of water by WATSPEC (Wigley 1977)

$$[\text{Ca}^{2+}] = 0.24 \times \text{spc} - 9.97, r^2 = 0.92 \quad (3)$$

$$[\text{HCO}_3^-] = 0.68 \times \text{spc} - 27.03, r^2 = 0.93 \quad (4)$$

where brackets denote species concentrations in mg/l and spc is specific conductivity in $\mu\text{S}/\text{cm}$ corrected for 25°C.

Diurnal variations in physico-chemical parameters of the spring S31

Figure 4 shows the diurnal changes of the spring S31 physico-chemistry during the dry weather of 21–23 September 2005. It can be seen that all the parameters show little change, and have no visible regular diurnal variation. That means the physical-chemistry of the spring is stable on the diurnal time-scale under dry weather.

Diurnal variations in physico-chemical parameters of the spring-fed pool water

As Fig. 4 shows, during dry weather all recorded parameters in the spring-fed pool show distinct diurnal fluctuations.

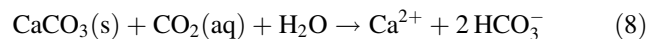
As displayed in Fig. 4b the P_{CO_2} of the pool water shows distinct daily variations. During the daytime periods the P_{CO_2} dropped in a few hours to a minimum far less than the spring water (14 times lower, Table 2), usually occurring round about 13:30 when the water temperature peaked (Fig. 4a). The maximum P_{CO_2} , even higher than the spring, usually was reached in the nighttime. Correspondingly, the pH (Fig. 4c) and SIc (Fig. 4d) of the pool water showed synchronous but anti-phase distinct daily variation with P_{CO_2} (Fig. 4b). During the day the pH and SIc rose about 1.1 greater than the spring water to a maximum of 8.20 and 1.1, respectively. These maximum pH and SIc were usually reached in the early afternoon (13:30). In nighttime periods the pH and SIc decreased again approaching the spring's values or even lower. Spc (Fig. 4e), $[\text{Ca}^{2+}]$ (Fig. 4f) and $[\text{HCO}_3^-]$ (Fig. 4g) of pool water showed synchronous anti-phase diurnal variation with temperature, pH and SIc, i.e., during the nighttime periods, spc, $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ of pool water reached their higher values of 422 $\mu\text{S}/\text{cm}$, 90.5 and 264 mg/l, respectively, while during the daytime periods, they decreased, approaching the lower values of 410 $\mu\text{S}/\text{cm}$, 87.8 and 256 mg/l, respectively (Table 2).

(a) *Causes of diurnal hydrochemical variations in the pool water* pH increase in streams may be caused mainly by photosynthesis of aquatic plants in the stream, which are using dissolved CO_2 for assimilation as soon as sunlight is

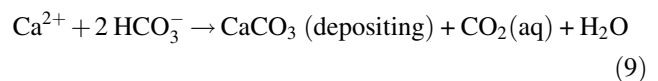
available. This results in a decreasing concentration of dissolved CO_2 in the stream. Since CO_2 partly reacts with water and produces free hydrogen (Eq. 5–7) it controls pH values.



In addition to this, free (surplus) CO_2 in water also dissolves solid calcium carbonate into calcium bicarbonate (Eq. 8).



However, the dissolution of calcium carbonate only lasts until the free CO_2 is completely used and equilibrium with the dissolved calcium bicarbonate is reached (“calcium carbonate–carbonic acid–equilibrium”). If the dissolved CO_2 is taken from the system, the inverse process occurs to keep the equilibrium, i.e., dissolved calcium bicarbonate deposits as solid calcium carbonate (Eq. 9):

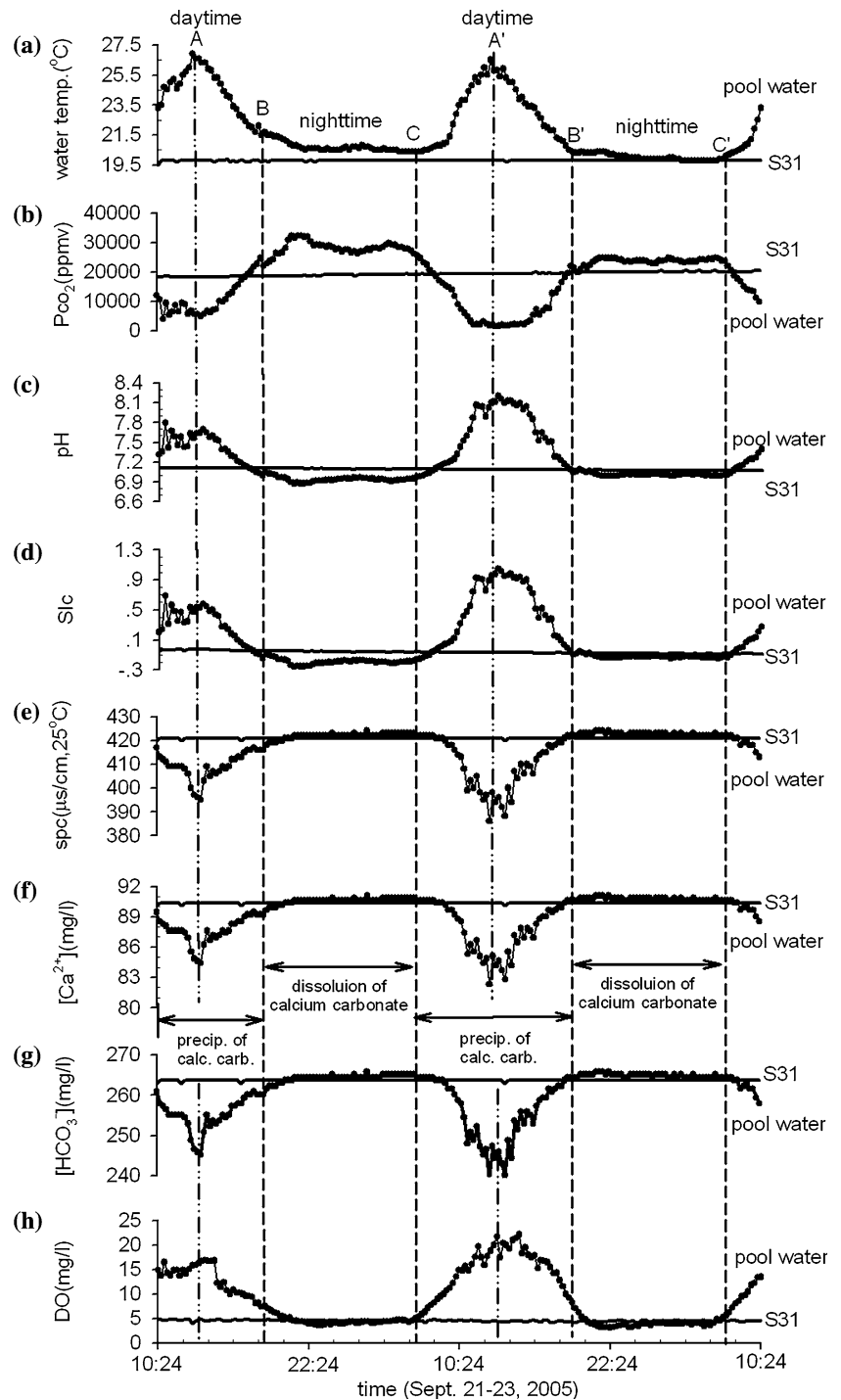


When photosynthesis is the main reason for the process it is termed “biological deposition”. Apart from consumption of CO_2 by photosynthesis, increase of water temperature and/or higher P_{CO_2} difference between water and the atmosphere can also reduce the concentration of dissolved CO_2 in the water (Hoffer-French and Herman 1989). If the lack of CO_2 in the water is caused by temperature- or pressure-driven exhalation of CO_2 the process is termed “physicochemical deposition”.

The observed diurnal cycle of pH in the spring-fed pool appears to be a consequence of both biological deposition and physico-chemical deposition. Triggered by sunlight, photosynthesis started soon after sunrise and reached the maximum at 13:30 (Fig. 4). This process accelerated deposition of calcium carbonate (Eq. 9), as evidenced by the decrease in spc, $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ (Fig. 4). This results in an ongoing decrease of the CO_2 concentration in the pool water (Fig. 4b) that simultaneously causes the pH and SIc to rise.

Apart from photosynthesis (Guasch et al. 1998), a rise in water temperature affects the concentration of dissolved CO_2 by reducing the solubility of the gas. Thus, increasing water temperature causes decreasing CO_2 levels. According to Plummer and Busenburg (1982), the Henry constant decreases when temperature increases. The curve “Only Temp” in Fig. 5 shows the change of P_{CO_2} in “pool water” if

Fig. 4 The diurnal cycle of the physico-chemical parameters of the karst spring S31 and the spring-fed pool, showing that the daytime deposition of calcium carbonate occurred, indicated by the decrease in $[Ca^{2+}]$ and $[HCO_3^-]$ to less than the spring, while nighttime dissolution of calcium carbonate was indicated by the increase in $[Ca^{2+}]$ and $[HCO_3^-]$ to greater than the spring. Note that there is almost no diurnal change for all parameters of the spring S31, indicated by the horizontal lines of all the parameters



only this temperature effect on the spring S31 is considered. It can be seen that the contribution (C_T) of temperature increase to the total decrease in pool water P_{CO_2} during daytime periods is not very important [C_T generally less than 30%, where $C_T = T/(T + P)$, T : decreased P_{CO_2} via increased temperature (relative to the spring S31) = $(P_{CO_2})_{S31} - (P_{CO_2})_{only-temp}$; P : decreased P_{CO_2} by photosynthesis = $(P_{CO_2})_{only-temp} - (P_{CO_2})_{pool}$]. In the night time, respiration and decreased temperature resulted

in higher total CO_2 concentrations and hence a gradual decrease in pH and S1c, which reduced calcium carbonate deposition or even made dissolution of calcium carbonate happen, and thus the increase of spc, $[Ca^{2+}]$ and $[HCO_3^-]$.

The contribution of P_{CO_2} difference between the spring water and the atmosphere to diurnal hydrochemical variations in the pool water can be neglected due to stable physico-chemistry of the spring water.

Table 2 Statistics on the daytime and nighttime variations of physico-chemical parameters of the karst spring S31 and the pool water at the weir 8.5 m to the spring

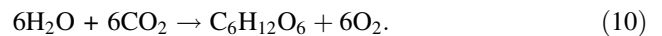
Monitoring site	S31		Pool water at weir	
	Nighttime (19:00, Sept.21–8:00, Sept.22, 2005)	Daytime (8:00–19:00, Sept.22, 2005)	Nighttime (19:00, Sept.21–8:00, Sept.22, 2005)	Daytime (8:00–19:00, Sept.22, 2005)
W.T. (°C)	19.7~19.8 ^a (19.79) ^b [0.12] ^c	19.7~19.8 (19.79) [0.07]	20.4~21.7 (20.7) ^b [1.61] ^c	20.4~26.5 (23.1) [8.4]
P_{CO_2} (ppmv)	18,621~19,498 (18,929) [1.42]	19,054~19,953 (19,500) [1.06]	22,029~32,359 (27,891) [84.7]	1,459~22,439 (7,886) [83]
pH	7.09~7.11 (7.1) [0.07]	7.08~7.10 (7.09) [0.05]	6.88~7.04 (6.94) [0.5]	6.97~8.20 (7.61) [5.42]
$SI_{calcite}$	-0.07~-0.05 (-0.06)	-0.08~-0.06 (-0.07)	-0.26~-0.09 (-0.19)	-0.10~1.05 (0.51)
Spc (µs/cm)	421~421 (421) [0.00]	420~421 (420.9) [0.03]	416~424 (422) [0.35]	386~423 (410) [2.6]
Ca^{2+} (mg/l)	90.37~90.37 (90.37) [0.00]	90.14~90.37 (90.37) [0.04]	89.2~91.1 (90.5) [0.38]	82.3~90.8 (87.8) [2.79]
HCO_3^- (mg/l)	263.6~263.6 (263.6) [0.00]	262.9~263.6 (263.6) [0.04]	260~266 (264) [0.40]	239~265 (256) [2.96]
DO (mg/l)	4.3~4.9 (4.6) [2.88]	4.2~4.9 (4.5) [3.58]	3.6~7.5 (4.5) [19]	5.0~22.1 (14.8) [32]

^a Minimum ~ maximum

^b Mean values ($N = 51$ for nighttime, and 46 for daytime)

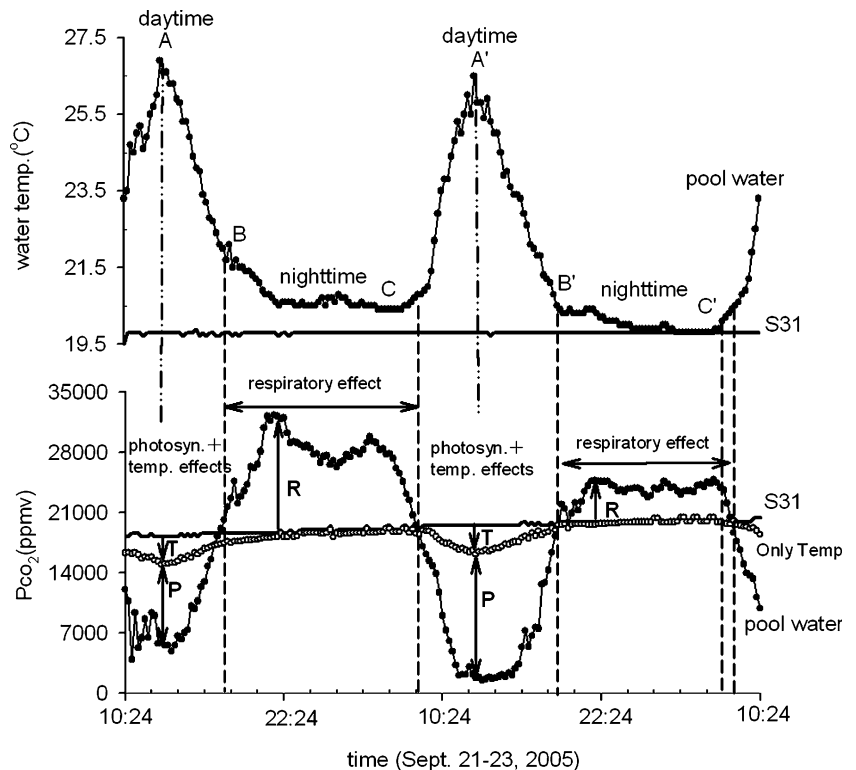
^c c.v. or coefficient of variation = (standard deviation/mean)%, c.v.s are not reported for SI_c values as these can be positive or negative

(b) *Independent confirmation of photosynthetic and respiratory activities in the pool aquatic ecosystem* Photosynthesis is the process by which plants, some bacteria, and some protists use the energy from sunlight to produce sugar. The photosynthetic process uses water and CO_2 and releases the oxygen. The overall reaction of this process can be written as:



On the other hand, respiration takes place in all living things, all the time. It is the release of energy from glucose or other organic substances inside living cells. There are two main types of respiration, aerobic and anaerobic. Aerobic respiration takes place in the presence of oxygen,

Fig. 5 The diurnal cycle of P_{CO_2} in karst spring S31 and the spring-fed pool and its controlling processes. T decreased P_{CO_2} by increased temperature only (temperature effect); P decreased P_{CO_2} by photosynthesis (photosynthetic effect); R increased P_{CO_2} by respiration (respiratory effect)



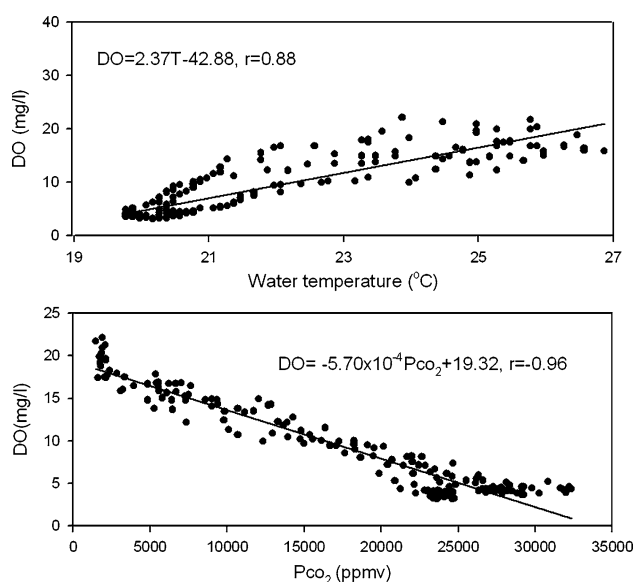


Fig. 6 Relation between DO and water temperature, and between DO and P_{CO_2} , showing the control of temperature on photosynthesis and thus on DO and P_{CO_2} , the latter two parameters being negatively correlated

i.e., glucose molecules react with oxygen molecules to form CO_2 and water molecules, with energy being released by the breaking of bonds in the glucose molecules. Therefore, aerobic respiratory process is reverse to photosynthetic process. From these descriptions, it is inferred that as an independent indicator of photosynthetic and respiratory activities, DO will show in-phase synchronous variation with water temperature and anti-phase synchronous variation with P_{CO_2} if photosynthetic and respiratory activities are active in the pool aquatic ecosystem. Figure 4a, b, h show it is really the case. When sun rises at 7:00, DO increases till 13:30 when water temperature peaks, and then decreases with water temperature. The diurnal variation in DO was from 3.6 to 22.1 mg/l, with daytime mean value of 14.8 mg/l, and 4.5 mg/l for nighttime mean value (Table 2). Figure 6 further shows that DO has good positive linear relation with water temperature and excellent negative linear relation with P_{CO_2} .

(c) *Comparison with similar works elsewhere in the world* In our previous work (Liu et al. 2006), diurnal variations of hydrochemistry were monitored at a spring and two pools in a travertine-depositing stream at Baishuitai, Yunnan, SW China. It was found that the measurements in the spring of the stream did not show any diurnal variations in the chemical compositions of the water. Diurnal variations, however, were observed in the water of the two travertine pools downstream. In one of them, a rise in temperature (thus more CO_2 degassing) during daytime and

consumption of CO_2 due to photosynthesis of submerged aquatic plants accelerated deposition of calcite, which is similar to the case of this study. In the other pool, where emerged aquatic plants flourished and grew out of the water (so photosynthesis was taking place in the atmosphere), the temperature-dependent root respiration underwater took place, which dominated until noon. Consequently, due to the release of CO_2 by the root respiration into water, which dominated CO_2 production by degassing induced by temperature increase, the increased dissolution of calcite was observed during daytime, which is just opposite to the case of this study.

Drysdale et al. (2003) measured at-a-station diurnal variations in carbonate hydrochemistry at Davys Creek, a tufa-depositing stream in central NSW, Australia. Major ion concentrations and continuously logged measurements of specific conductivity, pH and temperature showed that changes in the amount of calcium carbonate deposited upstream of the study reach were directly related to changes in diurnal water temperatures, which control the rate of CO_2 efflux to the atmosphere. The greatest upstream losses occurred during the mid-afternoon water temperature peak, whereas the lowest upstream losses occurred at sunrise, when water temperatures were at their lowest. Cloudy days at all times of the year produced small diurnal water temperatures ranges and, consequently, relatively small changes in upstream $CaCO_3$ loss through the day. Clear sunny days, especially during summer months, produced large diurnal water temperature changes, which in turn triggered diurnal changes in upstream $CaCO_3$ loss of up to 100 mg/l. These results are generally similar to those of this study. Unfortunately, the biological processes were not discussed separately in the Drysdale's work.

Summary and conclusions

Water temperature, DO, pH, and spc were monitored at high time-resolution (15 min) in the spring S31 and the spring-fed pool with flourishing submerged plants in Guilin, SW China under dry weather for periods of two days from 21 to 23 September 2005. $[Ca^{2+}]$ and $[HCO_3^-]$ were calculated through their linear relation with spc, and P_{CO_2} and SIc were calculated with WATSPEC software. Results show that there were not any diurnal variations in the physico-chemical parameters of the water for the spring. However, during daytime periods, pool water P_{CO_2} decreased to far less than the spring water in a few hours, pH and SIc increased to greater than the spring, and $[Ca^{2+}]$ and $[HCO_3^-]$ decreased to less than the spring. During nighttime periods, pool water P_{CO_2} returned to or even increased to greater than the spring water, pH and SIc decreased to less than the spring, and $[Ca^{2+}]$ and $[HCO_3^-]$

increased to greater than the spring. The decrease in $[Ca^{2+}]$ and $[HCO_3^-]$ to less than the spring during daytime periods implies daytime deposition of calcium carbonate, while the increase in $[Ca^{2+}]$ and $[HCO_3^-]$ to greater than the spring during nighttime periods implies nighttime dissolution of calcium carbonate. However, larger decrease in $[Ca^{2+}]$ and $[HCO_3^-]$ during daytime periods and less increase in $[Ca^{2+}]$ and $[HCO_3^-]$ during nighttime periods shows that deposition of calcium carbonate outweighs dissolution. Therefore, lithification in the submerged plant aquatic ecosystem may occur (Dupraz and Visscher 2005). In the field, some tufa deposits can be found on the aquatic plants' leaves and pool bottom near the weir. This is different from the case of emerged plant ecosystem, where dissolution of calcium carbonate may dominate, especially during daytime periods (Liu et al. 2006). The direction of the observed changes depended essentially on the illumination, indicating that daytime photosynthetic and nighttime respiratory activities in the pool aquatic ecosystem, which were further evidenced by the increase and decrease in DO during daytime and nighttime periods respectively, were the main processes involved. The large variations of the components of the carbonate system imply considerable changes of the capacities of CO_2 and O_2 in water.

The finding has implications for water sampling strategy in slow-flowing karst streams and other similar environments with stagnant water bodies such as estuaries, lakes, reservoirs, and wetlands, where aquatic ecosystem may flourish. Our data indicate that use of seasonal data sets without careful consideration of diurnal variability may impart significant error in calculations of annual carbon and oxygen budgets. These observations reinforce the need for higher temporal resolution measurements of oxygen and carbon system parameters in karst aquatic ecosystems. The finding has also implications for palaeoclimatic reconstruction with tufa deposits. The daytime deposition and nighttime dissolution of calcium carbonate controlled by submerged plants in a karst spring-fed pool indicate that the tufa deposits formed under this environment may provide only the paleoclimatic information (e.g., temperature) during daytimes but not nighttimes.

In addition, the results shown by this study may provide clues on the subject of diurnal cycles in natural and anthropogenic metal contaminated streams, the latter having important implications for many types of water-quality studies and for understanding trace-metal mobility (Fuller and Davis 1989; Cicerone et al. 1999; Nimick et al. 2003; Parker et al. 2007). This is due to the fact that the changes in temperature and pH are key factors in determining the amount of each metal that is adsorbed or desorbed on streambed materials, such as sediments (including tufa deposits) and aquatic plants.

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