

Diurnal Variations of Hydrochemistry in a Travertine-depositing Stream at Baishuitai, Yunnan, SW China

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Abstract. Diurnal variations of hydrochemistry were monitored at a spring and two pools in a travertine-depositing stream at Baishuitai, Yunnan, SW China. Water temperature, pH and specific conductivity were measured in intervals of 5 and 30 min for periods of 1 to 2 days. From these data the concentrations of Ca^{2+} , HCO_3^- , calcite saturation index, and CO_2 partial pressure were derived. The measurements in the spring of the stream did not show any diurnal variations in the chemical composition 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 day time and consumption of CO_2 due to photosynthesis of submerged aquatic plants accelerated deposition of calcite, whereas in the other pool, where aquatic plants flourished and grew out of the water (so photosynthesis was taking place in the atmosphere), the authors suggest that 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. This is the first time anywhere at least in China that the effect of root respiration on diurnal hydrochemical variations has been observed. The finding has implications for sampling strategy within travertine-depositing streams and other similar environments with stagnant water bodies such as estuaries, lakes, reservoirs, pools and wetlands, where aquatic plants may flourish and grow out of water.

Key words: root respiration, photosynthesis, aquatic plants, calcite precipitation/dissolution, CO_2 degassing, hydrochemistry, diurnal variations, travertine, China

1. Introduction

Travertine or tufa is a chemical sedimentary deposit that forms from spring-fed stream waters rich in dissolved carbon dioxide and calcium bicarbonate. It is found in many karst regions of the world, where it can

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form spectacular terraces, cascades and dams (Ford and Pedley, 1996; Pentecost, 1995). The chemical changes that take place once travertine-depositing spring waters emerge at the Earth's surface are well understood (Dreybrodt et al., 1992; Herman and Lorah, 1987; Liu et al., 1995; Liu et al., 2003); before any carbonate is deposited, the waters lose CO_2 as they equilibrate with ambient atmospheric conditions, which results in the waters becoming supersaturated with respect to the dissolved carbonate minerals. Carbonate deposition, usually as calcite, occurs once kinetic thresholds to mineral formation are overcome (Ford and Williams, 1989). Consequently, the point at which deposition commences is often located in stream channels well downstream of springs, and deposition may continue for a few kilometers thereafter (Liu et al., 1995). The hydrochemical evolution is also controlled by the physicochemical adjustment of the solution as it interacts with streambed geomorphology. Abrupt changes in stream longitudinal profile enhance CO_2 degassing, whilst in slowing moving zones (e.g., in travertine pools) it is considerably retarded (Liu et al., 1995). For a solution of given CO_2 and Ca^{2+} concentration, this solution–bed interaction governs precipitation kinetics, which not only control where deposition may occur, but also the rate at which the calcite is precipitated (Dreybrodt et al., 1997; Liu et al., 1995). At the solution–mineral interface, there is strong evidence that biogenic factors may be significant in travertine deposition (Pentecost, 1998), especially in standing water, where CO_2 removal by biogenic activity may be of equal or greater importance as removal by physicochemical means. Thus, travertine forming in lakes and low-velocity reaches of stream systems may have a strong biogenic influence (Pedley, 2000).

In recent years, travertine research has focused on refining our knowledge of specific depositional processes, particularly with respect to stream chemistry. For example, observed changes in water properties have been compared with measured deposition rates to confirm the validity of theoretical models (Liu et al., 1995), the three dimensional hydrochemistry of stream travertine pools has been evaluated (Lu et al., 2000), and links between seasonal climate, groundwater discharge, spring water concentrations and changes in the longitudinal distribution of travertine deposition have been investigated for river systems (Drysdale, 2002). Drysdale et al. (2003) also investigated the influence of diurnal temperatures on the hydrochemistry of a tufa-depositing stream in central NSW, Australia. Results showed that changes in the amount of CaCO_3 deposited upstream of the study reach were directly related to changes in diurnal water temperatures, which control the rate of CO_2 degassing to the atmosphere. To date, however, we know very little about the diurnal variations of hydrochemistry in a travertine-depositing stream under different biological environments, which are

a must in elucidating the mechanisms of biological effects on travertine deposition or erosion.

In this study, diurnal variations of hydrochemistry were monitored at a spring and two pools in a travertine-depositing stream at Baishuitai, Yunnan, SW China. The upstream travertine pool (No. 6) represents an environment where aquatic plants flourish and grow out of the water, so photosynthesis takes place mainly in the atmosphere, while the downstream travertine pool (No. 10) represents an environment where aquatic plants are submerged, so both photosynthesis and respiration take place entirely in the water. The spring is the source of the stream waters and acts as a background for comparison. In this paper, we aim to show the features of diurnal variations of hydrochemistry under the two environments, and then to elucidate the controlling processes responsible for the diurnal cycle of the hydrochemistry. This research is significant for two major reasons. Firstly, it is the first major attempt anywhere to reveal diurnal variations of hydrochemistry in a travertine-depositing stream under different biological environments. Secondly, it extends our understanding of contemporary hydrochemical processes in travertine-depositing streams, and thus provides more information for sampling design and interpretation of travertine paleoenvironments.

2. Study Site

Baishuitai is in southeastern Zhongdian County, Yunnan Province, SW China. Springs (Figure 1) abundant in calcium bicarbonate flow out from the mountainside in a forested area. About 100 m from the springs, a travertine platform (called Baishuitai in Chinese) with layered CaCO_3 has formed. It is a typical constructive karst landscape formed by calcite-supersaturated waters, and covers about 3 km² (Liu et al., 2003). It is believed to be one of the largest travertine deposits in China, and is an important natural tourism resource due to its scenic qualities and as the cradle of Donba Culture of the Naxi Minority.

Though Baishuitai lies in the subtropics, the region has considerable altitudinal range. There are four climatic zones present: a warm-temperate zone (altitude 2200–2500 m), a temperate zone (altitude 2500–3000 m), a cold-temperate zone (altitude 3000–3500 m) and a frigid zone (altitudes above 3500 m). Because of these climatic variations, plants near Baishuitai also have distinct vertical zonation. The native plants in the upper course of the Baishuitai River are protected quite well, therefore the forest cover can be up to 80% or more (Liu et al., 2003). However, native plants were seriously destroyed by agricultural activity in the lower reaches of the river; therefore the major component is secondary shrubs below an altitude of 2600 m asl.

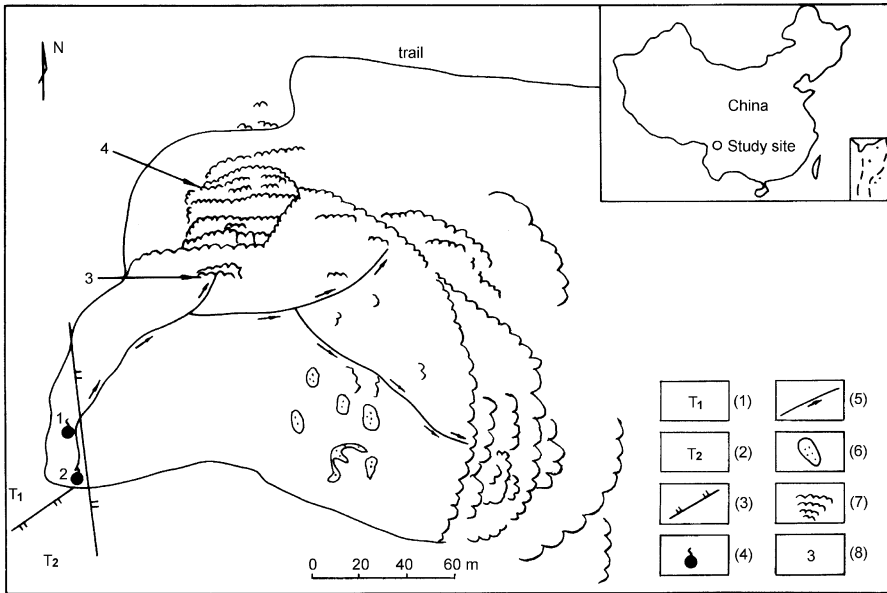


Figure 1. Distribution of the Baishuitai springs and travertines. (1) Lower Triassic shale and sandstone; (2) Middle Triassic limestone; (3) Fault; (4) Spring; (5) stream; (6) travertine pond; (7) travertine dam and terraces; (8) Monitoring sites: 1-Baishuitai spring No. 1; 2-Baishuitai spring No. 2, 3 and 4-travertine pool No. 6, and No. 10 respectively.

Baishuitai travertine deposits are formed on the limestone of the Triassic Beiya Formation. Due to intensive neotectonic movement and rock weathering, the limestone is highly fractured, and faults and fissures are well developed. This provides good conditions for rainfall infiltration and groundwater flow. However, due to the cut-off by a major northwest oriented fault, groundwater resurges at an altitude of about 2600 m asl, and forms the Baishuitai Spring. There are two main springs: No. 1 and No. 2 (Figures 1 and 2). During the contact of spring water with the atmosphere, a large amount of CO_2 is released and calcium carbonate has been deposited (Figures 1 and 2), and through time this natural wonder of colored travertine scenery has formed.

The temperature (about $11\text{ }^\circ\text{C}$) of the springs is approximately 3 degrees higher than the annual mean air temperature ($8\text{ }^\circ\text{C}$) at the altitude where the springs out-flow. This suggests that the spring water may be heated by a deep-seated geothermal source, especially considering that the high altitude recharge waters (ca. 4000 m) are significantly colder. Further support of this is shown by the evidence of hydrochemistry and stable carbon isotopes (Liu et al., 2003).

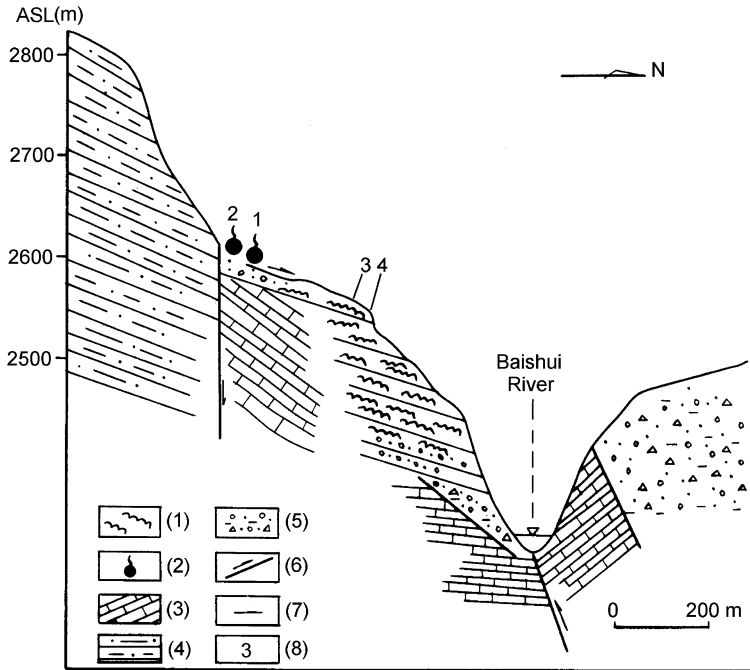


Figure 2. Cross section showing the geological conditions for the origin and formation of the Baishuitai travertine. (1) travertine; (2) spring; (3) Middle Triassic limestone; (4) Lower Triassic shale and sandstone; (5) fluvial deposits; (6) Fault; (7) flow direction; (8) Monitoring sites: 1-Baishuitai spring No. 1; 2-Baishuitai spring No. 2; 3 and 4-travertine pool No. 6, and No. 10 respectively.

3. Methods

3.1. CONTINUOUS MONITORING AND ANALYTICAL CHEMISTRY

The main field campaign was conducted in April 2003, during which time a WTW (Wissenschaftlich- Technische- Werkstätten) Technology MultiLine P3 multi-parameter data logger was programmed to collect continuous readings of specific conductivity (sp. Cond., as $\mu\text{S}/\text{cm}$ at 25°C), pH and temperature at 5 and 30 min intervals for periods of 1 to 2 days. The logger was calibrated prior to deployment using pH (4, 7 and 10) and conductivity ($1412 \mu\text{S}/\text{cm}$) standards. In 2005, for further examination, WTW multi-parameter instrument Multi-350i was used, which continuously recorded DO (dissolved oxygen), as well as specific conductivity, pH and temperature of water. 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.

In situ titrating was used to measure the $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$ of water with the Aquamerck Alkalinity Test and Hardness Test. The resolutions are 4 and 6 mg/l, respectively.

Seasonal 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^- .

3.2. ESTIMATING CO_2 PARTIAL PRESSURE AND CALCITE SATURATION INDEX FROM CONTINUOUS RECORDS OF TEMPERATURE, PH AND SPECIFIC CONDUCTIVITY

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

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

$$P_{\text{CO}_2} = \frac{(\text{HCO}_3^-)(\text{H}^+)}{K_{\text{H}}K_1} \quad (1)$$

where K_{H} and K_1 are the temperature-dependent Henry's Law and first dissociation constants for CO_2 gas in water, respectively.

SI_c is calculated from:

$$\text{SI}_c = \log\left(\frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_c}\right) \quad (2)$$

where activities are denoted by brackets, and K_c is the temperature dependent equilibrium constant for calcite dissociation. If $\text{SI}_c > 0$, water is supersaturated with respect to calcite, and calcite could deposit; if $\text{SI}_c < 0$, water is aggressive to calcite, and calcite dissolution could happen; and if $\text{SI}_c = 0$, the equilibrium reaches.

4. Results and Discussions

4.1. GENERAL HYDROCHEMICAL COMPOSITION OF THE BAISHUITAI SPRINGS

Table I gives the general hydrochemical compositions of the Baishuitai springs on April 19, 2003. It shows that Ca^{2+} and Mg^{2+} are the major cations in the waters, with molarity percentage of $>70\%$ and $>20\%$ respectively, and HCO_3^- is the major anion in the waters, with molarity percentage of $>90\%$. Thus, the hydrochemical type of the spring waters is $\text{HCO}_3\text{—Ca,Mg}$, which reflects the control of the middle Triassic limestone bedrock at the site.

Spring No. 1 has similar hydrochemical composition to spring No. 2, which indicates they may originate from the same aquifer.

4.2. DIURNAL VARIATIONS OF HYDROCHEMISTRY DURING DRY WEATHER

4.2.1. Calculation of SI_c and P_{CO_2} from data-logger data

To calculate the saturation index of calcite SI_c and CO_2 partial pressure 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 I), 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 SI_c and P_{CO_2} by using the data recorded by the data loggers. During the calculation, the concentration value in Table I was adopted for the each of the five ions. In the next step, to obtain the time-series of SI_c and P_{CO_2} , concentrations of Ca^{2+} and HCO_3^- must be determined. At the study site these concentrations under dry weather are linearly related to specific conductivity (Figure 3) by the relationships:

$$[\text{Ca}^{2+}] = 0.2 \times (\text{sp. cond.}) - 9, \quad r^2 = 0.996 \quad (3)$$

$$[\text{HCO}_3^-] = 0.69 \times (\text{sp. cond.}) - 6.8, \quad r^2 = 0.98 \quad (4)$$

where brackets denote species concentrations in mg/l and (sp. cond.) is specific conductivity in $\mu\text{s}/\text{cm}$ corrected for 25°C .

4.2.2. Diurnal Variations of Spring Hydrochemistry during Dry Weather

Figure 4 shows the diurnal changes of the spring No. 1 hydrochemistry during dry weather of April 15–16, 2003. It can be seen that all the parameters show little change, and have no visible regular diurnal variation.

Table 1. Hydrochemical compositions of the Baishuitai springs (on April 19, 2003)

Spring name	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	Water Temp. (°C)	pH	Specific conductivity (µs/cm)	SI ^c ^a	P _{CO₂} ^b (ppmv)	Hydro-chemical type
Spring No. 1	1.13	8.14	184.40	30.10	2.66	688.55	22.74	10.9	6.61	1000	-0.04	131,220	HCO ₃ -Ca,Mg
Spring No. 2	1.16	8.04	192.65	28.49	3.48	708.42	23.97	10.9	6.53	1009	-0.10	162,181	HCO ₃ -Ca,Mg

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

^b calculated CO₂ partial pressure of water by WATSPEC (Wigley, 1977).

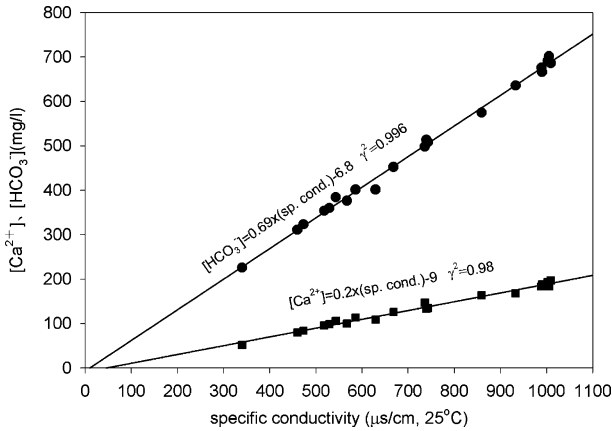


Figure 3. Linear relationships between specific conductivity vs. calcium and bicarbonate, respectively, for the spring and stream waters at Baishuitai, Yunnan, SW China.

4.2.3. Diurnal Variations of the Stream Hydrochemistry During Dry Weather

As Figures 5 and 6 show, during dry weather all recorded parameters in both the downstream pool No.10 and upstream pool No. 6 show distinct diurnal fluctuations.

In the following the fluctuations of the hydrochemistry are analyzed with respect to their causes.

(a) In downstream travertine pool No. 10

As displayed in Figure 5 the pH of the pool water shows distinct daily variations with the minimum usually occurring round about 8 a.m. when the sun rises. During the day the pH then rises about 0.4 to a maximum of 7.70. This maximum pH usually is reached in the late afternoon (19:00). At night time the pH decreases again approaching the stated minimum in the early mornings. Correspondingly, specific conductivity, $[Ca^{2+}]$, $[HCO_3^-]$ and P_{CO_2} of water show inverse diurnal variations, i.e., at about 8 a.m., specific conductivity, $[Ca^{2+}]$, $[HCO_3^-]$ and P_{CO_2} of water reach their maxima of 465 $\mu s/cm$, 83 mg/l, 307 mg/l, and 11400 ppmv, respectively, while during the daytime, they decrease approaching the minima of 387 $\mu s/cm$, 67 mg/l, 253 mg/l, and 4477 ppmv, respectively. The SI_c of water shows synchronous fluctuation as water temperature.

(b) In upstream travertine pool No. 6

Figure 6 displays pH fluctuations in the upstream travertine pool No. 6 recorded on April 17–18, 2003. Starting from a daily maximum of pH 7.2 at about 8:00 the pH continuously decreases during the day to a minimum of pH 7.05 at about 14:00 when the water temperature peaks, and then

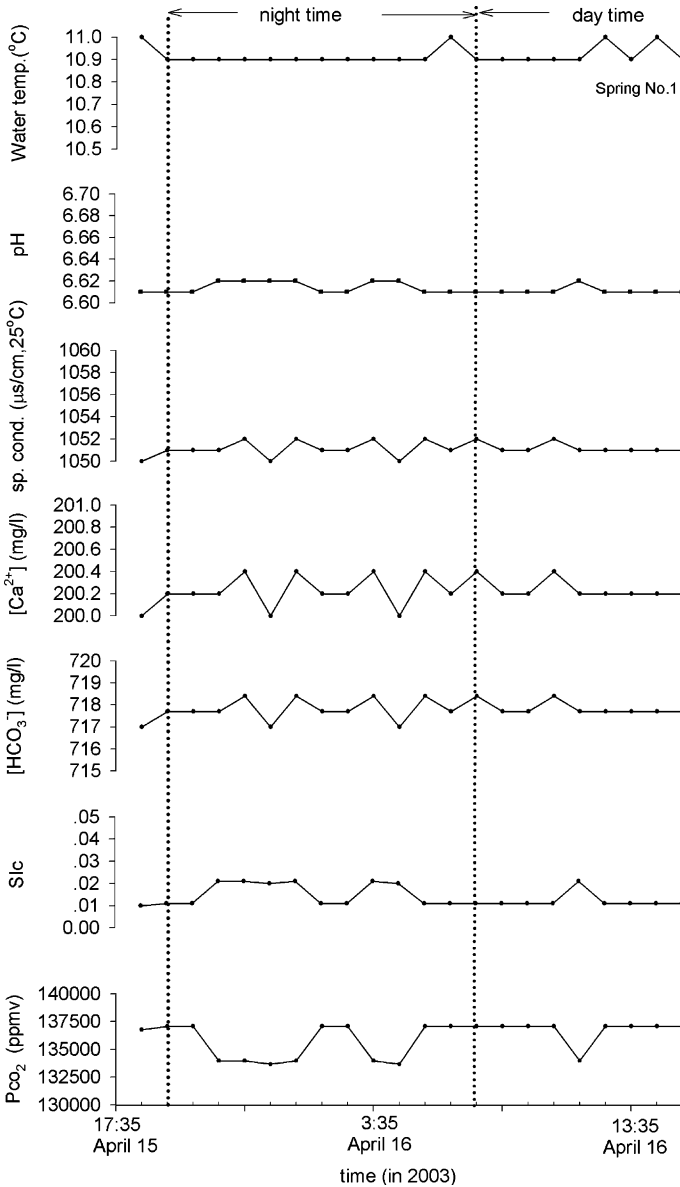


Figure 4. Diurnal variations of hydrochemistry of the spring No. 1. Note: water temp., pH and sp. cond. are logged temperature, pH and specific conductivity of water respectively by the data logger; $[HCO_3^-]$ and $[Ca^{2+}]$ are the concentrations of bicarbonate and calcium respectively calculated by their linear relationship with specific conductivity in Figure 3; and Sic and P_{CO_2} are the saturation index of calcite and CO_2 partial pressure of water computed by running the WATSPEC program (Wigley, 1977). The same below in Figures 5 and 6.

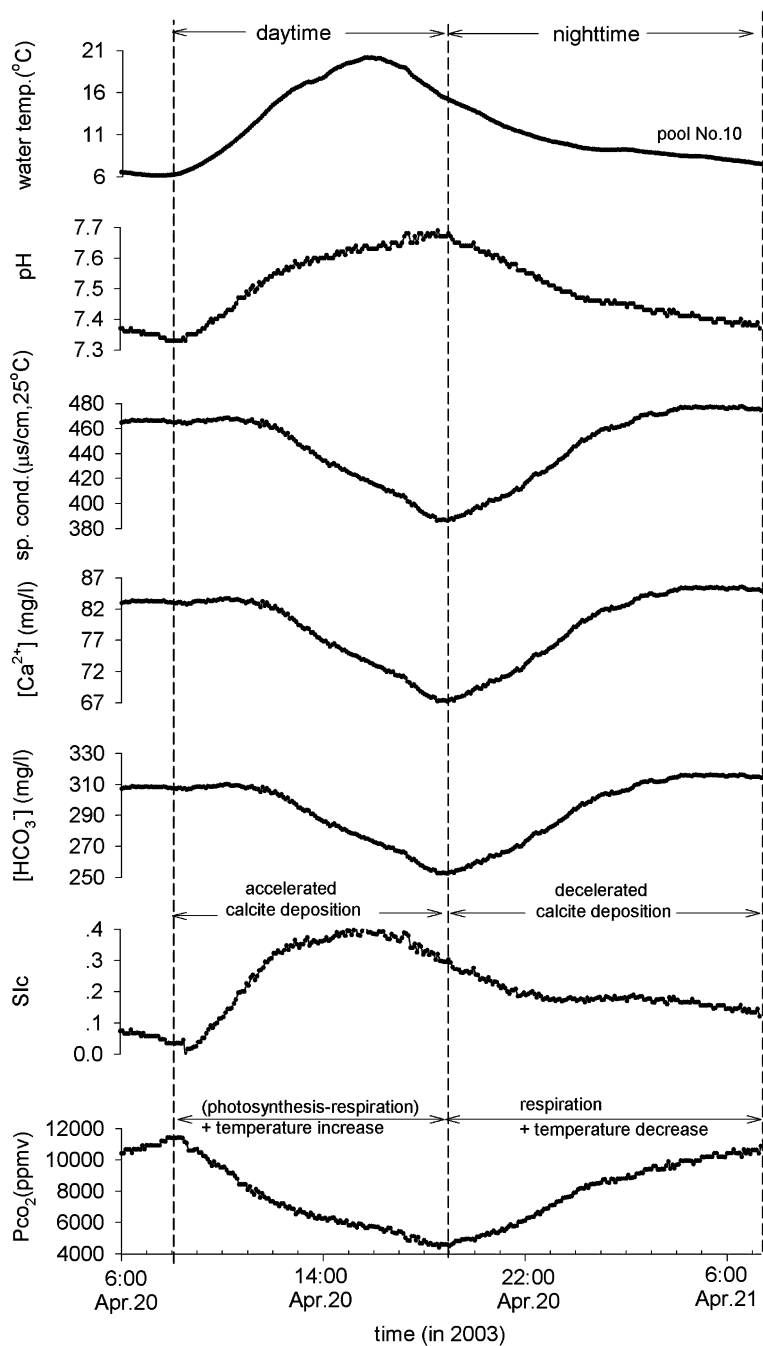


Figure 5. The diurnal cycle of the hydrochemistry in travertine pool No. 10 and its controlling processes.

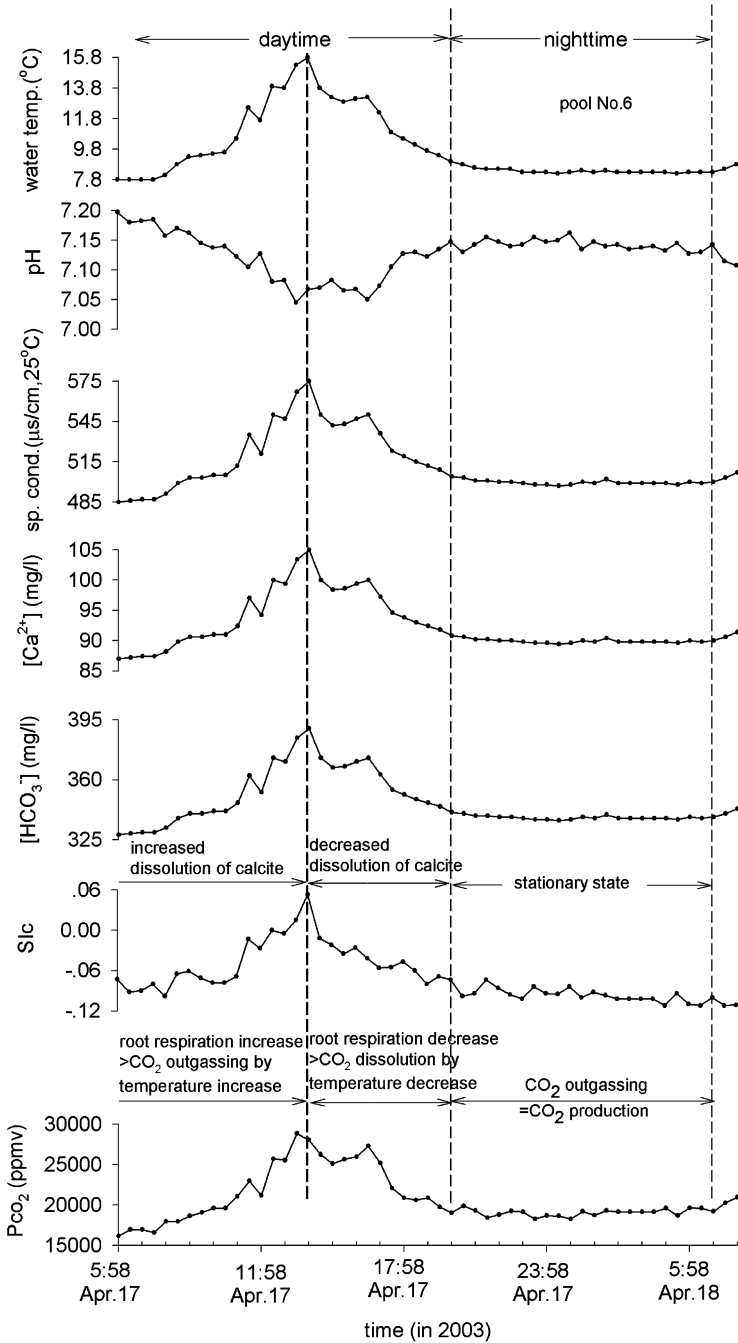


Figure 6. The diurnal cycle of the hydrochemistry in travertine pool No. 6 and its controlling processes.

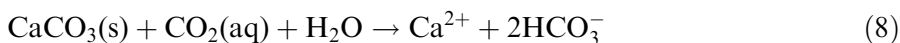
increases in the afternoon. Correspondingly, specific conductivity, $[Ca^{2+}]$, $[HCO_3^-]$, SI_c and P_{CO_2} of water show inverse variations, i.e., at about 8 a.m., specific conductivity, $[Ca^{2+}]$, $[HCO_3^-]$, SI_c and P_{CO_2} of water reach their minima of 490 $\mu S/cm$, 88 mg/l, 332 mg/l, -0.10 and 17947 ppmv, respectively, while in the morning, they increase approaching the maxima of 575 $\mu S/cm$, 105 mg/l, 390 mg/l, 0.05 and 28054 ppmv, respectively at 14:00, and then decreases in the afternoon. In night time all the parameters become more or less stable.

(c) Causes of diurnal hydrochemical variations in downstream travertine pool No. 10

According to Schwoerbel (1987), pH increase in streams may be caused mainly by photosynthesis of algae, phytoplankton and 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 (Equations 5–7) it controls pH values.



In addition to this, free (surplus) CO_2 in water also dissolves solid $CaCO_3$ into calcium bicarbonate (Equation 8).



However, the dissolution of $CaCO_3$ 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 precipitates as solid $CaCO_3$ (Equation 9). Due to the associated extraction of dissolved Ca from the water during this process, it is also called “de-calcification” (Equation 9):



When photosynthesis is the main reason for the process it is termed “biological de-calcification” (Winde, 2002). Apart from consumption of CO_2 by photosynthesis, increase of water temperature and/or higher CO_2 atmospheric partial pressure difference between water and the atmosphere can also reduce the concentration of dissolved carbon dioxide in the water. If the lack

of CO_2 in the water is caused by temperature- or pressure-driven exhalation of carbon dioxide the process is termed “physicochemical de-calcification”.

The observed diurnal cycle of pH in downstream travertine pool No. 10 appears to be a consequence of both biological decalcification and physicochemical de-calcification. Triggered by sunlight, photosynthesis started soon after sunrise and reached the maximum at 19:00, which was 3 h after insolation peaked at 16:00 (Figure 5). This process accelerated calcite precipitation (Equation 9), as evidenced by the decrease in specific conductivity, $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ (Figure 5). This results in an ongoing decrease of the CO_2 concentration in the stream (see P_{CO_2} in Figure 5) that simultaneously causes the pH to rise (Equations 3–5).

Apart from photosynthesis, 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 & Busenburg (1982), the Henry constant decreases by a factor of 1.5 from 6 °C (at 8:00) to 20 °C (at 16:00). Account of the total decrease in P_{CO_2} of water by a factor of about 2.6 from sunrise to sunset, it concludes that the effect of temperature dominates before 16:00 (Figure 5). Since both photosynthesis and water temperature are delayed reflections of insolation intensity in “normal” streams they oscillate in an almost identical rhythm. Therefore it is likely that their effects on the CO_2 concentration amplify each other. However, in downstream travertine pool No. 10, this may only be true



Photo 1. Travertine pool No. 10 and *in-situ* monitoring.



Photo 2. Travertine pool No. 6 and the flourishing aquatic plants growing out of water.

before 16:00. After this time, it seems that photosynthesis dominates (Figure 5).

In the night time, respiration and decreased temperature resulted in higher total carbon dioxide concentrations and hence a gradual decrease in pH, which reduces calcite deposition, and correspondingly the increase of specific conductivity, $[Ca^{2+}]$ and $[HCO_3^-]$ (Figure 5).

(d) Causes of diurnal hydrochemical variations in upstream travertine pool No. 6

Unlike the downstream travertine pool No. 10 (length×width×depth= 5 m×2 m×0.6 m), where aquatic plants were submerged and both photosynthesis and root respiration of the plants took place underwater (Photo 1), the upstream travertine pool No. 6 (length×width× depth= 4 m×1 m×0.5 m) represented an environment where aquatic plants flourished and grew out of water (Photo 2). This means that photosynthesis of the plants in pool No. 6 took place in the atmosphere, while root respiration took place underwater. According to Atkin et al. (2000), root respiration is temperature dependent. It increases as temperature increases, and decreases as temperature decreases. From Figure 6, one could conclude that root respiration dominated over CO_2 exsolution by temperature increase before about 14:00, when insolation peaked (evidenced by water temperature), which made the increase of P_{CO_2} in water, and thus the decrease of pH. The latter enhanced dissolution of calcite in the pool No. 6. So, the $[Ca^{2+}]$, $[HCO_3^-]$, specific conductivity and SIC of water

increased (Figure 6). However, after 14:00, as insolation decreased, root respiration decreased. This is the reason why all the hydrochemical parameters show a reversal after 14:00 and before about 20:00, when nighttime began. At nighttime, CO_2 degassing balanced CO_2 production, and the water reached steady state. So, all the hydrochemical parameters were more or less stable (Figure 6).

(e) Independent confirmation of biological processes

To obtaining independent confirmation of the biological processes, according to the suggestions by the anonymous reviewer, we went to the study site again for additional field investigation. We focus on travertine pool No. 6, where biological activity was more intensive. At this time, we used WTW multi-parameter instrument Multi-350i, which continuously recorded DO (dissolved oxygen), as well as specific conductivity, pH and temperature of water. As an independent parameter, DO could tell us more about plant photosynthesis and respiration. Unfortunately, almost all aquatic plants in pool No. 6 have been removed by local manager for maintaining enough travertine deposition. So, it was not possible to investigate the effect of plant root respiration on the diurnal hydrochemical variations this time. However, it was a good chance to examine diurnal hydrochemical variations at the time when plants are not active. This also provides interesting comparison. We found that after the plants were removed, the pattern of diurnal hydrochemical variation in pool No. 6 (Figure 7) was totally different than before, when flourished aquatic plants grown out of water. At daytime, pH increased but not decreases; conductivity (thus calcium and bicarbonate concentrations) and P_{CO_2} of water decreased but not increase (Figure 7). To compare with pool No. 10, where only some submerged aquatic plants exist, the pattern of diurnal hydrochemical variation at pool No.6 at this latter time is very similar. All these show the importance of photosynthesis by submerged plants and/or aquatic algae and temperature increase in diurnal hydrochemical variations. The daytime increase in DO content (Figure 7), as an independent parameter of photosynthesis, which consumed CO_2 and released oxygen, further provides support on biological process theory.

In addition, it was found from Figure 6 to Figure 7 that there was large increase in pH and SI_c , but huge decrease in P_{CO_2} of water. This may be related to the increase in photosynthesis of submerged aquatic plants and algae in summer season. On the other hand, higher temperature in summer may also contribute to this.

5. Summary

The Baishuitai data obtained in this study can only be considered in a descriptive manner as many other avenues of research are required to infill

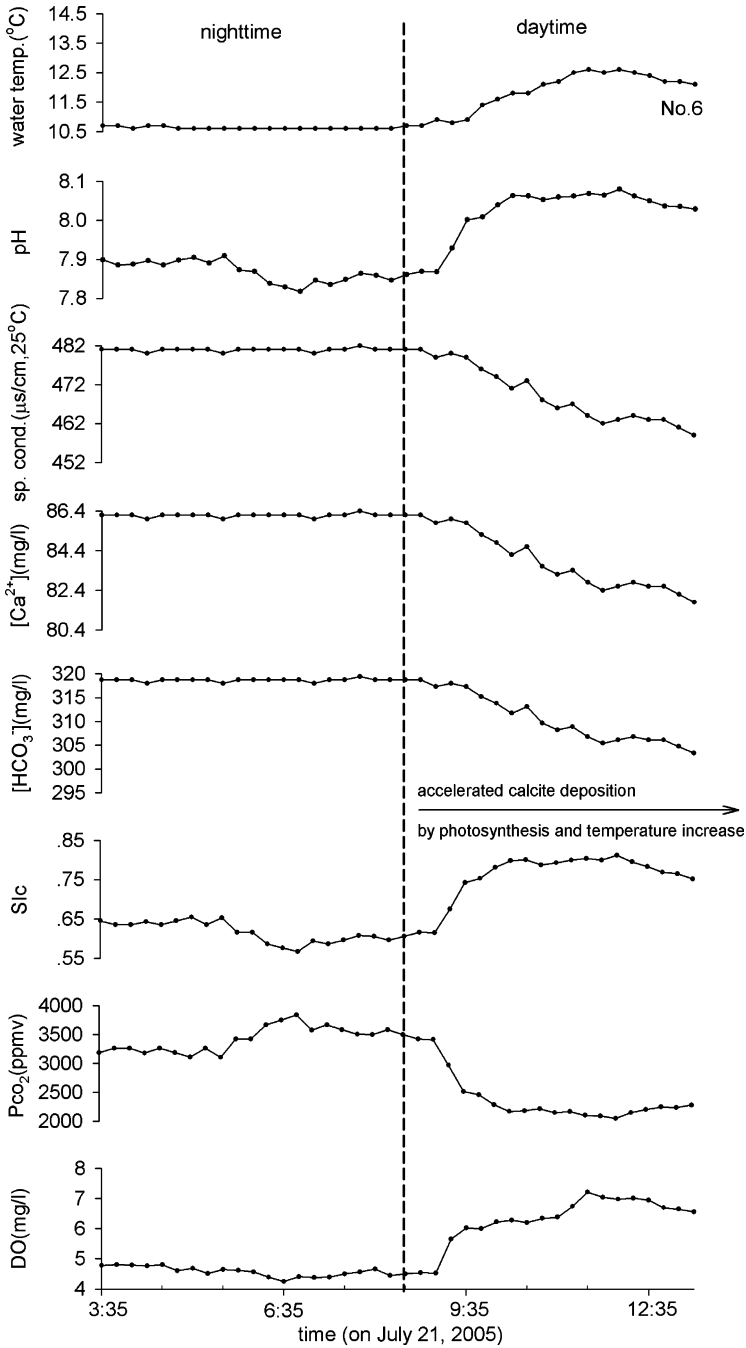


Figure 7. The diurnal cycle of the hydrochemistry in travertine pool No. 6 and its controlling processes after the flourishing aquatic plants were removed.

missing information on process dynamics. At this more descriptive level, the data clearly show, for pH, specific conductivity and carbon dioxide partial pressure, that within-pool biological controls are very important. With regard to the hydro-biogeochemical functioning of the pool No. 6 in 2003, an important issue is why the water was always oversaturated with respect to carbon dioxide. There are two primary reasons for this. Firstly, the water was supplied from the spring, which had much higher P_{CO_2} than atmosphere (about 500-fold). Secondly, the root respiration of aquatic plants contributed much CO_2 to water. Thus, the dissolved carbon dioxide changes that impact on the pH, specific conductivity and calcite saturation levels result from the following three primary processes:

1. Carbon dioxide laden inputs of the spring;
2. Within-pool biological processing; and
3. Carbon dioxide degassing to the atmosphere.

Descriptive processing of the information collected provides an important prerequisite for producing more detailed mathematical models that describe the dynamics of water quality change and which can be used to assess chemical flux. Thus the data and the hydro-biogeochemical framework presented in this paper provides an important step towards the production of reliable mathematical models which can then be used for environmental impact assessment in relation to contemporary issues of:

1. Climate variability (high and low temperature extremes);
2. biological effects on water quality change.

At last, though our finding about the influence of root respiration on water chemistry comes from a very small pool, the wider significance of the finding is evident in environments with stagnant water bodies (e.g. lakes, reservoirs, pools, wetlands) where aquatic plants may flourish and grow out of water.

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