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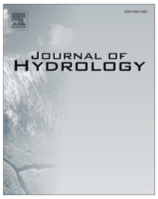

Diurnal hydrochemical variations in a karst spring and two ponds, Maolan Karst Experimental Site, China: Biological pump effects

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SUMMARY

A karst spring and two downstream ponds fed by the spring at the Maolan Karst Experimental Site, Guizhou Province, China, were used to investigate the effect of submerged plants on the CO_2–H_2O–$CaCO_3$ system during a time of spring base flow in summer when underwater photosynthesis was strongest. Temperature, pH, electrical conductivity (EC) and dissolved oxygen (DO) were recorded at 15 min intervals for a period of 30 h (12:00 29 August–18:00 30 August, 2012). $[Ca^{2+}]$, $[HCO_3^-]$, CO_2 partial pressure (pCO_2) and saturation index of calcite (SI_C) were estimated from the high-frequency measurements. Water samples were also collected three times a day (early morning, midday and evening) for $\delta^{13}C_{DIC}$ determination. A floating CO_2-flux monitoring chamber was used to measure CO_2 flux at the three locations. Results show that there was little or no diurnal variation in the spring water parameters. In the midstream pond with flourishing submerged plants, however, all parameters show distinct diurnal changes: temperature, pH, DO, SIc, $\delta^{13}C_{DIC}$ increased during the day and decreased at night, while EC, $[HCO_3^-]$, $[Ca^{2+}]$, and pCO_2 behaved in the opposite sense. In addition, maximum DO values (16–23 mg/L) in the midstream pond at daytime were two to three times those of water equilibrated with atmospheric O_2, indicating strong aquatic photosynthesis. The proposed photosynthesis is corroborated by the low calculated pCO_2 of 20–200 ppmv, which is much less than atmospheric pCO_2. In the downstream pond with fewer submerged plants but larger volume, all parameters displayed similar trends to the midstream pond but with much less change, a pattern that we attribute to the lower biomass/water volume ratio. The diurnal hydrobiogeochemical variations in the two ponds depended essentially on illumination, indicating that photosynthesis and respiration by the submerged plants are the dominant controlling processes. The large loss of DIC between the spring and midstream pond, attributed to biological pump effects, demonstrates that natural surface water systems may constitute an important sink of carbon (on the order of a few hundred tons of C km^2/a) as DIC is transformed to autochthonous organic matter. The rates of sedimentary deposition and preservation of this organic matter in the ponds, however, require quantification in future work to fully assess the karst processes-related carbon sink, especially under global climate and land use changes.

1. Introduction

Hydrochemical behavior in karst terrains exhibits marked annual, seasonal, and even diurnal and storm-scale variations (Liu et al., 2004, 2006, 2007, 2008). Thus, an increasing number of studies have focused on the karst critical zone because of its sensitivity to environmental changes and distinctive resource–environmental effects (De Montety et al., 2011; Hayashi et al., 2012; Yang et al., 2012; Zeng et al., 2012; Kurz et al., 2013).

Surface waters in karst terrains are rich in dissolved inorganic carbon (DIC) and provide a well-defined natural system to study gas exchange between water and atmosphere, calcite deposition, aquatic photosynthesis and respiration (Spiro and Pentecost, 1991). Previous studies have emphasized particular aspects of geochemistry or biology in these waters, but data on the interactions among physical, chemical and biological processes are still lacking. These mutually dependent processes should be discussed together, because consideration of water-rock-gas-organism interaction as a whole is required to understand the spatiotemporal hydrochemical

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variations in karst waters (Liu et al., 2010; Yang et al., 2012). Moreover, due to the dynamics and complexity of karst processes, there is still much to be learned about the biogeochemistry of karst waters, especially diurnal spatiotemporal variation (Liu et al., 2006, 2007, 2008; Yang et al., 2012).

A study of dissolved elemental and carbon isotopic composition in the major karst springs at the Maolan Karst Experimental Site, SW China (Maolan) has provided useful information about the characteristics of spring water. Because different sources of dissolved inorganic carbon (DIC) have different isotopic compositions, $\delta^{13}C_{DIC}$ is a direct reflection of the physical, chemical and biological processes in the water (Han et al., 2010). Identifying the transformation of DIC to organic carbon (OC) as evidenced by changes in CO_2, O_2, DIC, pH, $\delta^{13}C_{DIC}$ and estimating this contribution quantitatively are the purposes of this study.

Here we report on an investigation of an epikarst spring (Liu et al., 2007) and its two downstream ponds at Maolan. We have obtained high time-resolution monitoring records of the physical-chemical parameters for about a 30-hour period (12:00 29 August–18:00 30 August, 2012) when underwater photosynthesis was strongest. We also report selected $\delta^{13}C_{DIC}$ from the site. This research focuses on the physical chemistry of karst water and the evolution of $^{13}C_{DIC}$ influenced by major natural processes. The aim of this study is to understand diurnal hydrochemical variations and quantitatively estimate the C loss through the biological pump in a typical karst spring and its two downstream ponds under summer, sunny and base flow conditions. These conditions represent the time of most intensive biological activity. The results reveal spatiotemporal differences and their underlying mechanisms, which have implications for assessing karst processes as related to the global carbon sink (Liu et al., 2010).

2. Study area

The Maolan Karst Experimental Site in China (Maolan; Fig. 1) is well known for its dense virgin evergreen forests growing on cone karst, and is listed by UNESCO as a world heritage site (Libo Karst, one of the three clusters of South China Karst, whc.unesco.org). Annual rainfall in areas with virgin forest is about 1750 mm, about 80% of which falls in the monsoon season from April to September, July and August being the months with highest average precipitation (Zhou, 1987). Annual rainfall is 400 mm less in surrounding deforested areas due to absence of the forest microclimatic effect (Zhou, 1987). The mean annual air temperature at Maolan is about 17 °C, with hot summers (June–August) and cold winters (December–February). The bedrock is mostly dolomitic limestone of Middle to Lower Carboniferous age (Liu et al., 2007; Jiang et al., 2008).

The sampled spring is a typical Ca–HCO_3 type epikarst spring (here termed 'Maolan spring') with flow rate of 0.05–30 L/s (Liu et al., 2007). It is at the base of a cone karst slope covered by virgin karst forest. There is no net deposition of tufa at the spring and the calcite saturation index of the water there is near zero (Liu et al., 2007). Fig. 2 gives an oblique perspective of the spring and the receiving ponds with different amounts of submerged plants (chiefly *Charophyta*). The spring and two ponds have been modified by the addition of weirs to control outflow. The spring weir was built in 2002 for long-term monitoring of water stage and hydrogeochemistry (Liu et al., 2007), and the weirs for the two ponds were built in 2004 by the local population for freshwater fish farming; fishing was abandoned in 2011.

The spring discharge was 1.2 L/s and almost stable during the study period, and the surface areas of midstream and downstream ponds were 280 m^2 and 1300 m^2 respectively. The midstream pond volume was smaller (60 m^3) than the downstream pond volume (1300 m^3). The distances from the spring orifice sampling site to the midstream pond sampling site was 38 m, and the distance between the midstream and downstream pond sampling sites was 29 m.

3. Methods

3.1. Field monitoring and sampling

The field study was conducted on 29–30 August 2012 under summer, sunny and base flow conditions, when underwater photosynthesis was strongest. Two WTW® (Wissenschaftlich–Technische–Werkstaetten) Technology MultiLine® 350i's and one SEBA® multi-parameter data logger (Qualilog-16®) were programmed to measure pH, water temperature, dissolved oxygen (DO), and electrical conductivity (EC, 25 °C) at 15 min interval for 30 h (12:00 29 August–18:00 30 August, 2012) covering a complete diurnal cycle. The meters were calibrated prior to deployment using pH (4, 7 and 10), EC (1412 μs/cm), and DO (0% and 100%) standards. One WTW-350i® was located at the spring orifice to characterize discharging groundwater. The Qualilog-16® monitored conditions at the midstream pond and the second WTW-350i® monitored the downstream pond. The resolutions on pH, DO, EC and temp are 0.01, 0.01 mg/L, 1 μs/cm and 0.01 °C, respectively.

Water samples for $\delta^{13}C_{DIC}$ were collected three times (midday 29 August; evening 29 August; morning 30 August) at the three sites. The sampling site for the Maolan spring $\delta^{13}C_{DIC}$ differed from the location of the multi-parameter meter: the meter was put in the orifice measuring groundwater conditions just before emergence into the spring pool, whereas the $\delta^{13}C_{DIC}$ samples were collected in the spring pool, after some equilibration with surface conditions. The $\delta^{13}C_{DIC}$ samples were collected in pre-cleaned 30 mL glass vials, with no air space. One drop of saturated $HgCl_2$ solution was added to each sample to prevent microbial activity and all samples were kept at temperatures below 4 °C until analysis.

A floating CO_2-flux monitoring chamber (14 L volume with diameter of 40 cm, and surface area of 0.126 m^2) was placed on the surface of the waters to determine CO_2 efflux from the three sites. CO_2 flux was evaluated three times (midday 29 August; evening 29 August; morning 30 August) at each location by collecting five floating-chamber gas samples at 2-min intervals. The chamber was emptied between sampling and flushed with ambient air. The CO_2 concentration of the samples was measured by gas chromatography (Agilent-7890®) with a resolution of 0.01 ppmv.

3.2. Estimating CO_2 partial pressure and the calcite saturation index

We attribute EC fluctuations in the spring and ponds to Ca^{2+} and HCO_3^- variations induced by calcite precipitation or dissolution because other dissolved components are not involved in dissolution or precipitation reactions, no rainfall occurred during the sampling interval and evaporation is unlikely because of the high humidity (83% annually, www.163gz.com) of Maolan. In karst area with purely a bicarbonate type, Ca^{2+}, Mg^{2+} and HCO_3^- were previously correlated with EC at this site (Liu et al., 2007). The regressions were used to estimate concentrations of Ca^{2+} and HCO_3^- for further calculations, below. The relationships are:

$$[Ca^{2+}] = 0.15EC - 0.78, \ r^2 = 0.94, \quad (1)$$

$$[Mg^{2+}] = 0.04EC + 0.22, \ r^2 = 0.77, \quad (2)$$

$$[HCO_3^-] = 0.63EC - 4.70, \ r^2 = 0.99, \quad (3)$$

where brackets denote concentrations in mg/L and EC is electric conductivity in μS/cm at 25 °C (Liu et al., 2007).