Chemical Geology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Coupled control of land uses and aquatic biological processes on the diurnal hydrochemical variations in the five ponds at the Shawan Karst Test Site, China: Implications for the carbonate weathering-related carbon sink

Bo Chen [a,b], Rui Yang [a], Zaihua Liu [a,*], Hailong Sun [a], Hao Yan [a], Qingrui Zeng [a,b], Sibo Zeng [c], Cheng Zeng [a], Min Zhao [a]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, CAS, Guiyang 550081, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] School of Geographical Sciences, Southwest University, Chongqing 400715, China

ARTICLE INFO

Article history:
Received 27 November 2016
Received in revised form 17 February 2017
Accepted 4 March 2017
Available online xxxx

Keywords:
Diurnal hydrochemical variation
BCP effect
DIC fertilization effect
Rock weathering-related carbon sink
Land use and cover change

ABSTRACT

High-resolution hydrochemical data from five spring-fed ponds are presented to demonstrate the effect of different land uses and aquatic biological processes on the carbon cycle at a karst-analog test site. The results show that hydrochemical parameters including pH and the concentrations of HCO_3^-, Ca^{2+}, NO_3^-, partial pressures of CO_2 (pCO_2) and dissolved O_2 (DO) as well as carbon isotopic compositions ($\delta^{13}C$) of HCO_3^- in the pond water all displayed distinct diurnal variations, while those of the spring water itself were rather stable. The coupled dynamic behaviors of pCO_2, DO and NO_3^- indicate a significant influence from the metabolism of submerged plants in the ponds. In the afternoon, when photosynthesis is the strongest, the pCO_2 of the five pond waters was lower even than that of the ambient atmosphere, demonstrating the existence of a "biological carbon pumping (BCP) effect", similar to that in the oceans. It was determined that, in October (autumn), the BCP fluxes in the five spring-fed ponds were 156 ± 51 t C km^{-2} a^{-1} in P1 (Pond 1 – adjoining a bare rock shore), 239 ± 83 t C km^{-2} a^{-1} in P2 (adjoining uncultivated soil), 414 ± 139 t C km^{-2} a^{-1} in P3 (adjoining land cultivated with corn), 493 ± 165 t C km^{-2} a^{-1} in P4 (adjoining grassland) and 399 ± 124 t C km^{-2} a^{-1} of P5 (adjoining brushland), indicating the potentially significant role of aquatic photosynthesis in stabilizing the carbonate weathering-related carbon sink. In addition, by comparing the DIC concentrations and fluxes of DIC transformed into autochthonous organic matter (AOC) in the five ponds, the so-called "DIC fertilization effect" was found in which more AOC is produced in pond waters with higher concentrations of DIC. This implies that the carbon cycle driven by aquatic biological processes can be regulated by changing land use and cover, the latter determining the DIC concentrations. Further, the rock weathering-related carbon sink is underestimated if one only considers the DIC component in surface waters instead of both DIC and AOC.

1. Introduction

Inland freshwater ecosystems, particularly rivers, lakes and reservoirs, can affect regional carbon balances by storing, oxidizing and transporting terrestrial carbon and thus significantly influencing the terrestrial carbon budget (Cole et al., 2007). In earlier previous studies, dissolved inorganic carbon (DIC) transport through rivers into the ocean has been studied extensively; conversion from inorganic to organic carbon as well as the consequent carbon sequestration or release in freshwater ecosystems (Z. Liu et al., 2010; Y. Liu et al., 2010; Liu and Dreybrodt, 2015), however, is generally overlooked.

Recently, research has shown that autochthonous organic carbon (AOC) from DIC transformation by aquatic photosynthesis is an important part in river transported/buried carbon (Waterson and Canuel, 2008; Yang et al., 2016). Especially in karst basins, due to the rapid carbonate weathering which provides abundant DIC and the aquatic photosynthesis which utilizes DIC as its carbon source, the amount of AOC can be considerable and thus its corresponding contribution to karst-related carbon sinks must be considered (Liu and Dreybrodt, 2015). The karst-related carbon sink is a complex, combined effect including a series of physical, chemical and biological processes, and can be studied by understanding the spatiotemporal hydrochemical variations in the

* Corresponding author.
E-mail address: liuzaihua@vip.gyig.ac.cn (Z. Liu).

http://dx.doi.org/10.1016/j.chemgeo.2017.03.006

aquatic ecosystems (De Montety et al., 2011; Liu et al., 2015; Yang et al., 2015). Previous work has emphasized particular aspects of geochemistry or biology in karst waters (Liu et al., 2006, 2008; Parker et al., 2007; Z. Liu et al., 2010, Y. Liu et al., 2010; De Montety et al., 2011; Kurz et al., 2013), even specifically focusing on the influence of submerged plant metabolism (or primary producers) on stream water hydrochemistry, including oxygen dynamic and nutrient cycling (Clarke, 2002; Schulz and Köhler, 2006; Heffernan and Cohen, 2010; Parker et al., 2010; Poulson and Sullivan, 2010). There are also several studies showing that diurnal changes of dissolved organic carbon (DOC) are attributable to daily changes in the productivity levels of aquatic communities (Harrison et al., 2005; Spencer et al., 2007). However, research on the interactions among physical, chemical and biological processes is still lacking, and thus the driving mechanisms remain unclear and need to be further resolved.

It is common that natural karst catchments have mixed vegetation types, making data interpretation difficult, so, an experimental test site, controlling for all variables but one, can help simplify and understand the impact of different land covers on the karst hydrobiogeochemical processes, and improve the quantification of the related carbon budgets. With this requirement in view, five karst spring-pond systems of the same size but with different single types of vegetation cover were constructed at Shawan (Puding County, Guizhou Province, China), to investigate the diurnal hydrochemical variations in the ponds in different seasons. It was found that aquatic metabolism is the major driving force for the daily hydrochemical cycle and even causes strong Biological Carbon Pumping (BCP) effects. Moreover, higher DIC concentrations result in higher aquatic photosynthetic products, which are called "DIC fertilization effects" (Z. Liu et al., 2010; Yang et al., 2016), and indicate, for the first time, that carbon sequestration originating from water-carbonate rock-CO_2 gas-aquatic organism interaction could be regulated by land use and land cover changes, which result in changes in DIC concentrations, and are important to future carbon management in mitigating climate change.

Fig. 1. Five springs (S1 to S5, upper image) and the spring-fed ponds (P1 to P5, upper and lower image) with flourishing submerged plants and WTW data loggers and the floating chamber. The types of land uses feeding the springs are bare rock land (LUCC1), abandoned bare land (LUCC2), cultivated land (LUCC3), grassland (LUCC4), and shrubland (LUCC5).

2. Study site

The simulation test site (Fig. 1, 26°14′-26°15′N, 105°42′-105°43′E, 1200 m asl) is located in the Puding Comprehensive Karst Research and Experimental Station, Puding County, Guizhou Province, China. The climate is humid subtropical monsoon with annual mean air temperature of about 15.1 °C and mean annual precipitation of 1315 mm, 80% of which occurs during the rainy season from May to October (Yang et al., 2012).

Five concrete tanks LUCC (Land Use/Cover Change) 1 to LUCC5, each 20 m long and 5 m wide and 3 m deep, coated with epoxy resin to avoid the influence of possible concrete erosion on the tank hydrochemistry, were constructed at the site, filled with 2 m dolomitic limestone rubble in the lower part and topped with 0.5 m soil with the exception of LUCC1, which was left with rubble only. Construction was completed in January 2014. Tank LUCC1, with no soil and plants but only carbonate rubble was used to simulate the land-use condition in karst rocky desert. In Tank LUCC2, there was no induced plant growth but soil and carbonate rubble were used to simulate land-use conditions in bare land. Tank LUCC3 was planted with corn to simulate cultivated land-use. Alfalfa and Roxburgh rose were sown in the soils of Tank LUCC4 and Tank LUCC5 in January 2014 to simulate grass and shrub land-uses respectively (Fig. 1). A drainage hole was cut in each tank to simulate outlet of a karst spring (S1 to S5), which fed into an artificial pond (P1 to P5) with 3 m long, 50 cm wide, and 50 cm deep to simulate influence of groundwater on surface water (Fig. 1). Equal numbers of the locally dominant submerged plants, including Spirogyra, Hornwort and Charophyta, were transplanted in each spring-fed pond in January 2014 to simulate the influence of biological processes on the hydrochemistry of the pond waters.

3. Methods

3.1. Field monitoring

The field campaigns were conducted under sunny and steady flow conditions for 48 h on 26–28 April, 19–21 July, 24–26 October 2015 and 23–25 January 2016, two diurnal cycles each for spring, summer, autumn and winter respectively. We found similar diurnal hydrochemical variation patterns for all seasons, but highest range for autumn (September to November) and lowest range for winter (December to February). Therefore, for simplification and shortening the paper, we chosen the data for autumn and winter as a highest-lowest contrast to study climate influence on the BCP-effect. Five Manta Multi-parameter Data Logger 2.0 and five WTW Technology Multiline 350i were programmed at each spring vent and pond outlet (Fig. 1), respectively, to collect 15-min interval readings of water temperature (T), pH, electrical conductivity (EC, 25 °C), and dissolved oxygen (DO) for the daily cycles. The meters were calibrated prior to deployment using pH (4, 7 and 10), EC (1412 μs cm^{-1}), and DO (0% and 100%) standards. Resolution of pH, T, DO and EC was 0.01, 0.01 °C, 0.01 mg L^{-1} and 0.01 μS cm^{-1}, respectively. In addition, the flow rate of each spring (L min^{-1}) was measured at the beginning and end of the study periods.

3.2. Sampling and analysis

Two sets of water samples were passed through 0.45 μm Millipore filters into 20 mL acid-washed high-density polyethylene bottles for major cation and anion determination. The cation samples were acidified to pH < 2.0 with concentrated nitric acid to prevent complexation