JOURNAL OF ENVIRONMENTAL SCIENCES XX (2017) XXX–XXX

Available online at www.sciencedirect.com

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JES
JOURNAL OF ENVIRONMENTAL SCIENCES
www.jesc.ac.cn

Comparative study of carbonic anhydrase activity in waters among different geological eco-environments of Yangtze River basin and its ecological significance

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ARTICLE INFO

Article history:
Received 13 December 2016
Revised 16 May 2017
Accepted 16 May 2017
Available online xxxx

Keywords:
Yangtze River basin
Carbon sink
Eco-environments
Water body
Carbonic anhydrase (CA)

ABSTRACT

This study provides the presence of carbonic anhydrase (CA) activity in waters of the Yangtze River basin, China, as well as the correlation of CA activity with HCO_3^- concentration and CO_2 sink flux. Different degrees of CA activity could be detected in almost all of the water samples from different geological eco-environments in all four seasons. The CA activity of water samples from karst areas was significantly higher than from non-karst areas (PP3⁻ concentration (r = 0.672, P2 sink flux (r = 0.602, P = 0.076) in karst areas. This suggests that CA in waters might have a promoting effect on carbon sinks for atmospheric CO_2 in karst river basins. In conditions of similar geological type, higher CA activity was generally detected in water samples taken from areas that exhibited better eco-environments, implying that the CA activity index of waters could be used as an indicator for monitoring ecological environments and protection of river basins. These findings suggest that the role of CA in waters in the karst carbon sink potential of river basins is worthy of further in-depth studies.

Introduction

The increase in the atmospheric concentrations of carbon dioxide (CO_2) due to anthropogenic activities has led to several undesirable consequences, such as global warming and related changes (Lou et al., 2015; Ramanan et al., 2009). The rate of change in atmospheric CO_2 depends not only on human activities and ocean storage, but also on biogeochemical and climatological processes and their interactions with the carbon cycle (Falkowski et al., 2000; Manabe and Stouffer, 1993). The lithosphere is the Earth's largest carbon reservoir, and the quantity of carbon stored in carbonate rocks is estimated to be more than 6.0×10^{16} tons C (Cao et al., 2011). The karst ecosystem is an important component of the terrestrial ecosystem and the karst area covers about 12% of the world's land area (Liu et al., 2013). China has the largest karst area (346.3×10^4 km^2) in the world, with a coverage close to one-third of China's total land area (Jiang et

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http://dx.doi.org/10.1016/j.jes.2017.05.027
1001-0742 © 2017 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

al., 2010). The karst process involves carbonate dissolution or deposition as carbon is transferred among reservoirs in the carbon cycle, and is coupled to the water cycle as well as the calcium cycle (Yuan and Zhang, 2008). The karst process is considered to serve as an atmospheric carbon sink (He et al., 2012). The estimated annual absorption of atmospheric CO_2 by the carbonate system was about 6.08×10^8 tons, which may be an important part of the "missing carbon sink" (Jiang et al., 2013).

Organisms are one of the most active components of the Earth's surface system. Microorganisms and carbonic anhydrases play an important role in karst processes (Li et al., 2005a; Lian et al., 2011). Carbonic anhydrase (CA, EC4.2.1.1) is a metalloenzyme containing a zinc ion in its active site. It is widespread in animals, plants and prokaryotes, and can effectively catalyze the interconversion of CO_2 and HCO_3^- (Elleuche and Pöggeler, 2010; Smith and Ferry, 2000), which would then promote karst processes. The results of laboratory simulation experiments have indicated that after adding CA (bovine or microbial CA) to a karst system, the erosion rate of limestone would significantly increase (Liu and Dreybrodt, 1997; Li et al., 2005a, 2007, 2009). In contrast, some studies have shown a promoting effect of bovine CA or microbial CA on the sequestration of CO_2 in carbonate form (Favre et al., 2009; Li et al., 2010, 2013). Moreover, the photosynthesis of aquatic plants depends on CA. In their field monitoring experiments, Liu et al. (2010a) found that the global water cycle is likely to be an important CO_2 sink, through the absorption of CO_2 by water and subsequent enhanced consumption by carbonate dissolution and aquatic plant photosynthesis. Therefore, the influence of CA on karst carbon sinks is worthy of attention.

To clarify the actual contribution of CA to karst carbon sinks, it is necessary to investigate the distribution and activity of CA in natural karst ecological environments, including soils and waters, as well as in living organisms (Liu, 2001). Some studies have examined the characteristics of the distribution and activity of CA in soils among different karst ecological environments (Li et al., 2005b; He et al., 2013). However, the spatiotemporal distribution and activity of CA in waters of river basins have been less well reported. In our previous study, we investigated the spatial distribution and activity of CA in water samples from the Guijiang River basin, Guangxi, China (Shen et al., 2012). In this study we further investigated the spatiotemporal distribution and activity of CA in water samples from the Yangtze River basin, China. The water samples were collected in four different seasons from the mainstream and tributaries of the Yangtze River basin. The CA activity, HCO_3^- concentration and other physicochemical parameters in water samples were analyzed and compared among different geological eco-environments. The relationship between the CA activity in waters and the karst carbon sink was discussed. This study reports for the first time the presence of CA activity in waters of the Yangtze River basin, as well as its correlation with HCO_3^- concentrations and CO_2 sink flux. The results lay a foundation for further studies of the actual contribution of CA to karst carbon sinks, and provide a valuable reference for the scientific investigation of carbon sink potential in river basins.

1. Materials and methods

1.1. Site description

The Yangtze River is the third longest river in the world. It originates in the Qinghai–Tibet Plateau and extends about 6300 km eastwards to the northern East China Sea at around 31°30′ N and 121°30′ E (Fig. 1) (Yang et al., 2002). It flows through eleven provinces, *i.e.*: Qinghai, Tibet, Sichuan, Yunnan, Chongqing, Hubei, Hunan, Jiangxi, Anhui, Jiangsu, and Shanghai, covering a total area of 1.8085×10^6 km^2. The main stream is joined by a large number of tributaries. The major tributaries include the Yalongjiang, Minjiang, Tuojiang, Jialingjiang, Wujiang, Hanjiang, Xiangjiang, Yuanjiang, and Ganjiang. Four of these major tributaries (Jinshajiang, Jialingjiang, Minjiang and Wujiang) join in the mainstream of the upper Yangtze River (Hu et al., 2009).

Guizhou Province is regarded as the center of the karst areas of the Yangtze River basin, spanning Yunnan, Sichuan, Chongqing, Hunan and Hubei provinces, and to the southeast, connected to the karst areas in Guangxi and west of Guangdong. The total karst area including covering karst is 4.3×10^5 km^2, accounting for 28.5% of the total area of the region (Hu et al., 2000).

The precipitation and runoff of the Yangtze River basin change seasonally, and 70%–80% of precipitation is distributed in the rainy season from May to October (Yang et al., 2002). The annual mean temperature is below 4°C in the source area, 5–15°C in the mountainous areas, and 16–18°C in the middle and lower reaches (Chen et al., 2002).

1.2. Water sampling and analysis

Ten sampling sites representing different geological eco-environments were selected along the main stream and tributaries of the Yangtze River basin. The geographical positions of these sites are shown in Fig. 1. They are Shigu (SG), Ertan (ET), Gaochang (GC), Yibin (YB), Beibei (BB), Wulong (WL), Yichang (YC), Xiantao (XT), Waizhou (WZ), and Datong (DT). Except for the two sampling sites ET and WZ that were located in non-karst areas, the rest of the sampling sites were located in karst areas. The basic details of the various sampling sites are given in Table 1.

Water samples were collected from the main stream and six tributaries along the Yangtze River basin at ten representative sampling sites. The sampling sites SG, YB, YC and DT were located in the main stream of the Yangtze River and the sampling sites ET, GC, BB, WL, XT and WZ were located in the six tributaries, *i.e.*, Yalongjiang, Minjiang, Jialingjiang, Wujiang, Hanjiang, and Ganjiang, respectively.

Sampling was carried out in April, July, October and December 2013, corresponding to the spring, summer, autumn and winter seasons, respectively. The surface water samples were collected at depths of 0–50 cm. The CA activity, HCO_3^- concentration, temperature, pH and dissolved oxygen (DO) in the water samples were analyzed in the field.

The CA activity was determined from the rate of CO_2 hydration by following the change of pH traced on a chart recorder, as described earlier (Li et al., 2005b). The activity of CA in water samples was expressed as U/mL. Temperature, pH and DO were measured using the appropriate probes of a