Full Length Research Paper

The changing process of Carbon Dioxide under the conditions of different lithologies in Chaotian river basin

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According to the theory of global carbon balance, there are still missing carbon sinks. In order to find the missing carbon sinks, Scholars, through indoor and outdoor research, found that temperature, rainfall, CO_2 , partial pressure, lithology, and the ions in the water, and many other factors affect the geological carbon sink. Until now, few scholars have carried out research in the Chaotian river basin on the sources and changing process of CO_2 in the water in the process of geological carbon sinks. This text is based on Chaotian river as the research object, by selecting three sections, it was found that:1. The HCO_3^- of the river water mainly comes from the atmosphere in the non-Karst area, and almost half is from the atmosphere in the Karst area, but the atmospheric sources are slightly smaller than rock sources; 2. In the process of surface water in the non-Karst area flowing to the Karst area, the proportion of CO_2 gets smaller, with a corresponding increase in carbon sinks; 3. Dissolution rate of carbonates is faster than clastic, so it's faster to absorb CO_2 from the atmosphere. In the second cross-section, when the non-karst water flows into the carbonate rock area, the HCO_3^- concentration in the water increases immediately. At this time there is 60% HCO_3^-, which comes from the CO_2 in the atmosphere.

Keywords: Chaotian River basin, Different Lithology, CO_2, The process of changing

Introduction

According to the global carbon balance principle, there exist missing carbon (Yuan, 2001; Mackenzie and Mackenzie, 1995; Nikolai and Brian, 2006; Zaihua et al., 2010), and with economic development, the missing carbon has been constantly increasing from the 1980s, the average annual loss of due to carbon sinks is 1.0PgC /a (Siegenthaler and Sarmiento, 1993). In order to find the missing carbon, scholars explore a variety of ways, and most of the scholars think that geological carbon sinks play a decisive role, and argue that the geological process of weathering of rocks absorbs a large amount of CO_2 in the air. We found from the course geological study that: On the long term scale, carbonate and non-carbonate rocks for time scales are linked to atmospheric CO_2 sinks taking almost 50% (Qiu et al., 2004; Velbel, 1993), and short term scales are mainly carbonate weathering (Liu, 2012); in the study of the mechanism, geological chemistry(Meybeek , 1987), terrain(Raymo and Ruddimoll, 1992), temperature and rainfall (White and Slum, 1995), vegetation and so on can all affect the level carbon in the geologic process. Under indoor conditions of, the DIC (mainly HCO_3^-) of $CaCO_3$-CO_2-H_2O system is 13.6 times of CO_2-H_2O system

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(Dreybrodt , 1988), at a temperature of 15 ℃, and CO_2 partial pressure of water at 5000ppm. Pulina (1974) found the relationship between karst salt erosion volume and temperature and precipitation: The change of precipitation will have little impact on the dissolution rate in -5 ~ 5 ℃ temperature; the dissolution quantities will increase with the increase of precipitation in 16~20℃ temperature; in other words, when the flow is steady, the dissolution of the temperature range reaches the highest. Jianhua Cao, etc summarized the karst geological carbon's sequestration factors as temperature and rainfall, water power and water chemistry conditions and biological factors (Cao et al., 2011).

The ultimate goal of finding the factors that affect carbon sinks is to find the missing carbon, that is to say, the reason for the imbalance of CO_2 released to the atmosphere. On the global scope, we can adopt the method of (Nikolai et al., 2006); but in some basins, it's better to use more water chemical methods (Shengyou and Zhongcheng, 1997). These methods for studying some export of the basin can better estimate the annual geological carbon. By water chemistry method, it is generally believed that half of the Karst region's CO_2 is from the atmosphere, however, all the CO_2 in the Karst area is from the atmosphere, with the actual water chemistry containing NO_3^- (Perrin et al., 2008), SO_4^{2-} (Meyer et al., 2008; Xu and Liu, 2010) and other ions leading to the increase of the HCO_3^- content in the water. Part of this increase does not absorb CO_2 from the atmosphere and just change the carbon cycle in Karst areas, causing the excessive calculation of geological carbon .Therefore, how much CO_2 in the atmosphere is absorbed into the water on earth and the change of water flow in the process of research for the study of geological carbon sinks have a vital role.

Study area

Chaotian river located in Ling Chuan county in Guangxi Zhuang autonomous region, and its basin area is 476.34 Km^2. The Karst area covers an area of 162.81 Km^2, but non-Karst area with 303.43 Km^2. Chaotian river basin including the parts of Dayu town, Chaotian ,Ocean and Dajing Yao village. The area belongs to the subtropical Monsoon climate with mild climate and abundant precipitation, besides the annual rainfall is mainly concentrated from March to August. Its average annual rainfall is 1712.2mm, and runoff depth is 1126.6 mm and temperature is 19.6 ℃. It mainly contains the Quaternary Overburden Clay (Qh); the Carboniferous Yan Guan group (C_1y) limestone; Lower Devonian system (D3) limestone; Middle East Ridge group (D_2d) limestone, dolomite; Middle YuJiang group (D_2y) sandstone, shale; the Kaolin group (D_1n) system on sandstone; commission on the Lotus Hill group (D_1l) and purple rock (Figure 1). Vegetation in the study area is widely distributed, showing

that the non-Karst zone gives priority to trees, and the Karst area covered in shrubs. Its soil layer thickness is varied: The non-Karst area, due to being in the coastal hills, the soil thickness is smaller on the hillside, and generally is less than 0.50m, yet the valley soil thickness generally is within 1.50m; Changes in karst area is larger, what's more, rare Solum can be seen on the hillside, but the soil layer thickness is up to 10.00m in the peak-cluster depression .

Research Methods

This text is based on Chaotian River as the research object to select three monitoring sections: Shuang river section, Ganzhuang section and the outfall of Chaotian river. Every monitoring point is used for continuous monitoring approach, sampled once per month. Water samples for field monitoring have conductivity, temperature, pH, HCO_3^- and Ca^{2+} and other water quality parameters, HCO_3^- and Ca^{2+}, etc. which is measured by the German company Merck total alkalinity and hardness tester. And the measurement accuracies are 0.1mmol/L and 0.1mg/L. Mg^{2+} in water samples as accomplished by the Chinese academy of geological sciences institute of Karst geology.

In the calculation, for the non-Karst area, assuming that Cl^- of the river only comes from halite dissolution, and Na^+ mainly comes from the silicate rock weathering and the rock salt dissolution, and Ca^{2+}, Mg^{2+} are mainly from carbonate, silicate rock and evaporite, and SO_4^{2-} is from the evaporite, so there will exist: Na silicate rock = [Na river] - [Cl river], K = silicate rock river [K]; Ca silicate rock = Na silicate rock X (Ca/Na) silicate; Mg silicate rock = Na silicate rock X (Mg/Na) silicate, So for carbonate:(Mg + Ca) = [Ca] + [Mg] - Ca silicate rock - Mg silicate rock - [SO_4^{2-}] (Wu et al., 2011). The carbon sources in Karst area can be divided into three styles: One for the rock itself; the second for the air's source; the third for the soil source. According to the principle of balance, the equation can be expressed as:

$$HCO_{3\,CO_2}^- = HCO_{3\,total}^- - HCO_{3\,CaCO_3}^- \tag{1}$$

Where: ($HCO_{3\,CO2}^-$) is the atmospheric carbon source. The source is the sum of [Ca^{2+}+Mg^{2+}] molar mass minus the rock dissolved carbon source ($HCO_{3\,CaCO3}^-$). In general, the calculation formula is derived from the following equation:

$$Ca_{(1-X)}Mg_XCO_3 + CO_2 + H_2O \rightarrow 2HCO_3^- + (1-X)Ca^{2+} + xMg^{2+} \tag{2}$$

Now we think the pH of water can be used to determine the water in which exists carbon. It is generally believed that when the pH is in 7 ~ 9, the water contains mainly HCO_3^-, and CO_3^{2-} will be neglected (Liu et al., 2010).
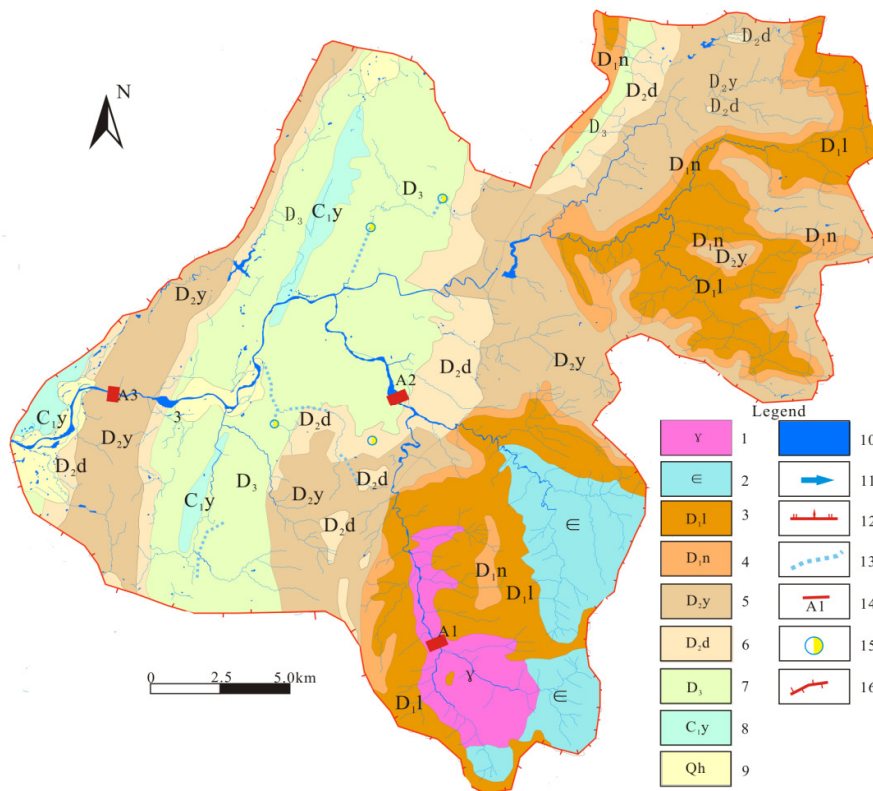
Figure 1. Geological sketch and Sampling points in Chaotian watershed (1, granite; 2, Cambrian sandstone; 3, Devonian sandstone under the EC Lotus Hill; 4, Devonian sandstone under the EC that kaolinite; 5, Devonian sandstone Yu River system; 6, mud Devonian limestone in the system Donggangling and dolomite; 7, Devonian limestone on the system; 8, under the EC Carboniferous limestone; 9 Quaternary clay and gravel cover layer; 10, surface waters; 11, surface water flows; 12, fault; 13, underground river; 13 ,sampling points; 15, skylights; 16, watershed; 17, across sections).

Table 1 The source of carbonate and silicate in Shuanghe watershed

Ca silicate	Mg silicate	Silicate source	Silicate source	The proportion of silicate weathering	The proportion of silicate weathering
0.085 mg/L	0.048 mg/L	0.132 mg/L	0.026 mg/L	83.5%	16.5%

Results and Discussion

In the case of Shuang river, to eliminate the error caused by multi-monitor, table 1 shows the monthly mean for the above formula. Similarly, more of the formulas will be used to calculate the source, comparing sections A1 and A2.

For A1 section: Each ion in average respectively: K^+: 0.667mg/L, Na^+: 1.877mg/L, Ca^{2+}: 6.842mg/L, Mg^{2+}: 2.614mg/L, SO_4^{2-}: 3.92mg/L; Then you can calculate the silicate rock weathering, Ca^{2+}: 0.119mol/L, $Mg2+$: 0.076mol/L, but these carbonate rock and weathering ions occupy calcium and magnesium ion concentration 0.044mol/L.Thus you can calculate for section A1 from the weathering silicate rocks accounting for 81.8%, and the carbonate rock weathering accounting for 18.2%, If all of the silicate weathering is from atmospheric CO_2, then the rest come from the weathering carbonate rocks. According to the method of formula (1 ~ 2) calculation, it can be calculated by the principle of balance: 60% of carbon is from the atmosphere, and 40% is from the weathering rock.

For A2 section: Each ion in average respectively: K^+: 0.59mg/L, Na^+: 1.05mg/L, Ca^{2+}: 43.74mg/L, Mg^{2+}: 4.21mg/L, SO_4^{2-}: 10.24mg/L, then you can calculate the silicate rock weathering, Ca^{2+}: 0.385mol/L, Mg^{2+}: 0.062mol/L. But this concentration is 0.715mol/L, so you can calculate out section A2 from the weathering silicate rocks accounting for 56.4%, and 44.6% of the carbonate rock weathering. If all of the silicate weathering is from atmospheric CO_2, then the rest come from the weathering carbonate rocks. According to the method of formula (1 ~ 2), it can be calculated by the principle of balance: 44.4% of carbon is from the atmosphere, and 55.6% is from the weathering rock.

It can be seen clearly that by the change of the three sections allogenic water, the smaller the Proportion of silicate rock weathering, the bigger the Proportion of carbonate rock weathering in the process of marching movement, at the same time, for air source the carbon source proportion gradually is reduced from top to bottom. Because carbonate rocks belong to the lava, the quantity of carbon sinks has multiplied on the whole.

Conclusion

Through the hydrochemical comparison of three sections, we can find that:1.the HCO_3^- of the river water mainly comes from the atmosphere in the non-karst area, and almost half is from the atmosphere in the karst area, but the atmospheric sources are slightly smaller than rock sources; 2. in the process of surface water in the non-karst area flowing to the karst area, the proportion of CO_2 gets smaller from the atmosphere, but a larger increase in carbon sinks; 3. disolution rate of the carbonate is faster, so it's faster to absorb CO_2 from the atmosphere. By the second section, when the non-karst water flows to the carbonate rock area, the HCO_3^- concentration in the water increases immediately. At this time there is 60% HCO_3^-, which comes from the CO_2 in the atmosphere.

Acknowledgement

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