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CO₂ source-sink in karst processes in karst areas of China

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The CO₂ source-sink of atmospheric greenhouse has a close relationship with karst processes. The corrosion of carbonate rocks leads to the sink of atmospheric CO₂, whereas the deposition of carbonate rocks gives off CO₂ into atmosphere, which is one of the sources of atmospheric CO₂. According to the exposed areas of carbonate rocks in China, the flux of atmospheric CO₂ consumed in karst processes is estimated at about $1.77 \times 10^{13} \text{ g CO}_2/\text{a}$. Considering the global karst area, the flux of atmospheric CO₂ consumed in corrosion may be an important part of the missing sink. And the sink has a tendency of continuous increase. The release of CO₂ from karst water is usually less than the sink of atmospheric CO₂ consumed in karst processes. But in active tectonic zone the release of high CO₂ concentration of mantle source in the geothermal karst water should not be neglected.

Figure 2 Distribution of exposed karst areas and monitoring stations of karst system in China. 1. exposed carbonate rocks; 2. reef; 3. monitoring station of karst system.

Introduction

Based on the estimates of CO₂ source-sink of atmosphere, IPCC (Houghton et al., 1990, 1992) and Tans et al. (1990) think that there is a missing sink of about 10–20% (Yang, 1996). In recent years many scientists tried to reveal the secret of the missing sink on the basis of their research (Xu, 1995), but so far there have been no reasonable results.

The conceptual model of a karst dynamic system on carbonate rock-water-CO₂ (gas) three-phase system (Yuan, 1993) clearly shows a close relationship between karst processes and atmospheric CO₂ (Figure 1), which provides a new way for further research of the

Figure 1 Conceptual model of karst dynamic system.

CO₂ source-sink and makes it possible to do a quantitative analysis on the relationship between karst processes and CO₂ source-sink of atmosphere based on the monitoring data of typical karst areas.

Exposed karst areas in China comprise about 900,000 km², distributed in different environments. To study and compare operating mechanism of the karst dynamic system under different environmental conditions, seven monitoring stations of karst dynamic system representing typical karst features in China were built in 1993 (Figure 2), where rainfall, air temperature, soil air CO₂ content and karst hydrochemical indices (water temperature, pH value, hardness, HCO₃⁻ and electric conductivity) have been monitored since 1993.

Simplification of model and estimation methods of relationships between karst processes and CO₂ source-sink of atmosphere

The conceptual model of a karst dynamic system can be simplified by the following equation:

where MeCO₃ represents CaCO₃, MgCa(CO₃)₂ and other carbonate compositions in actual karst dynamic system.

The chemical model shows a quantity relationship between CO₂ (carbon reservoir in atmosphere) and MeCO₃ (carbon reservoir in carbonate rocks), HCO₃⁻ (carbon reservoir in hydrosphere) in

Table 1 Corrosion loss of the standard limestone tablets in some monitoring stations in 1994 (unit: g)

Location	Huanglong	Maolan	Guilin	Zhenan	Beijing	Taizihe
Air above the ground	0.0151	0.0290	—	0.0068	—	0.0136
Surface of the earth	0.0170	0.0380	0.1456	0.0013	0.0336	0.0048
20 cm below soil surface	0.1690	0.1670	0.2222	—	0.0021	0.0014
50 cm below soil surface	0.1920	0.0520	0.2657	—	0.0018	0.0014
Mean value	0.0980	0.0710	0.2112	0.0041	0.0125	0.0053
Corrosion rate of unit area (g/cm ² ·a)	3.390×10 ⁻³	2.456×10 ⁻³	7.310×10 ⁻³	2.352×10 ⁻⁴	4.323×10 ⁻⁴	1.833×10 ⁻⁴

karst processes and carbon cycle. That is, corrosion of 1 mole MeCO₃ or production of 2 mole HCO₃⁻ needs to consume 1 mole CO₂ from atmosphere; conversely, deposition of 1 mole MeCO₃ can release 1 mole CO₂ into atmosphere. Therefore, besides direct measurement of CO₂, it is also possible to calculate flux of atmospheric CO₂ source or sink in karst processes depending on the model. The calculation for the atmospheric CO₂ sink needs detailed hydrochemical data or good corrosion test, and the deposition rate data are indispensable for calculating the atmospheric CO₂ source. All these data can be obtained from the seven monitoring stations of karst systems in China.

Estimation of atmospheric CO₂ sink in karst processes in China

In the seven monitoring stations of karst systems in China, field corrosion test of many standard limestone tablets (with surface area of 28.91 cm² and insoluble matter content of 0.97%) in different positions was carried out for one year. The mean value of rock tablet loss in one station represents the corrosion rate. Therefore, the corrosion rate of the seven monitoring stations can be obtained from the corrosion test results (Table 1). Combined with statistics of carbonate rock areas (after Li Datong, 1983), the flux of atmospheric CO₂ consumed in karst processes can be calculated by using the formula:

F = E × S × R × M_{CO2}/M_{CaCO3} (2)

where *F* is flux of CO₂ consumed in karst processes (g/a), *E* is corrosion rate of limestone tablet (g/cm²·a), *S* is the karst area (cm²); *R* is CaCO₃ content of the limestone tablet; *M*_{CO₂} and *M*_{CaCO₃} are the molar weights of CO₂ and CaCO₃ respectively.

The calculated results of the flux of atmospheric CO₂ consumed in karst processes in various karst types in China are shown in Table 2. The total flux of atmospheric CO₂ consumed is about 1.176 × 10¹³ g/a.

Using hydrochemical methods, the flux of atmospheric CO₂ consumed in karst processes in China can also be calculated by the formula:

F = 1/2 × [HCO₃⁻] × Q × M_{CO2}/M_{CaCO3} (3)

where [HCO₃⁻] is HCO₃⁻ concentration in karst water (g/l); *Q* is discharge of karst water (l/s), equal to product of karst area and the runoff module; *M*_{CO₂} and *M*_{HCO₃⁻} are molar weights of CO₂ and HCO₃⁻ respectively.

Table 3 gives the exposed areas of carbonate rocks, HCO₃⁻ concentration in karst water, runoff module of karst water (after 1:4,000,000 karst hydrogeological map of China by Li Guofen, 1992) in south and north China, and the flux of atmospheric CO₂ consumed in karst processes. Results of the hydrochemical method

Table 2 Distribution and CO₂ consumption of the main karst types in China

Karst type	Distribution	Exposed area (×10 ⁴ km ²)	Mean annual rainfall (mm)	Representative station	CO ₂ consumption (g/a)
Tropical and subtropical karst	Guangdong, Guangxi, Taiwan, Zhejiang, Yunnan, Guizhou, Hunan, Jiangxi, East Sichuan, West Hubei, etc.	44.6	1000–1850	Guilin	9.489×10 ¹³
High mountain and plateau karst	West Sichuan, Tibet, Kunlun Mountains	13.6	300–800	Huanglong	2.008×10 ¹²
Semiarid karst	Shanxi, Hebei, Henan, North Shaanxi, Shandong, etc.	13.2	400–600	Beijing	2.486×10 ¹¹
Temperate humid karst	Taizihe River basin, Huaihe River basin	1.6	800–1000	Taizihe	1.278×10 ¹⁰

Table 3 Parameters and calculation results of CO₂ consumption of carbonate rocks in south and north China

Distribution of carbonate rocks	Exposed area (×10 ⁴ km ²)	HCO ₃ ⁻ content in karst water (g/l)	Runoff module of karst water (l/s.km ²)	Atmospheric CO ₂ consumption (g/a)
North China	44.6	0.237	11.67	1.40×10 ¹³
South China	46.1	0.272	2.62	3.74×10 ¹²

show that the flux of atmospheric CO₂ consumed in karst processes in China is 1.774×10^{13} g/a. It is of a similar magnitude with that by the corrosion test method, so the estimates are valuable. Considering the global carbonate rocks of 22,000,000 km², one can gain a much more flux of atmospheric CO₂ consumption. Therefore, as a sink of atmospheric CO₂, the flux of atmospheric CO₂ consumed in karst processes should be taken into account for the global atmospheric CO₂ budget.

According to the data of corrosion rate in the Guilin monitoring station from 1993–1995, the flux of atmospheric CO₂ consumed in karst processes can be obtained by using equation (2), namely 6.129×10^9 g c/a, 10.744×10^9 g c/a, 11.582×10^9 g c/a. The sink figures show a tendency of continuous increase.

Estimation of atmospheric CO₂ source in karst processes in China

In China, tufa usually is deposited around karst springs and waterfalls, with the release of CO₂ into atmosphere. Because the chemical deposits of calcareous compositions are distributed in many small karst points, it is difficult to determine the deposit mass and estimate the release of CO₂ in any large karst area. A special case is provided to show the estimation method.

Huanglong tufa is used as an example to calculate the flux of CO₂ released from the karst waterfall by the deposit rate method. According to reports of Chen (1986) and Liu (1993), the mean deposit rate is 4 mm/a, and the tufa was deposited from 8,000 to 2,000 BP based on ¹⁴C dating. The tufa has a total thickness of 24 m in 6,000 years. It is about 3,500 m long and 300 m wide, mainly comprised of CaCO₃, with specific gravity of 2. The flux of CO₂ release is:

$$F = V/T \times \rho \times M_{\text{CO}_2}/M_{\text{CaCO}_3} \quad (4)$$

where V is the volume of the tufa (m³); T is the age of the tufa (a); ρ is the specific gravity of the tufa (t/m³); M_{CO_2} and M_{CaCO_3} are the molar weights of CO₂ and CaCO₃ respectively.

The calculation of flux of CO₂ release in Huanglong is 3,696 t/a. If extended to all karst areas in China or to a global scale, the calcareous deposits can produce a considerable flux of CO₂ release.

The distribution of calcareous deposits in various karst areas of the world indicate that most tufa deposits occur in the places on the boundary between liquid and gas. Examples are karst spring discharge points, waterfalls, dropwater points in caves and in karst areas near an active geothermal zone. The distribution area of deposits is much smaller than the corrosion area. Therefore, atmospheric CO₂ sink in karst corrosion processes can have a larger figure than the atmospheric CO₂ source from calcareous deposits. However, the strong release of high CO₂ concentration of mantle source in the geothermal karst areas should not be neglected.

Conclusions

1. CO₂ source-sink of atmospheric greenhouse has a close relationship with karst processes. When corrosion of carbonate rocks occurs, it results in the sink of atmospheric CO₂. When deposition of carbonate compositions happens, it will be a source of atmospheric CO₂.

2. Depending on the exposed areas of carbonate rocks in China, the estimate of flux of atmospheric CO₂ consumed in karst processes is about 1.77×10^{13} g CO₂/a. Considering the global karst area, the flux of atmospheric CO₂ consumed in corrosion may be an important part of missing sink. Besides, the sink has a tendency of continuous increase.

3. According to the preliminary research result, karst processes in epikarst zone can produce a bigger flux of atmospheric CO₂ in sink than in source.

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