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ORIGINAL ARTICLE

Role of hydro-geochemical functions on karst critical zone hydrology for sustainability of water resources and ecology in Southwest China

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Abstract Focusing on sustainability of water resources and ecology in the complex karst critical zone, we illustrated functions of the hydro-geochemical analysis on hydrology from the aspects of connection and interaction among hydrology–vegetation–soils/rock fractures along the karst subsurface profile. We reviewed isotopic and geochemical interpretations on tracing water sources for plant uptake, quantifying watershed outlet flow composition and residence times, and evaluating long-term evolution among climate–landscape–hydrology in the karst critical zone. In this paper, the application of the hydro-geochemical analysis on the above aspects in the karst areas of southwest China was summarized.

Keywords Hydro-geochemical analysis · Karst critical zone · Water resources · Vegetation Southwest China

1 Introduction

Karst landscapes, which form in settings with highly soluble lithologies, occupy roughly 12% of Earth's surface (Ford and Williams 2007). The karst region in Southwest China is one of the largest continuous karst areas in the world. It covers approximately 540×10^3 km^2 over eight provinces. The critical zone (CZ) extends from vegetation to the lower limit of groundwater and provides water and nutrients for food production and ecosystem services. Since karst systems allow extremely rapid infiltration of water and the solutes and particles transported by water, only limited amounts of water and nutrients remains in the upper thin soils and underlain epikarst zone for forest consumption in mountainous hillslopes and agriculture utilization in depression areas.

Karst CZ hydrological characteristics in the mountainous areas of southwest China are controlled by landscape and dissolved carbonate rock fractures. From the aspect of karst landform structure, surface and subsurface water flows from the high hillslopes into the low terrace and depression areas. Therefore, the high hillslopes with well-grown forest contribute a large proportion of water and nutrient resources needed for the maintenance of crops in the terrace and depression areas. Since the karst subsurface hydrological profile consists of a soil layer, epikarst zone, infiltration zone, and deep conduit flow zone (Perrin et al. 2003), the various flows with the profile present markedly different variations in time and interactions in space, which control the water fluxes and storages that constitute the basin-scale water balance. Understating variability of the multiple hydrological components and their interactions is critical for water resource utilization and allocation in the agro-forestry basin.

Deforestation for creating cultivation space from 1950 to 1980, and reforestation promoted by China government since the 1980s, changed karst CZ structure (e.g. soil erosion and vegetation alteration) and its service functions for water resources and the ecological system. Contemporaneously, temperature increased by 0.14 °C/decade, and hydrological extremes became more common, with increased droughts and heavy rainfall, both of which have impacted soil and water quality and the general quality of

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life. Climate change as well as de-/re-forestation would have strong impacts on future availability of karst water resources.

Isotopic and geochemical characteristics of water in various flows from karst KZ could be useful in assessing the vegetation-water–soil and/or rock interactions along the flow paths and in quantifying the residence and flux of water/solute. The chemical characteristics of subsurface water, the residence times, and the associated mixing processes allow the achievement of tracing water flow sources and understanding evolution of hydrological processes under climate and landscape changes.

In this context, we provide an overview about the role that hydro-geochemical functions play in revealing hydrological characteristics, such as plant consumption of water from soils/fractures, flow composition, and long-term evolution of climate-landscape-hydrology in the karst CZ. We briefly summarized the available research results in the karst areas of southwest China in terms of hydro-geochemical analyses.

2 Tracing water sources for plant uptake

Due to thin soils, plants in karst areas take water not only from the soils but also from shallow fractured rock zones (epikarst or subcutaneous zones). Strong heterogeneity of soils and rock fractures leads to irregular distribution of plant roots in the vertical profile. Therefore, the root distribution based method cannot be applied in tracing water sources for plant uptake. Since shallower soil water is generally more enriched in heavier isotopes due to evaporation, in comparison with the deeper soil and epikarst water, the hydrogen and oxygen stable isotope ratios of potential water sources for plant uptake are significantly different. Thus, stable isotope composition of water extracted by plant stems can be used to quantitatively determine the relative contributions of the different water sources.

As an example, proportions of the possible water sources contributed for the plant uptake of five typical species were analyzed at two sites in a karst plateau of Qingzhen, central Guizhou Province of China on the basis of δD and $\delta^{18}O$ values of plant stem water, soil water, and subcutaneous water (hillslope spring). Results show that most plants take water from the soil layers (less than 50 cm) and the subcutaneous zone, but proportions of these water contributions for plant uptake vary seasonally and depend on site-specific conditions and plant species. The average plant uptake of the subcutaneous water for all species is less than 30% of the total uptake amount in wet June and September, compared with more than 60% in dry December. Plants tend to take a larger proportion of water from the upper soil layer at the bush site than at the forest site in June and September (63% vs. 28% in July; 66% vs. 54% in September for all species in average). In December, however, 98% of water is taken from the subcutaneous zone at the bush site, which is much greater than 68% at the forest site. Compared to deciduous arbor, evergreen shrub takes a greater proportion of subcutaneous water in the December drought (Rong et al. 2011).

3 Quantifying watershed outlet flow composition and residence times

As precipitation recharges through the shallow epikarstic zone into deep karst aquifers, the flow movement is highly complex due to variable soil cover and heterogeneous karstification in the carbonate rock. The flow paths and residence time depends not only on basin surface features (topography and soils) but also fracture features (orientation, width and length, and connections). However, various water flows carry natural substances with different solutions of irons because of the chemical reactions that affect them within the system (dissolution, precipitation, mineralization…). Solutes of major ions or heavy isotopes of water Oxygen-18, deuterium, and tritium can be regarded as ideal natural tracers. They can be used to estimate the fractions and mixing of water from different sources, to assess the functioning of karst systems, and to determine origin and residence times of karst waters (Hartmann et al. 2014). TOC is commonly used for studying local pollutions and evaluating anthropogenic influences within karstic aquifers; it can be used as a relevant tool to characterize the behavior of the aquifer, to differentiate the water types which participate to the karstic flow (fast infiltration, unsaturated zone, saturated zone) and then, to evaluate their vulnerability (Batiot et al. 2003; Liu 2007, 2009).

As an example, stable isotopes (δD and $\delta^{18}O$) and hydro-chemical composition (sulfate ion) were analyzed for separating runoff components during rainy and dry periods based on the collected water samples of precipitation, overland flow, shallow epikarst flow (hillslope spring) and deep aquifer (depression sinkholes) in a small karstic basin of Chenqi in Guizhou Province, China. Results show that during the rainfall period, proportions of overland flow, epikarst flow, and deep aquifer flow from the basin outlet discharge were less than 10%, 28%–45% and 49%–62%, respectively. Meanwhile, as the epikarst flow contribution increased, the deep aquifer flow contribution decreased. After the rainfall ceased, the deep aquifer flow became a primary water resource, as its contribution to the basin total could increase to about 68%–88% (Chen et al. 2013).

4 Evaluating long-term evolution of climate-landscape-hydrology

Owing to the different solution kinetics of Mg and Ca minerals, the Mg/Ca ratio in karst water is often used to obtain information on residence times in karst systems advantageously combined with other time tracers, such as organic carbon (Batiot et al. 2003). The combining information can be used to reveal evolution among climate change, landscape, and hydrology (Liu 2007, 2009). In karst caves, drip water containing dissolved calcium and bicarbonate can precipitate calcium carbonate to form speleothems that contain paleoclimatic records (Lachniet 2009; McDermott 2004). The use of paleoclimatic records estimates possible future changes in water availability. Climate warming could lead to accelerated dissolution of carbonate rock and thus landscape changes. For example, temperature increase induced an increase of CO_2 production in soils, then an increase of the CO_2 concentration in the vadose zone of the system (cave), leading to a higher pCO_2 at the top of the phreatic zone, which in turn generated higher hardness values (Jeannin and Hessenauer 2013). Spatial variability in δ^{13}C-DIC is likely due to local differences in the relative proportions of young and old waters, mixing with brines containing CH_4, and variable sources of acidity that drive carbonate dissolution (Hutchins et al. 2013). High CO_2 concentrations due to high biodegradation activity leads to observed increase in water hardness (Jeannin and Hessenauer 2013). Using the reactions of carbonate equilibrium, it is possible to utilize geochemical data to estimate the rate of inorganic carbon that is sequestered from the atmosphere and liberated from the carbonate bedrock. Combining these data with the areal exposure of carbonate rocks can provide one approximation of the rate of landscape evolution (Griebler 2013).

An absolute-dated oxygen isotope record from Sanbao cave, central China, completes a Chinese-cave-based record of the strength of the East Asian monsoon that covers the past 224 000 years (Wang et al. 2001). In the karst areas of southwest China, it was found that land desertification (high rock exposure due to strong soil erosion and deforestation) resulted in the reduced net radiation and evaporation in the degraded areas, which could weaken the East Asian summer monsoon (Gao et al. 2016). Meanwhile, plant species shift the adaptability of their environments toward lower soil water and organic content in the thin soil, and higher light during karst rocky desertification in terms of measuring δ^{13}C of plant leaves from various species. The high and low δ^{13}C values of plant leaves were proven to be efficient in quantifying water use efficiency of various plants in relation with environmental changes (Rong et al. 2008).

5 Summary

Strong heterogeneous karstification in the carbonate rock combined with climate change and human activities leads to very complex situation in hydrology and thus impedes sustainability for water resources and ecology. However, unlike non-karst areas, marked variability in various hydrological components and isotopic and geochemical characteristics from karst KZ offers useful information to assess the flow paths and quantify the residence and flux of water/solute. Meanwhile, isotopic and geochemical characteristics from various plants, the dissoluble carbonate rock, and the climate reveal evolution in the vegetation-hydrology–landscape. Available research results in the karst areas of southwest China indicate that vegetation heavily relies on water remaining in shallow soils and rock fractures (e.g. to be highest of 98% uptake from epikarst at the bush site in December). However, most rainfall quickly infiltrates into deep aquifer (e.g. 68%–88% in the Chenqi basin) and only limited water perched on the epikarst zone after rainfall stopped. As temperature increases and hydrological extremes became more common, the current promotion of reforestation and sustainable water resources will face challenges.

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