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## Abstract

High-resolution measurements of rainfall, water level, pH, conductivity, temperature and carbonate chemistry parameters of groundwater at two adjacent locations within the peak cluster karst of the Guilin Karst Experimental Site in Guangxi Province, China, were made with different types of multiparameter sonde. The data were stored using data loggers recording with 2 min or 15 min resolution. Waters from a large, perennial spring represent the exit for the aquifer's conduit flow, and a nearby well measures water in the conduit-adjacent, fractured media. During flood pulses, the pH of the conduit flow water rises as the conductivity falls. In contrast, and at the same time, the pH of groundwater in the fractures drops, as conductivity rises. As  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  were the dominant (>90%) ions, we developed linear relationships (both  $r^2 > 0.91$ ) between conductivity and those ions, respectively, and in turn calculated variations in the calcite saturation index (SIC) and  $\text{CO}_2$  partial pressure (Pmath image) of water during flood pulses. Results indicate that the Pmath image of fracture water during flood periods is higher than that at lower flows, and its SIC is lower. Simultaneously, Pmath image of conduit water during the flood period is lower than that at lower flows, and its SIC also is lower. From these results we conclude that at least two key processes are controlling hydrochemical variations during flood periods: (i) dilution by precipitation and (ii) water-rock-gas interactions. To explain hydrochemical variations in the fracture water, the water-rock-gas interactions may be more important. For example, during flood periods, soil gas with high  $\text{CO}_2$  concentrations dissolves in water and enters the fracture system, the water, which in turn has become more highly undersaturated, dissolves more limestone, and the conductivity increases. Dilution of rainfall is more important in controlling hydrochemical variations of conduit water, because rainfall with higher pH (in this area apparently owing to interaction with limestone dust in the lower atmosphere) and low conductivity travels through the conduit system rapidly. These results illustrate that to understand the hydrochemical variations in karst systems, considering only water-rock interactions is not sufficient, and the variable effects of  $\text{CO}_2$  on the system should be evaluated. Consideration of water-rock-gas interactions is thus a must in understanding variations in karst hydrochemistry.