Isotopic Evolution and Epikarst Mixing in a Telogenetic Karst System: Implications for Contaminant Transport and Groundwater Movement

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There exists a limited understanding of hydrogeologic flow and contaminant transport within karst aquifers, particularly in the epikarst zone, which is highly susceptible to natural and anthropogenic contamination, such as agricultural runoff, due to the interconnected nature of the surface and subsurface. Understanding the storage, flow, and transport dynamics through the epikarst is fundamental to protecting and managing the water quality and quantity of karst aquifers. The epikarst is often where contaminants are located and also where mixing can occur between meteoric and groundwater sources.

Approximately 25% of the world's population relies on karst aquifers for potable water. Currently, federal and state water quality regulations do not recognize karst aquifers as unique entities with enhanced vulnerability to contamination. The National Pollutant Discharge Elimination System (NPDES) allows the US Environmental Protection Agency (USEPA) to regulate point source discharge (factory, house, etc.); however, non-point discharge (e.g. agriculture, forestry, mining, construction, etc.) is more difficult to monitor and regulate. Karst aquifers, especially in south-central Kentucky underlie vast agricultural areas and as such are subject to a broad spectrum of natural and anthropogenic contaminants. These aquifers feed local surface water bodies (rivers and lakes) that are relied upon for recreation, food, water supply, and income. Many surface water bodies in south-central Kentucky are under water quality study for harmful algal blooms, *Escherichia coli* (*E. coli*) loadings, and excessive nutrients (nitrogen, phosphorus). Proper understanding of how these contaminants are introduced to the karst aquifer and the subsequent transport is critical to reducing contamination and improving future water quality.

Crumps Cave in Warren County, south -central Kentucky, is a shallow epikarst cave underlying a large agricultural region near the town of Smiths Grove. The Crumps Cave Preserve, owned and managed by Western Kentucky University, encompasses an approximately 200 meter diameter sinkhole and the entrance to Crumps Cave. Crumps Cave consists of approximately 2050 meters of surveyed passage and averages a depth of approximately 15-20 meters below the surface. This epikarst cave offers a "snapshot" into the evolution and mixing of waters between the surface and the deep regional aquifer more than 45 meters below the surface.

While few tools exist to study the "black box" nature of epikarst dynamics, stable isotope hydrology offers an effective alternative to traditional karst investigative techniques, such as dye tracing, to evaluate flow dynamics and water-soil-rock interactions across a range of spatial and temporal resolutions, particularly with respect to recharge over long periods. Using stable isotopes of water ($^{18}O/^{16}O$ and $^{2}H/^{1}H$), recharge can be traced from meteoric sources through the epikarst, providing insight to the pathways of recharge, flow, mixing, and transport dynamics across multiple spatial and temporal scales in telogenetic karst systems. A secondary method performing base flow separation of multiple discrete storms was used to quantify epikarst storage by comparing recharge volumes with in-cave waterfall discharges.

During 2011-2013, weekly isotope samples were collected from rainfall and an epikarstic in-cave waterfall in Crumps Cave. All samples were collected in 10 mL screw cap vials with no head space and stored at 4°C. Analysis of all samples was conducted at the University of Kentucky's Earth and Environmental Science (UK EES) Stable Isotope Lab. Using the isotope data, along with 10-min in-cave waterfall discharge, precipitation, and geochemical data, the storm, seasonal, and annual transport dynamics of water through the epikarst were evaluated. Campbell Scientific CR10x dataloggers with pH, conductivity, temperature and pressure transducer sensors recorded 10-minute water geochemistry data and discharge of the in-cave waterfall. In a field adjacent to the cave entrance, an Onset HOBO U30 weather station recorded 10-minute meteorological conditions and precipitation.

While seasonal and storm pulses showed significant variation associated with changing atmospheric sources, the epikarst waterfall isotope signal remained constant across the dataset. This homogenizing effect implies mixing occurs in the shallow epikarst zone across both short and long time intervals. Previous estimates of baseflow separation of the waterfall indicated that the epikarst storage is potentially two to three orders of magnitude higher than at regional springs, revealing that storage in the epikarst can play a significant role in recharge and as a mixing zone for contaminant transport.

The results found in this study imply contaminants introduced to the epikarst during different seasons could mix at a rate that influences the contaminant signal throughout the year, particularly at baseflow. Contaminants introduced to the system may remain in the epikarst for longer time periods, possibly multiple seasons, and not flush through the epikarst into the groundwater in shorter time spans. This has significant implications for the assessment and execution of water quality monitoring and regulation.