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Abstract
The karst landscape at Mammoth Cave National Park, Kentucky, was formed by water through the dissolution of soluble rocks forming sinkholes, disappearing streams, emerging springs, closed depressions, and a combination of wet and dry caves. The Park's cave streams and pools provide a home to unique organisms. Surface waters in the Park tend to rapidly drain into subsurface geologic features and caves. This rapid infiltration makes the subsurface vulnerable to contamination. The objective of this investigation was to characterize chemical transport from the surface into the cave. The preliminary results were achieved by tracer studies and monitoring water chemistry along known flowpaths. The results presented in this paper are the outcome of several studies occurring between 2009-2012 in a partnership between Mammoth Cave National Park, Tennessee State University, Mammoth Cave International Center for Science and Learning, and U.S. Geological Survey. Processes that influenced chemical transport included storm intensity, time between storms, epikarst saturation, dispersion, dilution, and complex flow paths in the geology.

Introduction
The ecosystem within Mammoth Cave is dependant on adequate clean water for survival. To protect the waters, the Park has addressed the intense vehicle traffic in the parking areas with storm runoff filters. However, they are still concerned about surface chemicals entering the cave ecosystem. Currently, the National Park Service, in agreement with US Fish and Wildlife and Kentucky environmental regulators, has approved the limited application of road deicers on primary roads through the Park during snow or ice storms. However, the NPS lacks some essential quantitative information with regards to salt transport from land surface into the cave ecosystem. The chemical transport mechanisms including timing, contaminant load and concentration, and hydrologic response are not fully understood. The transport of contaminants into surface water and into the cave ecosystem could adversely impact the aquatic habitat of the rare and endangered species. The objective of this project was to identify and quantify processes important to chemical transport at Mammoth Cave National Park. The approach included monitoring water quality and quantity at points along selected flow routes into the cave.

Materials and Methodology
Three sites were selected for surface and subsurface monitoring stations (Figure 1). Site 1, Silent Grove sinking creek, is

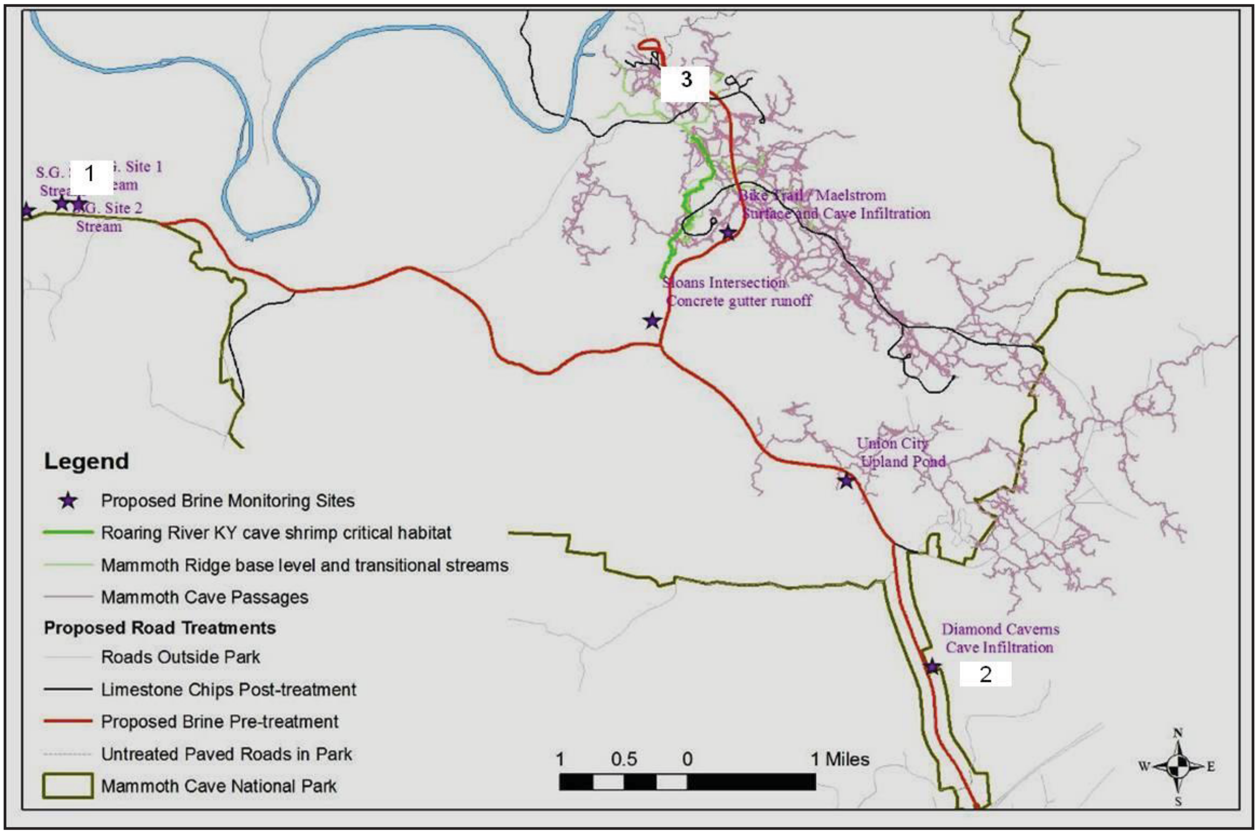

Figure 1: Three monitoring sites selected for monitoring in response to potential road brine application. 1. Silent Grove sinking stream, 2. Diamond Caverns, 3. Post Office-RV dump station. Roads and critical cave habitat are indicated on the map.

near the west edge of the Park. This site is adjacent to an off-park road that receives salt treatment during inclement weather. Site 2 was located near the south entrance to the Park coming from Interstate 65, at the private cave called Diamond Caverns. This site was selected because Diamond Cavern staff have observed rapid flow response during storms, and, the road is expected to be salted during snow events. Site 3, starts at the Post Office parking lot, which has been affiliated with quaternary ammonia compounds (Diehl, et al., 2012), and flows into the historic section of the cave.

Monitoring

YSI datasondes equipped with temperature, specific conductance, pH, dissolved oxygen, turbidity, Rhodamine-WT, and/or water depth probes were deployed along the flow paths at the monitoring sites. The sondes were serviced (calibrated, data uploaded, batteries replaced) every 2-3 weeks. Water samples were collected and analyzed for quaternary ammonia compounds (Hach, 2005) and/or chloride (Hach, 2012).

Results and Discussion

The transport of chemicals, such as salts, from the surface to the caves was studied at Mammoth Cave National Park, KY. Results from three sites are presented here. Site 1, Silent Grove sinking stream, is a road adjacent to the Park and was treated with rock-salt in the winter of 2011 and 2012. Two monitoring stations in the stream, one within 50 feet of the road and another one ~500 feet downstream, were instrumented with datasondes to monitor salt concentration in the stream. Salt spread during a cold spell was washed into the creek during a subsequent rain event. The salt concentration was diluted and dispersed as the water flowed from the road to the sink 500 feet downstream. A calibrated regression curve comparing known concentrations of salt to conductivity measures allowed us to extrapolate the chloride concentration in the stream. The highest chloride concentration was observed at the upstream site (76 mg/L). The chloride concentration was well below the action level of 600 mg/L.

Data compiled from several sites and summer storm-events were used to run correlations between specific conductance values in the first runoff and time-intervals between the storm events. We observed a weak correlation between increasing time intervals and increasing specific conductance. Although correlation does not imply cause and effect; it is reasonable to assume longer intervals between rain events allows for greater build up of potential dissolved solids.

Monitoring stations were set up at the road drainage ditch entering Diamond Caverns parking lot and in a cave pool below the tour route. A winter storm in February 2011 produced runoff that entered the cave and generated a decrease in the specific conductance of the cave pool. There was a short time period (<30 minutes) between the start of the rain and water entering the ditch. The specific conductance in the cave pool, which is an indicator of dilution, responded almost 5 hours later. This time lag was partly due to the flow path length and the head pressure needed to push water to the pool. A second wave of precipitation eight hours later evoked a conductivity response in the pool within a 2-hour time period. A third wave of rain evoked a cave-pool response in one hour. These data suggest that the response time in the cave to storms is partially a function of regolith and epikarst saturation.

A tracer study was conducted at the outfall of the Post Office parking lot storm filter (Embry, et al, 2012). This parking lot was the source of quaternary ammonia compounds (QAC) during several storms (Diehl, et al, 2012). The 175 mL of Rhodamine-WT tracer was released by storm runoff. It took approximately 1 hour and 15 minutes to travel from the discharge of the parking lot filter into Annette's Dome off Gratz Avenue. A monitoring station in the Devil's Cooling Tub at the other end of Gratz Avenue detected a smaller quantity of Rhodamine approximately 1 month and 2 days after tracer release. The average velocity of the tracer transport was estimated by dividing the relative distance from injection point (meters) by the time (minutes). The tracer traveled at an estimated speed of 3.3 meters per minute to reach Annette's Dome and Shaler's Brook. In comparison, the dye traveled at an average velocity of 0.01 meters per minute to reach the Devil's Cooling Tub. Another interesting fact was that the dye had to travel across a surface basin divide (Styx spring and Echo spring) to reach the Devil's Cooling Tub. This illustrates how complicated karst hydrology can be.

Summary

This project evaluated the transport of chemicals during storms at three locations. Data from Silent Grove sinking stream show that significant dilution and dispersion can occur within a 500-ft reach of surface stream. These dilution and dispersion processes are important factors for attenuating salt in road runoff. Additional data is being collected at other sites to determine if this pattern is applicable to other areas in the Park. Monitoring activities at Diamond Cavern area found that the response time in the cave was partially a function of epikarst saturation; the more saturated the epikarst, the quicker the response. Studies characterizing the transport from the Post Office into the cave reveal that surface chemicals can arrive in the cave in minutes or weeks after being released. Also, the tracer study illustrates how complicated karst hydrology can be when the dye moved across a surface basin divide.

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