WATER QUALITY MONITORING IN THE PERRY COUNTY KARST, MISSOURI

Brad Pobst and Sarah LaVern Taylor
Missouri Department of Conservation
Southeast Fisheries Division
2302 County Park Drive
Cape Girardeau, Missouri 63701
Brad.Pobst@mdc.mo.gov
LaVern.Taylor@mdc.mo.gov
573-290-5858

Abstract

The Perry County Karst of eastern Missouri has more than 670 known caves, the most of any county in Missouri. The caves are large, complex, flood-prone systems, which make contamination of groundwater and possibly drinking water a growing problem in this area. The diverse aquatic cave fauna that includes a unique cave-dwelling fish called the grotto sculpin, *Cottus* sp. cf. *carolinae*, is susceptible to water contamination. This project focuses on water quality on the surface and in the caves, and identifying nonpoint sources of water contamination. Components of the project include: (1) continuous water-quality monitoring with moored water-quality multi-probe sondes, (2) monthly grab samples of water for chemical, nutrient, coliform, and sediment analysis, (3) rainwater-runoff sampling of sinkholes unmodified or modified with vertical drains for chemical, nutrient, and sediment analysis, (4) SPMD and POCIS sampling for analysis of chemicals that are below detectable limits of traditional analytical methods, and (5) dye tracing and recharge delineation of the major cave systems. The data collected will provide managers needed information to protect groundwater and the populations of the grotto sculpin.

Key words: water-quality monitoring, groundwater contaminants, Grotto sculpin, *Cottus* sp. cf. *carolinae*, Perry County, Missouri

Introduction

Missouri contains over 6,200 caves in several karst zoogeographic regions. These regions include the Springfield and Salem plateaus, the Boone, Hannibal, St. Louis, Jefferson-Ste. Genevieve, and Perryville karsts, and an isolated Caney Mountain area (Elliott 2007). The Perryville Karst encompasses most of the eastern portion of Perry County, Missouri. Perry County leads the state in the number of known caves at more than 670, and it also boasts some of the longest caves, e.g. Crevice Cave (45 km), Moore Cave System (29 km), Mystery Cave (25.5 km), and Rimstone River Cave (22.8 km). The study area for this project is located within the Perryville Karst about 120 km (75 mi.) south of St. Louis, Missouri. The study area will be referred to as the Perry County Karst and totals approximately 59,000 ha (46,000 ac.). This area contains thousands of sinkholes ranging from a few meters to several hundred meters in diameter and can be from one to 30 meters deep. These sinkhole plains filter surface-water runoff into the cave systems below.

In addition to several caves of considerable length, the Perry County caves have a fairly species rich cave fauna. The diversity of cave life in Missouri was ranked by the Missouri Department of Conservation using the Cave Biodiversity Ranking system (Elliott 2007). Several caves within

the Perry County karst are ranked in the top 50 for biodiversity, e.g. Mystery (#3), Berome Moore (#4), Tom Moore (#8), Running Bull (#36), and Crevice Cave (#48). Five major cave systems in Perry County contain an endemic cave-dwelling fish called the grotto sculpin, *Cottus* sp. cf. *carolinae*. The undescribed but distinct grotto sculpin (Burr et al. 2001) was listed as a federal candidate species in 2002 and assigned a priority number of 2, indicating an imminent threat to the existence of the species.

The cave fauna is potentially threated by human impact because cave systems are potentially affected by the influx of surface waters. Water from the surface enters the groundwater supply via caves and natural percolation through the ground. Changes in land use bring new and almost certainly more serious threats to groundwater quality, and possibly to water quality in aquifers that supply drinking water. Aquifers in karst terrains are exceptionally sensitive to pollution and have higher potential for contamination than nonkarst aquifers. Previous limited surveys of karst groundwater in the study area indicated that ammonia, nitrite, nitrate, chloride, and potassium were detected within caves at levels high enough to be detrimental to aquatic life (Taylor, Webb, and Panno 2000, Vandike 1985). These compounds result primarily from cultivation. These same surveys also revealed that fecal contamination at 27 springs and caves was a serious problem (Taylor, Webb, and Panno 2000). The increase in contaminants is associated with population increase in the region. The largest population center and the focus of business and industry in the area is the town of Perryville. The region traditionally and still is dominated by agriculture, but now urbanization in the form of subdivisions is spreading out around Perryville. Continued population expansion, both suburban and rural, increases the potential for contaminated groundwater sources, however, little research has been conducted to see what the impacts of sedimentation and agricultural chemicals have on the karst system.

Another concern in the study area is the use of vertical drains to control erosion in sinkholes. A vertical drain is defined as "a well, pipe, pit, or bore in porous, underground strata into which drainage water can be discharged" (Natural Resources Conservation Service 2006) (Figure 1). These vertical drains could allow contaminated water to directly enter caves and aquifers without the benefit of natural filtration via percolation through the ground. Although the impact of vertical drains on water quality is poorly known, the installation of vertical drains into sinkholes is promoted by state and federal cost share practices in Perry, Ste. Genevieve, and Cape Girardeau counties, through the County Soil and Water Conservation Districts and the Natural Resources Conservation Service. In these counties, landowners are eligible to receive up to seventy-five percent cost-share to install vertical drains to stop erosion.

Figure 1 *Vertical drains installed in two sinkholes in a crop field.*

Very little water quality data has been collected from the study area. This project will be the initial phase to gather the required data to make informed decisions on the recharge areas of the cave systems, to determine water quality issues, to develop appropriate techniques to manage sinkholes, to develop educational tools that will inform citizens of the unique features that they live on, to help prevent the streams and springs in the study area from being listed on the 303(d) list, and to help prevent the grotto sculpin from being elevated from a candidate species to an endangered species. The data generated from this project will also be used to develop a Perry County Karst Watershed Management Plan which can be used, we hope, to guide future water-quality initiatives.

Materials and Methods

This project is divided into five subprograms. Each subprogram is designed to contribute to the overall assessment of water quality in the Perry County Karst, and to support ongoing and future scientific research. Figure 2 illustrates the station locations of each subprogram within the study area.

Continuous Deployment of Water-Quality Probes (Sondes). The first subprogram will be the continuation of preliminary water-quality research started in January 2006. Hydrolab and YSI multi-probe sondes were permanently moored at six cave and/or resurgence locations (Figure 2) in January, 2006, and will continue through August, 2010. These sites will allow for the determination of sea-

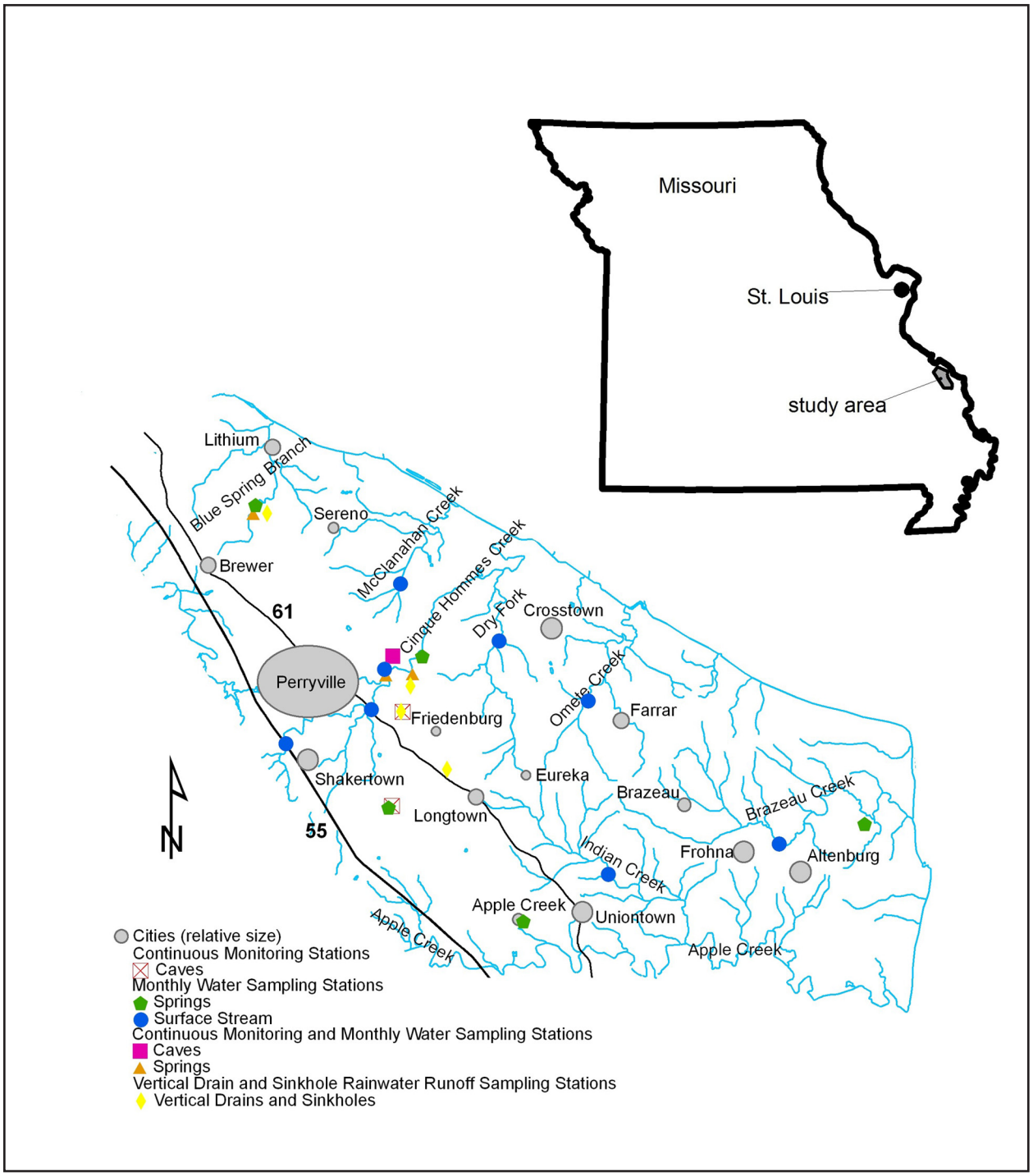

Figure 2. Study area showing continuous, monthly and vertical-drain, water-quality stations.

sonal fluctuations in urban and agricultural runoff, livestock waste, and septic runoff in the study area. Four of the six sites correspond with monthly water-grab-sample sites. Sonde data will be compared to data collected in the monthly water-grab-sampling subprogram.

Continuous deployment of water-quality probes will be placed in the same location of the thalweg of the resurgence and/or subsurface stream. Physical parameters are measured every 30 minutes and consist of: temperature, pH, specific conductivity, ammonium (NH_4^+-N), total ammonium nitrogen, turbidity and dissolved oxygen. Self-cleaning turbidity sensors are equipped with central wiper units to prevent fouling of other sensors with biological growth or debris. The sondes will be switched out monthly and the data will be downloaded and checked for accuracy. Sondes will then be post-calibrated, cleaned, internal batteries exchanged, and pre-calibrated for re-deployment the following month. *In-situ* field measurements of temperature, pH, specific conductivity, dissolved oxygen and turbidity will be recorded when the sondes are switched. Water velocity (m/sec) will be measured seasonally at each site in the thalweg of the resurgence and/or subsurface stream using a Marsh McBirney Model 201D Portable Water Current Meter with a 122-cm (4-ft.), top-setting wading rod.

Monthly Water Grab Samples. The second subprogram involves collecting water-grab samples from resurgences, springs, surface and/or subsurface streams at 17 sites (Figure 2) during each month from March 2007 to February 2009. The Cedar Spring site will be sampled seasonally (four grab samples per year) because of difficult access. Selection of sampling sites was based on past water-quality sampling data (Kraemer 2006 and MDC continuous monitoring). Sampling sites will allow for the determination of urban and agricultural runoff, septic runoff, and livestock waste in the study area. Water-grab samples will be collected according to U.S. EPA WAS Field Operations Manual (2004). Only flowing water will be sampled, thus, some sites will not be sampled during dry seasons of the year. Stagnant water will not be sampled to prevent biased water quality data that may be caused by evaporative concentration. Flow regime, e.g. runoff, base flow, or both, will be recorded. All samples will be analyzed for nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3), chloride (Cl^-), ortho-phosphate (PO_4^{3-}), total phosphorus (P_{total}), *Escherichia coli* (*E. coli*), total coliforms, total suspended solids, and the agri-chemicals in the atrazine family (only April through June). Selection of analytes was based on a review of the scientific literature dealing with karst water quality (Boyer and Alloush 2001, Graening and Brown 2000, Panno et al 2003, Taylor, Webb and Panno 2000). Atrazine will only be analyzed from April through June during the application period of the herbicide. A Hydrolab Quanta Water Quality Monitoring System will be used to measure temperature, pH, specific conductivity, turbidity and dissolved oxygen at each site. A ThermoOrion AQ4500 Turbidimeter will be used to measure turbidity at each site. Water velocity (m/sec) will be measured as noted above.

Sinkhole and Vertical-Drain, Rainwater-Runoff Sampling. The third subprogram involves sampling rainwater runoff at sinkholes and vertical drains at five to six sites for at least one rain event each month from March 2008 to July 2009. The sites have both unmodified and modified sinkholes with vertical drains (Figure 2). The sites will allow for the determination of seasonal fluctuations in agricultural runoff and sedimentation in the study area. Rainwater runoff samples will be collected using ISCO portable water samplers according to U.S. EPA NPDES Storm Water Sampling Guidance Document (1992). These samplers will be programmed to collect water during the first thirty minutes of a runoff event. A combination of monitoring local weather forecasts and notification by partnering agency personnel (NRCS, University Extension Service, Perry County Soil and Water Conservation District and MDC Field Offices) will be utilized to coordinate sampling during rain events. All samples will be analyzed for nitrate (NO_3^--N), nitrite (NO_2^--N), ammonia (NH_3-N), chloride (Cl^-), ortho-phosphate (PO_4^{3-}-P), total phosphorus (P_{total}), total suspended solids and atrazine. Atrazine will only be analyzed from April through June during the application period of the herbicide.

SPMD and POCIS. The fourth subprogram involves deployment of moored SPMD (semi-permeable membrane device) and POCIS (polar organic chemical integrative sampler) devices in resurgences, springs, surface and/or subsurface streams at five or six sites. Stations will correspond with continuously deployed, water-quality sonde

stations and/or monthly water-grab- sample stations. Samplers will be deployed for 30 days and then retrieved for analysis. These samplers will sequester trace levels of chemicals that cannot be detected by typical analyses of water grab samples. *In situ* field measurements of temperature, pH, specific conductivity, dissolved oxygen and turbidity will be recorded when the samplers are deployed and retrieved. Target analytes and procedures are currently in development.

Dye Tracing. The primary focus of the fifth subprogram is to conduct 36 water traces in the Perryville karst plain. These traces will help determine the full extent of the recharge area for Mystery, Crevice, Running Bull, Moore, and Rimstone cave systems. These traces are planned over a three-year time frame with an average of 12 traces each year. Scheduling and prioritization of water traces, as well as the selection of proposed dye types, have been planned based on review of existing water-trace data, proposed injection and monitoring locations, current cave mapping data, available dye types and analysis technologies and logistics required for injection. Schedule flexibility will be required to accommodate uncontrollable logistical circumstances such as weather conditions, property access and water availability. Dye monitoring receptors (packets of activated charcoal) will be used to absorb dyes from solution to determine if the dye was present within the water column at a particular location. For the traces proposed here, the receptor-monitoring points chosen are hydrologically significant groundwater resurgence points, cave streams and surface streams. The general water-tracing methodology established by Ozark Underground Laboratory (Aley 2007) will be used to conduct this work.

Results and Discussion

We are beginning the second year of this four-year study of water quality. Preliminary results after a few months of samples indicate that *E. coli*, chloride, atrazine, and turbidity could be some of the water-quality issues that may be impacting the Perry County Karst. Vulnerability mapping by Ozark Underground Laboratory indicates that most of the study area is vulnerable to groundwater contamination (Aley and Moss 2007). Within the sinkhole plain, only parts of the riparian corridors of the surface streams have moderate vulnerability. The rest of the landscape is high vulnerability because most of the runoff enters sinkholes with little to no filtration.

We hope that continuation of the water-sampling and dye-tracing studies will provide us with the data and watershed boundaries needed to assist with the drafting of the Perry County Karst Watershed Management Plan in three key ways: (1) long-term data sets will allow for interpretation of water-quality trends throughout the karst regions, (2) water-quality data will provide the needed information to develop or improve best management practices (BMPs) and cost-share practices, and (3) the dye-tracing study will delineate groundwater-recharge areas for five major cave systems to provide a better understanding of the relationships between surface-water and groundwater hydrology and biology.

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