Cover photograph is an aerial view of the Beaverdam Spring recharge area and discharge wetland. Photograph from Google Earth, 2012.
GEOLOGICAL SURVEY OF ALABAMA

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WATER QUANTITY AND QUALITY ASSESSMENT
FOR THE BEAVERDAM SPRING AREA OF
LIMESTONE COUNTY, ALABAMA

OPEN FILE REPORT 1305

By

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INTRODUCTION

Land use and climate can have tremendous impacts on the quantity and quality of shallow groundwater sources that supply water to springs that support unique biological habitats in the Valley and Ridge and Highland Rim physiographic sections of Alabama. Water in spring ponds and streams that originate from springs discharging from carbonate rocks have physical and chemical characteristics that support a unique assemblage of aquatic plants and animals.

Discovered in 1937, the spring pygmy sunfish was twice presumed extinct during the 70 years it has been known to science. It is limited primarily to headwater springs and historically occurred in three small disjunct spring complexes (Cave, Pryor and Beaverdam Springs) separated by up to 65 miles. Two of the three populations have disappeared. The Cave Springs population was extirpated in 1938 due to inundation by the formation of Pickwick Reservoir; the Pryor Springs population disappeared by the late 1960s, most likely due to dredging and chemical contamination. The single remaining native population occupies just 5 river miles of the Beaverdam Spring complex. Critical habitat was designated both for Beaverdam Springs and Creek, where the species survives, and for the Pryor and Branch Spring complex (Center for Biological Diversity, 2012).

ACKNOWLEDGMENTS

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PROJECT AREA AND LAND USE/LAND COVER

Beaverdam Spring is in rural southeastern Limestone County, about 2 miles west of the Madison County and city of Madison boundaries and about 2 miles north of the Greenbrier community (fig. 1). The project area covers about 10 square miles (mi²) and includes Beaverdam Spring, Moss Spring, Beaverdam Creek, and several tributaries to Beaverdam Creek.
Figure 1.—Location of the Beaverdam Spring project area.
Land use in the project area is dominated by row crop production. Corn, soybeans, and cotton are grown in most of the watershed, with the exception of some pasture with cows and horses, stream floodplains, and urban/residential areas. Wetlands are prominent in the Beaverdam Spring discharge area and in major stream floodplains (plate 1). Urban development extending westward from the city of Madison is a major land cover on the eastern side of the watershed (plate 1). The Beaverdam Spring recharge area contains about 1.3 mi² in the northwestern part of the project area. Land use in the recharge area is about 70 percent row crop agriculture and about 30 percent forest (plate 1).

**PHYSIOGRAPHY**

Beaverdam Spring is in the Tennessee Valley district of the Highland Rim physiographic section, which includes western Madison, Limestone, northwestern Morgan, northern Lawrence, and northern Colbert Counties and most of Lauderdale County (fig. 2). It is characterized by plateaus of moderate relief with elevations ranging from 600 to 800 feet underlain by chert in the north and limestone in the south (Sapp and Emplaincourt, 1975).

**ASSESSMENT PURPOSE, STRATEGY, AND AVAILABLE DATA**

The purpose of the Beaverdam Spring hydrogeologic assessment is to characterize the hydrogeology of the project area and to specifically identify the spring recharge area, groundwater flow paths, quantity of spring discharge, and water quality. These data will facilitate conservation practices for the protection of Beaverdam Spring, the spring pygmy sunfish, and its habitat.

Groundwater level data were collected from 13 privately owned water wells in the project area. One other private well was located but no access could be obtained. Two public water supply wells owned and operated by Madison Utilities are in the project area, but no water levels could be obtained. Water level data were used to construct a potentiometric water surface map to determine groundwater flow directions and groundwater production impacts. Groundwater residence time was estimated using isotopic data analyzed from water samples collected from the spring.

Beaverdam Spring discharges along a bluff line about 4,000 feet long and eventually flows into Beaverdam Creek. Since direct measurement of spring discharge is
not possible, a water budget method of estimating spring discharge was employed using surface-water discharge measurements from five Beaverdam Creek tributaries, Moss Spring, and Beaverdam Creek downstream from Beaverdam Spring. Measured discharges were subtracted from the downstream Beaverdam Creek discharge, leaving an estimated discharge for Beaverdam Spring.

Spring water quality was determined by analyses of water samples collected from the spring. Analytical parameters included physical parameters, metals, nutrients, inorganic non-metallics, and a limited number of organic constituents.

**HYDROGEOLOGY**

The central part of the Tennessee River watershed in Alabama, including the Beaverdam Spring project area, is underlain by a thick sequence of relatively flat-lying Paleozoic rocks, ranging in age from Middle Ordovician to Early Pennsylvanian. These rocks were less affected by the tectonic forces that formed the Appalachian fold and thrust belt to the southeast. With the exception of a few minor folds, rocks generally dip
south-southwest at 20 to 40 feet per mile (Osborne and Raymond, 1992; Jennings and Cook, 2008) in response to the position of the Tennessee River watershed on the southern flank of the Nashville Dome.

The stratigraphy in the project area consists of Lower to Middle Mississippian Fort Payne Chert and Middle Mississippian Tuscumbia Limestone (fig. 3). The overlying, younger Tuscumbia Limestone has been eroded by Beaverdam Creek and its tributaries exposing the older Fort Payne Chert in the stream flood plains (plate 2). The Fort Payne Chert is composed of very light gray to light-gray, thin- to thick-bedded, fossiliferous or bioclastic limestone, siliceous and dolomitic limestone, and dolomite with abundant nodules, lenses, and beds of light- to dark-gray chert (Copeland and others, 1975; Szabo and others, 1988). Bedded chert is common throughout the unit but is more concentrated near the base. The percentage of chert in the formation is variable from 20 to 80 percent (Holler, 1975). In areas underlain by the Fort Payne Chert, bedrock exposures are rare and are usually covered with dark-yellowish-orange to dark-reddish-brown regolith containing abundant detrital blocky chert. The formation has an average thickness of about 160 feet and is exposed as regolith in the eastern two-thirds of the project area, although relatively unweathered exposures exist along the bluff line where Beaverdam Spring discharges (plate 2).

The Tuscumbia Limestone overlies the Fort Payne Chert although in some areas it is lithologically indistinct (fig. 3). It is generally composed of a sequence of light-gray to light-brownish-gray coarse- to medium-grained bioclastic or micritic limestone, light-brownish-gray granular cherty calcareous dolomite, and randomly distributed light-gray and white nodular chert (Holler, 1975; Raymond and others, 1988). The Tuscumbia Limestone is exposed along the western margin of the Beaverdam Creek watershed (plate 2), and the average thickness of the unit is about 150 feet. The contact with the Fort Payne Chert is about 0.5 mile north from the discharge area for Beaverdam Spring (plate 2).

JOINTS

Joints are characterized as brittle fractures in rock with no displacement, caused by accommodation to stress. In the Tennessee Valley, joints are generally the result of tension. Joints are of particular interest because they provide permeability for the
**Figure 3.**—Typical stratigraphy for the Tennessee River watershed in Alabama (highlighted stratigraphic units underlie the Beaverdam Spring project area).
movement of groundwater, especially in carbonate rocks where they may be enhanced by solution. An investigation of joint systems in the Tuscumbia Limestone and Fort Payne Chert in northern Madison County by Mann and others (1996) revealed that the most prominent joint strike directions were N. 30° E., N. 60° W., and N. 75° W.

Mann and others (1996) also investigated the presence of lineaments in northern Madison County. Lineaments are linear features observed on aerial photographs or topographic maps that result from the alignment of stream channels, topographic relief, vegetation, or tonal anomalies. They are thought to be in part structurally controlled possibly by faults or zones of intense jointing and have been used to postulate the occurrence of groundwater. The investigation included analyses of high-altitude color-infrared photographs and identified dominant linear trends of N. 30° E. and N. 60° W., which agreed with the dominant trends of joints in the area.

Trends of joint and lineament directions determined by Mann and others for northern Madison County were shown to most likely extend into Limestone County and the Beaverdam Creek area by recent GSA investigations. Mapping of specific capacities in wells throughout the Tennessee River watershed by Cook and others (2009) and investigation of lineaments during the Beaverdam Spring project indicate that the N. 30° E. trend is the dominant joint/fracture direction in the Beaverdam Spring area.

**GROUNDWATER AVAILABILITY AND FLOW CHARACTERISTICS**

The source of groundwater and surface water in the Beaverdam Spring area is precipitation, which averages about 56 inches per year (Southeast Regional Climate Center, 2009). Availability and distribution of this water are controlled by processes, which include overland flow into streams and lakes, evaporation into the atmosphere, transpiration by vegetation, and infiltration into the subsurface as groundwater recharge. The surface hydrology of the project area is dominated by Beaverdam Creek and tributaries characterized by flashy runoff over relatively impermeable Paleozoic rocks. The groundwater system is characterized as relatively shallow, fractured, Paleozoic carbonate aquifers with widespread karst development. Groundwater yields are highly variable due to locally variable porosity and permeability that affect the water-bearing characteristics of an aquifer.
The Tuscumbia Limestone and Fort Payne Chert aquifer in the project area is primarily unconfined due to shallow depths and absence of confining layers that isolate groundwater from the water table and the land surface. Therefore, groundwater movement is controlled by gravity as water moves from topographic highs to topographic lows where it discharges as springs or to surface-water bodies. Groundwater movement in Paleozoic aquifers is preferential with respect to direction and velocity, related to the geometry and connectivity of fracture systems. Directions of groundwater movement can be determined from contour maps of water level elevations. There are three types of water level maps: Water table maps, potentiometric maps, and hybrid water table-potentiometric maps. Water table maps show the configuration of groundwater under water table conditions (unconfined). These water levels generally mimic land surface topography. Water levels used in the preparation of these maps can be from shallow wells, streams, springs, sink holes, and caves. Potentiometric maps represent groundwater levels in confined aquifers. Since confined groundwater is under hydraulic pressure, the elevation of the potentiometric surface is defined as the level that water rises in properly cased wells. The third type of water level map, common in the Tennessee River watershed, is a hybrid, composed of a mixture of water table, semi-confined, and/or confined water levels. Plate 3 shows water level contours constructed from water levels measured in 15 wells constructed in the Tuscumbia Limestone/Fort Payne Chert aquifer. Groundwater level contours in plate 3 generally conform to land surface topography so that the groundwater system in the project area is mostly unconfined. Plate 3 shows that groundwater generally moves from higher to lower elevation and discharges into streams forming the base flow component of surface-water flow. Flow directions are generally westward from the eastern watershed boundary of Beaverdam Creek and eastward from the western boundary of the watershed. In the recharge area of Beaverdam Spring, groundwater flow is generally southward from upland areas to the bluff line where the spring discharges (plate 3).

GROUNDWATER RECHARGE

Unlike the Coastal Plain where groundwater can move long distances from recharge areas in aquifers that exceed depths of 2,500 feet (Cook, 2004) or the Valley and Ridge and Piedmont where large, complex faults create pathways for movement of
recharge over long distances (Cook, 1997), groundwater recharge in much of the Tennessee River watershed is local. The recharge area for Beaverdam Spring was determined using a combination of topographic analysis and evaluation of groundwater level mapping. The recharge area for the spring is about 1.7 mi² and extends from the western Beaverdam Creek watershed boundary eastward to the eastward sloping topography near Oakland Spring Branch (plate 3). The northern extent of the recharge area is Huntsville Browns Ferry Road where the topography slopes northward (plate 3). The southern boundary of the recharge area is the bluff line where the spring discharges (plate 3).

Recharge rates are controlled by a number of factors including porosity and permeability, which in Paleozoic aquifers are mainly secondary and are characterized by leached fossils, fractures, and solution development. Most carbonate rocks in the Tennessee River watershed are indurated and thoroughly cemented, resulting in limited intergranular porosity. Therefore, fractures provide much of the porosity and permeability for groundwater movement and storage. Fractures are characterized as stress-relief (vertical) and bedding-plane (horizontal) and are typically non-uniform and can vary significantly over short distances (Bossong and Harris, 1987). The principal constituent of these rocks is calcium carbonate (CaCO₃), a compound which is readily soluble by several dilute acids that are normally present in precipitation and runoff. However, the most significant process affecting solution development in these carbonate rocks is the production of carbonic acid by percolating groundwater. As water moves downward through the regolith, it encounters carbon dioxide (CO₂), which is produced by decay of organic matter (Freeze and Cherry, 1979). Water and CO₂ combine to form carbonic acid, which dissolves limestone and aids in development of solution-enlarged fractures and cavities (Mann and others, 1996).

Recharge, originating from precipitation, may also be influenced by drought (fig. 4), seasonal precipitation (fig. 5), land surface slope, surface drainage, and the character of surface material. If the topography is relatively flat and surface materials are permeable, more surface water will infiltrate into local aquifers. Recharge may also be greater where faults and fractures are common and where they extend to the surface and connect surface water with aquifers (Bossong, 1988; Baker and others, 2005). Estimates of recharge can be useful in determining available
Figure 4.—Annual precipitation for the period 1980-2008 at the Huntsville Airport.

Figure 5.—Average monthly precipitation for the period 1908-2008 at the Huntsville Airport.
groundwater, impacts of disturbances in recharge areas, and water budgets for water-
resource development and protection. Numerous methods have been used for estimating
recharge, including development of water budgets, measurement of seasonal changes in
groundwater levels, groundwater flow velocities, and equating average annual base flow
of streams to groundwater recharge (Risser and others, 2005). Although it is desirable to
assess recharge in watersheds with unregulated streams that are not subject to surface-
water withdrawals, or discharges from wastewater treatment plants or industries, it is
unrealistic to expect that no human impacts occur in watersheds where recharge estimates
are performed.

As noted previously, average precipitation in the Tennessee River watershed is 56
inches per year. Precipitation is distributed as runoff, evapotranspiration, and
groundwater recharge. Sellinger (1996) described the various pathways of precipitation
movement that compose stream discharge and determine the shape of a stream
hydrograph (fig. 6). However, for the purposes of this report, pathways of precipitation
movement shown in figure 6 are combined into two primary components, runoff and base
flow. Runoff is defined as the part of total stream discharge that enters the stream from
the land surface. Bossong (1988) reported that runoff in the Tennessee River watershed
varies from 20 to 30 inches per year, depending on the location of the subject watershed
with respect to topography and geology. Base flow is the part of stream flow supplied by
groundwater, an essential component that sustains stream discharge during periods of
drought and is equated to groundwater recharge.

Separating runoff and base flow from total stream discharge can be accomplished
by several methods (Sellinger, 1996; Risser and others, 2005) including (1) recession
analysis (Nathan and McMahon, 1990), (2) graphical hydrograph separation (Meyboom,
1961), and (3) partitioning of stream flow using daily rainfall and stream flow
(Shirmohammadi and others, 1984). More recently, a number of computer models have
automated hydrograph separation techniques (Risser and others, 2005; Lim and others,
2005).

Beaverdam Spring discharges along a bluff line about 4,000 feet long and
eventually flows into Beaverdam Creek. Since direct measurement of spring discharge is
not possible, two methods of groundwater recharge estimation (water budget and
hydrograph separation) were used to estimate groundwater recharge in the project area
Figure 6.—Graphic and storm flow hydrograph illustrating pathways of movement of rainfall into streams (modified from Sellinger, 1996).
and the discharge from Beaverdam Spring. A water budget method was employed using surface-water discharge measurements from five Beaverdam Creek tributaries, Beaverdam Creek downstream from the Beaverdam Spring wetland, and Moss Spring. Discharge was measured on March 29, 2012, which is normally the wet season in Alabama. However, north Alabama was experiencing drought conditions at that time, so that streams were in base flow conditions. Two streams, Hardiman Branch and Oakland Spring Branch were dry (plate 4). A unit discharge of 1.16 cubic feet per mi² of drainage area was established for the area downstream from the Beaverdam Spring discharge and upstream from the Beaverdam Creek discharge monitoring point. The unit discharge was used to calculate total base flow discharge for the area downstream from the Beaverdam Creek discharge area, which when subtracted from the downstream Beaverdam Creek discharge, leaves the value of Beaverdam Spring discharge. This method yielded a spring discharge of 4.5 cubic feet per second (cfs) or 2,020 gallons per minute (gpm). The recharge rate calculated using the water budget values is 37.25 inches per year (in/yr).

The second method of groundwater recharge estimation employed discharge data from the nearest continuous discharge measurement station, analyzed using the Web based Hydrograph Analysis Tool (WHAT) automated hydrograph separation computer program (Lim and others, 2005; Purdue University, 2004). This program separates stream runoff and base flow, which is used to calculate volumes of groundwater recharge. The nearest long-term discharge data set was the U.S. Geological Survey monitoring site (gauging station 3576250) on Limestone Creek, which is adjacent to Beaverdam Creek to the west. Groundwater recharge using the WHAT program output was 15.03 in/yr. This value was checked using the Meyboom graphical hydrograph separation method (Meyboom, 1961), which yielded a value of 13.21 in/yr. When the average value from the methods (14.12 inches) is applied to the recharge area of Beaverdam Spring, the resulting discharge is 1.7 cfs or 766 gpm.

Although the recharge value obtained from the hydrograph separation methods is reasonable for karst terrains, the disparity in values between the water budget and hydrograph separation methods is most likely the result of a significantly larger recharge rate than the average rate for Tennessee Valley carbonate aquifers. This is probably caused by unusually high precipitation infiltration and aquifer permeability related to
minimal runoff and evapotranspiration rates due to row crop agricultural land use and a lack of vegetation in much of the recharge area and concentrated karst development.

GROUNDWATER WITHDRAWALS

An inventory of water wells by Geological Survey of Alabama Groundwater Assessment Program (GSAGAP) indicates that there are 16 wells in the Beaverdam Spring project area, which includes Beaverdam Spring and Beaverdam Creek. Two of the wells are used for public water supply (Hardiman and Williams wells, owned and operated by the Madison Water & Wastewater Board) (plate 5). Eight wells are currently used for domestic supply (BS2, BS3, BS4, BS5, BS6, BS7, BS12, BS14) (plate 5). Four wells may be capable of pumping, but are currently unused (BS8, BS9, BS10, BS13) (plate 5). Two wells are abandoned (BS1 and BS11) (plate 5).

The Hardiman and Williams wells pumped about 63,000 and 261,000 gallons per day (g/d), respectively for water year 2012 (Madison Water & Wastewater Board, 2013). The Williams well is outside of the Beaverdam Spring recharge area and most likely has no impact on the spring discharge. The Hardiman well is in close proximity to the spring recharge area, but no water level data could be obtained for the well. Therefore, no evaluation of spring discharge impact due to well pumpage could be performed. Per capita water use for Limestone County is 169 gallons per day (U.S. Department of Commerce, 2012; U.S. Geological Survey, 2009), therefore, a reasonable estimate for water withdrawals for families of four from the eight domestic supply wells is about 5,400 g/d. Only two wells are located in the Beaverdam Spring recharge area (BS5 and BS6) (plate 5). Both wells are currently used for domestic supply, but reduce the discharge of Beaverdam Spring by an almost undetectable amount. One surface-water withdrawal (irrigation pumping station) was observed immediately down gradient from bluff line where Beaverdam Spring discharges (plate 5). Although no volumes of pumpage are known, it is likely that withdrawals only occur during the agricultural growing season.

Total water withdrawals for the Beaverdam Spring project area (excluding withdrawals from the irrigation pumping station) are about 330,000 g/d. The Beaverdam Creek discharge measurement performed by GSAGAP in March 2012 (during base flow conditions and with no irrigation withdrawals) was about 9.63 million gallons per day.
Therefore, during base flow, withdrawals remove about 3.5 percent of the total flow of Beaverdam Creek in the project area.

**PHYSICAL PROPERTIES AND CHEMICAL AND ISOTOPIC COMPOSITION OF GROUNDWATER FROM BEAVERDAM SPRING**

Groundwater samples from Beaverdam Spring discharge were collected on March 29, 2012 and analyzed for physical properties and chemical and isotopic composition. The purpose of these analyses is to characterize the spring discharge with respect to water quality, geographic extent of recharge, and land-use impacts on recharge.

**PHYSICAL PROPERTIES**

Samples collected from the spring were processed and submitted to the GSA geochemical laboratory for analysis. Physical properties of groundwater were also tested in the field and included turbidity, temperature, hydrogen ion activity (pH), specific conductance (SC), oxidation reduction potential (ORP), and total dissolved solids (TDS).

Turbidity of the spring water was 0.8 nephelometric turbidity units (NTU), which is extremely clear water with minimal suspended particles. The temperature of the water at the spring discharge point was 16.3 degrees Celsius.

Hydrogen ion activity in an aqueous solution is controlled by interrelated chemical reactions that produce and consume hydrogen ions (Hem, 1985). The reaction of dissolved carbon dioxide with water is one of the most important mechanisms in establishing pH in natural water systems. Water collected from the spring had a pH of 6.2, which is slightly acidic and related to acidic precipitation that is normal for north Alabama.

Specific conductance is a measure of all dissolved substances in water and gives information about the length of time that groundwater has been in the subsurface and amounts of contaminants that are in the water. The SC of the water sample collected from Beaverdam Spring was 129 microsiemens per centimeter (μS/cm) which is relatively low but typical for shallow groundwater with relatively short residence time and little or no contaminants.
ORP, also referred to as redox potential (Eh) is a numerical index indicating the tendency of system/solution to acquire electrons and thus be reduced (Hem, 1985). Oxidation is the loss of electrons by a substance undergoing a chemical reaction. Conversely, reduction is the gain of electrons by a substance undergoing a chemical reaction. The more positive the ORP of a solution is, the higher is its tendency to be reduced (for example, to be reduced by oxidizing a new introduced species). Redox potential evaluations are very important in estimating the solubility of metals in natural water systems. However, temperature, pH, irreversible reactions, and other factors limit ORP interpretations. These measurements have been previously used by Garrels and Christ (1990) to monitor changes in systems. ORP in the water sample collected from the spring was 273 millivolts (mV), which indicates an oxidized subsurface environment, typical for shallow aquifers.

TDS is defined as the measure of the combined content of inorganic and organic substances contained in water. It is a measure of the mineralization and/or contamination in a water sample. The measured TDS from the spring sample was 95 milligrams per liter (mg/L), which indicates fresh, relatively uncontaminated groundwater.

CHEMICAL COMPOSITION

More than 90 percent of the dissolved solids in groundwater can be attributed to eight ions: sodium (Na\(^{+}\)), calcium (Ca\(^{2+}\)), potassium (K\(^{+}\)), magnesium (Mg\(^{2+}\)), sulfate (SO\(_4^{2-}\)), chloride (Cl\(^{-}\)), bicarbonate (HCO\(_3^{-}\)), and carbonate (CO\(_3^{2-}\)) (Fetter, 1994). The quantity of major cations and anions determines water types, which are used to characterize groundwater quality in specified areas. The water sample collected from Beaverdam Spring was analyzed for 60 constituents that include metals, inorganic non-metals, nutrients, and a selected group of organics. These constituents, when evaluated collectively and individually, provide information about water quality, land use impacts in the recharge area, and aquatic species and habitat impacts.

The U.S. Environmental Protection Agency (USEPA) compiled national recommended water quality criteria for the protection of aquatic life and human health in surface water for approximately 150 pollutants. These criteria are published pursuant to Section 304(a) of the Clean Water Act (CWA) and provide guidance for states and tribes to use in adopting water quality standards (USEPA, 2009). The criteria were developed
for acute (short-term exposure) and chronic (long-term exposure) concentrations. Selected constituents and concentrations for the water samples collected from Beaverdam Spring and their recommended acute and chronic maximum concentrations are shown in table 1 at the end of the chemical composition section.

**NUTRIENTS**

Excessive nutrient enrichment is a major cause of water-quality impairment. Excessive concentrations of nutrients, primarily nitrogen and phosphorus, in the aquatic environment may lead to increased biological activity, increased algal growth, decreased dissolved oxygen concentrations at times, and decreased numbers of species (Mays, 1996). Nutrient-impaired waters are characterized by numerous problems related to growth of algae, other aquatic vegetation, and associated bacterial strains. Blooms of algae and associated bacteria can cause taste and odor problems in drinking water and decrease oxygen concentrations to eutrophic levels. Toxins also can be produced during blooms of particular algal species. Nutrient-impaired water can dramatically increase treatment costs required to meet drinking water standards. Nutrients discussed in this report are nitrate (NO₃-N) and phosphorus (P-total and PO₄).

**NITRATE**

The USEPA Maximum Contaminant Level (MCL) for nitrate in drinking water is 10 mg/L. The USEPA national recommended water quality criteria for the protection of aquatic life and human health in surface water provides a standard of 690 micrograms per liter (µg/L) (0.69 mg/L) for total nitrogen concentrations (table 1). Typical nitrate (NO₃ as N) concentrations in streams vary from 0.5 to 3.0 mg/L. Concentrations of nitrate in streams without significant nonpoint sources of pollution vary from 0.1 to 0.5 mg/L. Streams fed by shallow groundwater draining agricultural areas may approach 10 mg/L, but those waters with nitrate concentrations in excess of 0.5 mg/L may have excessive algae growth, which may lead to eutrophication (Maidment, 1993).

The concentration of NO₃ as N for the water sample collected from Beaverdam Spring was 2.77 mg/L. This is more than five times above the suggested standard and indicates excessive nitrate in the groundwater system that most likely originates from row crop agriculture and animals in the recharge area. Total nitrogen was also 2.77 mg/L,
which is about four times the recommended concentration for the protection of aquatic wildlife (table 1).

PHOSPHORUS

Phosphorus in streams originates from the mineralization of phosphates from soil and rocks or runoff and effluent containing fertilizer or other industrial products. The principal components of the phosphorus cycle involve organic phosphorus and inorganic phosphorus in the form of orthophosphate (PO₄) (Maidment, 1993). Orthophosphate is soluble and is the only biologically available form of phosphorus.

The natural background concentration of total dissolved phosphorus is approximately 0.025 mg/L. Phosphorus concentrations as low as 0.005 to 0.01 mg/L may cause algae growth, but the critical level of phosphorus necessary for excessive algae is around 0.05 mg/L (Maidment, 1993). In many water bodies, phosphorus is the primary nutrient that influences excessive biological activity. These water bodies are termed “phosphorus limited.”

Total phosphorus in the spring water sample was 0.061 mg/L, and the concentration of orthophosphate was 0.031. The total phosphorus concentration is about 1.7 times the recommended concentration for the protection of aquatic wildlife (table 1). These values indicate elevated phosphorus concentrations that probably originate from row crop agriculture and animals in the Beaverdam Spring recharge area.

METALLIC AND INORGANIC NONMETALLIC CONSTITUENTS

Numerous metals are naturally present in streams in small concentrations. However, toxic metals in streams are usually a result of man’s activities. The water samples collected from Beaverdam Spring were analyzed for selected metallic constituents. Table 1 shows concentrations of metals and their relationship to recommended criteria for protection of aquatic life. Table 1 shows that only chloride, iron, and zinc were detected and none of those exceeded the recommended criteria for protection of aquatic wildlife.

Although not included in USEPA criteria, calcium, fluoride, potassium, magnesium, sodium, silica, sulfate, strontium, and vanadium were also detected in small concentrations in the water sample collected from the spring. These are naturally
occurring, common constituents in Alabama streams and are a result of dissolution or erosion of rocks and sediment.

Table 1.-- Concentrations of metallic constituents, nutrients, and pH detected in water samples collected from Beaverdam Spring, with comparisons with USEPA standards for protection of aquatic life.

<table>
<thead>
<tr>
<th>Metallic constituent</th>
<th>USEPA standards for protection of aquatic life (µg/L(^a))</th>
<th>Beaverdam Spring sample concentrations (µg/L)</th>
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<tr>
<td></td>
<td>Acute</td>
<td>Chronic</td>
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<tr>
<td>Aluminum</td>
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<td>Cadmium</td>
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<tr>
<td>Chromium (Cr(_3))</td>
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</tr>
</tbody>
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\(^a\) µg/L = micrograms per liter.
\(^b\) BDL = below detection limit.
\(^c\) Chromium reported as total chromium and is assumed to be primarily Cr\(_3\).

**ORGANIC CONSTITUENTS**

Organic compounds are commonly used in our society today. Frequently, these compounds appear in streams and groundwater aquifers. Many of these compounds are harmful to human health and to the health of the aquatic environment. Selected organic constituents including total organic carbon, oil and grease, and phenols were analyzed from the sample collected from Beaverdam Spring, in order to make a general determination of the presence of organic anthropogenic contaminants in the watershed.
Total organic carbon (TOC) analysis is a well-defined and commonly used methodology that measures the carbon content of dissolved and particulate organic matter present in water. Many water utilities monitor TOC to determine raw water quality or to evaluate the effectiveness of processes designed to remove organic carbon. Some wastewater utilities also employ TOC analysis to monitor the efficiency of the treatment process. In addition to these uses for TOC monitoring, measuring changes in TOC concentrations can be an effective surrogate for detecting contamination from organic compounds (e.g., petrochemicals, solvents, pesticides). While TOC analysis does not give specific information about the nature of the threat, identifying changes in TOC can be a good indicator of potential threats to a hydrologic system (USEPA, 2005). Typical TOC values for natural waters vary from 1 to 10 mg/L (Mays, 1996). TOC was below the detection limit in the sample from the spring.

Phenols are used in the production of phenolic resins, germicides, herbicides, fungicides, pharmaceuticals, dyes, plastics, and explosives (USGS, 1992). They may occur in domestic and industrial wastewaters, natural waters, and potable water supplies. The USEPA has set its water quality criteria, which states that phenols should be limited to 10,400 µg/L (micrograms per liter) (10.4 mg/L) in lakes and streams to protect humans from the possible harmful effects of exposure (USEPA, 2009). Phenols cause acute and chronic toxicity to freshwater aquatic life. However, Phenols were below the detection limit for the spring sample.

**ISOTOPE INVESTIGATIONS AND WATER AGE DATING**

Groundwater in the region surrounding Beaverdam Spring has been increasingly targeted for the region’s growing water needs. Expanding use of groundwater resources requires better knowledge of recharge and flow conditions. Groundwater evolution is a critical focus of the hydrogeological assessment of Beaverdam Spring, to develop a better understanding of the groundwater flow system, with respect to recharge mechanisms and groundwater residence times. Recent advances in analytical techniques make it possible to accurately measure extremely small concentrations of isotopes of key elements that enable the relatively accurate age dating of water. When combined with other geochemical and hydrogeologic information, isotopic data can help evaluate migration history and geochemical evolution of groundwater in aquifers, which can aid in
protection of groundwater sources and surface waters and aquatic habitats that rely on base flow contributions from groundwater sources. Isotopes can be used as tracers of water movement, since unique isotopic signatures are characteristic to particular recharge environments. As part of this investigation, groundwater samples from Beaverdam Spring were analyzed for anthropogenic, natural, and stable isotopes such as chlorofluorocarbon (CFCs), sulphur hexafluoride (SF6), carbon ($\delta^{13}C$), oxygen ($\delta^{18}O$), and hydrogen ($\deltaD$) (stable isotope compositions are expressed in terms of delta values ($\delta$), which are parts per thousand ($%$) differences from a standard). These analyses provide essential measurements to identify the environment from which groundwater originated and constrain the period of time during which recharge occurred.

Stable isotopes of hydrogen, oxygen, and carbon are ideal tracers of groundwater sources and evolution along flow paths. Hydrogen and oxygen isotopes are best used in tracing sources of groundwater since they integrally compose the water molecule (Cook and Herczeg, 1999). These measurements provide information about recharge and discharge processes and are successfully used in delineating recharge areas (Cook and Herczeg, 1999). Carbon occurs in all forms of organic life and is the basis of organic chemistry. Carbon stable isotopes have been used as tracers of carbonate evolution in groundwater, given their distinct range of values for specific reservoirs. Besides reflecting the water-rock interaction and any other additional geochemical reactions that may take place within the saturated zone and aquifers, $\delta^{13}C$ of groundwater dissolved inorganic carbon (DIC) is also a good indicator of the land-use/land-cover characteristics of the source area (Cook and Herczeg, 1999).

Groundwater originates primarily from precipitation that infiltrates soil layers and moves to the saturated zone. Groundwater transports anthropogenic atmospheric trace gases such as CFCs and SF6 that can provide a temporal characterization of groundwater recharge, essential in determining the geochemical evolution of water from the time it enters the recharge area to the time of discharge. When combined, the two isotopes of CFCs and SF6 can provide information about mixing processes, groundwater ages, and residence times with maximum resolution of about 50 years (Kazemi and others, 2006). These dating techniques have been employed worldwide and utilize relatively rapid and simplistic analytical procedures and unsophisticated sampling equipment to characterize
groundwater systems (Cook and others, 1995; Plummer and others, 2001; Oster and others, 1996; MacDonald and others, 2003; and others).

Results of such investigations can aid in the development of sustainable groundwater management strategies and improve risk assessments related to groundwater recharge, production, and contaminant transport.

**OXYGEN AND HYDROGEN STABLE ISOTOPES**

Ocean derived atmospheric waters are depleted in heavy isotopes ($^{18}$O and $^2$H) relative to the standard mean ocean water (SMOW). Isotopic ($\delta^{18}$O and $\delta$D) composition of precipitation depends on the fraction of water remaining in the air mass from which the rain or snowfall is derived (Ellis and Mahon, 1977). Depletion of $\delta^{18}$O and $\delta$D creates an isotopic signature in precipitation that has been correlated with seasonal change (changes in temperature and humidity), latitude, altitude, distance from the coast, and amount of precipitation (Dansgaard, 1964). Examples of geographic and topographic effects on depletion rates of $^{18}$O over North America include Fritz and Frape (1982) who found that the latitudinal effect is approximately 0.5 percent per degree of latitude and Poage and Chamberlain (2001) who determined that the altitudinal effect is about 0.30‰ per 100 meters of altitude increase. The cumulative effect of these physical parameters forms the isotopic character of precipitation, which is the source of surface-water runoff and recharge for groundwater aquifer systems.

Abundances of oxygen and hydrogen isotopes are measured (with an uncertainty of 1‰ for $\delta$D and 0.1‰ for $\delta^{18}$O) relative to an accepted standard, which is the SMOW, or Vienna SMOW (VSMOW) (Craig, 1961). The isotopic composition of sampled water is expressed in terms of relative difference of the ratio of heavy to light isotopes in the sample, compared to that of SMOW. The resulting compositional values are stated as positive (enriched) or negative (depleted) percentages relative to VSMOW. The average isotopic variation of global precipitation is defined by a linear regression of $\delta$D as a function of $\delta^{18}$O. Craig and Gordon (1965) estimated the mean worldwide isotope composition of precipitation to be $\delta^{18}$O = -4 per mil (‰) and $\delta$D = -22 ‰. The worldwide average correlation between hydrogen and oxygen isotope ratios in precipitation is given by the equation $\delta$D = 8 $\delta^{18}$O + 10‰, called the Global Meteoric Water Line (GMWL) (fig. 7).
Lambert and Aharon (2009) developed a local Tuscaloosa meteoric water line (TLMWL) from precipitation collected from the rain-gage station at the University of Alabama in Tuscaloosa. The TLMWL was developed using an average of multiple $\delta^{18}$O (a) and $\delta$D readings from precipitation samples collected during a 3-year period (2005-2008). The weighted annual (3-year) $\delta^{18}$O and $\delta$D mean values were -4.7‰ and -24.3‰, respectively (Lambert and Aharon, 2009) (fig. 7). These values are more enriched in the heavy isotopes compared to the Beaverdam Spring groundwater samples where the $\delta^{18}$O and $\delta$D values were -5.4‰ and -29.0‰, respectively (fig. 7). Latitudinally, the difference between the two locations (Beaverdam Spring recharge area: 34°42’50”W; Tuscaloosa: 33°12’35”W) is about 1.5°, which would account for about -0.35‰ of the difference in $\delta^{18}$O. Altitudinally, the Beaverdam Spring recharge area average elevation (625 ft) is about 400 feet higher than the average elevation of Tuscaloosa (223 ft). This would also account for about 0.35‰ of the difference in $\delta^{18}$O, thus explaining the increased depletion of heavy isotopes with respect to the mean stable isotope values for the TLMWL.

However, the Beaverdam Creek values should also be compared relative to the TLMWL regression. Figure 7 shows that the cross plot of Beaverdam Spring $\delta^{18}$O and $\delta$D values falls only slightly below (increase of $\delta^{18}$O) and to the right (decrease of $\delta$D) of the TLMWL. This indicates that the spring discharge is relatively young groundwater and is closely related to precipitation. The slight displacement of the Beaverdam Spring data from the TLMWL may be due to minor impacts of short residence time, evaporation, and water-rock exchange reactions.

Stable isotope values for Beaverdam Spring waters were confirmed by additional groundwater samples collected during the same time period from a well constructed in the Tuscumbia Limestone-Fort Payne Chert aquifer near Meridianville in Madison County. The well was at a similar latitude and altitude as Beaverdam Spring and had $\delta^{18}$O and $\delta$D values of -5.3‰ and -29.9‰, respectively (fig. 7). These values suggest a short recharge period with low evaporation rates of infiltrating water.
CARBON STABLE ISOTOPES

Carbon stable isotopes in groundwater DIC analysis offers information about groundwater regarding the source of recharge and the existence of water-rock interaction processes. Measurements of carbon stable isotope ratio ($^{13}\text{C}/^{12}\text{C}$) of groundwater DIC offer the possibility of estimating subsurface water transport rates (Mook, 2000). DIC concentrations are reported in parts per million per liter (ppm/L), whereas isotope ratios are reported in the conventional delta ($\delta$) notation in per mil ($\%\text{o}$). $\delta^{13}\text{C}$ data are reported relative to Vienna Pee Dee Belemnite (VPDB) and the standard deviation for the measurements is $\pm 0.2 \%\text{o}$ ($1\sigma$). Standard deviation of the measurements is based on sample replicates as well as internal and international standards. Uncertainties of the $\delta^{13}\text{C}$ measurements are $0.5 \%\text{o}$ VPDB.

Figure 7.—Cross plot of $\delta^{18}\text{O}$ and $\delta\text{D}$ values for water samples from Beaverdam Spring and a test well at Meridianville relative to the Global Meteoric Water Line and the Tuscaloosa Local Meteoric Water Line.
Unconfined, shallow aquifers have $\delta^{13}C$ signatures very similar to those of pore-water and source waters. Groundwater DIC content is dependent on carbon dioxide (CO$_2$) content of the soil. In open systems, such as the vadose zone, the continuous supplement of CO$_2$ increases the DIC concentration. Dissolution of CO$_2$ and formation of H$_2$CO$_3^-$ increase the acidity of the infiltrating water, which facilitates limestone dissolution. Closed conditions arise however, in recharge areas characterized by fast infiltration rates to the aquifer. Similarly, soils with very little or no carbonates behave as closed systems. In these systems, the final DIC concentration is extremely low (Clark and Fritz, 1997). The $\delta^{13}C$ signature of deeper, semiconfined, and confined aquifers depends on groundwater residence times and geochemical processes that occur along flowpaths.

The type of vegetation present in recharge areas exerts significant influence on the $\delta^{13}C$ signature of the soil CO$_2$, and the eventual $\delta^{13}C$ signature of groundwater. Three photosynthetic cycles influencing this signature are the Calvin or C$_3$, the Hatch-Slack or C$_4$, and the Crassulacean acid metabolism (CAM) (Ehleringer and others, 1991). Calvin plants are dominant in most terrestrial ecosystems and have an average $\delta^{13}C$ signature of -27‰ (Vogel, 1993). Hatch-Slack plants are characteristic of hot, open environments (for example, tropical and temperate grasslands) (Ehleringer and others, 1991) and have an average $\delta^{13}C$ of -12.5‰ (Vogel, 1993). Crassulacean acid metabolism plants are characteristic of desert environments and switch between C$_3$ and C$_4$ pathways of CO$_2$ fixation from day to night. Their characteristic $\delta^{13}C$ signature ranges between -13 to 27‰ (Clark and Fritz, 1997).

Distinctive $\delta^{13}C$ values for organic and inorganic carbon (-27‰ to -12.5‰ for plants, -2‰ to +2‰ for marine carbonates, and -12‰ to +2‰ for soil carbonates) have been used to identify sources of DIC in groundwater (Deines and others, 1974). Beaverdam Spring discharge water was sampled and analyzed for $\delta^{13}C$ of groundwater DIC. The $\delta^{13}C$ and DIC values are -11.6‰ and 16.9 ppm/L, respectively. Given the relatively low values of DIC and $\delta^{13}C$, it can be inferred that recharge occurs under closed conditions, with fast percolation rates of precipitation to the water table (for example karsts or fractured aquifer media) (Clark and Fritz, 1997). Under open conditions, $\delta^{13}C$ values would be closer to or lower than -14‰ due to the fractionation occurring between DIC (HCO$_3^-$ + H$_2$CO$_3$) and soil CO$_2$ (Zhang and others, 1995).
The groundwater signature in the recharge area is affected by (1) soil CO₂ derived from the decay of terrestrial vegetation and respiration of plant roots and (2) carbonate bedrock dissolution by carbonic acid or sulfuric acid and organic acids enriched in the infiltrating water from the root zone. During the first process, δ¹³C values of pore water are most likely to average about -25‰ (Mook, 2000). After meteoric water infiltrates to the water table (second process), water/rock reactions shift δ¹³C signature towards more positive values (greater than -14‰). This shift in isotopic composition is dependent on the degree of dissolution of carbonate minerals, groundwater residence times, and mixing degree with different signature waters. The δ¹³C value (-11.6‰) lies near the combined average δ¹³C values of soil CO₂ and carbonate dissolution (fig. 8). Therefore, groundwater δ¹³C signature is mainly controlled by two factors: soil CO₂ and carbonate dissolution. Under these conditions, carbonate dissolution along flowpaths is the main reaction affecting the δ¹³C signature after recharge water enters the aquifer system.

Figure 8.—Cross plot of δ¹³C and DIC in the water sample collected from Beaverdam Creek.
CHLOROFLUOROCARBON AND SULFUR HEXAFLUORIDE
GROUNDWATER AGE DATING

Chlorofluorocarbons (CFCs), organic compounds containing carbon, chlorine, and fluoride (F), commonly known as Freon, have been widely used as refrigerants, propellants, and solvents (Rossberg and others, 2006). Approximately 1 million tons of CFCs were produced worldwide by 1974. Due to their multiple applications, they are believed to be the most useful chemical compounds that have ever been produced and no natural source has been discovered (Lovelock, 1971). The atmospheric lifetime of trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), and trichlorotrifluoroethane (CFC-113), those species used to date relatively young groundwaters, is 40, 100, and 85 years, respectively (Badr and others, 1990). Industrial use of CFC-12 started in 1930s, CFC-11 in the 1950s, and CFC-113 in the 1970s (Plummer and Busenberg, 2000). These compounds dissolve in precipitation, become part of the hydrologic cycle, and can be identified in groundwater that has been recharged in the past 50 years.

The observed decreasing concentrations of CFCs in the atmosphere over the last decade or so resulted in ambiguity in CFC-based apparent age estimation. Therefore, sulfur hexafluoride (SF\(_6\)) has been used as an alternative to CFCs for gas-solubility water dating (Busenberg and Plummer, 1997). Production of SF\(_6\) began in the 1960s for use in high voltage electrical switches. SF\(_6\) is extremely stable and has an estimated atmospheric lifetime of 800 (Morris and others, 1995) to 3,200 years (Ravishankara and others, 1993). SF\(_6\) analyses can be conducted with a precision of 1 to 3% using GC-ECD techniques (Wanninkhof and others, 1991; Law and others, 1994). Therefore, although atmospheric mixing ratios are small (currently about 4 parts per trillion by volume (pptv)), dating using this method is possible from about 1970. SF\(_6\) accumulation in the atmosphere is extremely rapid with a current growth rate of approximately 6.9% per year (Geller and others, 1997). Records retrieved from previously dated groundwater, seawater concentrations (Law and others, 1994), production records, and atmospheric measurements (Ko and others, 1993; Elkins and others, 1996; Maiss and others, 1996; Geller and others, 1997; Levin and Hesshaimer, 1996) were used to reconstruct the historical atmospheric mixing ratio of SF\(_6\).
Groundwater evaluations conducted by simultaneously using different tracers offer important information about groundwater travel times and age frequency distribution for mixed waters (Böhlke, 2002). This information is invaluable for important resource-management decisions. If no biological or geochemical processes alter the CFCs and SF$_6$ concentrations in aquifers and their source is of atmospheric origin, apparent ages can be evaluated. Generally, four independent ages are generated from the three CFC compounds and SF$_6$ concentrations. These apparent ages can be used as a crosscheck on the sampling and analytical methods, and used to evaluate mixing processes.

Estimated apparent ages using both CFCs and SF$_6$ dating tools can be affected by factors such as excess air, recharge temperature, and degradation of CFCs. Excess air represents the air bubbles trapped in groundwater during the recharge process. This trapped air slowly dissolves in groundwater, increasing the CFC concentration and underestimating the estimated age. This is not an issue for waters recharged prior to 1990 but affects dating of waters recharged after 1990 because of declining atmospheric CFC concentrations (Plummer and Busenberg, 2000). CFCs solubility is estimated based on the recharge temperature. Overestimation of the recharge temperature will result in CFCs concentrations greater than actual values and overestimation of groundwater ages (Busenberg and Plummer, 1992). CFCs are degraded by microbial activity in soils with high organic content and in anoxic waters with sulfate-reduction or methanogenesis. CFC-11 is the most degraded CFC compound, which leads to a decrease in concentration and age overestimation (Kazemi and others, 2006).

Generally, CFC ages are considered reliable when all three compounds generate similar dates. If the three ages do not agree, CFC-12 is considered the most reliable, followed by CFC-113, and lastly CFC-11 (U.S. Geological Survey, CFC Laboratory, written communication, 2003). CFCs compounds, and especially CFC-11, degrade easily in poorly oxygenated waters. In contrast, SF$_6$ is stable in low-dissolved oxygen conditions (Robinson, 2004).

The water sample from Beaverdam Spring was collected from fractured chert at one of the spring discharge points. The sample was collected using a peristaltic sampling pump outfitted with viton tubing inserted as far into a fracture as possible to prevent introduction of air. Results of CFCs analysis revealed that the sample was supersaturated.
with CFCs, which indicates that the sample was contaminated with atmospheric gases, negating valid age estimation. Analytical results of SF$_6$ yielded an age greater than 40 years, which indicates concentrations of SF$_6$ larger than atmospheric concentrations, suggesting that other sources of SF$_6$ exist in the recharge area, also negating valid age estimation.

**SUMMARY**

The single remaining native pygmy sunfish population occupies just 5 river miles of the Beaverdam Springs complex. Critical habitat was designated both for Beaverdam Springs and Creek, where the species survives, and for the Pryor and Branch Spring complex. The purpose of the Beaverdam Spring hydrogeologic assessment is to characterize the hydrogeology of the project area and to specifically identify the spring recharge area, groundwater flow paths, quantity of spring discharge, and water quality. These data will facilitate conservation practices for the protection of Beaverdam Spring, the spring pygmy sunfish, and its habitat.

The dominant stratigraphy in the project area consists of Lower to Middle Mississippian Fort Payne Chert and Middle Mississippian Tuscumbia Limestone. The Fort Payne Chert has an average thickness of about 160 feet and is exposed as regolith in the eastern two-thirds of the project area, although relatively unweathered exposures exist along the bluff line where Beaverdam Spring discharges. The Tuscumbia Limestone is exposed along the western margin of the Beaverdam Creek watershed and has an average thickness of about 150 feet. The contact with the Fort Payne Chert is about 0.5 mile north from the discharge area for the spring.

The Tuscumbia Limestone and Fort Payne Chert aquifer in the project area is primarily unconfined due to shallow depths and absence of confining layers that isolate groundwater from the water table and the land surface. Therefore, groundwater movement is controlled by gravity as water moves from topographic highs to topographic lows where it discharges as springs or to surface-water bodies. Groundwater movement in Paleozoic aquifers is preferential with respect to direction and velocity, related to the geometry and connectivity of fracture systems.

The recharge area for Beaverdam Spring was determined using a combination of topographic analysis and evaluation of groundwater level mapping. The recharge area for
the spring is about 1.7 mi² and extends from the western Beaverdam Creek watershed boundary eastward to the eastward sloping topography near Oakland Spring Branch. The northern extent of the recharge area is Huntsville Browns Ferry Road where the topography slopes northward. The southern boundary of the recharge area is the bluff line where the spring discharges.

Since Beaverdam Spring discharges along a bluff line about 4,000 feet long and eventually flows into Beaverdam Creek, direct measurement of spring discharge is not possible. Therefore, two methods of groundwater recharge estimation (water budget and hydrograph separation) were used to estimate groundwater recharge in the project area and the discharge from Beaverdam Spring.

A unit discharge was established to calculate total base flow discharge for the area downstream from the Beaverdam Creek discharge area, which when subtracted from the downstream Beaverdam Creek discharge, leaves the value of Beaverdam Spring discharge. This method yielded a spring discharge of 4.5 cubic feet per second (cfs) or 2,020 gallons per minute (gpm). The recharge rate calculated using the water budget values is 37.25 inches per year (in/yr).

The second method of groundwater recharge estimation employed discharge data from the nearest continuous discharge measurement station, analyzed using the Web based Hydrograph Analysis Tool (WHAT) automated hydrograph separation computer program. This program separates stream runoff and base flow, which is used to calculate volumes of groundwater recharge. The nearest long-term discharge data set was the U.S. Geological Survey monitoring site (gauging station 3576250) on Limestone Creek, which is adjacent to Beaverdam Creek to the west. Groundwater recharge using the WHAT program output was 15.03 (in/yr). This value was checked using the Meyboom graphical hydrograph separation method, which yielded a value of 13.21 in/yr. When the average value from the methods (14.12 inches) is applied to the recharge area of Beaverdam Spring, the resulting discharge is 1.7 cfs or 766 gpm.

Although the recharge value obtained from the hydrograph separation methods is reasonable for karst terrains, the disparity in values between the water budget and hydrograph separation methods is most likely the result of a significantly larger recharge rate than the average rate for Tennessee Valley carbonate aquifers. This is probably caused by unusually high precipitation infiltration and aquifer permeability related to
minimal runoff and evapotranspiration rates due to the dominance of row crop agricultural land use and a lack of vegetation in much of the recharge area and concentrated karst development.

Groundwater samples from Beaverdam Spring discharge were collected on March 29, 2012, and analyzed for physical properties and chemical and isotopic composition. The purpose of these analyses is to characterize the spring discharge with respect to water quality, geographic extent of recharge, and land-use impacts on recharge. Physical properties of groundwater were also tested in the field and included turbidity, temperature, pH, specific conductance, oxidation reduction potential, and total dissolved solids.

Turbidity of the spring water was 0.8 nephelometric turbidity units, which is extremely clear water with minimal suspended particles. The pH was 6.2, which is slightly acidic and related to acidic precipitation that is normal for north Alabama. Specific conductivity was 129 microsiemens per centimeter, which is relatively low but typical for shallow groundwater with relatively short residence time and little or no contaminants. The oxidation reduction potential was 273 millivolts (mV), which indicates an oxidized subsurface environment, typical for shallow aquifers. Measured total dissolved solids were 95 milligrams per liter (mg/L), which indicates fresh, relatively uncontaminated groundwater.

Water samples collected from Beaverdam Spring were analyzed for 60 constituents that include metals, inorganic non-metals, nutrients, and a selected group of organics. These constituents, when evaluated collectively and individually, provide information about water quality, land use impacts in the recharge area, and aquatic species and habitat impacts.

The U.S. Environmental Protection Agency (USEPA) compiled national recommended water quality criteria for the protection of aquatic life and human health in surface water for approximately 150 pollutants. The concentration of NO₃ as N for the water sample collected from Beaverdam Spring was 2.77 mg/L. This is more than five times above the suggested standard for excessive algae growth and indicates excessive nitrate in the groundwater system that most likely originates from row crop agriculture and animals in the recharge area. Total nitrogen was also 2.77 mg/L, which is about four times the USEPA recommended concentration for the protection of aquatic wildlife.
Total phosphorus in the spring water sample was 0.061 mg/L, which is about 1.7 times the USEPA recommended concentration for the protection of aquatic wildlife. Elevated phosphorus concentrations probably originate from row crop agriculture and animals in the Beaverdam Spring recharge area.

Numerous metals are naturally present in streams in small concentrations. However, toxic metals in streams are usually a result of man’s activities. The water samples collected from Beaverdam Spring were analyzed for 14 metallic constituents included in the USEPA recommended water quality criteria for the protection of aquatic life and human health. Only chloride, iron, and zinc were detected and none of those exceeded the recommended criteria.

Although not included in USEPA criteria, calcium, fluoride, potassium, magnesium, sodium, silica, sulfate, strontium, and vanadium were also detected in small concentrations in the water sample collected from the spring. These occur naturally, are common constituents in Alabama streams, and are a result of dissolution or erosion of rocks and sediment.

Isotopes can be used as tracers of water movement, since unique isotopic signatures are characteristic to particular recharge environments. As part of this investigation groundwater samples from Beaverdam Spring were analyzed for anthropogenic, natural, and stable isotopes such as chlorofluorocarbons (CFCs), sulphur hexafluoride (SF₆), carbon (δ¹³C), oxygen (δ¹⁸O), and hydrogen (δD). These analyses provide essential measurements to identify the environment from which groundwater originated and constrain the period of time during which recharge occurred.

The δ¹⁸O and δD values for samples collected from Beaverdam Spring were -5.4‰ and -29.0‰, respectively. When these cross plotted values were compared to the Tuscaloosa Local Meteoric Water Line, they fall slightly below (increase of δ¹⁸O) and to the right (decrease of δD) of the line. This indicates that the spring discharge is relatively young groundwater and is closely related to precipitation. The slight displacement from the line may be due to minor impacts of short residence time, evaporation, and water-rock exchange reactions.

Carbon stable isotopes in groundwater dissolved inorganic carbon (DIC) analysis offers information about groundwater regarding the source of recharge and the existence of water-rock interaction processes. Beaverdam Spring discharge water was sampled and
analyzed for $\delta^{13}\text{C}$ of groundwater DIC. The $\delta^{13}\text{C}$ and DIC values are -11.6‰ and 16.9 ppm/L, respectively. Given the relatively low values of DIC and $\delta^{13}\text{C}$, it can be inferred that recharge occurs under closed conditions, with fast percolation rates of precipitation to the water table (for example karsts or fractured aquifer media).

Chlorofluorocarbons (CFCs), organic compounds containing carbon, chlorine, and fluoride (F), commonly known as Freon, have been widely used as refrigerants, propellants, and solvents. The atmospheric lifetime of trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), and trichlorotrifluoroethane (CFC-113) is 40, 100, and 85 years, respectively. These compounds dissolve in precipitation, become part of the hydrologic cycle, and can be identified in groundwater that has been recharged in the past 50 years. The observed decreasing concentrations of CFCs in the atmosphere over the last decade or so resulted in ambiguity in CFC-based apparent age estimation. Therefore, sulfur hexafluoride ($\text{SF}_6$) has been used as an alternative to CFCs for gas-solubility water dating. Production of $\text{SF}_6$ began in the 1960s for use in high voltage electrical switches. $\text{SF}_6$ is extremely stable and has an estimated atmospheric lifetime of 800 to 3,200 years.

Samples collected from Beaverdam Spring were analyzed for CFCs and $\text{SF}_6$. Results of CFCs analysis revealed that the sample was supersaturated with CFCs, which indicates that the sample was contaminated with atmospheric gases, negating valid age estimation. Likewise, analytical results of $\text{SF}_6$ yielded an age greater than 40 years, which indicates concentrations of $\text{SF}_6$ larger than atmospheric concentrations, suggesting that other sources of $\text{SF}_6$ exist in the recharge area, also negating valid age estimation.

**CONCLUSIONS AND RECOMMENDATIONS**

Beaverdam Spring is a spectacular natural resource with unique habitat and species, which should be protected and preserved. The hydrogeologic assessment performed by the Geological Survey of Alabama indicates that the spring is sourced from a limestone and chert aquifer with extensive karst development that results in local recharge and rapid infiltration of precipitation and runoff into the groundwater system. These hydrogeologic characteristics cause the spring to be vulnerable to drought and land-use changes that modify the quality and quantity of water infiltrating into the subsurface. This vulnerability includes a number of contaminants that influence groundwater quality, including nutrients and organic compounds. Excessive
concentrations of nitrate and phosphorus were measured in the spring discharge, most likely originating from row drop agriculture in the recharge area.

Additional scientific evaluations and continuous data collection is needed to formulate plans and actions that will protect the spring and spring habitat and species. Recommendations for future scientific evaluations include additional study and refining of the water budget for the spring area and collection of additional discharge data from Beaverdam Creek downstream from the spring to establish a rating curve. Once rated, discharge should be monitored continuously to detect changes in spring discharge. Water withdrawals in the spring recharge area should be identified and evaluated with regard to the spring water budget. Spring discharge samples should be collected regularly and analyzed for nutrients and organic compounds. Water temperature, turbidity, and specific conductance should be monitored continuously at one of the major spring discharge points. A source water protection assessment should be performed and updated regularly in the recharge area to identify threats to spring water quantity and quality.

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