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Do Limestone Quarries Act as "Engineered Sinkholes"? Analysis of Exfiltration of Groundwater from Limestone Quarries in the Boone Formation, Ozark Physiographic Province, Arkansas, USA

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Do Limestone Quarries Act as "Engineered Sinkholes"?
Analysis of Exfiltration of Groundwater from Limestone Quarries in the Boone Formation,
Ozark Physiographic Province, Arkansas, USA

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Abstract

Limestone quarries are a source of construction materials that are utilized in our everyday lives. Karst landscapes cover up to 15 percent of the Earth's surface, and limestone quarries are found in these environmentally sensitive regions where groundwater and surface-water interactions are dynamic and complex. Several studies have provided conceptual models of groundwater flow to and out of quarries. The goal of this research was to describe the geochemistry of water exfiltration from limestone quarries in karst regions via joints, fractures, faulting, or karst features and to determine if limestone quarries are "engineered sinkholes"; that is to say: did quarries, by nature of removal of overlying regolith and subsequent excavation into bedrock, act to increase infiltration into karst groundwater systems, potentially effecting some influence on groundwater chemistry? Water chemistry, water stable isotopes and dye trace data were used as means for characterizing groundwater flow out of and near limestone quarries. Connections between quarries and nearby springs were established based on evaporation indicated by water isotopes and similar trends in nitrate, calcium, chloride, and other water chemistry characteristics data. The dye trace conducted did not prove a connection between a dry quarry and nearby springs during the study period, further highlighting the complexities of groundwater flow in karst landscapes. Nitrate, pH, calcium, and alkalinity water chemistry characteristics between springs near quarries and springs near sinkholes were statistically different indicating that the differences in soil cover may have a great impact on water chemistry and nutrient transport. Because of the differences between sinkholes and quarries, applications of geologic time were considered for the formation of soil and karst features at active, dry, and lake quarry sites. Groundwater is flowing out of limestone quarries in karst landscapes via joints, fractures, and conduits even though signatures of quarry water was not found in all of the

monitored springs. The data from this study suggests that a deeper, regional groundwater flow path into large springs and spring-fed streams is the likely output of water from limestone quarries in karst landscapes.

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I.   Introduction

Limestone quarries are a source of construction materials and revenue in the United States and other countries. While limestone quarries benefit economies and provide an important resource, quarries create a potential for alteration and harm to the environment, particularly the aquatic environment of karst settings. Karst features, such as sinkholes, springs, caves, and other conduits, large and small, are characteristic of karst limestone terranes and provide a direct link between surface-water and groundwater. When a quarry is constructed in a karst area, the regolith, which provides a zone of hydraulic separation and filtration, is removed and contaminants are more easily introduced into the subsurface and groundwater. While several studies have determined that groundwater contributes flow to limestone quarries (Motyka and Postawa, 2000; Lolcama, Cohen, and Tonkin, 2002; Botta et al., 2009), few studies provide analysis of water flowing out of limestone quarries (Hobbs and Gunn, 1998; Miller, Lyons, and Davis, 1996); whereas what flows in must flow out under any long-term, near-equilibrium condition. Surprisingly no studies have attempted to find the connection of groundwater flowing out of quarries with karst groundwater through geochemical methods. The goal of this research is to describe the geochemistry of water exfiltration from limestone quarries in karst regions via joints, fractures, faulting, or karst features and to determine if limestone quarries are "engineered sinkholes"; that is to say: do quarries, by nature of removal of overlying regolith and subsequent excavation into bedrock, act to increase infiltration into karst groundwater systems, potentially influencing groundwater chemistry?

The quarrying of limestone is the main source of gravel and cement for roads and other construction purposes. More than $12.8 billion of crushed stone aggregate was produced in the United States in 2014. Of that production, almost 70% was crushed limestone and dolomite (U.S.

Geological Survey, 2015). As the human population increases, the demand for crushed aggregate for construction will increase for buildings, roads, and other structures.

Eventually, quarries exhaust the economically accessible resource or available land space. When a quarry has stopped production, the options applied for reclamation of the site are most commonly to fill the quarry with dirt and gravel—which often are much more permeable than original strata—or to let the quarry fill naturally with water (quarry lake). The properties of quarry/pit lakes differ from natural lakes in that quarry lakes usually are deeper and smaller, bound by very steep topographic relief, and can vary geochemically (Miller, Lyons, and Davis, 1996).

Regulations and guidelines of quarry reclamation vary by state in the United States. Virginia requires a reclamation plan for each quarry with the initial application of proposed mining. Mining below the water table requires plan detail on the impacts on the local hydrologic budget and minimizing water-quality impacts. Land-use upon reclamation of the quarry can be any legal land type; revegetation of the reclaimed area has specific guidelines (Reclamation Regulations for Mineral Mining, 2003). Nevada and other western states have stricter regulations for the quarry pit lakes because the common practice of strip-mining for sulfide metal ores ultimately results in acidic pit lakes. Where groundwater contamination is a concern, the design of the metal quarry must address concerns (Miller, Lyons, and Davis, 1996). In Arkansas, exhausted quarries can be reclaimed as lakes, timberlands, pastures, wetlands, or any combination of the previously listed (ADEQ, 1997). Lake quarries are not highly regulated in Arkansas as compared with other states. In the mid-1990s, The Arkansas Quarry Operation, Reclamation, and Safe Closure Act (Quarry Act) was established as law by the Arkansas Department of Environmental Quality (ADEQ). Under this act, all intended quarry operations

must submit a Notice of Intent to Quarry to the ADEQ prior to any quarry activities on the land. In these forms, a Notification of Intent to Reclaim Quarry must be signed, stating that the quarry will be reclaimed under Quarry Act regulations (ADEQ, 1997). However, no description of how the quarry will be reclaimed is required. Many quarries across the state existed before the Quarry Act was enacted. Some of those were grandfathered in and others stopped operation to avoid stricter regulations.

Karst regions inevitably include limestone quarries. Karst landscapes make up about 10 to 15 percent of the Earth's surface (Palmer, 2007). In these landscapes, the interconnectedness of surface and groundwater is complex and dynamic; therefore, the risk of contamination to groundwater by surface sources is increased. Natural surficial input points for surface water in karst systems include sinkholes, sinking springs, losing stream reaches, open fractures, and other permeable paths. Quarries may act as "engineered sinkholes", and furthermore quarries lack any regolith that often would be an isolation zone and filter for water that enters the subsurface. A study to determine sources of spring water in a sinkhole plain in Indiana found that more than 50 percent of a storm pulse through the spring was water from the vadose (soil and epikarst) zone (Lee and Krothe, 2001). The missing soil and epikarst (the zone between the soil and heavily karstified bedrock that has undergone limited weathering) zones also result in reduced evapotranspiration and increased effective rainfall infiltration in these quarry areas—a higher proportion of rainfall infiltrates into the subsurface (Hobbs and Gunn, 1998).

Forty percent of people in the United States get their drinking water from karst aquifers (USGS, 2012); therefore, understanding all inputs and pathways of surface water into groundwater is important. The chemicals that may enter the systems and their sources are also important when considering drinking water and the health of water bodies. The metal-ore pit

lakes of the west are known to be potentially harmful to groundwater and the environment surrounding those quarries. In a study by Miller, Lyons, and Davis (1996), groundwater was conceptually modeled to enter and flow out of the quarries. Monitoring groundwater within and proximal to the metal-ore quarries has provided insight as to when a geochemical equilibrium is reached in the quarry water and groundwater (Miller, Lyons, and Davis, 1996). Hobbs and Gunn (1998) discuss several impacts on water quality from limestone quarries. These include suspended-sediment load and fuel-oil spills. They also state that runoff from the land surface into the quarries occurs because of regolith removal; however, no impacts on water quality related to lithology, nearby land use, or evapoconcentration are discussed. Water chemistry depends on the lithology and source of the water. Limestone quarries are expected to be high in calcium and magnesium and other major ions depending on the specific rock type (Galas, 2003). Increased nitrate levels in karst systems are due to anthropogenic-based processes such as fertilizer application and animal agriculture (Peterson et al., 2002), as well as wet deposition from precipitation (Dentener et al., 2014). As water sits in a quarry, evapoconcentration is likely to occur unless inflow and outflow of the water are greater than evaporation processes (Eary, 1998).

Stable isotopes, in combination with major and minor ions, are useful tracers in karst aquifers (Lee and Krothe, 2001; Panno et al., 2001; Barbieri et al., 2005). Stable isotope data can help determine sources of the water and contaminants that may flow through the karst conduits. Water isotopes, oxygen and hydrogen, can be used to trace groundwater recharge of springs because values tend to vary spatially (Barbieri et al., 2005) and organic or geologic materials have minimal impacts on the water isotopic composition (Kendall and Caldwell, 1998). The two main factors that influence water isotopic composition are phase changes (evaporation, melting, or condensation) and mixing of water from multiple sources or recharges (Kendall and Caldwell,

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1998). Evaporation, which may occur in quarry lakes, is visible in oxygen isotope signatures, imparted through fractionation of light and heavy isotopes (Clark and Fritz, 1997). Water-stable isotopes in combination with ion concentrations of groundwater can also provide insight about mixing of multiple sources (Burns et al., 2001; Kendall, McDonnell, and Gu, 2001; Lee and Krothe, 2001). In addition to understanding groundwater mixing, ions can indicate the flow path of the ground water. High concentrations of ions often indicate that the residence time of water on a given flow path is long enough to allow dissolution and reflect the minerals and ions that the water comes into contact with (Kendall, McDonnell, and Gu, 2001; Hem, 1985).

Dye traces have been proven to aid understanding of groundwater flow in karst landscapes, where the flow of groundwater may be complex (Imes and Fredrick, 2002; Aley, 1988). From the slope of the dye concentration curve, we can determine if the flow is conduit based, diffuse, or both. This can be important for contaminants that may be introduced to the karst system and how they will flow through the karst conduits and groundwater (Wicks and Hoke, 2000).

While we know that groundwater can flow into limestone quarries (Motyka and Postawa, 2000; Lolcama, Cohen, and Tonkin, 2002) and will potentially flow out of quarries (Hobbs and Gunn, 1998; Miller, Lyons, and Davis, 1996), we still do not know the impacts on the groundwater quality. Especially the impacts that lake and exhausted quarries pose on groundwater quality. This research is important in the United States and worldwide to better understand anthropogenic processes and how they may alter groundwater quality in karst regions.

II. Geologic and Environmental Background

Limestones are a major component of the hydrogeologic framework of the Ozarks Plateaus in Northwest Arkansas. Multiple formations in the Ozarks Plateaus (Ozarks) are karstic. The karst landscape of the Ozarks region has often been demonstrated to be susceptible to contamination (Peterson et al., 2002; Kresse et al., in review; Brion et al., 2011; Adamski and Pugh, 1996). Karstified limestones of Northwest Arkansas, such as the Boone and Pitkin Formations, also make durable aggregate for construction purposes (Kline, 1999).

In this study, selected quarries all were in the Boone Formation. While the Pitkin Limestone is the more highly preferred aggregate rock due to the purity of the limestone (Kline, 1999), the Boone Formation outcrops and is accessible across a larger land area (Frezon and Glick, 1959). The Boone Formation is a Mississippian-age, cherty limestone that is the target of many aggregate quarries. Lithologic descriptions of the Boone Formation characterize the rock as being a finely crystalline limestone interbedded with gray chert (Frezon and Glick, 1959). The amount of chert varies vertically and horizontally, but comprises up to 90 percent of the Formation in some areas. Most descriptions of the Boone note the dissolutional karst features (sinkholes, springs, and caves) that are common throughout the Formation (McFarland, 1998). The St. Joe Member of the Boone Formation is at the base of the unit. Crinoid fossils, light gray to reddish brown color, and finely crystalline limestone characterize the St. Joe Member. In most places the Boone Formation is between 300 and 450 feet thick (including the St. Joe Member); the St. Joe Member is less than 100 feet thick. Over the Ozarks region, the Boone Formation has a general trend of dipping to the south (Frezon and Glick, 1959).

Throughout the Ozarks, the Boone Formation is often covered by soil and a thick, clayey regolith, or mantle, which can hide the surficial expression of karst features (Parse, 1995). The

thickness varies with lithology, structure, age of the landscape, jointing, and the location of the groundwater table in past and present. The regolith is also likely to be thicker on old, stable, low-gradient surfaces, as compared to steep slopes where wasting processes occur (Madole et al., 1991). Because the regolith can be more than 46 meters deep in some places, the karst features are often overlooked. Even though the regolith is a thick, usually low permeability mantle, the underlying karstified Boone Formation is still subject to dissolution processes (Parse, 1995). While the regolith may protect the groundwater from some contaminants, the regolith is not fully impermeable, and some water affected by surface processes infiltrates into karst conduits.

During the late Paleozoic a series of deformational events related to the Appalachian-Ouachita orogeny occurred in the Ozark Plateaus. These events resulted in faults, fractures, and joints that generally trend northeast-southwest and north-south in northwest Arkansas (Cox, 2009). Solution conduits have formed along faults, joints, fractures, and bedding planes because the openings provide an incipient, permeable flow path for water. Many karst features are known to form along these brittle-deformation zones (Ford and Williams, 2007). In the Missouri Ozarks, karst features have been proven to follow joint trends (Orndorff, Weary, and Sebela, 2001).

The economy for aggregate in the Ozarks Physiographic Province (Ozarks) is constant because states to the south (Mississippi and Louisiana, for example) that do not have hard rock to quarry and depend on Arkansas for the needed materials (Kline, 1999). Use of the rock coupled with the regional importance of the Boone Formation as an aquifer make understanding the influence of limestone quarries on groundwater quality of great import. As previously mentioned, studies show that groundwater flows into quarries – and some indicate that groundwater is flowing out of the quarries, but none of these quantifies or provides detail on the relation between the quarry and surrounding groundwater. The limestone quarries in the Boone

Formation of the Ozarks in northwest Arkansas and the aquifers that underlay the plateau hold the answer to this gap in knowledge. While the Boone Formation is limited to the Ozarks, the methods and findings of this study can be representative and applied to limestone quarries and groundwater flow in other karst regions.

III.   Methods

To better understand the effect of quarries on groundwater quality in karst regions, groundwater resurgences proximal to quarries were measured and analyzed. Preexisting data from springs near sinkhole clusters were gathered to compare to the water quality of springs near quarries. Quarry sites were chosen based on geology, topographic location, and availability of groundwater sampling locations. A variety of quarries were chosen to examine differences in active or inactive and lake (saturated zone) or dry (unsaturated zone). Water-quality samples and water isotope samples were collected at springs and gaining streams within a close proximity to the quarries. A dye trace was completed at one of the quarries to determine an existing connection between the quarry and groundwater.

A.   Quarry Site Selection

The limestone quarries were selected based on geology and availability and possible connection to groundwater sampling locations. All quarries in the study are located in the Boone Formation in the Ozark Plateaus of northern Arkansas. Coordinates of quarries located in the Boone Formation were gathered from Kline (1999) (Figure 1). Each of the selected sites had a spring located within a mile of the quarry (determined from topographic maps and ESRI ArcGIS). This resulted in 11 potential quarries for the study. The areas surrounding the quarries were field checked for additional springs.

Due to anthropogenic activities (filling of quarries to build subdivisions or roads) and inability to contact land owners, three quarry sites were selected as suitable and accessible for the study. A dry, inactive (Lead Hill Quarry), a wet, inactive (St. Joe Quarry), and a wet, active quarry (Sharps Quarry) were chosen from the eleven initial potential sites (Figure 1). Wet versus dry and active versus inactive quarries were chosen to provide insight into which types of quarries may have the largest effect on groundwater quality.

B.   Field Methods

An initial field-site reconnaissance was completed to determine if the quarry and surrounding springs would be useful in determining if water flows from the quarry into groundwater and if the quarry acts as an "engineered sinkhole". In many cases, landowner interviews were conducted to find the location of unmapped springs. Rock dip direction and geologic maps were useful in attempting to determine groundwater flow direction and springs that likely integrate flow from the quarry. Coordinates of the locations were recorded using the World Geodetic System of 1984 (WDS84) (Table 1). The topographic position of each quarry was also noted. Quarries at a topographic high will generally receive water from a smaller drainage basin than quarries at a topographic low which can result in different water-quality characteristics in the springs and lake quarries.

The Lead Hill Quarry (36° 21' 59.16" N, -92° 57' 56.77" W) is a dry, inactive quarry that is located on the top of a hill. On the northeast, eastern, and western sides of the base of the hill are several springs and seeps. The current landowner dug ponds where many of these springs are located to provide water for livestock. Three springs were used for sampling at this site (Figure 2). Sheep Field Spring (36° 22' 02.11" N, -92° 57' 30.23" W) is one of the springs that feeds a pond in the sheep field northeast of the quarry. Barn Spring (36° 21' 56.54" N, -92° 57' 39.09"

W) is another spring that feeds a larger pond east of the quarry. Brother Spring (36° 22' 10.10"N, -92° 57' 28.31" W) is a constantly flowing spring northeast of the quarry that has been modified to include concrete casing and a hose. The quarry is dry (above the water table); therefore, no water was collected from the quarry. Because of the ideal topographic location of Lead Hill Quarry, the abundance of springs at the base of the hill, and the likely hydraulic connection between the quarry and springs, a dye trace was conducted at the quarry.

The St. Joe Quarry (36° 01' 09.73" N, -92° 48' 21.68" W) is a wet, inactive quarry. Topographically, the quarry is located in the middle of a slope above Mill Creek. Water samples were collected from the western side of the quarry (Figure 3). A short stretch of an intermittent stream that was rapidly gaining water from groundwater discharge (36° 00' 56.4" N, -92° 48' 11.2" W) and flows into Mill Creek was sampled to the southeast of the quarry to see if groundwater is flowing out of the quarry. For the purposes of this study, the groundwater sampling location will be called the 'groundwater-fed drainage'.

Sharp's Quarry (36° 13' 53.30" N, -94° 11' 03.73" W) is an active quarry that has been mined below the water table in some sections of the quarry. The quarry is located at a topographic high with Puppy Creek flowing along the base of the eastern and southern walls of the quarry. The sump inside the quarry was sampled with permission from the quarry operators (Figure 4A). Field Spring (36° 13' 22.17" N, -94° 11' 13.24" W) was sampled in a field south of Sharp's Quarry. The spring forms a pool of water, in which water cress (a plant that only grows where cool water is present year-round, often indicative of groundwater input) grows, in the field that flows into Spring Creek (Figure 4B). The exact location of upwelling was unclear.

Table 1. A brief description and coordinates (degrees, minutes, seconds) of the quarry and spring sites of the study.

Name	What is it?	Latitude	Longitude
Lead Hill Quarry	Dry, inactive Quarry	36 21 59.16	-92 57 56.77
Sheep Field Spring	Spring, feeds pond	36 22 02.11	-92 57 30.23
Brother Spring	Spring, cased	36 22 10.10	-92 57 28.31
Barn Spring	Spring, feeds pond	36 21 56.54	-92 57 39.09
Sharps Quarry	Active Quarry, wet	36 13 53.30	-94 11 03.73
Field Spring	Spring	36 13 22.17	-94 11 13.24
St. Joe Quarry	Wet, inactive quarry	36 01 09.73	-92 48 21.68
Gaining Drainage	Gaining drainage near quarry	36 00 56.4	-92 48 11.2

Water Sample Collection

Water samples were collected from the quarries and springs under base-flow and storm-flow hydrologic conditions. The samples were analyzed for major ions, metals, nutrients, total organic carbon, and water isotopes (oxygen and hydrogen isotopes). Major ions, metals, total organic carbon, and nutrients samples were analyzed by the environmental laboratory in the Technical Services Division of the Arkansas Department of Environmental Quality (ADEQ). The saturation index of calcite and partial pressure of carbon dioxide of the quarries and springs were calculated from the major ions. Isotope analysis was completed at the University of Arkansas Stable Isotopes Laboratory (UASIL). Deuterium excess in the water isotope values were calculated and the isotopic values were compared to the local meteoric water line. Temperature, pH, and specific conductance were observed and recorded while samples were being collected.

Isotope precision methods as described by Gehre et al. (2004) and Nelson (2000) are utilized by the University of Arkansas Stable Isotope Laboratory (UASIL). To overcome memory effects of the high temperature conversion elemental analyzer (TC/EA), four or five samples are injected (Gehre et al., 2004). The water samples are split into hydrogen and carbon

monoxide by the TC/EA before being sent to the mass spectrometer. The results from the mass spectrometer are then normalized by two water standards to produce the results that are published (Nelson, 2000). The goal of the isotope precision methods at UASIL is to be better than 1‰ for δD and 0.5‰ for $\delta^{18}O$.

Locations of water-sample collection varied by site. For the wet quarries, water samples were collected from the most easily accessible location. At Sharps Quarry, the water samples were collected from the northern side of the sump in the western section of the quarry. Water samples from the St. Joe Quarry were collected at the upper western side of the quarry where an overgrown access road leads down to the water. For the springs, water samples were collected at the point where the most water seemed to be upwelling or as close to that point as possible. Field Spring, associated with Sharps Quarry, was sampled on the northwest side of the pool created by the upwelling of the spring. The gaining stream segment, associated with the St. Joe Quarry, was sampled at a bedrock portion of the drainage where water discharge appeared to increase (coordinates listed in the "Field Methods" section above). Barn Spring and Sheep Field Spring, associated with Lead Hill Quarry, were both sampled on the western side of the ponds where the highest discharge from the spring occurred. Water samples from Brother Spring, near Lead Hill Quarry, were collected from the hose protruding from the encased spring, which faces east.

The calcite saturation index of each of the water samples was calculated using major ions and field parameter data. The graphical interface of *Phreeqc*, a computer program for geochemical calculations available through the U.S. Geological Survey, was used to input temperature, pH, and the major ions (calcium, magnesium, sodium, alkalinity, chloride, nitrate, potassium, zinc, and sulfate) of the water samples to calculate saturation indices. The saturation index equation is :

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$$SI = logIAP/K \qquad (1)$$

where SI is the saturation index; IAP is the ion activity product, which are the concentrations of calcium and carbonate for calcite; and K is the thermodynamic equilibrium constant (Ford and Williams, 2007).

For this study, the calcite saturation index was the important result from *Phreeqc* because the Boone Formation is a karstic limestone that is actively undergoing geochemical processes, including dissolution and mineral precipitation. Calcite dissolution (negative saturation index) and precipitation (positive saturation index) of the limestone was determined by the saturation index. Percent error, a charge balance between cations and anions that provides a quality-control criterion for assessment of general chemistry data quality, was also calculated by *Phreeqc*.

The partial pressure of carbon dioxide (P_{CO2}) was calculated for each of the water samples to better understand the dissolutive properties of the waters. Henry's Law, which states that the partial pressure of the gas and the concentration of the gas are proportional at equilibrium and constant temperature, was used to calculate P_{CO2}:

$$C_{CO2} = K_H \times P_{CO2} \qquad (2)$$

where K_H is the temperature dependent constant for Henry's Law; and C_{CO2} is the concentration of carbon dioxide in solution (Palmer, 2007).

K_H was calculated using *olm*, a Python package that is capable of performing geochemical calculations (Covington et al., 2015). The concentrations of carbon dioxide, as molality, were calculated by *Phreeqc*. P_{CO2} has the strongest influence on dissolution rates (Covington et al., 2015); therefore, more carbon dioxide in the water results in a higher dissolution rate.

Atmospheric P_{CO2} is 0.0004 atm at sea level (Palmer, 2007), soil P_{CO2} ranges from 0.01 to 0.1 atm (Brook et al., 1983), and cave P_{CO2} ranges from 0.001 to 0.01 atm (Palmer, 2007).

C.   Sinkhole Related Spring Selection

The sinkholes were used to understand if the limestone quarries have similar effects on water-quality characteristics as sinkholes. As the sinkholes in the mantled karst of northwest Arkansas generally have a mantling cover of regolith of varying thickness and the quarries do not, differences between the water quality data from the sinkholes and quarries are expected. Sinkholes in the Ozark Plateaus physiographic region of Arkansas were digitized using ESRI ArcGIS and historical and new U.S. Geological Survey (USGS) topographic maps. Hachure marks on the topographic maps indicate depressions which were called sinkholes in this case. Depressions containing water on the topographic maps or on Google Earth were not labeled sinkholes.

Preexisting water-quality data of springs from the National Water Quality (NWQ) portal were added to the map and compared to the sinkhole locations. The NWQ portal includes data from the U.S. Geological Survey National Water Information System (NWIS) and the U.S. Environmental Protection Agency (EPA). The water-quality data for the springs includes date, time, coordinates, pH, alkalinity, chloride, sulfide, magnesium, sodium, potassium, nitrate, and calcium.

To compare the sinkholes to quarries, springs within at least three kilometers of a group of sinkholes (more than two sinkholes within 1 kilometer proximity) in the Ozarks Plateau physiographic region of Arkansas were selected to represent potentially sinkhole-recharged springs. The Boone Formation generally dips slightly to the south – about 10 feet per mile

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(Frezon and Glick, 1959); therefore, selected sinkhole springs were usually south of sinkhole groups. From these specifications, three springs were selected to represent sinkhole-recharged springs (Figure 5). The springs are located in Benton and Washington Counties in Arkansas. The water-quality data from the sinkhole-recharged springs were compared to the water quality data collected at the springs near the quarries to answer the research question of limestone quarries being engineered sinkholes.

Phreeqc and *olm* were also used to calculate the calcite saturation index and partial pressure of carbon dioxide of the sinkhole-recharged springs using Equations 1 and 2. Because preexisting data were used for the sinkhole springs, the saturation index analysis in *Phreeqc* was completed using fewer attributes than the quarry and spring water samples that were collected for this study. Dissolution or precipitation of calcite was determined for the spring water near sinkholes. The calcite saturation indices and the partial pressures of carbon dioxide of the sinkhole related spring water were compared to the springs near quarries to determine if differences occur in the water chemistry between the two sets of springs. Percent error of the ion exchange was also calculated by *Phreeqc* as a quality-control. P_{CO2} also provides information on the dissolutive nature of the waters.

D.   Dye Trace

Fluorescein dye and carbon samplers were used to determine the connection between the quarry and surrounding springs in the dye trace. Lead Hill Quarry was the chosen location of the dye trace because the topographic high position of the quarry and the many springs around the base of the hill allowed for an ideal dye trace location.

Placement of Carbon Samplers

Carbon samplers were placed at spring and stream locations where water carrying the dye that was injected into the quarry may resurge (Table 2; Figure 6). Because many of the springs near Lead Hill Quarry have been made into ponds, the carbon samplers were placed at the outlets of the ponds using wooden stakes and zip-ties. Where springs had not been converted to ponds, the carbon samplers were placed as close to the outlet of the spring as possible and in direct flow. In the streams to the south and east of the quarry, carbon samplers were connected to rocks with zip-ties and wire, and placed in the part of the channel with the most flow. At many of the sites, multiple carbon samplers were installed as a precaution against damage or loss because some of the areas were inhabited by livestock and wildlife. A total of seventeen carbon samplers were placed around the Lead Hill Quarry.

The carbon samplers were initially placed in all of the locations around Lead Hill Quarry on February 9, 2016 prior to the dye trace to detect any background interferences or dyes in the system. A week later, February 16, 2016, the initial carbon samplers were collected, and new carbon samplers were installed. After the dye was introduced to the quarry, carbon samplers were collected daily for the first week, then every other day after that. Single carbon samplers were installed after the first two weeks of background collection. The collection of the carbon samplers was spaced logarithmically to the maximum of two weeks in the dye sample locations. Carbon samplers were kept refrigerated until the elution process began.

Introduction of Dye

Fluorescein dye was chosen for the dye trace because the dye resists adsorption to inorganic materials (soils and sediments), is effectively adsorbed to activated carbon samplers,

and is the cheaper option of potential dyes. However, fluorescein is likely to have some interference from organic material (algae) and will degrade in the sunlight. The acceptable range of peak emissions for fluorescein is 510.7 to 515.0 nanometers (Aley, 2002).

Prior to introducing the dye at the field site, the fluorescein powder was mixed in 5-gallon buckets with water. A ratio of 2 gallons of water per 1 pound of dye was the target mixture of the dye. Only three 5-gallon buckets were used and each bucket contained 3.33 pounds of dye and five gallons of water. The dye powder was mixed into the water until all of the powder was dissolved.

The fluorescein dye was introduced to the Lead Hill Quarry system on February 22, 2015, prior to a rain event. Three locations in the lowest level of the quarry were chosen for the placement of dye. The first location was a low spot in a rubble pile in the lowest level of the quarry. Dye quickly flowed downward through the voids between the rocks and all 5-gallons of the dye mixture were in the ground at the first location by 9:58. The second location where dye was introduced was about 40 feet to the east of the first injection point, at a low place at the edge of the rubble pile and near a few trees. Some soil was dug away until rocks too large to lift away were reached. The hole where the dye was dumped was about 8 inches deep. In this location the dye was quickly introduced to the soil and rock system. Within three minutes of the initial pour of dye into the second location, 5 gallons of fluorescein dye was completely soaked into the medium of soil and rock by 10:05. The third location of the addition of dye was another low spot in the lowest level of the quarry, along a fracture. Soil was dug away from the bedrock in this location to a depth of about five inches. In this final location, the introduction of dye to the system took the longest. Under time restriction, the dye was poured into the holes and covered

Table 2. The names, coordinates, elevation, distance from injection location, and a brief description of the springs and streams where carbon samplers were placed for the dye trace at Lead Hill Quarry.

Site Name	Latitude	Longitude	Elevation (feet)	Distance from Injection Site (miles)	Description
Dump Site	36° 21' 59.66" N	92° 57' 56.15" W	1112	0	Three sites located in the lower level of Lead Hill Quarry.
Sheep Field Spring 1	36° 22' 02.11" N	92° 57' 30.23" W	856	0.42	Spring with visible upwelling, covered in water cress.
Sheep Field Spring 2	36° 22' 3.65" N	92° 57' 29.06" W	859	0.45	Spring converted to pond.
Barn Spring	36° 21' 56.54" N	92° 57' 39.09" W	859	0.31	Spring converted to pond.
Lonny's Ravine	36° 22' 0.10" N	92° 57' 42.86" W	903	0.24	Two springs within 10 feet of each other. Bugs placed in both springs.
Pond West	36° 22' 3.73" N	92° 58' 6.61" W	1007	0.19	Spring converted to pond.
Hog Spring	36° 21' 59.96" N	92° 58' 9.94" W	1031	0.22	Spring
Brother Spring	36° 22' 10.10" N	-92° 57' 28.31" W	858	0.49	Spring emerging from casing built around spring.
East Fork of West Sugarloaf Creek	36° 22' 8.96" N	92° 57' 24.93" W	810	0.54	Creek flowing along eastern side of Lead Hill Quarry.
Bruce Chaney	36° 21' 44.76" N	92° 57' 55.55" W	873	0.32	Creek flowing along southern side of Lead Hill Quarry. Flows into Sugarloaf.

with rocks to prevent degradation of the dye from sunlight. The 5-gallons of dye were introduced at this location by 10:21.

Prior to introducing the dye at the field site, the fluorescein powder was mixed in 5-gallon buckets with water. A ratio of 2 gallons of water per 1 pound of dye was the target mixture of the dye. Only three 5-gallon buckets were used and each bucket contained 3.33 pounds of dye and five gallons of water. The dye powder was mixed into the water until all of the powder was dissolved.

The fluorescein dye was introduced to the Lead Hill Quarry system on February 22, 2015, prior to a rain event. Three locations in the lowest level of the quarry were chosen for the placement of dye. The first location was a low spot in a rubble pile in the lowest level of the quarry. Dye quickly flowed downward through the voids between the rocks and all 5-gallons of the dye mixture were in the ground at the first location by 9:58. The second location where dye was introduced was about 40 feet to the east of the first injection point, at a low place at the edge of the rubble pile and near a few trees. Some soil was dug away until rocks too large to lift away were reached. The hole where the dye was dumped was about 8 inches deep. In this location the dye was quickly introduced to the soil and rock system. Within three minutes of the initial pour of dye into the second location, 5 gallons of fluorescein dye was completely soaked into the medium of soil and rock by 10:05. The third location of the addition of dye was another low spot in the lowest level of the quarry, along a fracture. Soil was dug away from the bedrock in this location to a depth of about five inches. In this final location, the introduction of dye to the system took the longest. Under time restriction, the dye was poured into the holes and covered with rocks to prevent degradation of the dye from sunlight. The 5-gallons of dye were introduced at this location by 10:21.

The Elution Process

   After each collection from the field locations, the carbon samplers were eluted. Each of the carbon samplers was rinsed in deionized water for three to five minutes to remove any organic matter that might have been on the packets or the charcoal. The carbon samplers with more algae growing on them were rinsed for a longer period of time. An eluent mixture of about 20 milliliters of 70% isopropyl alcohol and 5 to 6 flakes (approximately 0.25 grams) of potassium hydroxide was prepared in two-ounce plastic multipurpose cups. Enough of the eluent was made for all of the sampling locations. About one tablespoon of charcoal was added to each of the eluent solution cups. The charcoal sat in the eluent for about an hour to elute dye. Aley (2002) methods indicated that one hour is the ideal time because organic influence may occur after that time.

   Once the elution process was complete, the samples were analyzed for dye by a spectrophotometer. Three milliliters of the eluent was transferred to a macro cuvette, which was then inserted into a Shimadzu Spectrofluorophotometer RF-5301PC. The spectrophotometer can detect fluorescein dye in the eluent to as little as 0.010 ppb. Pre-installed fluorescein detection parameters were used to detect the dye. The excitation wavelength was 420 nanometers with a slit width of 5 nanometers and the emission wavelength range was 480 to 550 nanometers with a slit width of 3 nanometers. The expected wavelength of the fluorescein dye is 510.7 to 515.0 nanometers (Aley, 2002). Sensitivity was set to high and the recording range was 0 to 50 nanometers.

E.   Spring Basin Delineation

Surface watershed basins were delineated for several springs of the study using StreamStats (U.S. Geological Survey, 2012). Karst watersheds often are not coincident with surface watersheds and are often difficult to delineate due to the complexities of the flow paths and natural variations in water levels (Brahana, 1997). Discharge from springs, along with other hydrologic and geologic parameters, can be used to constrain spring-basin boundaries (Brahana, 1997); however, no discharges from springs were measured in this study. StreamStats does not consider karst conduits and flow paths when delineating basins; however, the program provides a general area that would be the topographic drainage basin. Basins are delineated in StreamStats by utilizing ArcGIS, ArcHydro, the National Hydrography Dataset (NHD), the U.S. Geological Survey (USGS) 3D Elevation Program, and the USGS National Streamflow Statistics (USGS, 2012). Images, shapefiles, and drainage basin areas were the desired outputs from StreamStats to gain more knowledge about the springs and what may control the water chemistry. Once the spring basins were delineated, the land-use percentages of the basin area were determined to normalize chemical characteristics of the groundwater samples.

F.   Statistical Analysis

A series of statistical analyses were completed using R to determine the water-quality relation between the quarries, springs, and sinkholes. The first step was to check that the data are normally distributed. As the sample size of the data is small, a normal distribution cannot be determined. Therefore, non-parametric tests were used to determine if the data are statistically different. The Wilcoxon Rank Sum Test was used for comparisons between the lake quarries and springs within proximity to the quarries and between the springs near quarries and springs near sinkholes. An alpha value of 0.05 was used to determine if the spring groupings were statistically

different. The water chemistry of the samples was organized into boxplots to have a visual comparison of the data.

IV.   Results

A.   Field Observations

Storm-flow

The storm-flow samples were collected on December 14, 2015 after a two-day rain event during which Fayetteville, Arkansas received 2.37 inches of rain (NOAA's NCEI, 2016). At Sharp's Quarry, water levels were three feet higher than normal levels. The water was rushing into the sump from all directions and from bedding planes in the rock at similar elevations (Figure 7). Quarry operators also noted that the water in the sump was cloudier than normal conditions. The Lead Hill Quarry springs appeared to be the same as the initial visit to the site; however, the ground was fully saturated and water was seeping from places that were normally dry. At the St. Joe Quarry, water was dripping audibly into the quarry lake below.

Base-Flow

Base-flow sampling was conducted on February 8 – 9, 2016 after receiving only 0.15 inches of rain in Fayetteville, Arkansas in the month prior to sampling (NOAA's NCEI, 2016). At Sharp's Quarry the water in the sump was significantly lower (approximately 6 feet) than the storm-flow sampling. However, water was still flowing into the sump from bedding planes. Field Spring was completely dry so sampling was moved about 100 feet to the south to a pool of water surrounding a large sycamore tree. An old foundation from a well or spring house was at this location. The sampling locations around Lead Hill Quarry displayed no visible changes in discharge due to lack of precipitation. Stains from geochemical weathering were visible on the

sides of the St. Joe Quarry walls due to runoff and water flowing in between beds in the Boone Formation. From the staining and audible dripping during storm-flow we can presume that water is entering the quarry from surface flow and groundwater flow. The drainage sampled near the St. Joe Quarry was gaining groundwater in some areas and then losing completely before reaching Mill Creek. The discharge was significantly less than the storm-flow collection. However, water was still flowing at the sampling location in the gaining drainage.

B.   Sample Water Chemistry

Water samples collected from springs and limestone quarries were analyzed for major ions, metals, and nutrients. Temperature, pH, and specific conductance were field parameters measured for each of the samples. The calcite saturation index was calculated for each of the water samples, indicating that both quarry lakes are supersaturated with respect to calcite and all springs, except for the spring near St. Joe Quarry, were undersaturated (Table 5). The partial pressure of carbon dioxide (P_{CO2}) in springs near quarries ranged from 0.00335 to 0.0321 atm and the P_{CO2} in the quarries ranged from 0.000827 to 0.00281 atm (Table 5).

Storm-flow Water Samples

The storm-flow water samples were collected from springs and quarries on December 14, 2015, after receiving 2.39 inches of rain (NOAA's NCEI, 2016) in Fayetteville, Arkansas. Due to dilution of groundwater by recharge from rain water, specific conductance (median during storm-flow was 199 µS/cm) and alkalinity (median during storm-flow was 208 mg/L) were lower than the base-flow samples collected at the same locations. Temperatures of the water at the sampling locations were higher during storm-flow (median of 11.78 °C), reflecting surface temperatures (Table 3).

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Base-flow Water Samples

The base-flow water sample collection from springs and quarries occurred on February 8 and 9, 2016. In the month prior to collecting the base-flow samples, Fayetteville, Arkansas had received 0.15 inches of rain (NOAA's NCEI, 2016). The specific conductance and alkalinity were higher during base-flow than storm-flow with a median of 636 µS/cm and 322 mg/L, respectively (Table 3). Median water temperature at sampling locations was about two degrees (9.8 °C) lower than the storm-flow sampling.

C.   Water Chemistry Related to Sinkholes

Water-chemistry data for springs located within 3 kilometers of a group of at least two sinkholes were downloaded from the National Water Quality (NWQ) portal. The four selected springs related to sinkholes were in Benton and Washington counties of Arkansas. The available data for the sinkhole spring sites included pH, alkalinity, chloride, sulfate, nitrate, calcium, magnesium, potassium, and sodium (Table 4). Median nitrate for the sinkhole springs was 6.75 mg/L. Alkalinity for the sinkhole springs had a median value of 103.5 mg/L. The calculated calcite saturation index for each sample was negative; therefore, the springs are undersaturated with respect to calcite (Table 5). Partial pressure of carbon dioxide (P_{CO2}) values ranged from 0.0136 to 0.0550 atm (Table 5). The saturation index and P_{CO2} for sinkhole spring 1, collected on August 29, 2007, could not be calculated because the data were missing an alkalinity value.

D.   Water Stable Isotopes

Spring δD values ranged from -72.61‰ to -36.72‰ and $\delta^{18}O$ values ranged from -10.53‰ to -4.8‰ (Table 6). The limestone quarry water samples exhibited heavier water isotope compositions, as compared to the springs, ranging from -47.08‰ to -19.43‰ for δD

Table 3. Storm-flow and base-flow water sample results from springs and quarries.

Site*	Storm or Base**	Temp. (C)***	Cond. (µS/cm)	pH	Alk. (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Nitrate (mg/L)	Calcium (mg/L)	Mg (mg/L)[1]	Potassium (mg/L)	Sodium (mg/L)
SQ	Storm	9.27	162	7.90	110	10.1	39.6	4.11	61.0	3.01	1.80	6.21
FSSQ	Storm	8.03	113	7.29	66.9	2.51	3.44	<0.15	18.3	3.08	15.9	0.532
SFLHQ	Storm	11.78	206	7.10	308	9.01	12.4	5.05	67.9	35.2	2.41	4.56
BarnLHQ	Storm	15.18	230	6.91	295	1.43	6.34	0.183	61.4	30.7	0.789	1.34
BSLHQ	Storm	13.96	199	7.01	208	5.14	11.2	0.181	45.2	21.1	0.840	3.96
SJQ	Storm	11.65	129	7.98	108	1.46	4.50	0.260	42.9	1.20	0.425	1.14
SpSJQ	Storm	13.21	361	7.56	252	12.0	6.62	1.93	102	1.47	4.10	4.74
SQ	Base	9.8	380	7.68	144	11.0	10.8	3.76	63.2	2.37	1.85	7.32
FSSQ	Base	4.1	572	7.11	176	33.4	35.8	1.67	69.0	2.60	11.6	27.1
SFLHQ	Base	13.8	741	7.01	341	13.9	18.2	8.00	77.6	44.0	1.85	6.02
BarnLHQ	Base	12.9	636	6.95	342	2.05	8.74	0.262	74.1	39.7	0.949	1.65
BSLHQ	Base	10.6	638	7.06	322	6.36	15.8	1.05	68.1	38.5	0.830	3.24
SJQ	Base	5.5	251.3	8.14	124	1.34	5.71	0.224	47.5	1.24	0.493	1.24
SpSJQ	Base	7.8	685	7.32	342	14.0	5.91	0.627	132	1.51	1.99	6.50

* Sites were assigned IDs to shorten names: SQ = Sharp's Quarry, FSSQ = Field Spring near Sharp's Quarry, SFLHQ = Sheep Field Spring near Lead Hill Quarry, BarnLHQ = Barn Spring near Lead Hill Quarry, BSLHQ = Brother Spring near Lead Hill Quarry, SJQ = Saint Joe Quarry, SpSJQ = spring fed drainage near Saint Joe Quarry.

** Storm = Storm-flow; Base = Base-flow

***Temperature

[1] Mg = Magnesium

Table 4. Values for the sinkhole springs, acquired from the National Water Quality portal.

Site[1]	Date	pH	Alk.* (mg/L)	Cl (mg/L)	Sulfate (mg/L)	Nitrate (mg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)
SS 1	4/8/1994	6.3	89.5	7.2	4.5	8.3	31	2.0	3.0	4.7
SS 1	7/13/1994	7.0	113	7.3	1.8	6.6	46	1.7	1.6	6.1
SS 1	8/29/2007	6.1	NA	7.8	3.8	7.0	55	2.3	2.8	6.1
SS 2	7/13/1994	6.9	104	8.1	2.3	6.9	45	1.8	1.9	6.2
SS 3	7/20/1994	6.8	91.0	11	4.7	4.9	37	1.6	2.7	7.4
SS 4	5/4/1994	6.7	129	12	5.4	5.1	49	1.2	0.9	11

[1] SS = Sinkhole Spring

* Alk. = Alkalinity

Table 5. Henry's Law constant (K_H) and the partial pressure of carbon dioxide (P_{CO2}), as calculated by *olm*, and saturation index of calcite ($SI_{calcite}$) and percent error of the ion exchange, as calculated by *Phreeqc*, for quarries, springs, and sinkhole springs.

Site	Base-Flow K_H	Base-Flow P_{CO2} (atm)	Storm-Flow K_H	Storm-Flow P_{CO2} (atm)	Base-Flow $SI_{calcite}$	Base-Flow Percent Error	Storm-Flow $SI_{calcite}$	Storm-Flow Percent Error
SQ	0.0544	0.00281	0.0554	0.00130	0.13	1.90	0.05	4.02
SpSQ	0.0668	0.0124	0.0579	0.00335	-1.2	8.33	-0.49	-0.630
SFLHQ	0.0476	0.0321	0.0509	0.0234	-0.18	-1.48	-0.16	0.860
BarnLHQ	0.0490	0.0320	0.0456	0.0321	-0.43	19.4	-0.31	23.0
BSLHQ	0.0530	0.0261	0.0474	0.0202	-0.55	1.03	-0.23	1.93
SJQ	0.0634	0.000827	0.0511	0.00114	0.14	-0.260	0.29	-1.35
SpSJQ	0.0584	0.0151	0.0486	0.00690	0.42	-1.17	0.31	-2.23
SS 1 (04/08/94)	0.0342	0.0550			-1.6	-14.8		
SS 1 (07/13/94)	0.0342	0.0136			-0.60	-3.92		
SS 2	0.0342	0.0158			-0.74	-2.28		
SS 3	0.0342	0.0176			-0.97	-4.24		
SS 4	0.0342	0.0311			-0.82	-5.47		

and -7.54‰ to -0.78‰ for δ^{18}O. Isotopic values of the water samples were compared to the

Local Meteoric Water Line (LMWL) for northwest Arkansas (Knierim, 2015) and the Global

Meteoric Water Line (GMWL) (Craig, 1961) to determine differences in water sources and

effects of evaporation (Figure 8). The two isotopically heaviest samples were both from the

Saint Joe Quarry; indicating that the water in the quarry undergoes evaporation. Field Spring

near Sharp's Quarry was the lightest sample, which is within the expected range of winter

surface water isotopic compositions. Deuterium excess for springs ranged from 0.780‰ to

17.7‰ and -13.2‰ to 13.2‰ for the limestone quarries.

The base-flow sampling of Sharp's Quarry and Field Spring near the quarry resulted in

similar water isotopic compositions. Sharp's Quarry had an isotopic composition of -37.5‰ for

Table 6. Water isotope (δD and δ^{18}O) values for the spring and quarry samples and the calculated deuterium excess values for each sample.

Site	δD (‰)	δ^{18}O (‰)	d^* (‰)
BarnLHQ1	-38.1	-5.79	8.19
BarnLHQ2	-37.6	-4.80	0.780
BSLHQ1	-46.2	-7.74	15.8
BSLHQ2	-37.5	-6.43	14.0
SFLHQ1	-45.3	-7.03	10.9
SFLHQ2	-39.0	-7.08	17.7
SJQ1	-19.4	-0.780	-13.2
SJQ2	-22.3	-1.46	-10.6
SpSJQ1	-46.0	-7.13	11.1
SPSJQ2	-40.3	-6.80	14.2
SpSQ1	-72.6	-10.5	11.6
SpSQ2	-36.7	-5.62	8.24
SQ1	-47.1	-7.54	13.2
SQ2	-37.5	-5.99	10.5

*d = deuterium excesss

δD and -5.99‰ for δ¹⁸O and Field Spring had an isotopic composition of -36.7‰ δD and -5.62‰ δ¹⁸O. The deuterium excess values for Sharp's Quarry and Field Spring during base-flow are also differ by just more than 2‰, at 10.5‰ and 8.24‰, respectively.

Hydrograph separation curves, which can be used to determine flow paths of water, of the springs were not interpreted because discharge was not recorded for this study. However, comparing the water isotope values of the quarries and springs to soil and cave water isotope values was beneficial when determining the source of the spring waters. Knierim (2015) collected soil and cave water isotope values from a cave developed in the Boone Formation and overlying soils in northwest Arkansas. The median values for soil water were -41.6‰ δD and -6.2‰ δ¹⁸O and the median values for cave water were -37.2‰ δD and -5.7‰ δ¹⁸O (Knierim, 2015). The median values of the springs near quarries were -39.60‰ δD and -6.91‰ δ¹⁸O, which are statistically different from both the cave and soil water samples (Appendix B).

E.   Dye Trace

Fluorescein dye was introduced to Lead Hill Quarry on the morning of February 22, 2016. Eight springs and two creeks surrounding the Lead Hill Quarry area were monitored daily for a week after two rainfall events (February 23, 2016 and March 8-12, 2016) and then weekly after those storms. After 35 days (as of 3/28/16) and 4.27 inches of rain in the Lead Hill, Arkansas area (NOAA's NCEI, 2016) the fluorescein dye had not been recovered at any of the springs or creeks surrounding the Lead Hill Quarry area.

A groundwater-level measurement was recorded with an electrical tape at the land owner's domestic well near Lead Hill Quarry in an attempt to understand groundwater flow in the area. The top of the well casing was at the same elevation as the land, which was located at

877 feet above sea level. The depth to water from land surface was 47.71 feet, or 829.3 feet above sea level. The East Fork of West Sugarloaf Creek, east of the well location, is located at about the same elevation (824 feet above sea level), which would indicate that groundwater flows into the creek.

F.   Spring Basin Delineation

The spring-basin delineation was computed by StreamStats to better understand the influences on spring water chemistry near the limestone quarries. Basins for two of the spring locations were computed because only surface-water basins are available on StreamStats (U.S. Geological Survey, 2012). The watershed basin for the groundwater-fed drainage near St. Joe Quarry was calculated to be 0.035 square miles. Figure 9A, shows that the groundwater-fed drainage-basin does not actually include St. Joe Quarry; however, water from the quarry may still flow to the groundwater-fed drainage because the limestone is karstified and fractured. The basin for Lonny's Ravine at Lead Hill Quarry was computed to be 0.039 square miles (Figure 9B). While Lonny's Ravine was not sampled for water isotopes or water chemistry, the basin delineation gives us an idea of the watershed and can be expanded for the other springs at Lead Hill Quarry. Other than major creeks and streams, no location on StreamStats was adequate for delineating the basin for Field Spring near Sharp's Quarry.

The drainage basins of the St. Joe Quarry groundwater-fed drainage and the Lead Hill Quarry Lonny's Ravine were used to calculate percent land use in the watersheds. In both basins forests and grasses constituted most of the land use. Houses or barns were also present in each basin, therefore a small percentage of the basins were classified as urban. These land use results can assist in determining the sources of nutrients found in the quarry and spring samples.

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V.   Discussion

A.   Connecting Springs to Quarries

To determine any connection between quarries and the nearby sampled springs, water isotopes, water chemistry, and a dye trace data were analyzed to better understand groundwater flow in the complex karst systems that have been anthropogenically altered. By applying these different analyses, some springs can be linked to quarries; conduit or fracture flow is the likely flow path of the groundwater.

Water Stable Isotopes

Water-isotope data indicated that evaporation and mixing between rainfall from different storm events had occurred in the quarries and springs. Samples from the Saint Joe Quarry plot below the Local Meteoric Water Line (LMWL) indicating that the water in the quarry had undergone evaporation. The two samples from the groundwater-fed drainage near St. Joe Quarry show no evaporation based on water isotopic composition. Barn Spring near Lead Hill Quarry was another sample that plotted below the LMWL, which may be a result of two situations: Firstly, Lead Hill Quarry is a dry quarry, but some puddling of water on the bedrock occurs after rainfall. Evaporation of some of the water in the puddle is likely to occur before the water moves into the subsurface via fractures and conduits in the bedrock. Secondly, the isotopic signature from Barn Spring may be evidence of evaporation of soil water. In a study by Hsieh et al. (1998), the enrichment of ^{18}O during evaporation of soil water can increase $\delta^{18}O$ values by up to 4.5‰. Soil water evaporation could explain the nearly 1‰ $\delta^{18}O$ enrichment of the base-flow water sample at Barn Spring. The cluster of samples located near or on the LMWL likely indicate that the water has undergone mixing of water with different sources. Precipitation events originating

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in the Pacific Ocean or Arctic would have high deuterium excess values and storm events

originating in the Gulf of Mexico and somewhere more equatorial generally would have a lower

deuterium excess (Clark and Fritz, 1997). The combinations of these two types of storms become

mixed in the groundwater, resulting in an isotopic composition that is similar to the averages in

rainfall (the LMWL). The one spring that was the most negative in respect to both δD and $\delta^{18}O$

is Field Spring near Sharp's Quarry. This sample was collected during the stormflow event in

December 2016 and is representative of winter surface-water isotopic values that do not show the

mixed, time-averaged isotopic composition that occurs during longer residence time in

groundwater flow.

From the water-isotope values, only one quarry and one nearby spring were similar

indicating that a significant component of spring flow was quarry-water input. Sharp's Quarry

and Field Spring had similar isotopic composition during the base-flow sampling. The isotopic

signatures of the quarry and spring are not exactly the same because Field Spring has $\delta^{18}O$

enrichment which could be due to some evaporation of the water or mixing.

When the spring and quarry water isotopic compositions were compared to soil and cave

water isotopes from Knierim (2015), the values were statistically different. The median

deuterium isotope value for the spring and quarry water samples was between the median cave

and soil values, which may indicate that mixing of soil and cave water occurred in the

groundwater of the sampled locations or may be indicative of differences inherent between sites.

Evaporation of the water in the quarries and Barn Spring resulted in a higher median oxygen-18

value for the spring and quarry water samples compared to the soil and cave median oxygen-18

values. The comparison of the spring and quarry isotopic values to soil and cave isotopic values

further supports that mixing of the groundwater occurs at the sampling locations as determined by the clustering of isotopic values near the Local Meteoric Water Line.

Water Chemistry

The quarry samples water-chemistry data and the nearby spring samples data were compared to determine whether the samples were statistically different. After using the Wilcoxon Ranked Sum Test, only four out of fifteen chemical characteristics of the water samples were statistically different. The statistically different water-chemistry characteristics were pH, alkalinity, hardness, and magnesium. Important chemical tracers, such as nitrate, chloride, sulfate, and specific conductance, were similar between quarries and nearby springs.

From the calculated calcite saturation indices, the quarry water samples were all supersaturated and most of the springs are undersaturated. The quarries are expected to be supersaturated because the water is sitting in the quarry and chemically interacting with freshly exposed limestone and crushed limestone. The concentration of all solutes, including calcium, are increased as water the in the lake quarry is evaporated (Eary, 1998). Following the increased solute concentrations, Eary (1998) states that calcite precipitation is the first chemical divide that occurs in lake quarries that are undergoing evapoconcentration. However, no precipitation of calcite is visibly occurring in St. Joe Quarry. The one spring that was supersaturated during both stormflow and base-flow sampling was the groundwater-fed drainage near St. Joe Quarry. Recall that the water stable isotopes did not suggest a connection between St. Joe Quarry and the nearby groundwater-fed drainage. The high specific conductance and calcium values of the groundwater-fed drainage near the St. Joe Quarry might indicate long residence time of the water (Hem, 1985). Therefore, the oversaturation of the groundwater-fed drainage may not be entirely related to the quarry and more so on diffuse groundwater flow. The unsaturated state of the

waters from the other springs indicates that the water had a short residence time, which means that conduit flow paths are likely (Hem, 1985).

The supersaturation with respect to calcite of the quarries could also be explained by degassing of carbon dioxide in the water within the quarries. P_{CO2} has the strongest influence on dissolution rates (Covington et al., 2015); therefore, the dissolved CO_2 in the quarries waters was likely the cause of high calcite saturation indices. Degassing of CO_2 results in an increase in saturation indices and a decrease in dissolution rates (Covington et al., 2013). A positive saturation index, indicating supersaturation, could be a result from the CO_2 in quarry waters reaching equilibrium with the air. The P_{CO2} values of the quarry waters were lower than the spring values, and more similar to atmospheric values. Most of the springs had P_{CO2} values within the range of soil P_{CO2} values (Brook et al., 1983), meaning that the majority of the spring waters may be soil water. This suggests that the springs sampled near the quarries in this study have shallow flow paths.

However, other water characteristics, such as specific conductance, indicate that the spring waters may have conduit flow paths. Specific conductance can be used to understand the flow in and out of the quarries. If storm-flow and base-flow water samples are highly variable, then groundwater flow is likely predominantly conduit flow (Andreo et al., 2002). The boxplot of specific conductance during storm-flow and base-flow (Figure 10) indicates that the specific conductance is variable between the different flows. Statistically, the specific conductance values of the water samples from the quarries and springs during storm-flow and base-flow are significantly different. Therefore, we can assert that the water is moving through the springs and quarries primarily via conduit flows.

Temperature, pH, and specific conductance were found useful in determining aquifer behavior by Andreo et al. (2002); however, other studies have found calcium, magnesium, sulfate, nitrate, and chloride useful in determining flow paths and aquifer characteristics. The temperature values of the springs and quarries appear to be dependent on surface temperature; however, more measurements or continuous monitoring of temperature would provide more information on the groundwater flow characteristics of each spring. The pH of the samples does not vary greatly between the quarries and springs other than the quarries being slightly more alkaline as the water has higher solute concentration (Eary, 1998). The variability in specific conductance has already been discussed. Gunn (1981) used calcium and magnesium values to determine the components of flow in a karst setting. When comparing the results of the spring data to the Gunn (1981) values, nearly all values of calcium and magnesium are above the ranges found in their study area in New Zealand. Equilibria is the main limiting factor on calcium concentration in water (Hem, 1985); therefore the state of calcium equilibrium in the water between the Gunn (1981) study and this study are likely different. Because spring waters of this study exhibit higher calcium concentrations, the solubility of calcium in the waters can likely be explained by low temperatures that occur during the winter study period and high partial pressure of carbon dioxide from soil carbon dioxide. Sulfate has been used as a tracer, alongside water isotopes, in karst landscapes in Indiana. A few of the springs of this study near quarries (Sheep Field Spring and Brother Spring) have sulfate values that fit in the sulfate range (13 to 24 mg/L) of vadose flow given by Lee and Krothe (2003) which would suggest that some groundwater flow in the unsaturated zone occurred in those springs. Nitrate and chloride are other chemical components often used in tracing groundwater especially in areas influenced by agriculture or urbanization (Hem, 1985; Kresse and Hays, in review; Kresse et al., 2014); however, the nitrate

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and chloride ranges between the quarries and nearby springs are not statistically different. Because the land use near the quarries and related springs are similar, major differences in nitrate and chloride should not be expected. Sheep Field Spring had the highest nitrate value which is likely due to the spring being in a sheep pasture. The high nitrate values in Sheep Field Spring also support the unsaturated-zone flow as indicated by sulfate values. The calculated land use percentages from the drainage basins supports the likely influence of pastures on the nitrate values. Increased nitrate from human waste is unlikely because the urban percentages were small in the spring drainage basins.

Dye Trace

After more than 40 days and 6.19 inches of rain (NOAA's NCEI, 2016) no dye was observed in any of the seven springs or two streams where carbon samplers were located. Four potential explanations of the missing dye have been formulated:

1. Rainfall since the injection of dye has been insufficient to saturate the local flow system and move the dye. While Lead Hill, AR received 6.19 inches of rain after the injection of the dye (NOAA's NCEI, 2016), the rainfall events were spread out and occurred after weeks of no rain in many cases.

2. The dye moved through the groundwater to an unexpected location. In this case, the groundwater flow path may have been to the north where no carbon samplers were located because of a lack of springs in that area within a close proximity to the quarry. A deep and complex flow path to a location outside of the observed area may also be likely as the area has many karst features, such as caves and springs.

3. From the groundwater level observed in the land owner's well, the dye may have discharged into the East Fork of West Sugarloaf Creek. The dye may have become too

diluted in the creek to be adsorbed to the carbon samplers and observed by the spectrophotometer.

4. The aquifer had a very slow, diffuse flow or the dye was perched in the system. After the dye injection, there was not enough time for the dye to move through the aquifer. If the dye was perched, a large rain event would be required to move the dye, which would relate to the first proposed explanation of the missing dye.

The dye trace results provide no indication of a link between Lead Hill Quarry and the nearby springs and streams. Despite which hypothesis might explain the missing dye, the dye trace further proves the complexities of studying groundwater flow in karst landscapes and the likelihood of a deeper groundwater flow system of water exfiltration out of quarries.

In comparing the quarries to the nearby springs, some conclusions can be made: 1) the base-flow water-isotope values indicate a connection between Sharp's Quarry and nearby Field Spring, 2) the majority of the chemical characteristics of the water samples are not statistically different, and 3) the calcite-saturation index of the groundwater-fed drainage near St. Joe Quarry is positive, indicating supersaturation. However, some of the results from this study also show no connection between the quarries and the springs, such as the dye trace at Lead Hill Quarry and most of the water isotope values. Even if the water from the quarries is not flowing to the observed springs, the water is flowing somewhere. Qualitative observations of runoff during storm events suggest that water is readily transmitted through the soil and to the underlying bedrock; therefore, the quarries are likely to influence groundwater quality. In the fractured and karstified Boone Formation, groundwater flow and potential effects on water quality should be considered during active mining of the limestone and reclamation of the quarries.

The data from water stable isotopes, water chemistry, and the dye trace suggest that some limestone quarries and nearby springs may be connected, indicating that water flows out of the quarries into the groundwater. Even though a signature of the quarries was not discernable in every spring, water is still likely flowing out of the quarries via fractures, joints, and conduits as indicated by rapid loss of water (and dye) at the quarry sites and high variability in specific conductance. Not every spring or stream around the quarries was sampled in this study, so more data likely would show more connections between limestone quarries and groundwater. The springs near quarries were still used in the comparison of groundwater near quarries and near sinkholes because the influence of quarries on groundwater flow is apparent as outlined in the discussions above.

B.   Comparing "Engineered Sinkholes" and Naturally Forming Sinkholes

Springs near quarries and springs near sinkholes were compared as two different populations to determine if limestone quarries act as "engineered sinkholes". The majority (six out of nine) of the chemical components of water chemistry were statistically different between springs near quarries and springs near sinkholes. Chloride, potassium, and sodium were the chemical characteristics of the springs that were similar (Appendix A).

Nitrate

Nitrate values between springs near quarries and springs near sinkholes were statistically different based on a Wilcoxon Ranked Sum Test (p-value = 0.0075). The differences in nitrate values between the quarries and sinkholes (Figure 11) suggests that nitrate cycling is different between quarry and sinkhole areas. Soil stores nitrate (Peterson et al., 2002) and the quarries lack soil; therefore, nitrate introduced to the quarries moves to the groundwater more quickly.

However, both sets of data have maximum values of nitrate around 8 mg/L (below the U.S. Environmental Protection Agency's Safe Drinking Water Act requirement), indicating that the quarry-related springs may have some flow paths that would allow for the storage of nitrate. Because the limestone quarries only make up a small percentage of the drainage basins, storage of nitrate in the soil elsewhere in the basin is plausible.

Because the quarry related springs and sinkhole related springs have nitrate values higher than background values, 0.4 mg/L (Kresse and Hays, in review; Kresse et al, 2014), the influence of land use is visible in the groundwater quality. The quarry related spring with the highest nitrate values is Sheep Field Spring near Lead Hill Quarry. The land use, a pasture for sheep, likely influenced the nitrate values for Sheep Field Spring, which is likely sourced from soil water and surface infiltration.

C.   Influences of Time on Karst Processes In and Near Limestone Quarries

When considering geologic time, the quarries are new features on the landscape that have not had the time to undergo processes that take longer than a human lifetime to see results, such as the formation of soils. Because soil seems to be the biggest difference in the limestone quarries and sinkholes, I consider how removal of soil might influence water flow and karstification. Figure 12 is a flow chart of processes that would occur in the different types of quarries (dry, lake, or active) to aid or limit karstification of the bedrock.

Active Quarries

Active quarries in limestone, such as Sharp's Quarry, are still being mined which seems to limit karstification of the bedrock. Any acids, from soil processes, rain, or other acid producing processes both natural and anthropogenic, introduced to the active quarries that would

normally aid in the dissolution process are quickly buffered by dust, gravel, boulders, and walls of the freshly exposed bedrock (Eary, 1998). Water that enters the quarry will become oversaturated with respect to calcite once coming in contact with the carbonate (Eary, 1998); therefore, less dissolution of the bedrock is likely to occur.

While dissolution of the bedrock may be limited, the propagation of fractures from blasting has been documented in limestone quarries with preexisting joints and fractures (Hobbs and Gunn, 1998; Lolcama, Cohen, and Tonkin, 2002). Sharp's Quarry had water flowing into the quarry along bedding planes during both storm-flow and base-flow (Figure 7). Some of the water may have been flowing along paths that existed before quarrying began, but it is likely that the blasting of the bedrock has increased the number of fractures as well as the diameter of the fractures. These fractures, in addition to the removal of rock may have rerouted the flow of groundwater. Hobbs and Gunn (1998) also conceptualize the rerouting to spring discharge into active quarries when the mining has reached below the water table and the water is pumped out of the quarry. With these changes of increased groundwater flow into the active quarries and the example of Sharp's Quarry, the quarries appear to act as "engineered springs". Once the active quarry becomes exhausted and the water level in the quarry is restored to the water table level then the water may return to the original flow path.

Dry Quarries

Dry quarries, Lead Hill Quarry for example, are above the water table and require significant hydraulic potential and soil for karst formation processes to occur in the unsaturated (vadose) zone. While some water may move into the fractures of the bedrock post-mining, minimal dissolution of the bedrock is likely to occur because the water will become oversaturated quickly. With time, soils will begin to form in and around the dry limestone

quarries. The soil will move into the fractures and joints that can be modified by dissolution, which provide an input to the karst pathways of the bedrock. In this stage, hydraulic gradients, hydraulic conductivity, and porosity of the soils and bedrock are important for the movement and flow of water into the subsurface to aid in the formation of karst features (Ford and Williams, 2007). As plants and microorganisms grow in the soil, respiration and decay in the soil will occur which produces carbon dioxide. The carbon dioxide in the soil enhances the solubility of carbonates, which ultimately results in the dissolution of the bedrock along the joint and fractures and eventually along bedding planes (Ford and Williams, 2007). The formation of conduits is very likely to occur in and around the dry limestone quarries over geologic time as long as the system has sufficient hydraulic potential. The thick Boone Formation regolith is also likely to form over the quarries over time which may result in the quarries actually looking like sinkholes on the surface and will provide more storage space for soil carbon dioxide.

Other types of reclamations of quarries, such as forests or fills, were not a part of this study; however, the evolution of those types of reclaimed quarries over time can be conceptualized here. The forest quarries are likely to evolve similarly to the dry quarries, such as Lead Hill Quarry; however, vegetation cover might influence soil formation. An increased rate of soil production might result in increased rates of karstification in forest quarries compared to the dry quarries left as bedrock. Another reclamation type is to fill the quarry either with soil or human-produced waste. Filling the dry quarries with soil would likely speed up the karstification process, similar to the forested reclamation type. The landfill approach to quarry reclamation is the worst for the groundwater quality. Harmful metals, bacteria, and nutrients can enter the groundwater through the fractures in the quarry walls (Hobbs and Gunn, 1998). Many states no

longer allow this type of reclamation unless a sufficient liner is used in an attempt to protect groundwater.

Lake Quarries

Lake quarries, St. Joe Quarry for example, are an expression of the groundwater table and will not form soil, unless the groundwater table drops. Because soils are not forming in lake quarries, karst dissolution processes depend on the saturation index of the water. From the study, all of the water samples from lake quarries were oversaturated with respect to calcite (Table 5); therefore, dissolution is not likely to occur in lake quarries.

While fractures along the walls of the lake quarries are likely not growing in diameter from dissolution, some water is still flowing out of the quarries via these fractures. The water in the lake quarries is a representation of the groundwater level at that location. For the water levels to be kept relatively constant, an equilibrium of groundwater flow into the quarry and out of the quarry must be met. Therefore, protecting the quality of the water in the quarry is important. Monitoring surface processes, such as farming or urban development, near the lake quarries is necessary for the protection of the groundwater. Nutrients could enter the lake quarries through runoff and result in eutrophication of the lake (Botta et al., 2009). One option for protecting the water in the quarry from runoff is a riparian zone of trees, bushes, and other plants (Neri and Sánchez, 2010). Neri and Sánchez (2010) concluded that vegetation management should be a key part of limestone quarry restoration to prevent potential harmful runoff from reaching the groundwater. The plants in the riparian zone will increase the amount of soil carbon dioxide along edges of the quarry. During rain events, soil carbon dioxide charged waters may flow into the quarry by runoff or into the fractures in the bedrock beneath the soil layer, aiding the dissolution of the carbonates (Ford and Williams, 2007).

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VI.   Conclusions

Quarries, similar to sinkholes, are often represented by hachure marks on topographic maps. The visual similarities of sinkholes and quarries brings about questions of water flow around the quarries, especially in limestone quarries where karst features may influence flow. Groundwater flow in and out of limestone quarries was conceptualized in previous studies. In this study, means of tracing groundwater flow out of limestone quarries via water chemistry, water stable isotopes, and a dye trace were established. Comparisons of water quality near sinkholes and quarries were used to determine if limestone quarries act as "engineered sinkholes".

Limestone quarries are common where limestone bedrock outcrops at the land surface because the quarries are a source of gravel, cement, and other construction materials. As the human population continues to grow, the demand for construction materials will increase as new schools, homes, and highways are built. Regions, like northwest Arkansas, that have a limestone bedrock resource, the Boone Formation, will continue to supply the demand for the materials. While the chert in the Boone Formation makes mining difficult at times, the abundance of limestone is an economic resource to the region. The quarries in the Boone Formation can be found across the Ozark Physiographic Province (Ozarks), active and inactive. The state of Arkansas has loose regulations for the reclamation of exhausted limestone quarries. The common types of reclamation include lake, pasture, forest, or fill. For this study, both active and inactive quarries were utilized, as well as the lake and pasture reclamation types.

Groundwater flow out of quarries was determined by water stable isotopes, water chemistry, and a dye trace. The water stable isotopes provided the most likely connection between the limestone quarries and nearby springs. Water chemistry between the quarries and

springs were similar for the majority of the chemical components of the water samples. The dye trace provided no connection between the quarry and nearby springs. While the groundwater moving through the limestone quarries may not be evident in some of the springs observed in this study, the movement of water via fractures and joints in the limestone is occurring. A deeper, regional groundwater flow path is likely occurring in these karstified landscapes, as indicated by the dye trace and spring water chemistry results. These findings further prove the complexities of groundwater flow paths in a karst landscape.

When looking at a topographic map, quarries and sinkholes both appear as depressions. From comparing water quality data between springs near sinkholes and springs near quarries, the two types of depressions may not be as similar as one would originally think. Quarries lack the soil and regolith that protects groundwater and serves as a storage zone for sinkholes.

Water chemistry and water isotope samples were collected at quarries and springs in northern Arkansas and a dye trace was completed to understand groundwater flow out of the quarries. During storm-flow sampling, the discharge of water into Sharp's Quarry and St. Joe Quarry was visibly higher compared to base-flow sampling. Storm-flow samples had specific conductance and alkalinity values that were lower than base-flow samples; however, water temperatures during storm-flow were higher than base-flow values, which reflected surface air temperatures. The water samples indicated that the quarry lakes are supersaturated while all of the springs, except the spring near St. Joe Quarry, were undersaturated. Water isotope values of the springs near quarries ranged from -72.61‰ to -36.72‰ for δD and -10.53‰ to -4.8‰ for $\delta^{18}O$. Isotope values of the quarries ranged from -47.08‰ to -19.43‰ for δD and -7.54‰ to -0.78‰ for $\delta^{18}O$. Quarry samples were heavier indicating that the water in the quarries had been exposed to evaporation processes. The fluorescein dye used in the dye trace at Lead Hill

Quarry was not observed at any of the springs or creeks in the immediate surrounding area during the duration of the study.

Data from springs that were located near several sinkholes was downloaded from the National Water Quality Portal. All of the springs near the sinkholes had a negative calcite saturation index, indicating that the water flowing out of the springs was undersaturated. Nitrate values of the springs near sinkholes were higher than background nitrate values for the Ozarks.

This research has provided an analysis of groundwater flow out of quarries. While the flow out of quarries may not be evident in all springs near a quarry, flow of groundwater out of quarries via fractures, joints, and conduits is likely to happen in karst landscapes. Further analysis of regional springs and streams may provide a better connection between the quarries and groundwater as deeper flow paths likely occur in the observed karst landscape. Because of the changes in groundwater flow in and near the quarries, best management practices during the mining process and during the reclamation efforts must be considered in karst regions. The question of limestone quarries acting as "engineered sinkholes" relates to the way that water flows through the quarries and how potential contaminants may enter the groundwater. The quarries in their present state may not act as "engineered sinkholes", but in geologic time, a thick regolith will have formed over the Boone Formation bedrock. At that point in time, when the quarries have the regolith storage that sinkholes have, quarries will likely act as "engineered sinkholes". Perhaps quarries with a soil and regolith mantle already exist in the regions of the world where ancient civilizations quarried rock for their infamous architectural achievements.

Further investigations should be considered to obtain more data to better understand the flow of groundwater in and around limestone quarries in karst landscapes. More samples of base-flow and storm-flow water should be collected from the springs observed in this study as well as

other springs and spring-fed streams in the area. Dye traces should be completed at the other quarries to fully understand the flow path of water in and around the quarries, if landowner permission allows the vivid dye to be injected to the quarry and eventually the groundwater. Methods similar to those explained in this study should be used in other karst regions where limestone quarrying is prominent to better understand flow paths in and around quarries and how they change before, during, and after the mining of limestone.
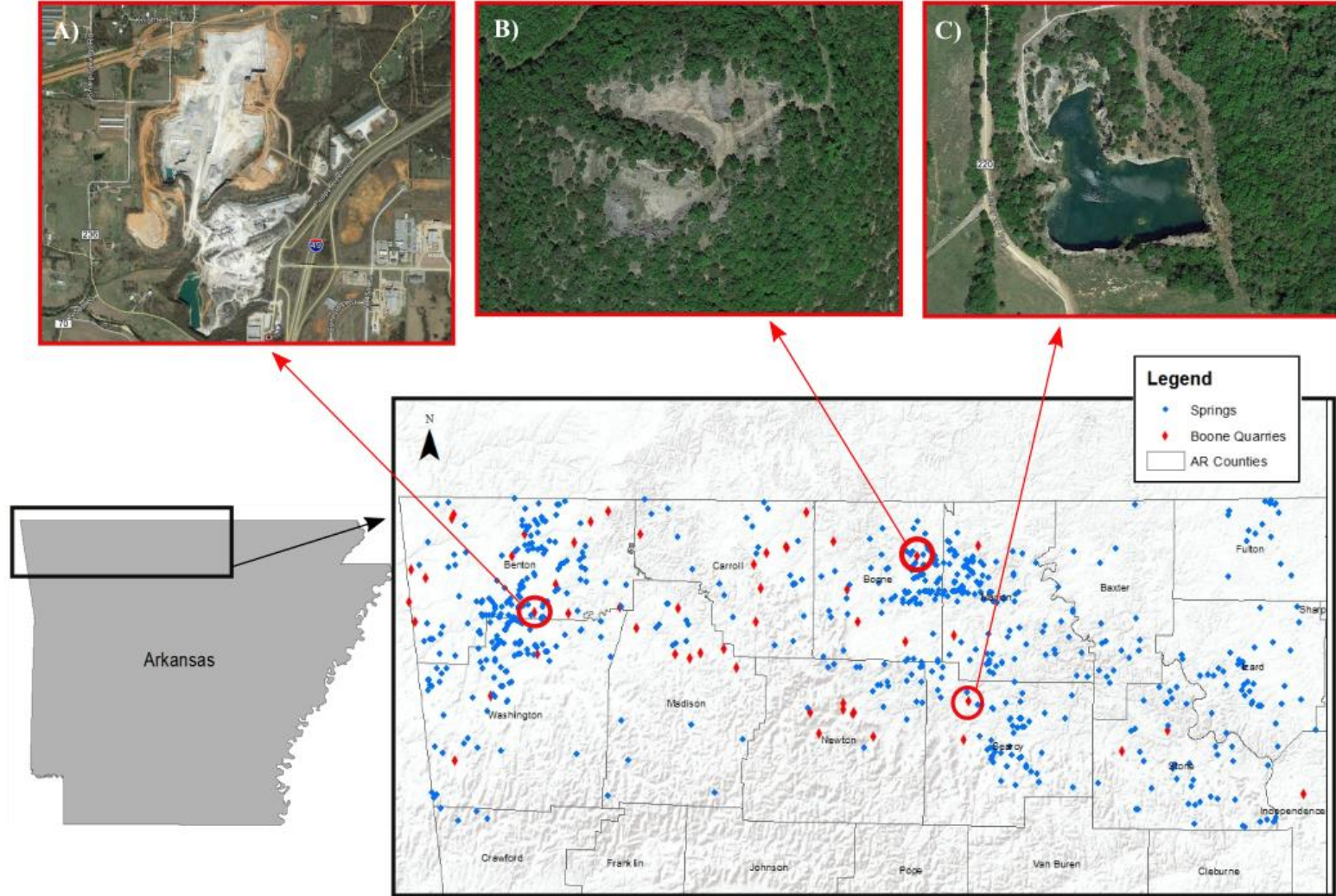
Figure 1. A map of quarries in the Boone Formation (red diamonds) as defined by Kline (1998) and springs (blue circles) from U.S. Geological Survey topographic maps. Google Earth (2016) images of the three limestone quarries in Northwest Arkansas used in this study (A: Sharp's Quarry, B: Lead Hill Quarry, C: St. Joe Quarry).

Figure 2. A Google Earth (2016) image of the Lead Hill Quarry area indicating locations of springs. The pictures are of A) Brother Spring, B) Sheep Field Spring, and C) Barn Spring.
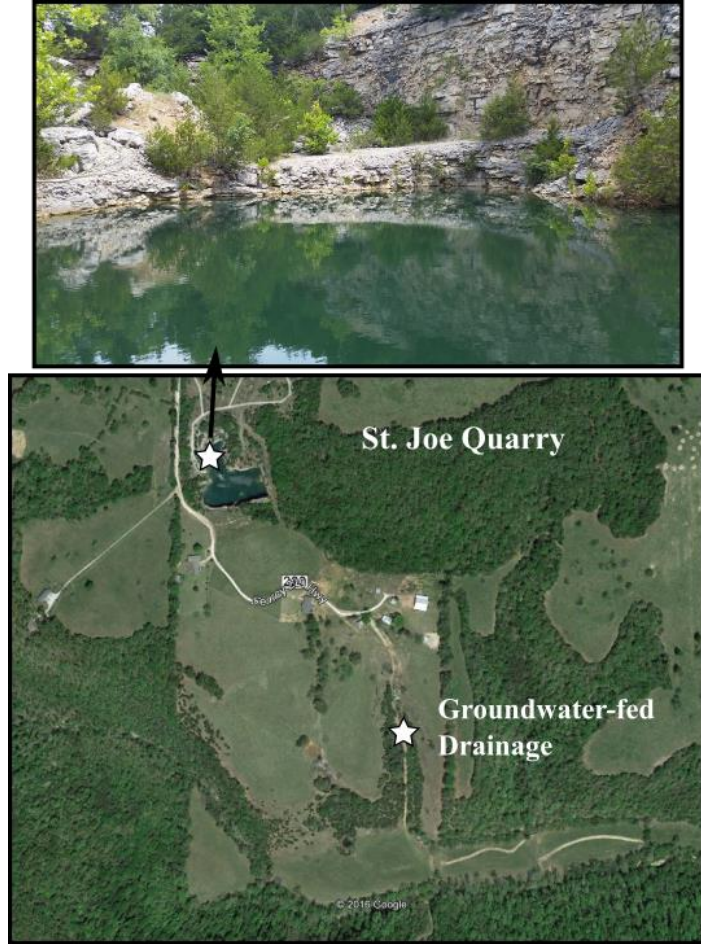
Figure 3. A Google Earth (2016) map of the St. Joe Quarry area (bottom) and a picture taken from the water sample collection point in St. Joe Quarry. The groundwater-fed drainage is labeled on the map.
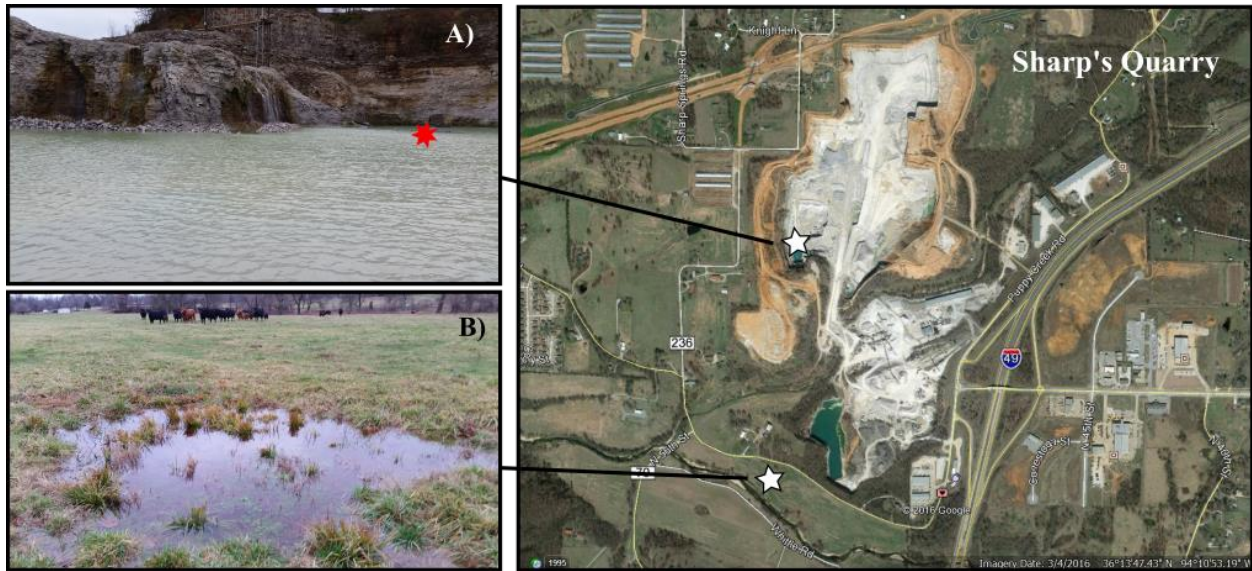
Figure 4. A Google Earth (2016) map of the Sharp's Quarry area with pictures of the sample location inside of the quarry (A) and Field Spring (B). The red 7-sided star in picture A was the location of the base-flow water sampling as water level was lower in the quarry.
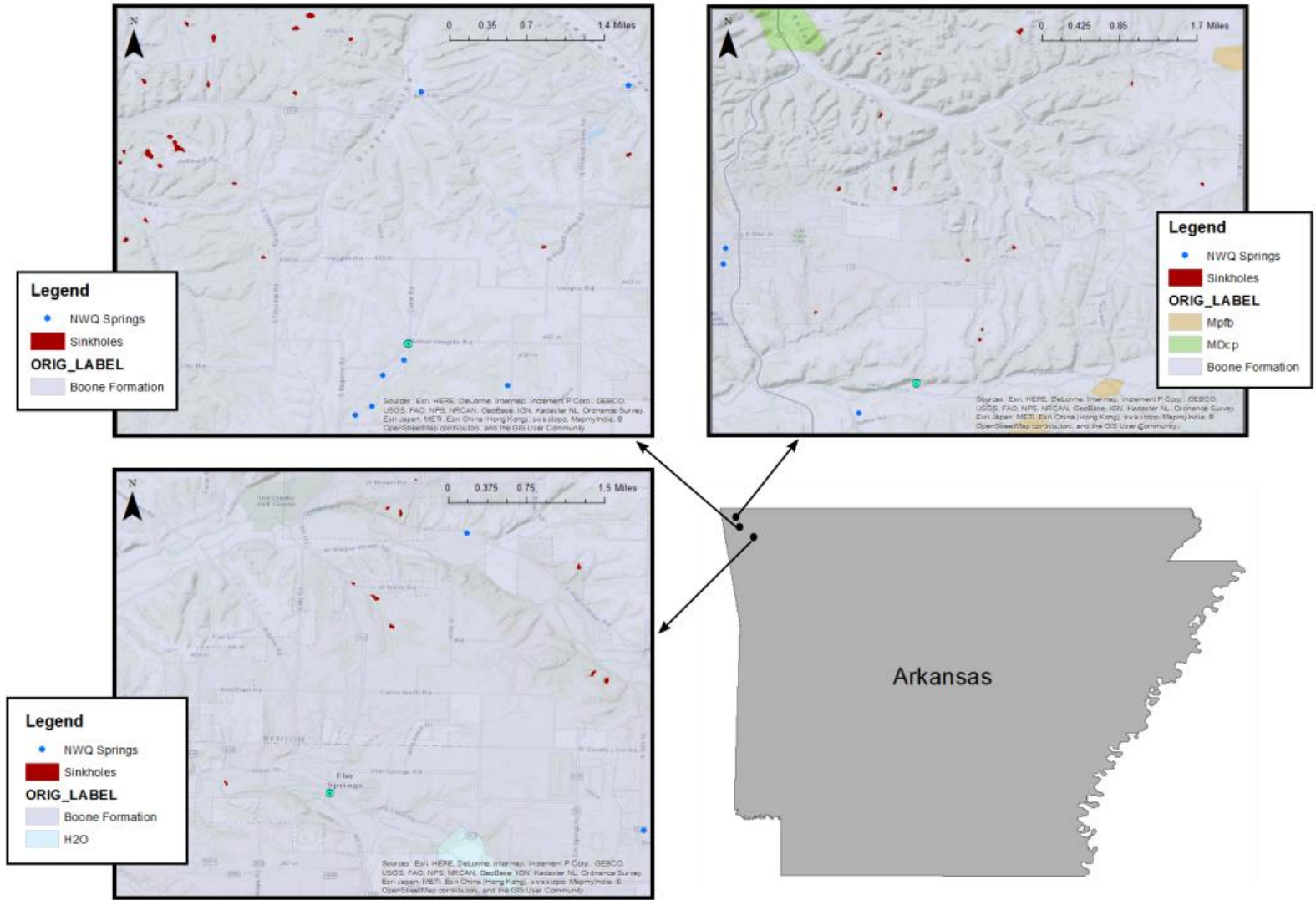
Figure 5. Topographic maps of the selected springs (blue circle with center) near sinkholes clusters (red polygons). The Arkansas geologic map was applied to the maps to display the Boone Formation.
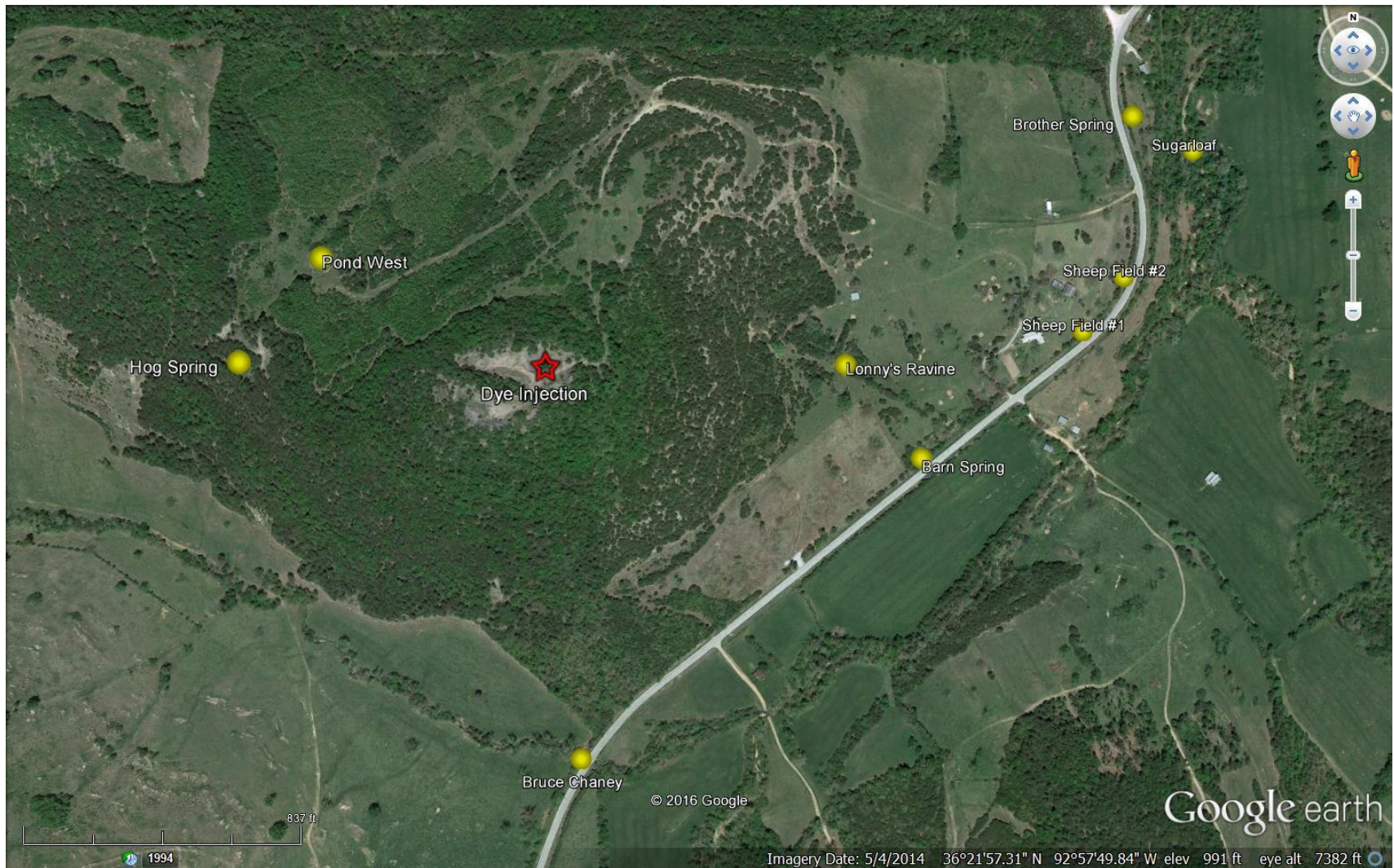
Figure 6. Locations of the dye injection point ("Dump" indicated by the star) and the carbon samplers in streams and creeks (points). Image from Google Earth (2016).

Figure 7. A picture of the Sharp's Quarry sump where water samples were collected during stormflow. Water can be seen entering the sump from bedding planes in the quarry walls.
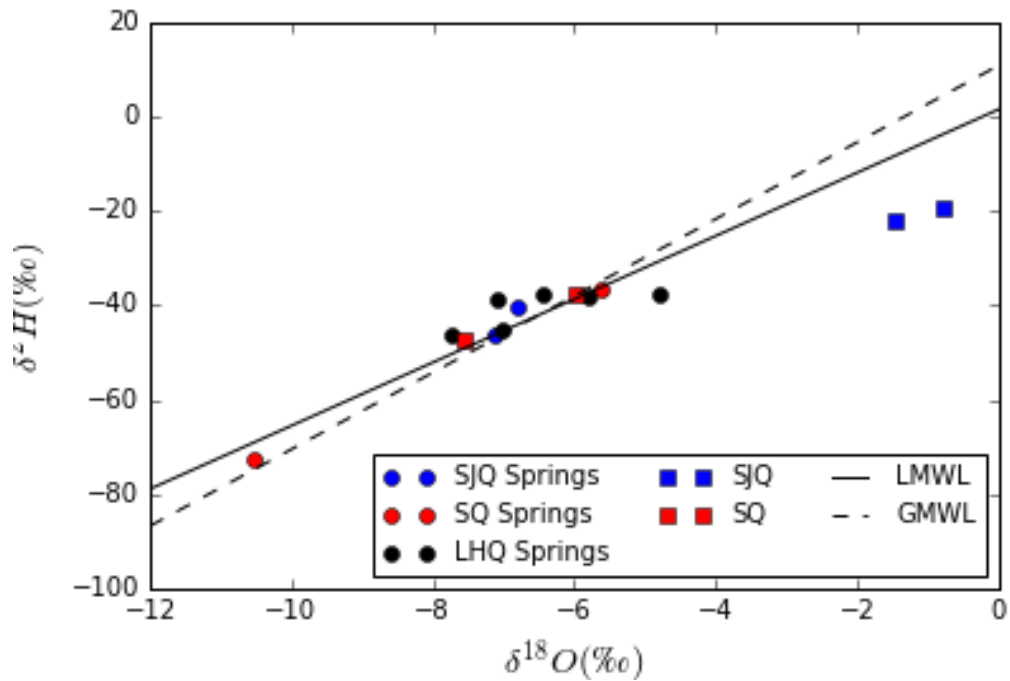

Figure 8. A plot of the δD and $δ^{18}O$ isotopes of quarries (squares) and springs (circles), compared to the Global Meteoric Water Line (GMWL) and Local Meteoric Water Line (LMWL) (Knierim, 2015). The quarries and springs are color coded by location: St. Joe Quarry (SJQ) area is blue, Sharp's Quarry (SQ) area is red, and Lead Hill Quarry (LHQ) area is black. The error associated with the isotopic values is as large as the symbols (1‰ for δD and 0.5‰ for $δ^{18}O$).
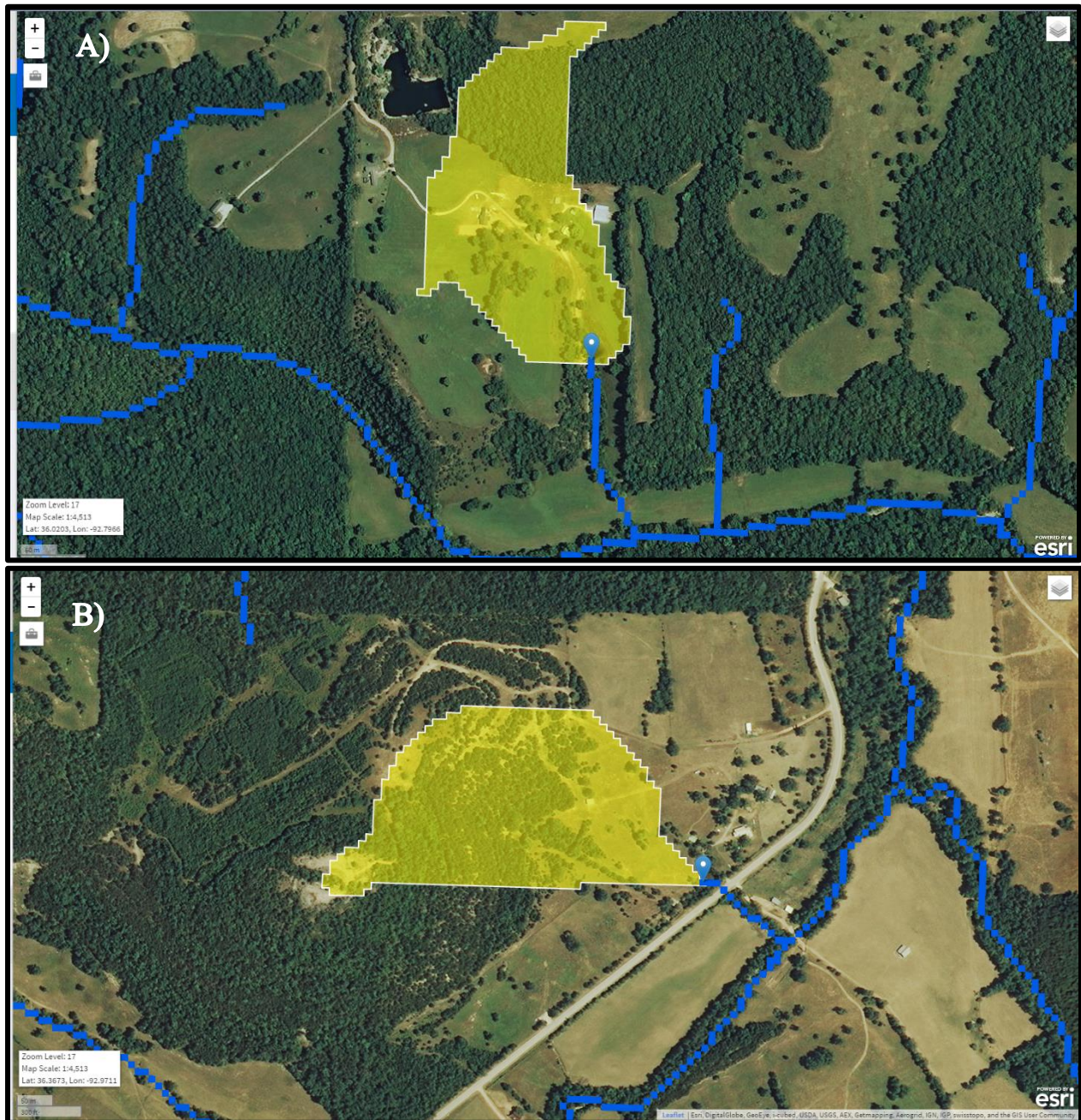
Figure 9. Maps of the A) St. Joe Quarry groundwater- fed drainage basin and B) the Lead Hill Quarry Lonny's Ravine basin from StreamStats outlined by yellow shapes. Streams are indicated by the blue points (U.S. Geological Survey, 2012).

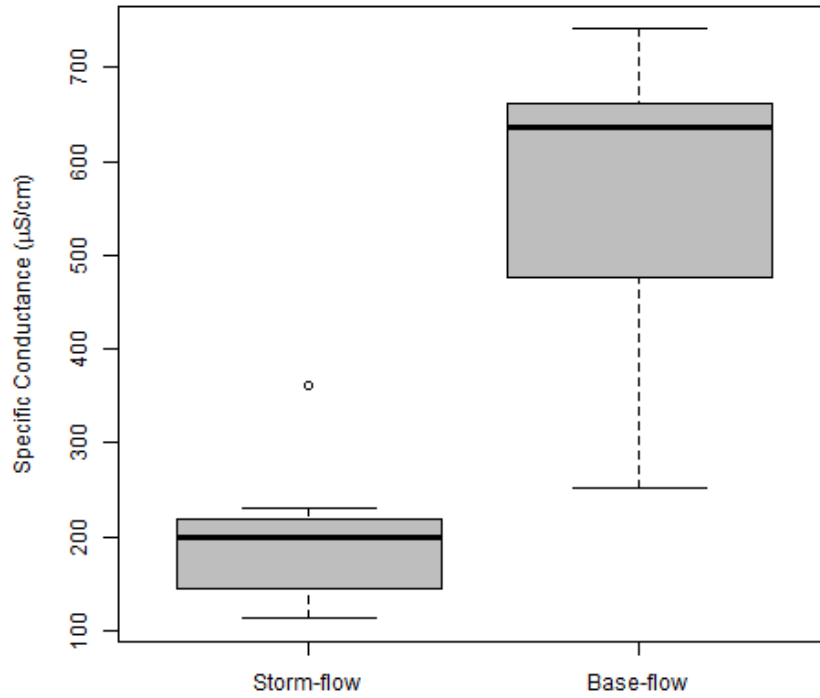**Figure 10.** A boxplot of specific conductance of the quarries and nearby springs during storm-flow and base-flow.
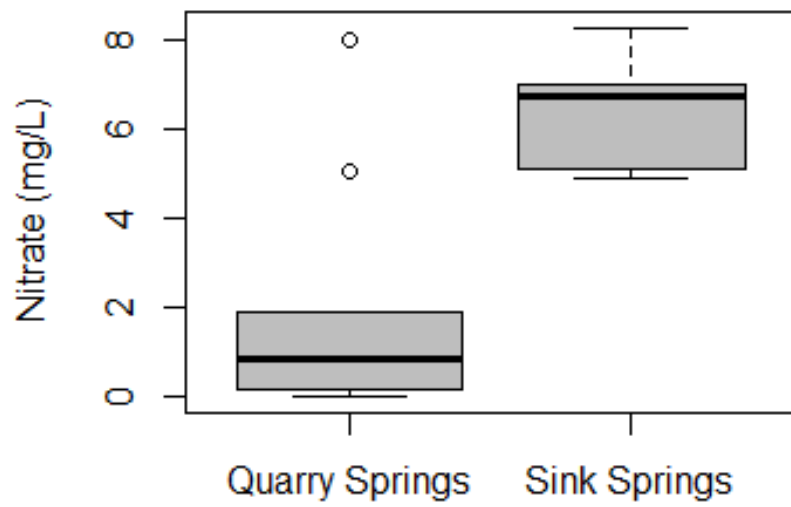

Figure 11. A boxplot of nitrate data of springs near quarries ("Quarry Springs") and springs near sinkholes ("Sink Springs").
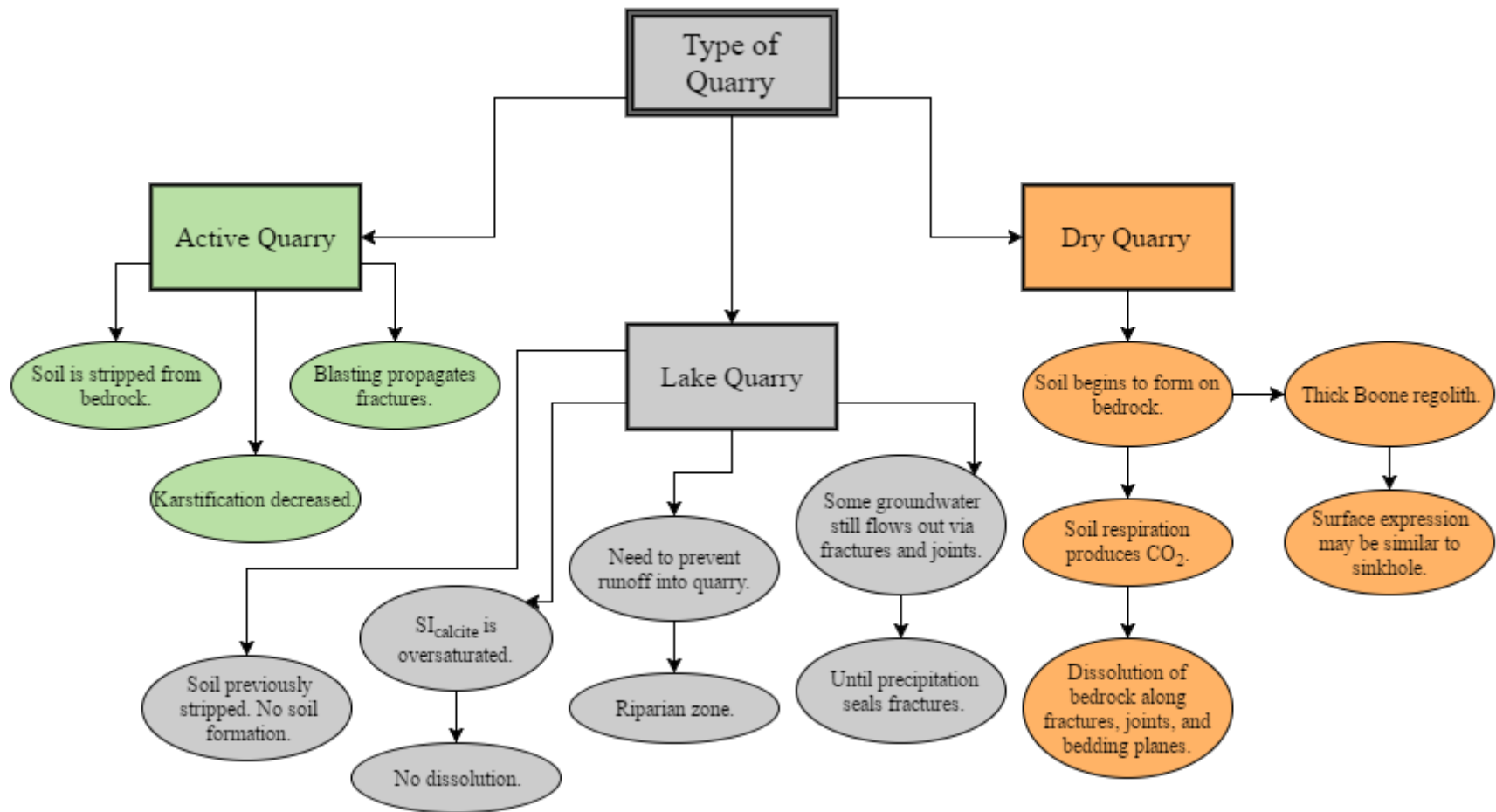
Figure 12. A flowchart of the types of quarries and the processes that occur in the quarries to limit or enhance karst feature formation over geologic time.

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VIII. Appendix

A. Tables of p-values calculated for statistical comparisons of water chemistry components of quarries, springs near quarries, and springs near sinkholes. The shaded cells indicate p-values that are statistically different (less than 0.05). The p-values were calculated using the Wilcoxon Ranked Sum Test.

Alkalinity

	Quarry	Spring near Quarry	Spring near Sinkhole
Quarry	----	0.028	
Spring near Quarry	0.028	----	0.017
Spring near Sinkhole		0.017	----

Calcium

	Quarry	Spring near Quarry	Spring near Sinkhole
Quarry	----	0.106	
Spring near Quarry	0.106	----	0.022
Spring near Sinkhole		0.022	----

Chloride

	Quarry	Spring near Quarry	Spring near Sinkhole
Quarry	----	0.374	
Spring near Quarry	0.374	----	0.828
Spring near Sinkhole		0.828	----

Magnesium

	Quarry	Spring near Quarry	Spring near Sinkhole
Quarry	----	0.036	
Spring near Quarry	0.036	----	0.031
Spring near Sinkhole		0.031	----

Nitrate

	Quarry	Spring near Quarry	Spring near Sinkhole
Quarry	----	0.839	
Spring near Quarry	0.839	----	0.007
Spring near Sinkhole		0.007	----

pH

	Quarry	Spring near Quarry	Spring near Sinkhole
Quarry	----	0.006	
Spring near Quarry	0.0006	----	0.003
Spring near Sinkhole		0.003	----

Potassium

	Quarry	Spring near Quarry	Spring near Sinkhole
Quarry	----	0.119	
Spring near Quarry	0.119	----	0.793
Spring near Sinkhole		0.793	----

Sodium

	Quarry	Spring near Quarry	Spring near Sinkhole
Quarry	----	0.945	
Spring near Quarry	0.945	----	0.056
Spring near Sinkhole		0.056	----

Sulfate

	Quarry	Spring near Quarry	Spring near Sinkhole
Quarry	----	0.733	
Spring near Quarry	0.733	----	0.003
Spring near Sinkhole		0.003	----

B. Other p-values, calculated using the Wilcoxon Ranked Sum Test, which was used in this study.

Components of comparison		p-value
Spring and quarry water – δD	Knierim (2015) soil water δD	0.009
Spring and quarry water – $\delta^{18}O$	Knierim (2015) soil water $\delta^{18}O$	0.005
Spring and quarry water – δD	Knierim (2015) cave water δD	0.001
Spring and quarry water – $\delta^{18}O$	Knierim (2015) cave water $\delta^{18}O$	0.005
Specific conductance – Storm-flow	Specific conductance – Base-flow	0.001

C. Land use percentages for drainage basins at Lead Hill Quarry and St. Joe Quarry.

Land Use	Percent
Lead Hill Quarry	
Urban	1 %
Herbaceous/Woody	14%
Forest	54%
Bare Soil/Seedbed	8%
Grasses	23%
St. Joe Quarry	
Urban	16
Herbaceous/Woody	13%
Forest	29%
Grasses	42%