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V. Brahana
University of Arkansas, Fayetteville, brahana@uark.edu

J. Nix
Ouachita Baptist University

C. Kuyper
Ouachita Baptist University

T. Turk
National Oceanographic and Atmospheric Administration

F. Usrey
National Park System

See next page for additional authors

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Geochemical Processes and Controls Affecting Water Quality of the Karst Area of Big Creek near Mt. Judea, Arkansas

V. Brahana[1*], J. Nix[2], C. Kuyper[3], T. Turk[4], F. Usrey[5], S. Hodges[5], C. Bitting[6], K. Ficco[7], E. Pollock[8], R. Quick[9], B. Thompson[10], and J. Murdoch[11]

[1]U.S. Geological Survey (Research Scientist Emeritus) and Department of Geosciences (Emeritus Professor), University of Arkansas, Fayetteville, AR 72701
[2]Department of Chemistry (Emeritus Distinguished Professor), Ouachita Baptist University, Arkadelphia, AR 71923
[3]Department of Chemistry Water Lab, Ouachita Baptist University, Arkadelphia, AR 71923
[4]National Oceanographic and Atmospheric Administration, Research Fisheries Biologist (Retired), Seattle, WA 98115
[5]National Park System, Buffalo National River, 402 N. Walnut, Suite 136. Harrison, AR 72601
[6]HC 73 Box 182 A,Marble Falls, AR 72648
[7]Department of Karstology, University of Nova Gorica, Slovenia
[8] Director, University of Arkansas Stable Isotope Lab, Fayetteville, AR 72701
[9]Woodward Clyde Consulting Group (retired); ADEQ (retired), Little Rock, AR 72118
[10]Tyson Foods, Inc. (Retired), Fayetteville, AR 72701
[11]Department of Biological and Agricultural Engineering (Retired), University of Arkansas, Fayetteville, AR 72701

*Correspondence: brahana@uark.edu

Running Title: Geochemical Processes and Controls Affecting Water Quality of the Karst Area of Big Creek near Mt. Judea

Abstract

Karst regions typically are considered to be vulnerable with respect to various land-use activities, owing to the intimate association of surface and groundwater and lack of contaminant attenuation provided by most karst aquifers. Inasmuch as the soluble rocks of the karst landscape can be dissolved to create large, rapid-flow zones that compete successfully with surface streams, groundwater and subsurface flow represent a much larger component of the hydrologic budget in karst regions than in areas where non-soluble rocks predominate. Karst areas typically are distinguished by being unique, but some general approaches can be applied to characterize the hydrology of the area. These approaches include an evaluation of the degree of karstification, the hydrologic attributes of the groundwater flow system, the baseline water quality, the time-of-travel through the karst flow system, and the general flux moving through the system. The nature of potential contaminants and their total mass and range of concentrations are critical to understanding the potential environmental risk.

This study describes the characterization of the baseline water quality of the shallow karst Boone aquifer and surface streams and springs to determine major processes and controls affecting water quality in the region, and to assess 2 years of waste spreading. Parameters evaluated include major constituents, contaminants and their breakdown products from the industrial operation of a concentrated animal-feeding operation (CAFO) on Big Creek, the indicator pathogen, *E. coli*, dissolved oxygen, selected trace metals, and other ancillary water-quality attributes that are directly observable in the environment. Determination of pre-CAFO water quality was accomplished by sampling approximately 40 sites that included wells, springs, and streams.

Introduction

The recent (2012) Arkansas Department of Environmental Quality (ADEQ) issuance of a permit for a CAFO near Big Creek, slightly more than 10 kilometers (km) upstream from the Buffalo National River near the town of Mt. Judea, Arkansas (Figure 1), made Arkansas citizens aware of the potential for the CAFO to introduce solutes and pathogens that could degrade surface and groundwater in the area. The initial permit did not consider or discuss groundwater or karst, nor did it establish baseline water quality.

The waste generated from 6,503 hogs exceeds more than 7.5 million liters per year, and it must be continually removed to avoid overfilling the waste lagoons. Pig feces and urine spread on pasture land overlying karst has generated significant concern that the CAFO will create health problems for the many tourists who utilize the Buffalo, as well as many of the downstream landowners in Big Creek valley who use

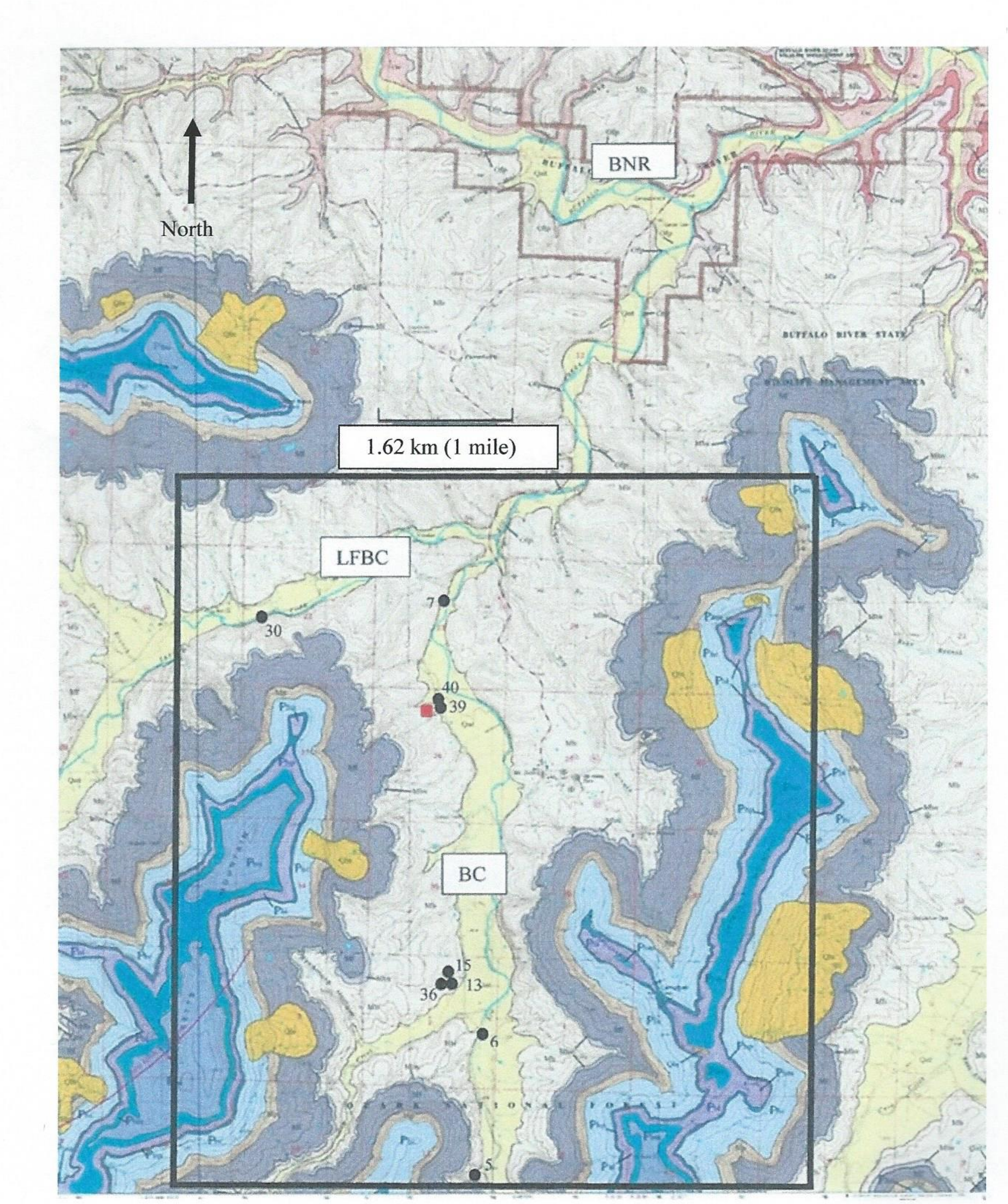

Figure 1. Geologic map of the study area, indicating the extent of karst where the Boone Formation (light grey color) occurs at land surface. BNR is Buffalo National River; BC is Big Creek and LFBC is Left Fork of Big Creek. The CAFO is shown by the red square, and the spreading fields for waste mostly lie between 7 & 6 on the west side of Big Creek. The study area is outlined by the black rectangle. Numbers 6 & 7 are referenced to Table 2. Numbers 5 & 30 are the furthest extent of groundwater tracing in the study area from dye input at 36, which has an altitude greater than any of the dye-receiving sites. The geologic base map is from Braden and Ausbrooks (2003). Topographic base map is from USGS (1980). Color legend for the map is in Figure 2.

the groundwater for domestic and stock water supplies. Canoeists and swimmers are particularly concerned because much of the drainage area of Big Creek has been karstified, which means that contaminated water with concentrated pig waste can move rapidly through open voids in the subsurface with little or no attenuation, and resurface in Big Creek, Left Fork Big Creek, or springs that drain the impacted area that lie downgradient. The main drain of this highly interactive groundwater/surface water system is the Buffalo National River (BNR on Figure 1). Insofar as the canoeists and swimmers cannot escape direct contact with river waters of the Buffalo (an Extraordinary Resource Water), citizen concerns seem warranted, and served as justification for conducting this study.

Physical Setting of the Study Area

Hydrologically, the study area includes the drainage basin of Big Creek including the waste-spreading fields of the CAFO, and the region surrounding site 30 on Left Fork of Big Creek (LFBC on Figure 1), which has been shown by dye tracing to receive groundwater flow beneath the topographic divide separating the two surface-drainage basins. The Boone Formation (from the base of the Batesville Formation to the bottom of the St. Joe Formation) is shown in Figures 1 and 2 as the light gray color in the central and northwest parts of the study area. The study area lies completely within Newton County.

The Boone Formation occurs across northern Arkansas in a broad outcrop band coincides with the Springfield Plateau physiographic province. This formation becomes karstified during weathering to facilitate groundwater capture of surface water, including the Mt. Judea area. Although this geologic unit encompasses about 35 percent of the land area of the northern two tiers of Arkansas counties, specific details of its hydrogeology are only generally documented in the literature. and its water-transmitting capacity and its ability to attenuate contamination has seldom been discussed other than to reference the entire area as a mantled karst (Aley 1988, Aley and Aley 1989, Imes and Emmett 1994, Adamski et al. 1995, Funkhouser et al. 1999, Braden and Ausbrooks 2003, Mott 2003, Hobza et al. 2005, Brahana et al. 2011, Kosič et al. 2015). Given this general cursory treatment, there exists a faulty claim that lack of obvious karst topography at air-photo scales is evidence that karst in the outcrop of the Boone Formation does not exist. The claim is inaccurate.

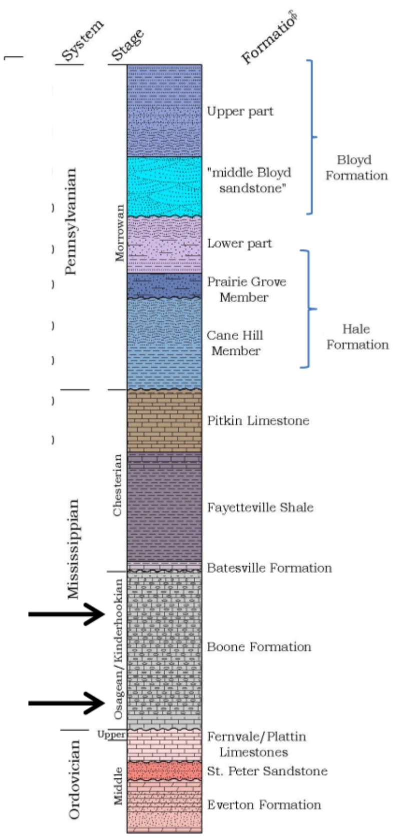

Figure 2. Stratigraphic column of the study area, showing the extent of karst where the Boone Formation (light grey color) occurs at land surface. Arrows identify the chert-rich interval of the formation. Total thickness of the Boone is about 110 m. Figure modified from Braden and Ausbrooks (2003).

The Boone Formation is a relatively thick unit, about 110 m with variable lithology, including limestone, chert, and minor thin shaley limestone layers. The soluble limestone of the Boone contrasts with the highly insoluble, brittle chert, which can occupy as much as 70 percent of the entire thickness of this formation. For the most part, the Boone contains no less than 50 percent chert, except in its upper and lower pure-limestone measures (Liner 1978). The Boone Formation is nearly flat-lying, and has numerous, thin interbedded limestone layers forming couplets with thin, areally continuous chert layers through much of its middle and lower sections of the formation (Hudson and Murray 2003). Brittle fracturing, a result of about 200 meters of total uplift in the distal, far-field of the Ouachita orogeny has allowed groundwater to chemically weather and karstify the formation (Liner 1978, Brahana et al. 2014).

The physical attributes of the chert at a regional scale appears to be near-uniform thickness, but in the field under close, non-magnified inspection, contact boundaries between the chert and limestone reflect thickening and thinning that one would expect in soft, non-indurated sediment, typically on the order of several centimeters. Whereas individual chert layers may possess similar thickness, different layers vary significantly, with some of the thicker chert units greater than 30 cm. The limestone lithologies in this interval range from less than 10 cm to several m.

The low permeability of the chert results in segregation and vertical isolation in this part of the groundwater flow system, which typically has been developed only in the limestone layers where the rock has been dissolved and karstified. The systematic orthogonal jointing resulting from the uplift and the long duration of weathering near the land surface are responsible for introduction of aggressive recharge and dissolution from the land surface to the hydrologically connected groundwater (Adamski et al. 1995, Davis et al. 2000, Funkhouser et al. 1999, Brahana et al. 2011).

Problem to Be Addressed

Significant land-use changes from a CAFO on karst required an accurate characterization of groundwater flow and the establishment of baseline water quality. Defining geochemical processes and controls was an essential first step in addressing these data gaps.

The CAFO is comprised of a 6,503-head facility for 2500 farrowing sows, 4000 piglets, and 3 boars; it was permitted to be constructed on the Boone Formation. In addition to the large structures housing the swine, two lagoons approximately one acre each were included as temporary holding facilities for urine, feces, and wash water from the operation. In addition, about 243 hectares of pasture land for waste were also approved on land underlain by the Boone Formation, or in the valleys with thin alluvial deposits directly overlying the Boone (Braden and Ausbrooks 2003). The waste generated from this CAFO is equivalent to the waste generated by a city of 17,000 people (Tietz, 2006).

In addition to the lack of characterization of 1) karst, 2) basic hydrogeology, and 3) a baseline assessment of water quality (Brahana and Hollyday 1988, Edmunds and Shand 2008), the risk of similar environmental and water-quality problems occurring on the Buffalo had been well-documented elsewhere (Quinlan 1989, Quinlan et al. 1991, Funkhouser et al. 1999, Varnell and Brahana 2003, Palmer 2007, Gurian-Sherman 2008, Brahana et al. 2014, Kocic et al. 2015). The waste generated from 6,503 hogs of this size exceeds more than 7.5 million liters per year, and it must be periodically removed to avoid overfilling the waste lagoons (Pesta 2012). Insofar as the swimmers, fishermen, and canoeists cannot escape primary contact with water in the Buffalo National River, which has been classified as an ERW, this research was undertaken as part of a sequence of karst hydrogeologic studies to fill in the missing scientific gaps that were not addressed in the original permitting and approval process.

Water samples from wells, springs, and streams in the study area were collected during the summer and fall of 2013 prior to waste spreading from the CAFO. Sampling was conducted in the field by teams of volunteers using approved U.S. Geological Survey methods (Wilde 2006). Prior to collecting each water sample, field parameters of temperature, specific conductance, and pH were measured and reported. Site location was determined using a Garmin Colorado global positioning system, with latitude and longitude recorded in degrees and decimal minutes, to four significant figures of decimal minutes.

Sampling and Sample Preservation

Grab samples were obtained at each of approximately 40 sites and shipped to the Ouachita Baptist University Water Lab. Samples were taken to accurately represent water-quality at the time of collection. Each sample was divided into 5 fractions, and appropriate preservation initiated for each subsample as indicated below.

Methods

Raw Unacidified {R_u] Sample: An untreated aliquot was placed in a 500 mL plastic bottle and placed on ice. This subsample was used for the lab determination of alkalinity, turbidity, and specific conductance.

Raw Acidified (sulfuric acid) [R_a] Sample: a sub-sample was placed in a 250 mL plastic bottle then acidified with sulfuric acid to pH 2 then placed on ice. This subsample was used for the determination of total phosphorus, total Kjeldahl nitrogen, and ammonia nitrogen.

Filtered Acidified [F_a] Sample: A 25- mL subsample was filtered through a 0.45 micron filter using a syringe and a plastic Swinex filter holder. The sub-sample was then acidified to pH 2 with nitric acid then placed on ice. This subsample was used for the determination of sodium, potassium, calcium, magnesium, iron, manganese, copper, and zinc.

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Filtered Unacidified [F_u] Sample: A 25-mL subsample was filtered through a 0.45 micron filter then placed in a 25-mL plastic bottle then placed on ice. This fraction was used for the determination of nitrate nitrogen, chloride, and sulfate.

Microbial Sample: Microbial samples were collected in 125 mL sterile cups, with no filtration and no acidification ($_{\text{raw}}$). The sample was placed on ice, and transported to the analyzing laboratory (University of Arkansas Water Lab) within 8 hours from sampling.

Laboratory and Field Analyses

Major constituents and nutrients were analyzed by the Ouachita Baptist University Water Lab in Arkadelphia, Arkansas. Cations were analyzed with an inductively coupled plasma optical emission chromategraphy (ICP-OEC), and anions were analyzed by high performance liquid chromatography (HPLQ). Pathogens were analyzed by the Arkansas Water Quality Lab (AWQL) on the campus of the University of Arkansas. This lab accommodated the short holding-time requirements. *E. coli* data reported in this paper were taken from the BCRET (2015) report, with analyses provided by AWQL using Idexx Quanti-tray equipment following Standard Methods in Water and Wastewater Analysis, method 89223-B. Stable isotopes of deuterium and oxygen-18 and dissolved selected trace constituents were analyzed by the University of Arkansas Stable Isotope Lab (UASIL) using Thermo Scientific iCAP Q inductively-coupled plasma mass spectrometer. Dissolved oxygen data were collected by the USGS using a dissolved oxygen logger that sampled every 15 minutes. The logger was deployed in Big Creek, and calibrated biweekly, following the procedure of Green and Usrey (2014).

Quality Assurance

Quality assurance, holding times, and sampling procedures employed in this study followed U.S. Geological Survey protocols (Wilde 2006). The Ouachita Baptist University Water Laboratory maintains an internal and an external quality assurance program, which includes periodic blind audits, checks for both precision and accuracy, and field blanks. The laboratory is certified by the ADEQ for each of the parameters reported. The minimum detection limits (MDL) for each parameter are given in Table 1.

Table 1. Chemical parameters analyzed by the Ouachita Baptist University Lab, and their minimum detection limits (MDL).

Parameter	MDL (in mg/L)
Major Anions	
Chloride	0.11
Sulfate	0.12
Alkalinity	1.08
Major Cations	
Sodium	0.06
Potassium	0.002
Calcium	0.079
Magnesium	0.006
Nutrients	
Ammonia Nitrogen	0.006
Nitrate Nitrogen	0.006
TKN	0.027
Total Phosphorus (low range)	0.008

Results and Discussion

Major Constituents

Water-quality data and synthesis from the major constituents indicate that the dominant processes controlling dissolved species in the water are dissolution, which is to be expected from precipitation recharging shallow aquifers, especially in karst regions. Mixing is also a predominant process, owing to the close interaction of surface and groundwater in karst settings, wherein recharge from surface precipitation events dilutes dissolved species in the groundwater. Background concentrations of dissolved chloride in groundwater were less than 5 mg/L, and concentrations of dissolved nitrate typically in the range of 1 mg/L or greater (Figure 3). Surface water samples typically had concentrations less than the mean for chloride, caused by dilution from upstream sources; nitrate experienced similar dilution, with reported concentrations not uncommonly between 0.1 to 0.5 mg/L (Figure 3).

Groundwater from the Boone Formation wells, springs, and surface water from Big Creek all are calcium- bicarbonate type (Figure 4). Deep wells beneath the cover of terrigenous sediments show the effect of less mixing, being more mineralized but still dominantly a calcium bicarbonate waters (Figure 4). Shallow wells and springs in the upper, overlying younger sediments (Figure 2) are indicative of less dissolution (Figure 3), with greater components of chloride and sulfate, typical of shales. Insofar as these are natural inorganic chemical solutes derived from dissolution and modified by mixing, and within EPA guidelines, none are considered to be hazardous to the overall health of water quality in Big Creek valley.

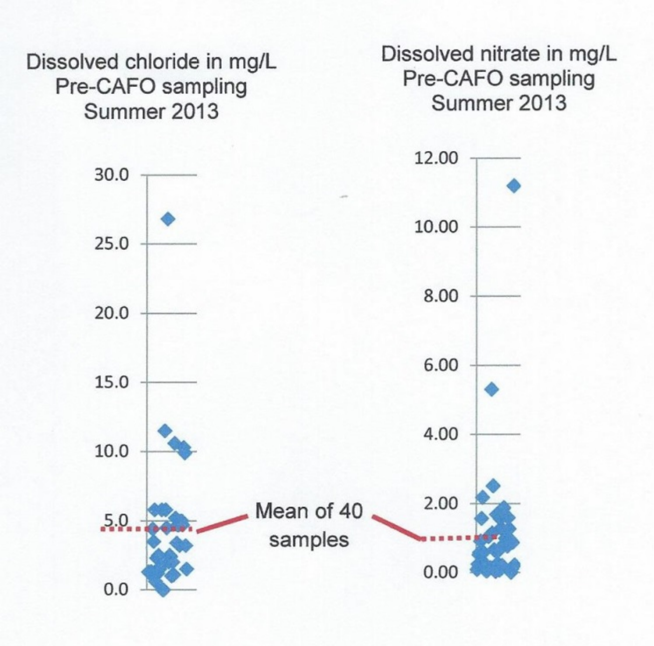

Figure 3. Concentration of dissolved chloride and nitrate sampled during the summer of 2013, prior to spreading of hog feces and urine on the spreading fields. The mean chloride concentration of 40 samples, which included groundwater from wells and springs and surface water from streams in the study area, was 4.5 mg/L. The mean nitrate concentration of 40 samples in the study area was 1.15 mg/L. Mean concentrations are shown by the dotted line. All units of concentration are mg/L

Microbes

Microbes are microscopic organisms that live in the guts of warm-blooded animals; they move into the environment upon defecation by the host, and they have the potential to be pathogenic to animals and humans when entrained in water and ingested. *E. coli* are an indicator organism of bacterial microbes. They are sampled to assess risk from primary contact with natural waters (Usrey 2013). In Big Creek, *E. coli* were sampled by the Big Creek Research and Extension Team (BCRET), as well as, the Karst Hydrogeology of the Buffalo National River (KHBNR) team. The Arkansas Pollution Control and Ecology Commission [APCEC] established criteria (APCEC 2015) for *E. coli* limits for impairment of surface waters in the state, and for those having a drainage basin greater than 26.24 km^2 (10 $miles^2$) it was 410 colonies per 100 milliliters (col/100 mL). This limit for *E. coli* requires "no exceedance of more than 25% of samples from no less than eight samples taken during the primary contact season or during the secondary contact season" (ADPCE 2015).

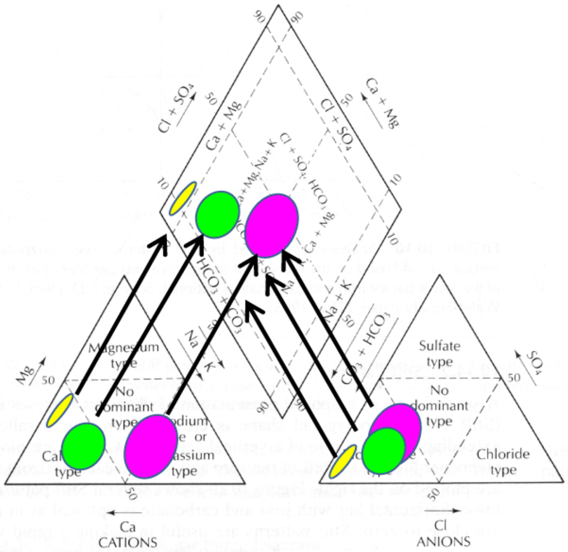

Figure 4. Piper diagram [modified from Hem (1993)] showing the general water-quality types in the exposed area of the Boone Formation (green), area of deeply buried Boone Formation with slow-flow karst attributes (yellow), and area of exposed, overlying, nonkarstified sandstone and shale aquifers (pink). These indicate that dissolution is the dominant geochemical process, coupled with mixing. This plot is based on pre-CAFO (2013) water samples. Figure 6 shows a cross-sectional view that identifies the general location of where these water types typically are found.

E. coli concentrations of single grab samples greater than 410 col/100 mL are not uncommon in streams, wells, and springs in the Big Creek drainage basin. For example, sites sampled during the summer of 2016 [6/14/2016 through 8/08/2016] (Figure 5) by KHBNR reflect extreme fluctuations that are attributed to multiple factors. These concentrations varied from less than 10 to 6,200 col/100 mL. Other examples included 6/24/14 *E.coli* concentrations in Big Creek which were 28,150 col/100 mL at site 6 , and 24,950 col/100 mL at site 7 (BCRET 2014).

Rapid changes in concentrations of microbes are a common expectation and have been observed in the Boone aquifer elsewhere (Marshall et al. 1999, Ting 2005), caused by mobilization of *E. coli* by resuspension in rapidly flowing surface and groundwater. Microbes have mass, and are deposited on the base of the flow systems when velocities slow during flow recession. Turbulence from rapid recharge

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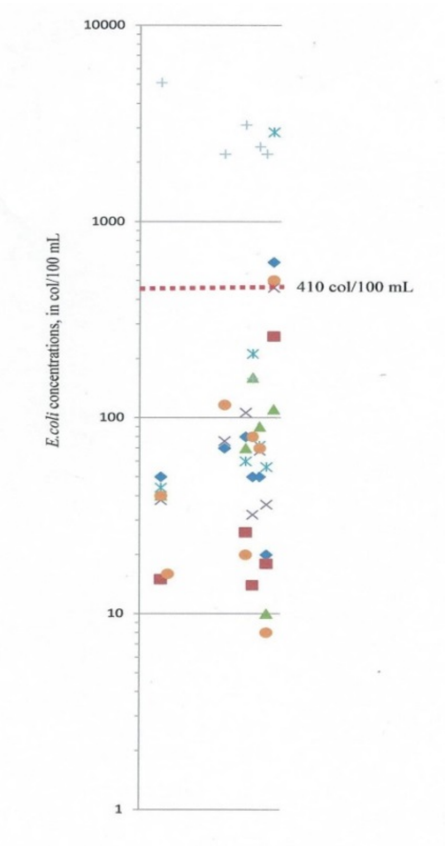

Figure 5. Semi-logarithmic plot of *E. coli* concentrations (in colonies/100 mL) for eight sampling intervals between 6/14/16 and 8/8/16. Samples were collected by the KHBNR team. Different patterns on the graph show different sampling periods. The red dashed line at 410 col/100 mL represents the *E. coli* concentration limit for Big Creek (non-extraordinary waters) the primary period. To be classed as impaired, a stream must be above this limit for five successive samples made during a 30-day period.

from storms resuspends the *E. coli* from the floor of the flow system, accounting for orders of magnitude increases. A key consideration here is that many of the *E.coli* persist in groundwater for periods of many months because of the lack of exposure of groundwater to ultraviolet rays, as well as to cooler groundwater temperatures. Although some die off of *E. coli* occurs in the subsurface, most organisms are entrained alive in the bottom sediment and have been shown to be viable for months (Whitsett 2001, Hamilton 2002). The dynamic nature and flow-path heterogeneity of karst flow ensures that each flow reach has a continuous and viable supply of these bacteria to share with downgradient receiving streams.

The similarity in timeframe and exceedingly high concentrations of *E. coli* at KHBNR sites is consistent with the connectivity of surface and groundwater in this watershed. Connectivity has been shown to directly impact the quality of downstream water in numerous other karst settings and locations (Winter et al. 1999, Palmer 2007).

Nutrients

Nutrients are compounds that are essential for plant and animal nutrition, and for this study the focus was primarily on nitrate. Animal feces are rich in nutrients, and too great an agricultural application rate can produce water-quality problems in receiving streams and groundwaters (Peterson et al. 2002, Sauer et al. 2008, Jarvie et al. 2014). Figure 7 shows a plotof nitrate concentrations versus time for two BCRET sites (BCRET 2016), 6 (upstream CAFO) and 7 (downstream CAFO) [Figure 1]. The dissolved nitrate concentrations from site 7 are greater than site 6 for the period of record, explained in part by the inflow of groundwater to Big Creek from springs which occur in the bed of the stream upgradient from site 7. Also notable are objectionable algal densities downgradient from these substream springs (Figure 8). Larger springs have been dye-traced from dye-injection well, site 36 (Figure 1) surrounded on 3 sides by spreading fields, and site 39 (Figure 1) across a county road and 200 m from the CAFO.

Summer 2013 analyses of nitrate in water in Big Creek valley (Figure 3) indicate that in some areas of the valley, the natural system had received more nutrients than could be adequately assimilated by crops, with dissolved concentrations of NO_3 as great as 11.3 mg/L analyzed from springs. Maximum EPA limits for nitrate are 10 mg/L, and although these elevated concentrations were present before the CAFO started, the groundwater system was obviously stressed during this time. In other locations in the valley where adequate dilution occurs, concentrations of dissolved nitrate typically are less than 1.0 mg/L.

Dissolved Oxygen

Dissolved oxygen (DO) concentrations in Big Creek were sampled by the U.S. Geological Survey at station 07055814 Big Creek at Carver. Automated probes sampled at 15-minute intervals, and were calibrated on a biweekly basis. Results from 2014 show a diurnal pattern of high concentrations during daylight hours, and low concentrations during the nighttime, which is typical. During daylight, algae in the creek generates oxygen, which is added to the water as it absorbs sunlight (due to photosynthesis). At night, oxygen is removed from the water, thus depleting DO from streams and rivers as part of a natural cycle. However, if measurements show the DO

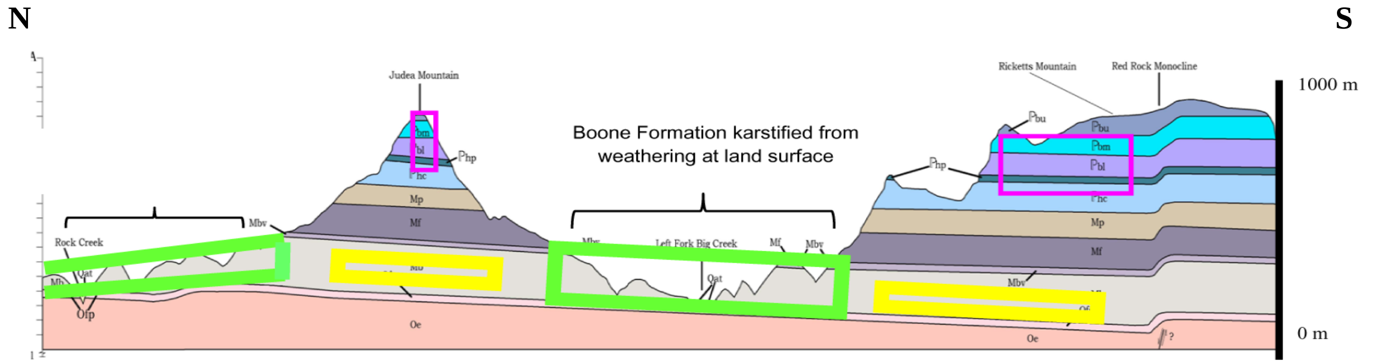

Figure 6. Generalized cross section showing typical water-quality types in the exposed area of the Boone Formation (green rectangles), area of deeply buried Boone Formation with slow-flow karst attributes (yellow rectangles), and area of exposed, overlying, nonkarstified sandstone and shale aquifers (pink rectangles). The line of section is along west edge of study area. Figure modified from Braden and Ausbrooks (2003).

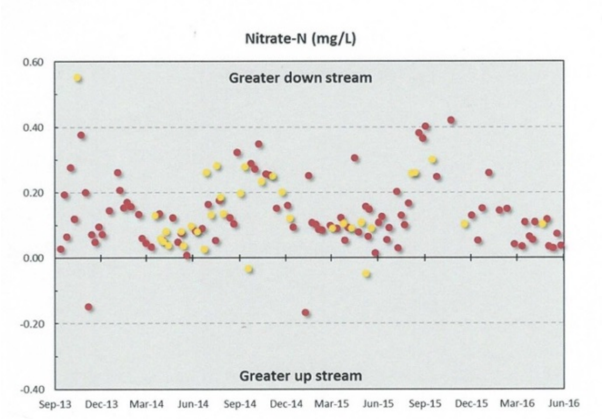

Figure 7. Plot of nitrate in mg/L verses sampling date showing the relation between upstream (Site 6-Figure 1) versus downstream BCRET sites (Site 7-Figure 1). Source of data and graph is BCRET (2016). Negative values for upstream site are necessary to plot the two stations together. Actual concentrations are positive.

Table 2. Periods of DO exceedence of Regulation 2 standards (APCEC 2015) during selected 8+ hour intervals in the summers of 2014 and 2015. Data are from U.S. Geological Survey (2016), site 07055814 Big Creek at Carver downstream from the study area.

Date	Start Time	Stop Time	Minimum Measured DO (mg/L)	Minimum DO Allowed (mg/L)
8/24/2014	2:45	11:00	4.4	5.0
8/25/2014	2:45	11:30	4.4	5.0
8/30/2014	3:15	12:00	4.5	5.0
9/1/2014	4:15	12:45	4.2	5.0
10/8/2014	5:45	15:15	5.8	6.0
8/10/2015	3:15	12:45	4.5	5.0

Figure 8. Objectionable algal densities on Left Fork of Big Creek downstream from an anomalously large spring (Brahana, 1997) at site 30 (Figure 1). Under high flow conditions, groundwater and dye were traced to site 30 beneath the topographic divide that separates Big Creek from Left Fork Big Creek.

concentration in the stream has dropped below the critical level, the stream is classified as impaired.

Minimum concentration of DO in this part of the Ozarks during the critical period is 5 mg/L for times when the water temperature is greater than 22^o C. Big Creek fell below 5.0 mg/L on multiple occasions during the summers of 2014 and 2015 (Table 2). Recently reported results from the National Park System conducting ongoing 15-minute DO monitoring of Big Creek during the summer of 2016 showed ongoing continuation of depressed DO.

As a comparison of DO on Big Creek to a nearby stream, DO concentration in the Little Buffalo River, slightly more than 10 km upstream from the confluence of Big Creek and the Buffalo River, was below 6 mg/L only 1 time for less than 3 hours total for the period measured during the sampling interval of summer 2013. The drainage basin of the Little Buffalo River has a similar distribution of land use and population as Big Creek, but it does not contain any CAFOs.

Trace Metals

Trace metals are dissolved cationic constituents that typically occur in water in very small concentrations (parts per billion or µg/L). Trace metals serve as effective tools for hydrogeologists to determine if groundwater contamination is occurring. If the trace metals can be connected with a specific land use, they may also serve as valuable indicators to suggest the potential contamination source. Relevant

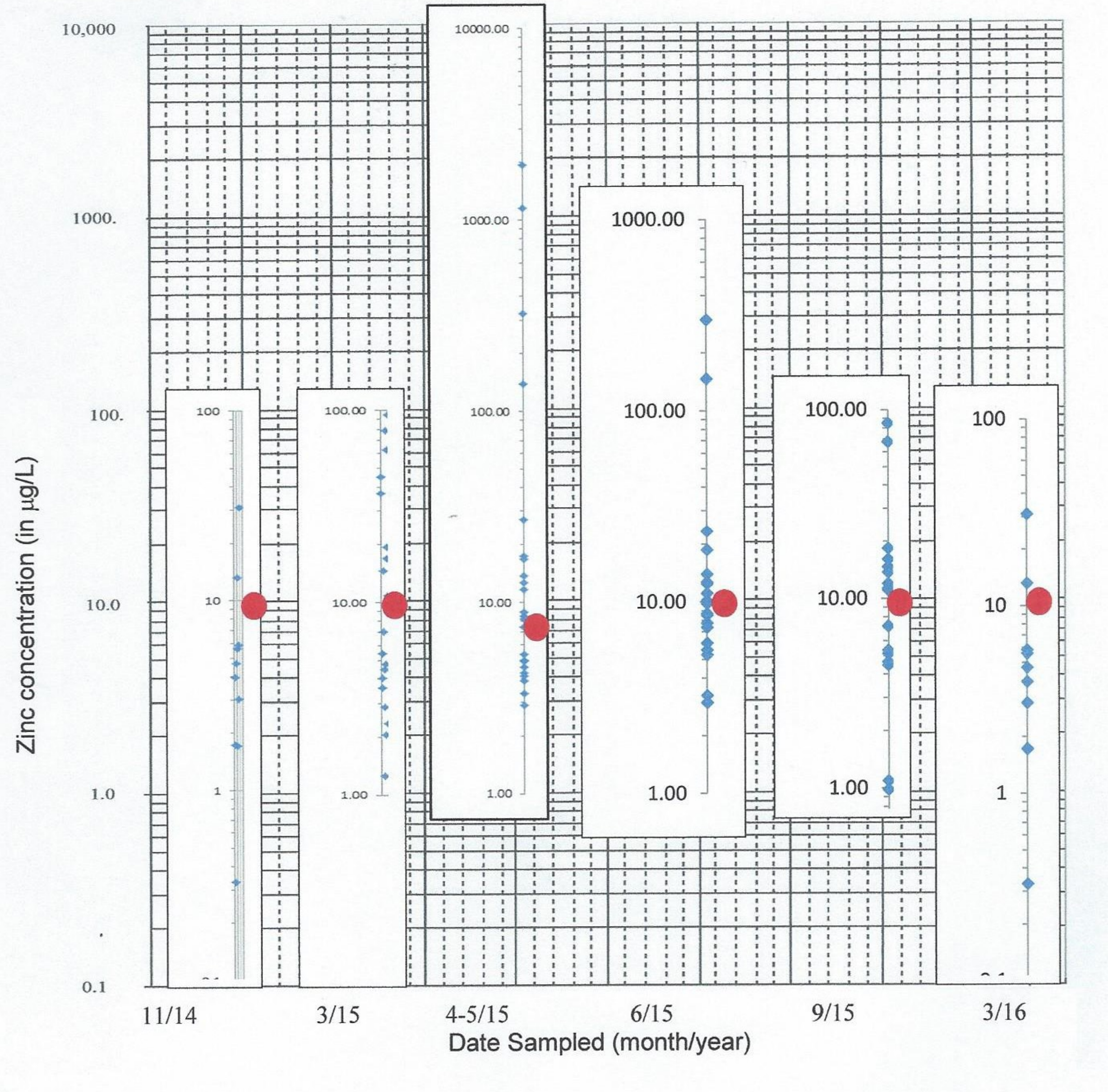

Figure 9. Dissolved zinc concentrations in groundwater and surface water in µg/L (ppb) plotted by date sampled, plotted on semi-logarithmic paper in blue diamonds. QA/QC values are shown by the red circles, and reflect the iCAP MS value for 10 µg/L standard for each suite of analysis by date. Precise sampling dates and hydrogeologic conditions during sampling are November 15, 2014 (low flow); March 17-18, 2015 (intermediate flow); April 13-May 11, 2015 (high flow); June 3-4, 2015 (high flow); September 8,2015 (intermediate flow); and March 7, 2016 (low flow).

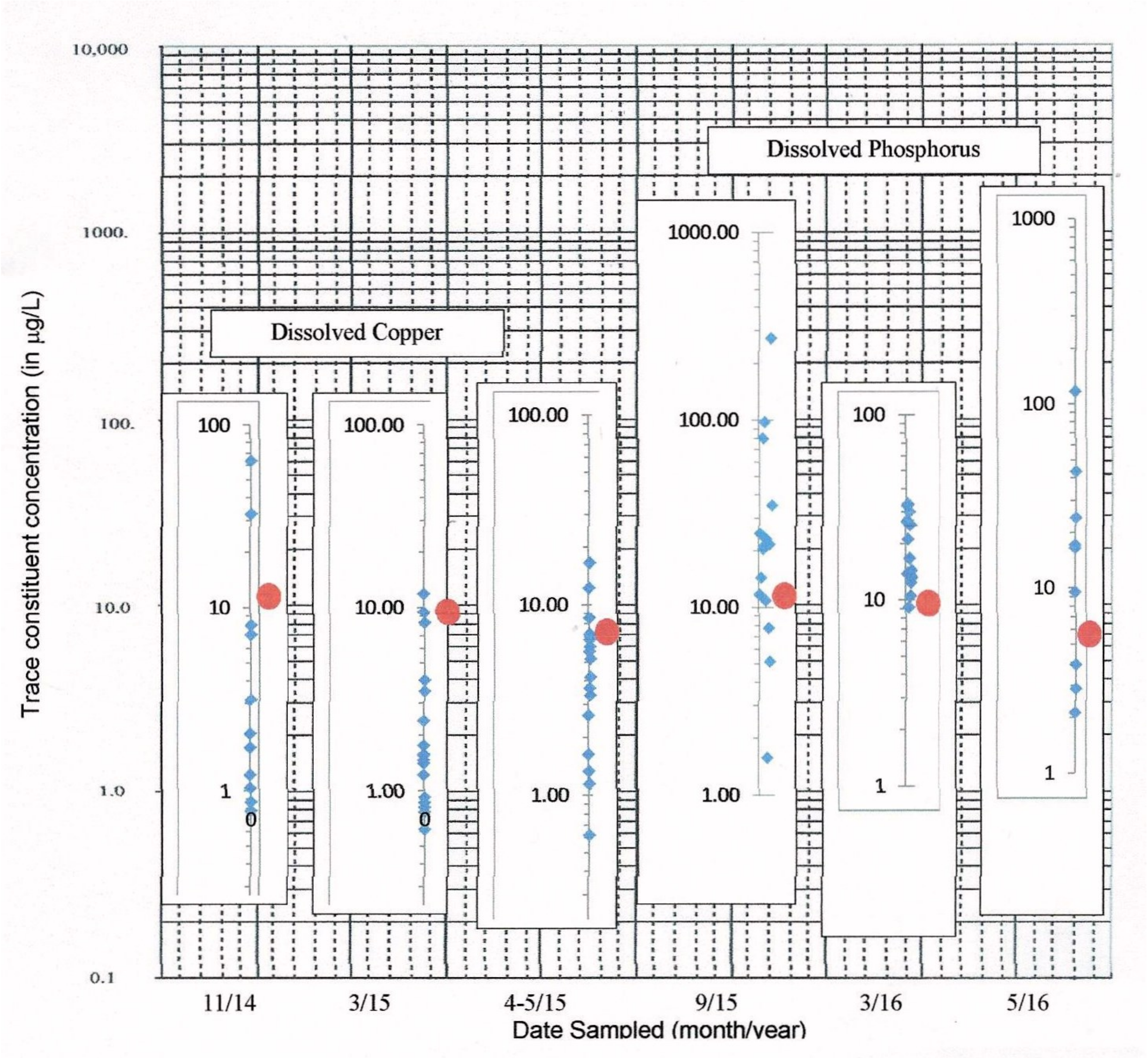

Figure 10. Dissolved copper and phosphorus concentrations in groundwater and surface water in µg/L (ppb) plotted by date sampled, plotted on semi-logarithmic paper in blue diamonds. QA/QC values are shown by the red dots, and reflect the iCAP MS value for 10 µg/L standard for each suite of analysis by date. Precise sampling dates and hydrogeologic conditions during sampling are November 15, 2014 (low flow); March 17-18, 2015 (intermediate flow); April 13-May 11, 2015 (high flow); September 8,2015 (intermediate flow); March 7, 2016 (low flow); and May 10, 2016 (intermediate flow).

to this study, two of these trace metals are reported to be additives to pig feed (Jacela et al. 2010), including zinc (Zn), and copper (Cu). Phosphorus (P), a non-metal was also included in this study because its isotope ^{31}P is an indicator constituent of animal feces. Selected Zn analyses are shown in Figure 9, and Cu and P are shown in Figure 10. Seven trace-constituent sampling campaigns were undertaken between November 15, 2014, and May 10, 2016.

Preliminary results of this part of the sampling program revealed that two specific regions of the study area had anomalously high concentrations of Zn, Cu, and P. These locations included sites 13, 15, and 36 (Figure 1), which are surrounded by spreading fields that lie immediately upgradient from these springs and well, and sites 39 and 40 (Figure 1), wells that are down-gradient and within 200 m of the CAFO infrastructure and its ponds. Concentrations of trace constituents in these two general areas typically varied from one to two orders of magnitude greater than samples from surface water.

Stable Isotopes

The stable isotope ratios, deuterium/protium

($^{2}H/^{1}H$) and oxygen -18/oxygen-16 ($^{18}O/^{16}O$) were analyzed for each of ten water samples collected during a single sampling interval on March 7, 2016. The results are shown in Figure 11, and may be synthesized as lying on the global meteoric water line. The $\delta^{18}O$ values in units of per mil ($^{o/oo}$; parts per thousand against standard mean ocean water) have been plotted against the $\delta\ ^{2}H$ values for each of the samples, and are shown superimposed on the global meteoric water line (Craig 1961, White 1988). This close relation of the data to the meteoric water line gives us confidence that the interpretation that the source of the water comes wholly from precipitation, and that no geochemical processes (evaporation, addition of deep thermal water) are acting on the water to shift the data above or below the line. The global meteoric water line can be defined by an equation:

$$\delta\ ^{2}H = 8.0 \times \delta\ ^{18}O + 10\ ^{o/oo}$$

(Craig 1961) that relates the average relationship between H and O isotope ratios in natural terrestrial waters, expressed as a worldwide average (Standard Mean Ocean Water).

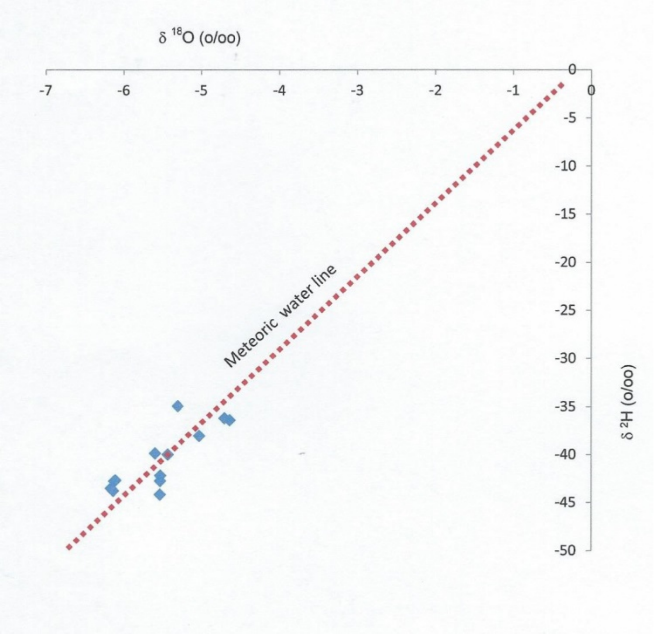

Figure 11. The stable isotopes of hydrogen and oxygen have been plotted for samples collected on March 7, 2016, and they lie on the meteoric water line. Data are shown as blue diamonds, and the meteoric water line is dashed, in red. Units of measurement are per mil (o/oo).

Ancillary Observation

Field observations of streams, springs and wells in Big Creek basin provide a good general overview of the general health of the integrated natural water system. During late-summer low-flow conditions when evapotranspiration is at its greatest, many of the tributaries and even the main stem of Big Creek cease to flow on land surface, a common occurrence on karst lands elsewhere. Water that has been trapped and pooled on the surface is evaporated, and commonly leaves a crust on the dry streambed (Figure 12). These reaches in the study area in the summer of 2013 smelled like a poultry CAFO, and the fields upgradient that supplied recharge to the creeks were reported (not verified) to have received poultry litter. The presence of the evaporative crust does establish the fact that solutes are present in the stream water.

Figure 12. During the summer of 2013, when precipitation declined and evapotranspiration increased, surface streams Big Creek and Left Fork of Big Creek displayed sections downstream from animal production fields that pooled, evaporated, and left a crust of dissolved minerals on the streambed. This evaporative crust was thicker, more odoriferous (strong poultry litter-like smell), and far more extensive than any personal observations of the coauthors had experienced during their careers in this region. It is shown here as white covering of the streambed.

Summary

Data from major constituents indicate that the dominant geochemical processes controlling water quality in Big Creek basin are dissolution and mixing with meteoric water, which is to be expected in a region underlain by karst. Groundwater in the Boone Formation from wells and springs, and surface water from Big Creek and its tributaries are a calcium-bicarbonate type, with various contributions from animal husbandry and other land-use activities on the land surface. Deep wells beneath the cover of terrigenous sediments show the effect of less mixing and dilution, being more mineralized but still dominantly calcium bicarbonate type (Figure 4). Shallow wells and springs in the overlying younger sediments are indicative of less mineralization, with greater concentrations of chloride and sulfate, typical of shales with interbedded sandstones.

Observations of objectionable algal densities and nuisance water-plant growth are indicative of excessive nutrients that have been added to the water from activities on the land surface. At this time, Big Creek basin does not typically experience water quality that exceeds acceptable EPA limits. However, numerous observations indicate that Big Creek basin has greater nitrate concentrations at its downstream sample site 7 (BCRET 2016). U.S. Geological Survey DO and BCRET and KHBNR *E. coli* data also document that Big Creek does qualify as an impaired stream during some summertime periods. Because Big Creek drains the fifth largest subbasin to the Buffalo, and animal husbandry is the dominant land use, we need to carefully manage the feces and urine we allow to leak into its flow paths.

All data suggest that it is important to incorporate karst and hydrogeology into our permitting process for CAFOs on soluble rock if we intend to preserve these environments and their contained water resources (Kosič et al. 2015). Groundwater is hidden from view, but it plays a dominant role in the hydrologic budget of karst. Considering the fact that the Buffalo National River is the main drain for all waters flowing from Big Creek, the many users of the river deserve a scientifically accurate assessment of the risks of primary contact with water for any number of intended uses. It is our opinion that water-quality in Big Creek valley is being degraded, and ongoing monitoring of both surface and groundwater is essential.

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