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Stable Isotope and Geochemical Characterization of Nutrient Sources
in the Big Creek Watershed of Northwest Arkansas

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Geology

by

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Oklahoma State University
Bachelor of Science in Geology, 2015

August 2019
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This thesis is approved for recommendation to the Graduate Council.

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Abstract

The establishment of a concentrated animal-feeding operation (CAFO) in Newton County, Arkansas near Big Creek, a tributary of the Buffalo National River, has raised concern over potential degradation of water-quality in the watershed. In this study, isotopic tools were combined with standard geochemical approaches to characterize nutrient sources and dynamics in Big Creek. An isotopic and geochemical reference library of potential nutrient sources in the Big Creek watershed was established by direct sampling of representative potential sources, including septic-system effluent, poultry litter, swine and cattle manure, and CAFO waste lagoons. Representative nutrient sources and Big Creek stream samples were analyzed for $\delta^{15}\text{N-NO}_3$, $\delta^{18}\text{O-NO}_3$, $\delta^{18}\text{O-PO}_4$, and a cation and anion suite. Big Creek stream samples were also analyzed for $\delta^{18}\text{O-H}_2\text{O}$ and $\delta^2\text{H-H}_2\text{O}$. Nutrient concentrations and isotopic data provide evidence of modification of potential nutrient source signatures by nitrification, atmospheric deposition, evaporation, and denitrification. Chloride-to-bromide ratios of stream samples indicated an anthropogenic influence in Big Creek that could have resulted from any combination of the analyzed sources. Samples taken from the CAFO waste lagoon, a septic system, field and parking-lot runoff, fertilizer, and hog manure exhibited different $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ as compared to stream samples. Stream $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ cannot be explained by direct input of any one of these potential sources without modification of isotopic composition by mixing or fractionation. Big Creek NO_3 isotope values (-7.59‰ to 9.10‰ $\delta^{15}\text{N-NO}_3$ and -3.41‰ to 6.71‰ $\delta^{18}\text{O-NO}_3$) were similar to NO_3 values expected from nitrification of nitrogen stored in soils sampled in the watershed (3.8‰ to 6.6‰ $\delta^{15}\text{N-NO}_3$ and 3.4‰ to 4.8‰ $\delta^{18}\text{O-NO}_3$). The NO_3 isotope data indicate stream NO_3 is derived in part from NO_3 stored in soils. Discrimination of nutrient source input to Big Creek using $\delta^{18}\text{O-PO}_4$ was complicated by overlap between

potential source $\delta^{18}\text{O}$ and stream $\delta^{18}\text{O}$. Stream equilibrium $\delta^{18}\text{O-PO}_4$ values indicated the influence of both isotopically light and heavy phosphate sources in Big Creek, and the in-stream biological processing of PO_4 . The results of this study highlight the importance of effective agricultural, residential, and urban best-management practices in protecting the quality of our waterways.

Acknowledgements

First, I would like to thank my thesis advisor Dr. Phillip Hays for his guidance and patience throughout this process. He always made time for my many questions and I am grateful to have had the opportunity to learn from him. Thank you to my thesis committee members Erik Pollock and Dr. Andrew Sharpley for their guidance and suggestions. Special thanks to Erik for his help in the stable isotope lab and to Dr. Sharpley for lab funding assistance.

I could not have completed this project without the generous support of the Arkansas Water Resources Center USGS 104B Grant Program. Thank you for the opportunity to conduct research in a beautiful landscape. I want to thank Tim Glover, Keith Trost, Jennifer Purtle, Erin Scott, Brian Haggard, and the AWRC staff for their help in sample collection, analyzing my many samples, and completing my grant proposal and report. Thank you to Ron and Chris Thurston for welcoming me and allowing me to sample at your home. Thank you to Lindsey Conaway and Barry Shaulis at the UASIL and Daniel Snow at the UNWSL for their assistance in completing sample analyses.

Lastly, I would not be where I am today without the continuous love and encouragement from my family. I cannot fully express my gratitude for all you have done for me over the years. Thank you for always believing in me. Thank you, Timothy, for your endless reassurance and for keeping me going – I could not have done it without you.

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I. Introduction

Anthropogenic nutrient inputs have the capability to transform the landscape and permanently alter ecosystems. Understanding sources, processing, and transport pathways of nutrients is critical to nutrient management and water-resource protection. The production of poultry, beef, and swine, and the use of manure from these animals as fertilizer can contribute nutrients to streams and groundwater (Heathwaite and Johnes, 1996). Rural and suburban residential land use has the potential to provide excess nutrients due to the use of septic systems and the interconnectedness of surface water and groundwater, resulting in ultimate delivery of nutrients to streams (Kaushal et al., 2006). Storm-water runoff and waste-water treatment plant drains in urban land use areas can add nutrients to watersheds (Anderson et al., 2002). Nitrogen and phosphorus are the primary constituents of concern released by these practices.

Nutrients are essential to the health of aquatic life in streams; however, elevated phosphorus and nitrogen concentrations are associated with eutrophication, which causes the creation of harmful anaerobic conditions and a reduction in biodiversity (Millennium Ecosystem Assessment, 2005). Nitrogen contamination can be extremely harmful to humans; it has been linked to blue baby syndrome, properly known as infant methemoglobinemia (Comly, 1945), and cancer of the digestive tract (National Research Council, 1981).

Increased agricultural land use in the Big Creek watershed, particularly the recent establishment of a Concentrated Animal-Feeding Operation (CAFO) near Mt. Judea in Newton County, AR, has raised concern for the nutrient enrichment and degradation of water-quality (Figure 1). Big Creek is a tributary of the Buffalo National River (BNR). In the Big Creek watershed, as for the larger Buffalo River watershed, the complex distribution of land use and nutrient sources, combined with the occurrence of karst terrain with rapid connection of

groundwater and surface water, creates a challenging technical problem for understanding nutrient dynamics.

Traditional methods of geochemical analysis often fall short of providing adequate characterization of nutrient sources in watersheds. This study applied a combined approach of traditional water-quality analysis and stable-isotope geochemistry in characterizing nutrient concentrations, sources, transport pathways, and transformation processes in the Big Creek watershed. The objectives of this research are (1) to establish a database on isotopic compositions of potential nutrient sources; (2) to employ NO_3 isotopes for characterizing sources, transport, and transformations; (3) to characterize stream PO_4 isotopes and identify sources and biological cycling; and (4) to characterize water sources and pathways through the application of water isotopes.

II. Background

A. C&H Farms

C&H Hog Farms was established in 2013 and is located 0.5 miles from Big Creek, approximately 6 miles upstream of the BNR (Figure 2). The farm is regulated as a point source under the National Pollutant Discharge Elimination System (NPDES) general permit program. The NPDES requires many specifications be met before operation, including a manure management plan. C&H Farms has a 6,500-hog capacity, two barns, two in-house shallow waste pits, and two open-air waste lagoons lined with clay. The manure-management plan involves land application of the generated manure onto 670.3 acres of surrounding property, including Fields 1 and 12 in Figure 2. Soil-sample data were used to determine the amount of waste that could be applied to applications fields, and to develop best-management practices aimed at avoiding pollution of surface waters (Hovis, 2014). A table of abbreviations can be seen in Table

A in the Appendix.

The authorization of the farm was met with protest from Arkansas residents and from groups such as the Buffalo River Watershed Alliance and the National Park Conservation Association due to its location in the Buffalo River watershed. In 2013, the owners of C&H Farm sought assistance from their county extension agent in order to determine potential impacts on the BNR from their operation. This led to the allocation of funding from the Arkansas Governor's office, approved by a subcommittee of the Arkansas General Assembly, for a comprehensive case study of C&H Farms. The Big Creek Research Team (BCRET) was established for this purpose in October 2013, and presently continues to monitor potential impacts of C&H Farm on the Big Creek watershed (BCRET, 2014a). The BCRET consists of hydrogeology specialists, soil experts, and agricultural engineers, among other specialists. A review Panel identified three major potential threats to the water-quality of Big Creek associated with C&H Farm: 1) leakage from holding ponds; 2) contamination of surface water and groundwater due to land application of manure; and 3) build-up of soil nutrient levels due to over-application (Bolster et al., 2014).

B. Buffalo River and the Big Creek Watershed

Mt. Judea is a rural, unincorporated community in the Ozarks of northwest Arkansas. Agricultural practices such as hay cultivation and the raising of beef cattle, swine, and chickens have long been prevalent in the area. The headwaters of Big Creek originate in Newton County: Big Creek flows north past the town of Mt. Judea where it meets with Left Fork Big Creek to flow into the upper section of the BNR (Figure 2).

The BNR was established as America's first National River in 1972. The headwaters of the BNR begin in Newton County, Arkansas. The BNR is characterized by dramatic bluffs and

steep topography, both of which contribute to the flashy nature of runoff events (Panfil and Jacobson, 2001). Only 44% of the BNR drainage area is managed by the National Park Service, the U.S. Forest Service, or the state of Arkansas; the large percentage of private ownership raises concerns for water-quality impacts to the river (Scott and Smith, 1994). A land-use study by the Arkansas Water Resources Center (AWRC) concluded that in Newton County, agricultural land use increased by more than 40,000 acres from 1965 to 1992 (Scott and Hofer, 1995). Big Creek watershed contains 18% agricultural land and 79% forested land (BCRET, 2015).

Numerous studies have been conducted in the Buffalo River watershed. A summary of water-quality data from 1985-1995 showed a trend of increasing $\text{NO}_3\text{-N}$ concentrations in the middle portion of the BNR, directly correlating with the highest percentage of pasture land (Mott, 1997). Big Creek was found to be a significant NO_3 contributor to the BNR, with a $\text{NO}_2+\text{NO}_3\text{-N}$ load of 40 lbs./day and a mean $\text{NO}_2+\text{NO}_3\text{-N}$ concentration of 0.12 mg/L. The mean $\text{NO}_2+\text{NO}_3\text{-N}$ concentration for BNR tributaries was 0.15 mg/L with a maximum value sampled at Gilbert Spring of 0.79 mg/L. Mean total phosphorus (TP) concentration for Big Creek was 0.013 mg/L. Mean TP for the river corridor was 0.015 mg/L and mean $\text{NO}_2+\text{NO}_3\text{-N}$ concentration was 0.06 mg/L. (Mott, 1997).

A study of water-quality at the BNR from 1991-2001 compared base-flow and surface-runoff, or storm-flow conditions (White et al., 2004). Maximum, minimum, median, and mean values from this study are presented in Table 1. The majority of samples had nutrient concentrations less than the minimum reporting level, particularly during base-flow conditions. Median values for $\text{NO}_2+\text{NO}_3\text{-N}$, TN, and TP were higher during surface-runoff conditions than during base-flow conditions. Parameters that experienced significant increase over time from 1991-2001 include $\text{NO}_2+\text{NO}_3\text{-N}$, $\text{NH}_3+\text{organic nitrogen}$, and TN (White et al., 2004).

Table 1. Water-quality data in the Buffalo National River (White et al. 2004).

	Base Flow Samples				Surface Runoff Samples			
	Min	Max	Median	Mean	Min	Max	Median	Mean
SpC ($\mu\text{S}/\text{cm}$)	163	273	216	217	88	277	191	188
DO (mg/L)	5	13.1	9.4	9.3	5.2	15.5	9.1	8.9
pH	6.8	8.4	7.9	7.9	6.5	8.6	7.6	7.7
NH ₃ -N (mg/L)	<0.01	0.041	<0.02	<0.02	<0.01	0.19	<0.02	<0.03
NO ₂ ⁻ -N (mg/L)	<0.001	0.02	0.01	0.01	0.003	0.02	0.01	0.009
NH ₃ + organic N (mg/L)	0.06	0.2	0.2	0.16	0.07	2.5	0.2	0.32
NO ₂ ⁻ + NO ₃ ⁻ -N (mg/L)	0.03	0.27	0.05	0.09	0.04	0.75	0.14	0.18
TN (mg/L)	0.09	0.37	0.23	0.21	0.12	2.63	0.3	0.48
TP (mg/L)	0.004	0.04	0.01	0.017	0.003	0.791	0.021	0.071
DP (mg/L)	0.003	0.02	0.01	0.008	0.003	0.047	0.01	0.012
PO ₄ ³⁻ (mg/L)	0.01	0.02	0.01	0.01	0.01	0.036	0.01	0.015

< below method detection limit

SpC: specific conductance

DO: dissolved oxygen

A study by Moix and Galloway of water-quality in the BNR shows nutrient concentrations near or below their respective reporting limits, with nitrogen-based nutrient concentrations similar to the Mott, 1997 study (2005). Mott and Steele quantified the effects of pasture runoff on water chemistry of the Buffalo River and found that cattle grazing adjacent to the river caused higher nutrient concentrations downstream as well as fecal coliform concentrations 50 times greater than samples taken further upstream (1991).

The Big Creek Research Team (BCRET) began monitoring water-quality in Big Creek in September 2013. Nitrogen concentrations remain below the drinking water standard of 10 mg/L; however, NO₃-N concentrations downstream of the farm are greater than those measured at an upstream site (BCRET, 2016; 2014b). The geometric mean of NO₃-N concentrations in a groundwater well near C&H Farms has gradually increased each water year of monitoring (April 1 to March 31). Seasonal Kendall Tau tests indicated a statistically significant increase in NO₃-N concentration from April 2015 to April 2018 in an ephemeral stream and a groundwater well near C&H Farms. Kendall tests of chloride and specific conductance for the ephemeral stream

and well samples revealed no statistically significant change during the same time period. These data suggest that elevated NO₃-N concentrations may be influenced by sources containing low chloride and specific conductance (BCRET, 2018).

Nutrient concentrations upstream and downstream of the CAFO are low relative to similar regional watersheds (Sharpley et al., 2017). Flow-adjusted nutrient concentration data in Big Creek from 2014-2017 showed NO₃ decreased with increasing flow. Concentrations of TN decreased with increasing flow, then increased with increasing flow after a minimum value occurred. Concentrations of TP increased with rainfall events and were stable during base-flow (Sharpley et al., 2017). A 2016 Big Creek study found TN for Big Creek ranged from 0.07 mg/L upstream of the CAFO to 0.23 mg/L at the confluence of Big Creek and the BNR, TP ranged from <0.02 mg/L at the confluence to 0.14 mg/L upstream, and NH₃-N ranged from <0.002 mg/L upstream to 0.1 mg/L at the confluence. (Roland, 2016).

Fields and Halihan (2016) conducted Electrical Resistivity Imaging (ERI) surveys and soil sampling in the Big Creek watershed. ERI surveys exhibited the potential for rapid transport pathways in fields applied with C&H farms manure slurry. Zinc and magnesium were lower in soil samples from unapplied sites when compared to applied sites. Soil sample $\delta^{15}\text{N-N}$ ranged from 3.8‰ to 6.6‰ across all sites (Fields and Halihan, 2016).

C. Geology, Hydrogeology, and Soils

The study area is located on the edge of the Springfield Plateau and Boston Mountains in the Ozark Mountains of Arkansas (Figure 1). The sedimentary rock units in the region are nearly flat-lying and have been arched into the broad Ozark dome. Streams have incised large, deep valleys to expose the Mississippian carbonate Boone Formation, with younger, Pennsylvanian clastic formations capping the surrounding hills (Chandler and Ausbrooks, 2003).

Middle and Upper Ordovician dolostone, sandstone, and limestone units underlie the study area and are exposed along the BNR. The Boone Formation outcrops at the surface across most of the study area, including the location of C&H Farms. The Boone Formation contains coarse-grained fossiliferous and fine-grained limestones interbedded with chert (which can constitute more than 70% of the Formation) and is approximately 120-400 feet thick. Sinkholes and springs are abundant in the Boone Formation. Where the Boone Formation is present at the surface, it is overlain by clay-rich weathered regolith of varying thickness. The Short Creek Oolite, an oolitic biosparite and biomicrite, is part of the Boone Formation and is present along Highway 74 in Mt. Judea. The St. Joe Limestone Member of the Boone Formation is a thin-bedded crinoidal limestone with interbedded thin shaly limestones, with phosphate nodules present near the lower contact. The St. Joe Limestone is 10-30 feet thick and is present along Big Creek and the BNR (Chandler and Ausbrooks, 2003).

The Upper Mississippian Batesville Formation lies above the Boone Formation. In the study area, this interval mostly consists of the Hindsville Limestone Member, a thin-bedded crystalline limestone containing pyrite. The Fayetteville Shale, an Upper Mississippian black fissile clay shale, and the Pitkin Limestone, an Upper Mississippian crystalline, fossiliferous limestone, lie above the Batesville Formation. The Lower Pennsylvanian Hale Formation lies above the Pitkin. The lower Cane Hill Member of the Hale is a clay to silty shale with iron nodules. The upper Prairie Grove Member of the Hale is a bluff-forming quartz sandstone. The Lower Pennsylvanian Bloyd Formation tops the bluffs overlooking Big Creek and the Buffalo River. The Lower part of the Bloyd consists of interbedded siltstones and sandstones, the middle Bloyd sandstone is a quartz or iron-cemented sandstone, and the Upper part of the Bloyd is interbedded sandstones and shales. Unconsolidated Quaternary alluvium deposits cover much of

the area immediately adjacent to Big Creek (Chandler and Ausbrooks, 2003). Structurally, faulting, jointing, and fracturing of rocks in the Ozarks has occurred during numerous periods of uplift (Hudson and Cox, 2003).

The Springfield Plateau Aquifer consists of the Boone Formation and has highly varied permeability due to the fractured nature of the Boone (Imes and Emmett, 1994). The numerous fractures and faults facilitate dissolution of the carbonate Boone Formation, which contributes to the secondary porosity of the aquifer and the karst topography present in the study area. The hydrogeology of the Springfield Plateau Aquifer is typical of karst, with connection between surface water and groundwater, rapid response to storm events, and bimodal porosity distribution (Imes and Emmett, 1994; Hays et al., 2016). Rapid transport of storm flow equates to little attenuation of contaminants such as NO_3 . A component of flow separate from focused flow in the aquifer – diffuse flow in primary matrix porosity – exists, which maintains base-flow to springs and streams during dry periods (Peterson et al. 2002).

Recharge to the aquifer occurs by infiltration of precipitation in the outcropping area and by flow through overlying units where covered (Adamski et al., 1995; Hays et al., 2016). Diffuse recharge through overlying regolith constitutes a small part of the total recharge. Most recharge occurs rapidly through pathways such as sinkholes, fractures, and losing streams (Brahana et al., 2005). Discharge occurs primarily through seeps and springs, groundwater withdrawal, and to the underlying Ozark aquifer in places where the confining unit is absent (Harvey, 1980; Imes and Emmett, 1994; Hays et al., 2016). The water in the aquifer is dominantly calcium-bicarbonate type. Values of pH range from 6.0 to 9.1 with a median of 7.2; $\text{NO}_3\text{-N}$ ranges from 0.01 to 20.00 mg/L with a median of 1.80 mg/L (Kresse et al., 2014). Concentrations of surface-derived components such as NO_3 , PO_4 , and chloride increase during storm events. Rock-derived

components such as calcium, magnesium, and HCO_3 decrease during storm events (Adamski, 1987; Pollock et al., 2011).

Background NO_3 concentrations in the Springfield Plateau Aquifer are important to addressing potential NO_3 inputs to groundwater via point or non-point sources. Although $\text{NO}_3\text{-N}$ concentrations across the watershed are generally well below the EPA Maximum Contaminant Level (MCL) of 10 mg/L as nitrogen (U.S. EPA, 2002), concentrations above background levels can result in environmental effects such as eutrophication of streams. A conservative estimate for background $\text{NO}_3\text{-N}$ concentration was determined to be 0.4 mg/L based on previous studies (Kresse et al., 2011).

The Ozark confining unit underlies the Springfield Plateau Aquifer and overlies the Ozark Aquifer. The Ozark confining unit restricts flow between the Springfield Plateau aquifer and the Ozark aquifer, however, the leakance of the confining unit varies due to local structural and lithologic differences. Devonian and Mississippian age shales and dense limestones make up the Ozark confining unit, which has a thickness of 20 to 40 feet in Newton County, Arkansas. The Ozark aquifer is a thick sequence of shales, limestones, dolomites, and sandstones with a high degree of secondary porosity and permeability, much like the Springfield Plateau aquifer. While rocks of the Springfield Plateau aquifer consist primarily of calcite, those of the Ozark aquifer consist primarily of dolomite. Water in the Ozark aquifer is calcium-magnesium bicarbonate type. When exchange occurs between the Ozark aquifer and Springfield Plateau aquifer, the calcium-to-magnesium ratio can differ (Imes and Emmett, 1994; Hays et al., 2016).

Soils in fields proximal to Big Creek are sandy loam, silty chert loam, and clay loam. Mean soil phosphorus in the top 4 inches was 41 mg/kg for Field 1 and 54 mg/kg for Field 5 (BCRET, 2014b). BCRET conducted a Ground Penetrating Radar assessment of Fields 1 and 5

in 2013. Soil depth to bedrock was greater than 49 inches for all transects. The soil-bedrock interface for both fields was wavy in nature, suggestive of cutter and pinnacle karst (BCRET, 2014b). Cutters are soil-filled enlarged joints separated by pinnacles of upward-protruding limestone (Zhou et al., 2000). These features provide rapid transmission of surface runoff to the underlying groundwater. Thin soils and conduits for rapid transmission of contaminants make groundwater in the Ozarks vulnerable to nutrient inputs (Al-Qinna et al., 2014).

D. Stable Isotopes

The stable isotopic compositions of oxygen, hydrogen, and nitrogen are reported in delta (δ) notation in parts per thousand, or permille (‰). Delta values are calculated by:

$$\delta (\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \quad (1)$$

where R is the ratio of the heavy to the light isotope (e.g. $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, $^{15}\text{N}/^{14}\text{N}$). Values are reported relative to atmospheric N_2 for $\delta^{15}\text{N}$ and Vienna Standard Mean Ocean Water for $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

Nitrate

This study applied a dual-isotope approach to NO_3 . As nitrogen moves through a watershed, $\delta^{15}\text{N}\text{-NO}_3$ source signatures are often obscured by fractionating processes. This limits the utility of $\delta^{15}\text{N}\text{-NO}_3$ alone as a tracer. Many recent publications have included $\delta^{18}\text{O}\text{-NO}_3$ along with $\delta^{15}\text{N}\text{-NO}_3$ in order to delineate NO_3 sources (Burns and Kendall, 2002; Mayer et al., 2002; Anisfeld et al., 2007). Organisms most often preferentially uptake the light isotope (^{14}N) over the heavy isotope (^{15}N). This causes the product (anything created by the organism) to be isotopically lighter than remaining material (reactant or substrate) (Kendall, 1998). In biologically formed NO_3 , one oxygen atom is taken from atmospheric O_2 , while two come from water (Hollocher, 1984). In synthetic fertilizers, oxygen is primarily derived from atmospheric

O₂ (Clark and Fritz, 1997). This allows for the discrimination of NO₃ from natural and anthropogenic sources.

The principal transforming processes responsible for nitrogen-isotope distribution in natural systems are fixation, assimilation, mineralization, nitrification, volatilization, and denitrification. Fixation is facilitated by bacteria, lightning, fertilizer production, etc. and converts atmospheric N₂ into more useable forms of nitrogen, which can cause a -3 to +1‰ change in δ¹⁵N (Fogel and Cifuentes, 1993). Assimilation is the uptake of nitrogen by organisms and favors the incorporation of the light isotope (¹⁴N), with a large range of enrichment factors in aquatic environments (-27 to 0‰) and less variation in enrichment factors in soils (-1.6 to +1‰) (Fogel and Cifuentes, 1993; Kendall, 1998). Mineralization, also known as ammonification, is the production of NH₄ from soil organic matter and causes a small +/- 1‰ change in the nitrogen isotopic signature. Volatilization is the loss of NH₄ from soils to the atmosphere and results in a residual solution that is enriched in δ¹⁵N (Kendall, 1998).

Nitrification is a biologically mediated multi-step oxidation process: NH₃ or NH₄ is converted to NO₂, then NO₂ is oxidized to NO₃. Nitrification produces N₂O as a by-product. The extent of fractionation due to nitrification depends on the size of the reservoir. Fractionations are minimal in nitrogen-limited systems. Reported δ¹⁵N enrichment factors associated with nitrification range from -12 to -29‰ (Shearer and Kohl, 1986). During nitrification, the NO₃ produced takes one oxygen atom from atmospheric O₂, and two oxygen atoms are taken from water (Hollocher, 1984). Thus, δ¹⁸O of NO₃ produced by nitrification can be estimated with measured δ¹⁸O of stream water and atmospheric O₂ of 23.5‰ (Kroopnick and Craig, 1972).

Denitrification is the reduction of NO₃ to N₂. Denitrification also produces N₂O. This process occurs in anaerobic conditions and causes the δ¹⁵N of residual NO₃ to increase

exponentially as NO_3 is used up, dramatically obscuring the source signal. Denitrification can skew the N-isotopic signature from the source by 5‰ to 40‰. Denitrification causes a 1:2 change in $\delta^{18}\text{O}\text{-NO}_3:\delta^{15}\text{N}\text{-NO}_3$ (Böttcher et al., 1990). Water movement through the soil has an effect on denitrification. Water introduces oxygen and delivers N_2 gas from the soil; as oxygen availability and N_2 diffusion decrease, the rate of denitrification increases and the produced $\text{N}_2\text{O}:\text{N}_2$ ratio decreases (Davidson et al., 2000). Available carbon in soil can promote denitrification by increasing oxygen consumption (Firestone and Davidson, 1989). Isotopic signatures of N_2O have been used as indicators of denitrification and nitrification in ecosystems. Uptake of N_2O and reduction to N_2 by denitrifying organisms in soil increases the $\delta^{15}\text{N}$ of N_2O by 1‰ to 27‰ and increases the $\delta^{18}\text{O}$ by 5‰ to 42‰ (Snider et al., 2009).

Nitrogen availability in a watershed is dictated by land use, biological activity, and seasonal changes. One major source of nitrogen in watersheds is agricultural activities (Howarth et al., 2012). Nitrogen is often leached from soil, making soil a significant nitrogen source in watersheds. Nitrification proceeds rapidly in warm and moist conditions, increasing NO_3 concentration. Mineralization in soil increases as microbial activity increases. Microbial activity is directly related to soil temperature and water content. Seasonal changes in runoff and plant nitrogen uptake are a large factor in the availability of nitrogen. Transformations of nitrogen are integral to the removal of NO_3 – different forms of nitrogen are more readily released from the watershed. Nitrogen inputs to agricultural systems include synthetic and organic fertilizers and the atmosphere (Zaman et al., 2012). Nitrogen transformations and transport in watersheds are affected by soil type, vegetation, soil moisture, and depth to groundwater (Schlesinger et al., 2006).

Typical ranges of $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ of various sources can be seen in Figure 3. Sources relevant to this particular study (manure, septic, fertilizer) show a high degree of overlap. Animal and human waste are indistinguishable in most cases using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. Under ideal circumstances with minimal fractionation, synthetic fertilizer and manure signatures will be distinct and the nitrogen source recognizable. Organic fertilizers have a $\delta^{15}\text{N-NO}_3$ of +2 to +30‰, while artificial fertilizers exhibit a $\delta^{15}\text{N-NO}_3$ of -4 to +4‰ and a $\delta^{18}\text{O-NO}_3$ of +18 to +22‰, generally. Most soils have a $\delta^{15}\text{N-NO}_3$ of +2 to +5‰ (Kendall, 1998). Denitrification causes an increase in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. Determining initial isotopic composition of the NO_3 and whether denitrification is occurring is critical in source tracing projects. Few techniques are available to identify the presence of denitrification in a system. If Mn^{3+} and Fe^{3+} oxides exist in the system, Mn^{2+} and Fe^{2+} will be generated via iron and manganese reduction following denitrification according to the redox series. Also, denitrification is associated with increased alkalinity due to the oxidation of organic matter (Kendall, 1998).

A study of six watersheds with different land uses utilized NO_3 dual-isotope analysis to determine sources and processes affecting NO_3 concentrations (Burns et al., 2009). Mean $\delta^{15}\text{N-NO}_3$ for both forested watersheds was 1.9‰ and mean $\delta^{18}\text{O-NO}_3$ was 2.8 and 3.8‰, which is consistent with nitrification of soil nitrogen as the dominant source. The $\delta^{15}\text{N-NO}_3$ values for the suburban watershed ranged from 4 to 8‰, which suggests a septic-waste source; however, as seen in Figure 3, the source boxes for a waste source and a nitrified source overlap in this range. The $\delta^{18}\text{O-NO}_3$ values for the suburban watershed lie outside the expected range for soil or waste sources – this points to a significant atmospheric NO_3 contribution to the stream. All samples collected in agricultural watersheds had $\delta^{15}\text{N-NO}_3$ values suggesting an animal or human waste source (greater than 5‰, most greater than 9‰). The large range of $\delta^{15}\text{N-NO}_3$ values observed in

the agricultural streams indicates a large fractionation of about 10‰ during denitrification, which occurs during “riparian” denitrification when NO₃ availability is not limiting the rate of denitrification. Lower fractionation values would suggest an NO₃-limited denitrification process. This study used plots of δ¹⁵N-NO₃ vs. δ¹⁸O-NO₃, δ¹⁵N-NO₃ vs. 1/NO₃ concentration, and δ¹⁵N-NO₃ vs. ln NO₃ concentration to characterize their data (Burns et al., 2009). When δ¹⁵N-NO₃ is plotted as a function of 1/NO₃ concentration, mixing of two solutions with different δ¹⁵N-NO₃ values and NO₃ concentrations is linear. When denitrification is occurring, the residual solution δ¹⁵N-NO₃ value increases in proportion to the logarithm of the fraction of NO₃ remaining. Therefore, a plot of δ¹⁵N-NO₃ vs. ln NO₃ concentration is linear when denitrification is occurring in the system (Kendall, 1998).

Phosphate

Phosphorus has only one stable isotope, therefore it has no utility as an isotopic tracer in nutrient source studies as the lack of heavy and light isotopes precludes any fractionation or source signature. The δ¹⁸O of PO₄, however, can be used to identify PO₄ sources and transformation processes. Phosphate only exchanges oxygen with water through biological mediation at typical surface temperatures (Longinelli et al., 1976). Hence, a change in δ¹⁸O-PO₄ from source signatures indicates either mixing of sources or alteration due to oxygen exchange. The δ¹⁸O-PO₄ value will be carried towards isotopic equilibrium with water as PO₄ undergoes biological uptake and cycling (McLaughlin et al., 2006). Theoretical isotopic equilibrium values for δ¹⁸O-PO₄ in stream samples can be calculated by applying the following equation derived from Longinelli and Nuti, 1973:

$$\delta^{18}O_{phosphate} = \frac{T(^{\circ}C) - 111.4}{-4.3} + \delta^{18}O_{water} \quad (2)$$

where T(°C) is the temperature of the water.

Phosphorus is readily sorbed onto stream sediments; therefore, sediments can act as a continuous nutrient source in surface waters. Other sources of PO₄ in surface waters include point sources, such as septic tanks, and non-point sources, such as natural and artificial fertilizers and urban runoff (Paytan and McLaughlin, 2012). Phosphorus from agricultural runoff was diluted during transport through karst in a 2014 study in the Savoy watershed (Jarvie et al., 2014).

A study in the Illinois River watershed used $\delta^{18}\text{O-PO}_4$ as a tracer for sources and cycling of phosphorus (Breaker, 2009). The $\delta^{18}\text{O-PO}_4$ value for poultry litter water extract in this study was 20.0‰, commercial fertilizer water extract was 18.2‰, septic tank leachate was 12.3‰, waste water effluent was 25.2‰, and runoff from a litter amended pasture was 10.6‰. Stream samples from the Illinois River, Osage Creek, Spring Creek, and little Osage Creek ranged from 20.8‰ to 11.4‰. Increased $\delta^{18}\text{O-PO}_4$ values were seen downstream in the Illinois River (14.2‰ upstream, 20.8‰ downstream), which reflects input from both waste water effluent and poultry litter. The runoff sample showed a lower $\delta^{18}\text{O-PO}_4$ than the poultry litter water extract, indicating PO₄ consumption and reprecipitation in the field caused a change in $\delta^{18}\text{O-PO}_4$. The $\delta^{18}\text{O-PO}_4$ values increased upstream to downstream by only 0.7‰, despite the 25.2‰ $\delta^{18}\text{O-PO}_4$ value of waste water effluent from the waste-water treatment plant near Spring Creek. This reflects the occurrence of equilibrium processes of phosphorus in Spring Creek: as phosphorus is consumed, dissolved inorganic phosphates are precipitated in equilibrium with stream water $\delta^{18}\text{O}$ values (Breaker, 2009).

Water

Stable isotopes of water have long been used as indicators of the origins of waters; $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are particularly useful due to their conservative and predictable behavior. Mixing of

water from multiple sources and phase changes are the two principal factors that account for varying isotopic signatures of hydrogen and oxygen in waters. As seawater is evaporated and carried inland as water vapor, the vapor becomes isotopically lighter in composition as an increasing fraction of the vapor is condensed and lost as precipitation. This is the primary, low-temperature fractionating process for isotopes of water (Clark and Fritz, 1997).

III. Methods

A. Field Methods

To develop a database of isotopic compositions and geochemical characteristics of nutrient sources, samples were taken from sites representative of potential sources. Nutrient source samples were chosen based on the dominant agricultural practices in Northwest Arkansas. The waste-holding ponds at C&H Farms were sampled once early in the study; a second sample collection was attempted in order to remain within acceptable holding times for geochemical analyses but was denied. The waste-holding pond at the University of Arkansas Swine Farm at Savoy, AR was sampled on two separate dates. The two Savoy samples were used for comparison and to support the viability of the samples from the C&H holding ponds. Hog manure was sampled at the University of Arkansas Swine Farm due to sampling restrictions at C&H Farms. The University of Arkansas Applied Broiler Research Unit provided a broiler-litter sample for analysis. Fresh and aged cattle-manure samples were taken from a grazing field (field 1) near Mt. Judea. Manure and litter samples were extracted with deionized water for analysis and data were weighted to 200 mg/L for consistency. A residential septic-system sample was collected near Bella Vista, AR after a failed sampling attempt near Mt. Judea. Runoff samples from three fields (field 1, field 5A, and field 12) near Mt. Judea were collected during a large rainfall event from BCRET flumes equipped with automatic samplers (Figure 2). The three fields

sampled have all been used for cattle grazing and hay production, and fields 1 and 12 have been amended with waste from C&H Farms. Parking-lot runoff was collected during a rain event in Mt. Judea. A commonly used artificial fertilizer variety, 13-13-13 (13% nitrogen, 13% phosphorus, and 13% potassium), was obtained for sampling and dissolved in deionized water for analysis. Artificial fertilizer data were weighted to 200 mg/L for consistency. Stream-bottom sediment was collected from four stream collection sites on Big Creek. Stream sediments were dried, and the silt and clay fractions were separated for analysis. Stream sediments were analyzed for %N, $\delta^{15}\text{N-N}$, PO_4 concentration, and $\delta^{18}\text{O-PO}_4$.

Four stream sites were chosen for water and stream-bottom sediment sample collection: the confluence of Big Creek with the Buffalo River, Big Creek upstream and downstream of Mt. Judea, and an ephemeral stream between C&H Farms and Big Creek (Figure 2, Table 2).

Table 2. Latitude and longitude of Big Creek stream sampling sites.

	Ephemeral Site	Upstream Site	Downstream Site	Confluence Site
Latitude	35° 55' 25.91"	35° 53' 31.9"	35° 56' 19"	35° 58' 39.38"
Longitude	93° 4' 15.24"	93° 4' 6.23"	93° 4' 21.6"	93° 2' 36.54"

A BCRET automatic sampler is present at the ephemeral stream site. A two-liter sample was collected from both the ephemeral stream (sample 5A) and the automatic sampler (sample 5B) early in the study after rainfall. A four-liter sample was collected from the ephemeral stream twice after rainfall (S1 and S2 samples). Four-liter samples were collected from the three Big Creek sites twice during base-flow conditions (B1 and B2 samples) and twice after rainfall (S1 and S2 samples). All stream and runoff samples were measured for pH, temperature, and specific conductance at the time of collection. Hydrologic conditions during sampling are contained in Table 3.

Table 3. Hydrologic conditions and sampling dates of stream and runoff samples.

Sample	Sampling Date	Hydrologic Conditions*
B1 Samples	7/17/17	No rain for 7 days, discharge at base-flow conditions
B2 Samples	9/23/17	No rain for 7 days, discharge at base-flow conditions
S1 Samples	3/30/17	2.134 cm rainfall
S2 Samples	4/17/17	1.778 cm rainfall
Samples 5A and 5B	5/2/16	2.184 cm rainfall
Field Runoff Samples	5/1/17	10.262 cm rainfall
Parking Lot Runoff	11/15/17	1.473 cm rainfall

* Rainfall data are from the National Weather Service Harrison station. Rainfall values are totaled from the date of sampling plus the previous two days.

All stream and source samples were kept refrigerated until analysis. All stream and source samples except artificial fertilizer were filtered to 0.45 μm prior to analysis. Appendix Table B contains the samples collected and the analytes measured for individual samples.

B. Analytical Methods

Geochemical Analysis

Sample pH and specific conductance values were measured in the field using Orion meters. Alkalinity titrations were performed using a Hach digital titrator with 1.60 eq/L sulfuric acid, and alkalinity was calculated using the inflection point method (Rounds, 2006). All samples except stream-bottom sediment were analyzed for TN, DOC, and cations at the University of Arkansas Stable Isotope Laboratory (UASIL). A Shimadzu TOC-V was used to measure TN and DOC. Samples were prepared for measurement of cations by diluting samples at a 1:100 ratio with weak HNO_3 after filtration. Cations were analyzed using a Thermo Fisher iCapQ Quadrupole Mass Spectrometer with a CETAC ASX-560 Auto-sampler. Nitrogen isotopic ratios and %N of sediment were analyzed simultaneously at the UASIL on a Carlo Erba NC 2500

elemental analyzer interfaced to a Thermo Scientific Delta Plus XP continuous flow isotope ratio mass spectrometer (CF-IRMS).

All samples except stream-bottom sediment were sent to the AWRC for analysis of anions, TP, NH₃-N, and NO₃+NO₂-N. Anions were measured with a Dionex ion chromatograph ICS-1600. A Lachat QuickChem 8500 was used to analyze NH₃-N, TP, and NO₃+NO₂-N. Orthophosphate concentration was measured on a Seal AQ3 autoanalyzer at the University of Nebraska Water Sciences Laboratory (UNWSL). Analytical methods, reporting limits, and method detection limits for anions, TP, NH₃-N, NO₃+NO₂-N, and PO₄ concentrations are contained in Table 4.

Table 4. Reporting limits (RL), method detection limits (MDL), and methods of anion analyses.

	NH ₃ -N (mg/L)	Br ⁻ (mg/L)	Cl ⁻ (mg/L)	F ⁻ (mg/L)	NO ₃ ⁻ +NO ₂ ⁻ -N (mg/L)	NO ₃ ⁻ -N (mg/L)	SO ₄ ²⁻ (mg/L)	TP (mg/L)	PO ₄ ³⁻ (mg/L)
RL	0.05	--	0.5	0.1	0.05	0.02	0.5	0.02	--
MDL	0.01	0.015	0.15	0.042	0.02	0.004	0.032	0.005	0.02
Method	EPA 351.2	EPA 300.0	EPA 300.0	EPA 300.0	EPA 353.2	EPA 300.0	EPA 300.0	APHA 4500-P	EPA 365.1

-- no reporting limit

EPA Environmental Protection Agency

APHA American Public Health Association

Isotopic Analysis

Isotopic analysis of NO₃ was conducted at the UASIL. The microbial denitrifier method was utilized to convert NO₃ to gaseous N₂O with denitrifying bacteria (*Pseudomonas aureofaciens*) (Sigman et al., 2001, Coplen et al., 2012). The denitrification process, which under natural conditions continues to generate N₂, was stopped with the generation of N₂O through use of genetically modified denitrifier strains in order to analyze nitrogen and oxygen isotopes of NO₃ simultaneously. Complete conversion from NO₃ to N₂O prevented the inherent fractionation in the denitrification process from influencing isotopic signatures due to the

nitrogen mass balance between product and reactant. After conversion to N_2O , $\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-NO}_3$ were measured on a Thermo Scientific Gas Bench II interfaced to a Thermo Scientific Delta Plus XP CF-IRMS. Reference standards for the analysis were USGS 32, USGS 34, and USGS 35.

Isotopic analysis of $\delta^{18}\text{O}\text{-PO}_4$ was conducted at the UNWSL. Samples were prepared according to the preparation methods described in McLaughlin et al. (2004) and McLaughlin et al. (2006). Soluble phosphate was coprecipitated with magnesium hydroxide and a series of dissolution and precipitation reactions resulted in silver phosphate. The $\delta^{18}\text{O}$ of silver phosphate was analyzed using high temperature pyrolysis on a Eurovector EA Isoprime continuous flow IRMS. Reference standards for the analysis were USGS 34, USGS 35, and potassium phosphate and sucrose reference standards obtained from Elemental Microanalysis.

Water isotopes were measured using a high-temperature reduction unit (TC/EA) interfaced to a Thermo Scientific Delta plus XP IRMS. Isotope precision methods as described by Gehre et al. (2004) and Nelson (2000) were followed for analysis of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of Big Creek stream samples by the UASIL. Four isotopically distinct standards were used for analysis: USGS 47 and three house standards (UASIL L, UASIL H and UASIL R).

C. Interpretive Methods

The minimum and maximum were calculated for all source sample analytes. The minimum, maximum, mean, and median were calculated for all stream sample analytes. The TN, DOC, and cation analyses yielded values below the detection limit that could not be reliably estimated, known as left-censored data. Censored data means were computed using the Kaplan-Meier method. Chloride-to-bromide ratios were analyzed for potential source and stream samples. A chloride-to-bromide ratio of 400 is the theoretical maximum for natural waters;

chloride-to-bromide ratios of over 400 are indicative human-influenced waters (Thomas, 2000). Wilcoxon Rank Sum Tests were conducted to compare select analytes between stream sampling sites.

D. PARCC

Data quality indicators were used in this study to assess quality assurance and quality control of collected data. Indicators include precision, accuracy, representativeness, comparability, and completeness (PARCC). Precision is a measurement of agreement between a series of duplicate measurements. Laboratory duplicates of collected samples were used in order to estimate analytical precision. Accuracy is the proximity of an observed value to an accepted reference value. Measurement of accuracy was conducted with both laboratory and reference standards. Representativeness is the degree to which collected data represent true environmental conditions of the system or system component of interest. Regional agricultural practices were considered during nutrient source selection, and sampling was conducted for as many sources as possible within budget and time constraints. Stream sites were sampled multiple times under varying hydrologic conditions in order to assure representation of both high-flow and base-flow conditions. However, rain events prior to stream sampling were smaller than planned.

Comparability refers to the equivalency of datasets. Comparability was achieved by following approved sampling plans and applying proper sampling and analysis techniques. Completeness measures the quantity of valid data collected compared to the planned amount that was determined necessary to address research questions. In this study, all planned samples were collected and analyzed. A small number of samples did not contain enough analyte to accurately measure (U.S. EPA, 2014).

IV. Results

A. Potential Nutrient Sources

Potential nutrient source samples in this study exhibit distinct geochemical signatures. Manures, waste lagoon, and fertilizer samples had higher concentrations of most analytes when compared to runoff and stream samples. Potential nutrient source anion concentrations can be seen in Table 5, with minimums and maximums in Table 6. Source sample $\text{NH}_3\text{-N}$ concentrations ranged from 0.11-1040.00 mg/L with little to no $\text{NO}_3\text{-N}$ (range: 0-0.380 mg/L). Manure, septic and waste pond $\text{NH}_3\text{-N}$ ranged from 7.93 – 1040.00 mg/L.

Field 1 runoff $\text{NO}_3\text{-N}$ concentration was 0.380, the highest of all potential nutrient sources. Of all potential sources, the CAFO solids pond (6) had the highest $\text{NH}_3\text{-N}$ and alkalinity. Artificial fertilizer (9) had the highest bromide, TN, and PO_4 . Chicken litter (4) had the greatest concentration of fluoride, chloride, $\text{NO}_3+\text{NO}_2\text{-N}$, and SO_4 , along with the highest specific conductance of all source samples. Hog manure (2) had the highest DOC and TP.

Total nitrogen data were compared to nutrient data from AWRC. TN comprises organic nitrogen, NH_3 , NO_2 , and NO_3 . The sum of $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{NO}_3+\text{NO}_2\text{-N}$ was consistently higher than TN concentration, indicating TN data do not precisely represent field conditions. Recommended holding times for TN and DOC analysis were exceeded for most source and stream samples, rendering TN and DOC data potentially less accurate. Orthophosphate data from UNWSL were compared to TP data; TP is a measure of all forms of phosphorus in a sample (orthophosphate, condensed phosphate, and organic phosphate). In 34% of samples analyzed, PO_4 concentration was higher than TP. In source samples, TP ranged from 0.033 to 400.400 ppm, and PO_4 ranged from 0.25 to 860.14 mg/L.

Table 5. Anion and nutrient concentrations of potential source samples.

#	Sample Name	NH ₃ -N mg/L	Br mg/L	Cl mg/L	F mg/L	NO ₃ +NO ₂ -N mg/L	NO ₃ -N mg/L	SO ₄ mg/L	TN ppm	DOC ppm	TP mg/L	PO ₄ mg/L	pH	SpC μS/cm	Alkalinity mg/L as CaCO ₃
1A	Old Savoy Lagoon	354.00	--	444.15	0*	0.16	0.105	24.71	--	--	--	--	7.77	6770.0	1187.8
1B	Fresh Savoy Lagoon	227.00	0*	542.87	0*	0.17	0*	43.06	<1	<2.14	52.950	16.75	--	--	--
2	Hog Manure	432.08	0*	81.64	376.94	0.23	0*	54.51	193.30	721.20	400.400	280.70	6.08	5260.0	89.0
3	Fresh Cow Manure	307.00	0.119	98.42	3.35	0.14	0*	0*	0.21*	<2.14	38.200	14.05	7.19	1732.0	490.3
4	Chicken Litter	673.04	0*	1125.17	851.27	1.36	0*	3857.46	<1	<2.14	81.028	347.40	6.28	7310.0	503.7
6	CAFO Solids Pond	1040.00	0*	586.68	0*	0.22	0*	43.62	<1	<2.14	75.200	121.70	8.16	4581.0	4134.5
7	CAFO Liquids Pond	448.00	0*	472.33	0.63	0.12	0.108	6.18	<1	<2.14	110.400	91.30	7.96	3314.0	2987.2
8	Old Cow Manure	7.12	0*	14.62	0.22	0.05	0*	0*	<1	<2.14	34.110	19.26	7.06	297.7	245.6
9	Synthetic Fertilizer	173.60	1.280	231.88	4.08	0.80	0*	112.28	391.60	138.00	203.160	860.14	6.95	63.6	--
10	Septic Effluent	83.90	0.097	52.43	0*	0.06	0*	20.46	79.40	43.89	7.662	7.66	6.55	1313.0	278.0
11	Field 1 Runoff	0.51	--	2.68	0.15	0.34	0.380	2.52	<1	<2.14	0.712	0.57	7.50	51.0	--
12	Field 5A Runoff	0.39	0*	2.12	0.15	0.8	0.372	2.29	1.19	7.26	0.868	0.83	7.28	68.0	45.5
13	Field 12 Runoff	0.14	0*	1.24	0.14	0.19	0.218	2.04	0.26*	4.69	0.368	0.25	7.35	60.0	15.2
32	Parking Lot Runoff	0.11	0.006*	E 0.34	0*	0.08	0.181	1.42	<1	3.59	0.033	0.83	6.62	51.7	--

* below method detection limit

E below reporting limit and above method detection limit

-- no data

< left-censored data

B samples collected during base-flow conditions

S samples collected after rainfall

SpC specific conductance

Table 6. Anion and nutrient concentration minimums and maximums of potential source samples.

	Max	Max Sample	Min	Min Sample
NH₃-N (mg/L)	1040.00	CAFO Solids Pond	0.11	Parking Lot Runoff
Bromide (mg/L)	1.280	Synthetic Fertilizer	0	--
Chloride (mg/L)	1125.17	Chicken Litter	0.34	Parking Lot Runoff
Fluoride (mg/L)	851.27	Chicken Litter	0	--
NO₃+NO₂-N (mg/L)	1.36	Chicken Litter	0.08	Parking Lot Runoff
NO₃-N (mg/L)	0.380	Field 1 Runoff	0	--
SO₄ (mg/L)	3857.46	Chicken Litter	0	--
DOC (ppm)	721.20	Hog Manure	<	--
TN (ppm)	391.60	Synthetic Fertilizer	<	--
TP (ppm)	400.400	Hog Manure	0.033	Parking Lot Runoff
PO₄ (mg/L)	860.14	Synthetic Fertilizer	0.25	Field 12 Runoff
pH	8.16	CAFO Solids Pond	6.08	Hog Manure
Specific Conductance (µS/cm)	7310.0	Chicken Litter	51.0	Field 1 Runoff
Alkalinity (as CaCO₃) (mg/L)	4134.5	CAFO Solids Pond	15.2	Field 12 Runoff

< multiple left-censored samples equal to minimum value

-- multiple samples equal to minimum value

Chloride-to-bromide ratios were calculated to determine potential anthropogenic influences in Big Creek (Table 7). A chloride-to-bromide ratio of 400 is the theoretical maximum for natural waters; chloride-to-bromide ratios of over 400 are indicative human-influenced waters (Thomas, 2000). Fresh cow manure and septic effluent were the only sources sampled with a chloride-to-bromide ratio over 400. The chloride-to-bromide ratio of fresh cow manure was 827.04, and septic effluent had a chloride-to-bromide ratio of 540.52.

Runoff samples had lower NH₃-N, chloride, TP, PO₄, specific conductance, and alkalinity when compared to other source samples. Of all runoff samples, Field 1 had the highest concentration of NH₃-N, chloride, fluoride, NO₃-N, and SO₄. Field 5A had the highest concentration of NO₃+NO₂-N, TN, TP, and specific conductance. Parking lot runoff had the highest concentration of bromide. Potential source cation concentrations are found in Tables C and D in the Appendix, with minimums and maximums in Table 8. Runoff samples had consistently low cation concentrations compared to other sources.

Table 7. Chloride-to-bromide ratios of potential source samples and stream samples containing sufficient bromide.

	#	Sample Name	Bromide (mg/L)	Chloride (mg/L)	Chloride Bromide
Potential	3	Fresh Cow Manure	0.119	98.42	827.04
Source	9	Synthetic Fertilizer	1.280	231.88	181.16
Samples	10	Septic Effluent	0.097	52.43	540.52
	14	Upstream S1	0.006	2.788	464.67
	16	Upstream B1	0.01	1.196	119.60
	17	Upstream B2	0.011	2.007	182.45
	18	Downstream S1	0.002	1.495	747.50
Stream	21	Downstream B2	0.019	2.595	136.58
Samples	23	Confluence S2	0.005	2.249	449.80
	24	Confluence B1	0.008	1.950	243.75
	25	Confluence B2	0.019	2.845	149.74
	26	Ephemeral S1	0.007	2.649	378.43
	27	Ephemeral S2	0.015	3.930	262.00

Cation concentrations for potential source samples were greater than stream sample cation concentrations. Sample 1A, old Savoy lagoon, was highest in most rare earth metals. Hog manure had the highest concentration of magnesium and manganese. Artificial fertilizer had the maximum concentration of aluminum, chromium, cadmium, tin, and 12 other cations. Chicken litter was highest in sodium, potassium, iron, cobalt, nickel, copper, zinc, arsenic, selenium, and five other cations.

Potential source $\delta^{15}\text{N-NO}_3$ ranged from -15.40‰ to 54.79‰, and $\delta^{18}\text{O-NO}_3$ ranged from -7.15‰ to 59.06‰ (Figure 3 and Table 9). Instrument precision for both $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ was $\pm 0.3\%$. The fresh Savoy lagoon, fresh cow manure, and CAFO liquids pond samples did not contain sufficient NO_3 to obtain isotopic ratios. The old Savoy lagoon sample had an unusually enriched $\delta^{18}\text{O-NO}_3$ value of 59.06‰, consistent with values expected of atmospheric NO_3 , but potentially indicative of in-lagoon exchange processes. The CAFO solids pond sample $\delta^{15}\text{N-NO}_3$ was 4.21‰, and $\delta^{18}\text{O-NO}_3$ was -7.15‰, within the typical range of $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ for

Table 8. Cation minimums and maximums of potential source samples.

PPB	Maximum	Maximum Sample	Minimum	Minimum Sample
Aluminum	257	Synthetic Fertilizer	1.11	Parking Lot Runoff
Antimony	5.59	Synthetic Fertilizer	0.000179	Synthetic Fertilizer
Arsenic	1.16	Chicken Litter	<	Parking Lot Runoff
Barium	16.8	Synthetic Fertilizer	0.539	Synthetic Fertilizer
Beryllium	0.0911	Fresh Savoy Lagoon	0	--
Bismuth	0.0257	Old Savoy Lagoon	<	--
Boron	108	Chicken Litter	0.0901	Synthetic Fertilizer
Cadmium	0.0203	Synthetic Fertilizer	<	--
Calcium	521	Chicken Litter	1.28	Synthetic Fertilizer
Cerium	0.0359	Synthetic Fertilizer	<	--
Cesium	0.13	Chicken Litter	<	--
Chromium	5.84	Synthetic Fertilizer	<	Field 1 Runoff
Cobalt	1.19	Chicken Litter	<	Field 5A Runoff, Parking Lot Runoff
Copper	225	Chicken Litter	<	--
Dysprosium	0.0603	Synthetic Fertilizer	0.000227	Parking Lot Runoff
Erbium	0.0444	Synthetic Fertilizer	<	Parking Lot Runoff, Septic Effluent
Europium	0.0317	Old Savoy Lagoon	<	Parking Lot Runoff, Septic Effluent
Gadolinium	0.0397	Synthetic Fertilizer	<	Parking Lot Runoff
Gallium	0.191	Synthetic Fertilizer	0	--
Holmium	0.032	Old Savoy Lagoon	<	--
Indium	0.0368	Old Savoy Lagoon	<	--
Iron	246	Chicken Litter	0.62	Parking Lot Runoff
Lanthanum	0.0316	Old Savoy Lagoon	<	--
Lithium	4.8	Fresh Savoy Lagoon	0	--
Lutetium	0.0304	Old Savoy Lagoon	<	--
Magnesium	6547	Hog Manure	4.42	Parking Lot Runoff
Manganese	159	Hog Manure	0.0398	Parking Lot Runoff
Neodymium	0.0663	Synthetic Fertilizer	<	CAFO Solids Pond, Parking Lot Runoff
Nickel	26.4	Chicken Litter	<	--
Potassium	86578	Chicken Litter	9.23	Parking Lot Runoff
Praseodymium	0.0319	Old Savoy Lagoon	<	--
Rhenium	0.03	Old Savoy Lagoon	<	--
Rubidium	56.9	Chicken Litter	0.00252	Parking Lot Runoff
Samarium	0.0326	Old Savoy Lagoon	<	Parking Lot Runoff, Septic Effluent
Scandium	0.0333	Old Savoy Lagoon	<	--
Selenium	0.0756	Chicken Litter	0	--
Sodium	37201	Chicken Litter	<	Synthetic Fertilizer, Parking Lot Runoff
Strontium	10.9	Chicken Litter	0.0611	Synthetic Fertilizer
Terbium	0.0326	Old Savoy Lagoon	<	--
Thallium	0.0388	Old Savoy Lagoon	<	--
Thorium	0.0481	Old Savoy Lagoon	<	--
Thulium	0.0331	Old Savoy Lagoon	<	--
Tin	163	Synthetic Fertilizer	0.00386	Old Savoy Lagoon
Uranium	3.05	Synthetic Fertilizer	<	--
Vanadium	4.84	Synthetic Fertilizer	0.00543	Septic Effluent
Ytterbium	0.0884	Synthetic Fertilizer	<	Septic Effluent
Yttrium	0.844	Synthetic Fertilizer	0.00281	Septic Effluent
Zinc	284	Chicken Litter	<	--

< below method detection limit

-- multiple samples equal to minimum value

both manure and septic waste and NH₄ in fertilizer and rain. Manures δ¹⁵N-NO₃ varied dramatically but exhibited a smaller range of δ¹⁸O-NO₃.

Hog manure δ¹⁵N-NO₃ was -2.78‰, old cow manure δ¹⁵N-NO₃ was 20.19‰, and chicken litter δ¹⁵N-NO₃ was 54.79‰. For these three samples, δ¹⁸O-NO₃ ranged from 16.09‰ to 39.68‰. Artificial fertilizer was slightly enriched in δ¹⁵N compared to the typical range. Old cow manure δ¹⁸O-NO₃ was more enriched than the typical range of manure δ¹⁸O-NO₃. Chicken litter exhibited signs of denitrification, with enriched δ¹⁵N-NO₃ and δ¹⁸O-NO₃. Septic δ¹⁵N-NO₃ and δ¹⁸O-NO₃ values fell within expected ranges for septic waste. Runoff samples exhibited heavy δ¹⁵N-NO₃ and δ¹⁸O-NO₃. Runoff δ¹⁸O-NO₃ ranged from 32.14‰ to 56.07‰, and δ¹⁵N-NO₃ ranged from -15.40‰ to 0.21‰.

Table 9. Potential source sample δ¹⁵N-NO₃ and δ¹⁸O-NO₃.

#	Sample Name	δ ¹⁵ N (‰)	δ ¹⁸ O (‰)
1A	Old Savoy Lagoon	4.77	59.06
2	Hog Manure	-2.78	16.09
4	Chicken Litter	54.79	37.82
6	CAFO Solids Pond	4.21	-7.15
8	Aged Cow Manure	20.19	39.68
9	Synthetic Fertilizer	13.28	30.80
9D	Synthetic Fertilizer Duplicate	15.40	18.73
10	Septic Effluent	18.70	2.21
11	Field 1 Runoff	-3.18	33.37
11D	Field 1 Runoff Duplicate	-2.82	32.14
12	Field 5A Runoff	0.21	34.19
13	Field 12 Runoff	-3.16	38.85
32	Parking Lot Runoff	-15.40	56.07

D = duplicate

The following samples did not contain sufficient NO₃ to obtain an isotopic ratio:

1B Fresh Savoy Lagoon

3 Fresh Cow Manure

7 CAFO Liquids Pond

Soil $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ were calculated from $\delta^{15}\text{N-N}$ after Fields and Halihan (2016). The $\delta^{18}\text{O}$ of NO_3 produced by nitrification of nitrogen was estimated with measured $\delta^{18}\text{O}$ of stream water (-6.68‰ to -4.96‰) and atmospheric O_2 of 23.5‰ (Kroopnick and Craig, 1972). Estimates of $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ produced by nitrification of nitrogen stored in soils sampled in the watershed range from 3.8‰ to 6.6‰ $\delta^{15}\text{N-NO}_3$ and 3.4‰ to 4.8‰ $\delta^{18}\text{O-NO}_3$. Stream-bottom sediment $\delta^{15}\text{N-N}$ ranged from -2.26‰ to 5.07‰ (Table 10), which overlaps the range for measured $\delta^{15}\text{N-NO}_3$ (dissolved) of stream samples. Stream-bottom sediment %N ranged from 0.023% upstream to 0.286% downstream.

Table 10. Nitrogen isotopic ratios and percent nitrogen of stream sediment samples.

#	Sample Name	$\delta^{15}\text{N}$ (‰)	%N
28	Upstream	4.57	0.023
28D	Upstream Duplicate	2.61	0.025
29	Downstream	5.07	0.286
30	Confluence	2.18	0.154
31	Ephemeral	-2.26	0.053

D = duplicate

Potential nutrient source $\delta^{18}\text{O-PO}_4$ values are documented in Table 11 and shown in Figure 4. Source $\delta^{18}\text{O-PO}_4$ values were extremely variable. Stream-bottom sediment $\delta^{18}\text{O-PO}_4$ was -78.8‰ and 101.0‰. Manure and septic $\delta^{18}\text{O-PO}_4$ ranged from 21.0‰ to 81.6‰. Waste lagoon $\delta^{18}\text{O-PO}_4$ ranged from -0.7‰ to 30.5‰. Fertilizer $\delta^{18}\text{O-PO}_4$ was 19.9‰, and runoff sample $\delta^{18}\text{O-PO}_4$ ranged from 8.5‰ to 38.6‰.

Both a fresh and an old cow manure sample were taken from field 1 for comparison. Fresh cow manure did not contain sufficient NO_3 to obtain isotopic ratios. Aged cow manure $\delta^{18}\text{O-PO}_4$ was 15.8‰ higher than fresh manure. Fresh manure had higher ammonia, bromide, chloride, fluoride, and TN compared to old manure.

Two samples were collected from the Savoy waste pond to determine the viability of the dated samples from the C&H waste ponds. The more recent savoy lagoon sample (1B) did not contain sufficient NO_3 to determine isotopic ratios. Sample 1B had lower $\text{NH}_3\text{-N}$ and higher chloride, $\text{NO}_3+\text{NO}_2\text{-N}$, and SO_4 compared to sample 1A. The average % difference between cation concentrations between 1B and 1A was 65%. Analyte concentrations of sample 1A, along with samples from the CAFO lagoons, should be regarded as potentially less accurate due to increased sample holding times.

Table 11. Potential nutrient source $\delta^{18}\text{O-PO}_4$ values.

#	Sample Name	$\delta^{18}\text{O}$ (‰)
1B	Savoy Lagoon-Fresh	-0.7
2	Hog Manure	81.6
3	Fresh Cow Manure	45.9
4	Chicken Litter	21.0
6	CAFO Solids Pond	30.5
7	CAFO Liquids Pond	23.3
8	Aged Cow Manure	61.7
9	Synthetic Fertilizer	19.9
10	Septic Effluent	28.1
11	Field 1 Runoff	8.5
12	Field 5A Runoff	15.2
13	Field 12 Runoff	32.0
32	Parking Lot Runoff	38.6
29	Downstream Sediment	101.0
31	Ephemeral Sediment	-78.8

Sample 1A Old Savoy Lagoon was not tested
 Upstream and Confluence sediment did not contain
 sufficient PO_4 to obtain an isotopic ratio

B. Stream Samples

Stream sample anion concentrations are shown in Table 12, and anion statistics in Table 13. Stream samples contained little $\text{NH}_3\text{-N}$ (range: 0-0.06 mg/L) and slightly more $\text{NO}_3\text{-N}$ (range: 0.046-0.809 mg/L). Ephemeral stream samples contained higher $\text{NO}_3\text{-N}$ compared to other stream sites. A Wilcoxon Rank Sum Test was conducted with a 95% confidence interval

Table 12. Anion and nutrient concentrations of stream samples.

#	Sample Name	NH ₃ -N mg/L	Br ⁻ mg/L	Cl ⁻ mg/L	F ⁻ mg/L	NO ₃ ⁻ +NO ₂ ⁻ -N mg/L	NO ₃ ⁻ -N mg/L	SO ₄ ²⁻ mg/L	TN ppm	DOC ppm	TP mg/L	PO ₄ ³⁻ mg/L	pH	SpC μS/cm	Alkalinity mg/L as CaCO ₃
14	Up S1	0*	0.006*	2.788	0.153	0.17	0.185	3.182	<1	1.46*	0.030	0.015*	7.82	84.7	53.6
15	Up S2	E 0.01	0*	1.382	0.149	E 0.03	0.167	3.865	<1	1.01*	0.052	0.003*	7.89	95.8	55.6
16	Up B1	E 0.04	0.01*	1.196	0*	0.20	0.180	3.876	<1	1.06*	0.024	0.439	8.05	119.1	25.3
17	Up B2	E 0.02	0.011*	2.007	0.021*	0.09	0.046	4.261	<1	1.52*	E 0.010	6.290	7.64	235.0	55.6
18	Down S1	E 0.01	0.002*	1.495	0.157	0.25	0.288	3.706	<1	1.90*	0.076	0.010*	7.63	114.5	23.3
19	Down S2	0.06	0*	1.830	0.158	0.14	0.152	5.321	<1	1.49*	0.026	0*	7.75	162.9	53.6
20	Down B1	E 0.02	0*	1.623	0.002*	0.18	0.152	4.295	<1	1.81*	0.020	0.157	7.57	180.7	65.7
21	Down B2	E 0.02	0.019	2.595	0.007*	0.45	0.398	4.820	<1	2.53	0.004*	0.703	7.54	276.0	96.0
22	Con S1	0.06	0*	1.919	0.155	0.29	0.305	4.852	<1	2.10*	0.030	0.010*	7.87	147.9	94.0
23	Con S2	0*	0.005*	2.249	0.169	0.12	0.146	6.787	<1	1.37*	0.028	0.022*	8.10	200.7	69.8
24	Con B1	E 0.04	0.008*	1.950	0.206	0.31	0.277	4.723	<1	1.14*	0*	0.185	8.00	217.7	65.7
25	Con B2	0*	0.019	2.845	0.335	0.08	0.055	5.006	<1	1.63*	0*	0.031	7.44	263.0	85.9
26	Eph S1	0*	0.007*	2.649	0.149	0.77	0.809	2.168	0.28*	0.86*	0.062	0.002*	7.16	313.0	131.4
27	Eph S2	0*	0.015	3.930	0.146	0.65	0.692	3.127	0.10*	0.53*	0.030	0.016*	7.48	394.0	166.8
5B	Ephemeral ISCO	E 0.03	0*	3.015	0.907	0.51	0.586	2.561	--	--	--	0	7.79	339.0	--

* below method detection limit

E below reporting limit and above method detection limit

-- no data

< left-censored data

B samples collected during base-flow conditions

S samples collected after rainfall

for NO₃-N and PO₄ concentrations between the upstream and downstream sites. No statistically significant difference was observed. Stream sample NO₃+NO₂-N concentrations ranged from 0.03 mg/L to 0.77 mg/L. Stream samples contained low TP (range: 0-0.076 mg/L), while PO₄ concentration varied from 0 to 6.290 mg/L. The upstream B2 sample had the maximum concentration of PO₄, one magnitude higher than other stream samples. The TP value for upstream B2 (0.010 mg/L) did not reflect this high PO₄ concentration (6.290 mg/L).

Anion data were grouped by stream sites and summary statistics were generated. The median of samples taken from the ephemeral stream was highest in chloride, NO₃-N, NO₃+NO₂-N, TP, specific conductance, and alkalinity of all stream locations, and was consistently lowest in SO₄, DOC, and PO₄. Chloride, SO₄, specific conductance, and alkalinity increased downstream, with concentrations lowest upstream, moderate concentrations downstream, and concentrations highest at the confluence of Big Creek and the BNR. Fluoride, TP and PO₄ concentrations decreased downstream, with concentrations highest upstream and lowest at the confluence.

Table 13. Anion and nutrient concentration statistics of stream samples.

	Max.	Max. Sample	Min.	Min. Sample	Mean	Median
NH₃-N (mg/L)	0.06	Con S1	0	--	0.02	0.02
Bromide (mg/L)	0.019	Down B2	0	--	0.007	0.006
Chloride (mg/L)	3.930	Eph S2	1.196	Up B1	2.232	2.007
Fluoride (mg/L)	0.907	Eph ISCO	0	Up B1	0.181	0.153
NO₃+NO₂-N (mg/L)	0.77	Eph S1	0.03	Up S2	0.28	0.20
NO₃-N (mg/L)	0.809	Eph S1	0.046	Up B2	0.296	0.185
SO₄(mg/L)	6.787	Con S2	2.168	Eph S1	4.170	4.261
DOC (ppm)	2.53	Down B2	0.53	Eph S2	1.46	1.48
TN (ppm)	0.28	Eph S1	<	--	0.03	0
TP (ppm)	0.076	Down S1	0	--	0.028	0.027
PO₄ (mg/L)	6.290	Up B2	0	--	0.053	0.016
pH	8.10	Con S2	7.16	Eph S1	7.72	7.75
Specific Conductance (µS/cm)	394.0	Eph S2	84.7	Up S1	210.0	200.7
Alkalinity (as mg/L CaCO₃)	166.8	Eph S2	23.3	Down S1	74.5	65.7

< multiple samples below method detection limit

-- multiple samples equal to minimum value

Anion data were grouped by hydrologic conditions and summary statistics were generated. Base-flow samples exhibited the highest median $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NO}_3+\text{NO}_2\text{-N}$, TP, and PO_4 concentrations. Specific conductance ranged from 84.7 to 394.0 $\mu\text{S}/\text{cm}$ in stream samples. Base-flow stream samples had higher specific conductance than storm-flow samples. Bromide, chloride, fluoride, SO_4 , DOC, and alkalinity were highest after rainfall. Table 7 includes stream sample chloride-to-bromide ratios. The stream samples that contained a chloride-to-bromide ratio over 400 include upstream S1 (464.67), downstream S1 (747.5), and confluence S2 (449.8).

Cation concentrations in stream samples are shown in the Appendix in Tables E and F and statistics in Table 14. Sample 5A from the ephemeral stream had the maximum concentration of all stream samples for sodium, aluminum, potassium, manganese, iron, arsenic, and most rare earth metals. Copper was only found in detectable concentration in sample 5A. The downstream B2 sample had the highest lithium and uranium concentration. The upstream B2 sample had the highest magnesium, and the ephemeral S2 sample had the highest calcium and chromium.

Cation concentrations were grouped by stream site and summary statistics were generated. When medians were compared, sodium, magnesium, calcium, chromium, arsenic, strontium, tin, and uranium increased from the upstream site to the confluence site. The ephemeral stream site had the highest median concentration of lithium, boron, calcium, vanadium, chromium, and tin. Aluminum and iron were also highest at the ephemeral site: the median concentrations of aluminum and iron were one magnitude higher at the ephemeral site compared to other stream sampling sites. The ephemeral site had the lowest median concentration of magnesium of all stream sampling sites. Cation concentrations were grouped by

hydrologic conditions and summary statistics were generated. Samples taken during storm-flow conditions had greater median concentrations than those taken following rainfall for aluminum, chromium, manganese, gallium, tin, and most rare earth metals.

Table 14. Cation statistics of stream samples.

PPB	Max.	Max. Sample	Min.	Min. Sample	Mean	Median
Aluminum	7.76	Eph In-Stream	<	--	0.832	0.37
Antimony	0.00111	Con S1	0.143	Eph S1	0.000371	0.000322
Arsenic	0.0531	Eph In-Stream	0	--	0.0086	0.00506
Barium	1.63	Con S1	0.786	Down S1	1.1	1.08
Boron	1.17	Eph In-Stream	0.18	Eph S1	0.49	0.496
Calcium	136	Eph S2	25.5	Up S1	73.1	69.1
Chromium	0.0483	Eph S2	<	--	0.0128	0.0104
Cobalt	0.00427	Eph In-Stream	<	--	0.00372	0
Dysprosium	0.00325	Eph In-Stream	<	--	0.000495	0.000302
Erbium	0.0017	Eph In-Stream	<	--	0.000315	0.000284
Gadolinium	0.00336	Eph In-Stream	<	--	0.000518	0.00017
Gallium	0.00916	Eph In-Stream	0	--	0.00153	0.00153
Holmium	0.000989	Eph In-Stream	<	--	0.0000879	0
Iron	4.7	Eph In-Stream	<	--	0.645	0.379
Lanthanum	0.0139	Up S2	<	--	0.00216	0.000783
Lithium	0.0713	Down B2	0	--	0.0238	0.0238
Lutetium	0.000579	Eph ISCO	<	--	0.0000711	0
Magnesium	71.8	Up B2	27.5	Eph S1	45.3	44.3
Manganese	0.358	Eph In-Stream	<	Con S2	0.0692	0.0259
Potassium	138	Eph In-Stream	13.1	Eph S2	33.1	23.2
Praseodymium	0.00407	Eph In-Stream	<	--	0.000526	0.000293
Rhenium	0.000472	Eph In-Stream	<	--	0.0000657	0
Rubidium	0.131	Eph In-Stream	<	Up S2	0.0145	0.00756
Selenium	0.0126	Con B2	0	--	0.00236	0
Sodium	62.1	Eph In-Stream	21.7	Up S1	35.4	33.5
Strontium	2.38	Con B2	0.964	Eph In-Stream	1.57	1.49
Terbium	0.00109	Eph In-Stream	<	--	0.0000953	0
Thulium	0.000777	Eph In-Stream	<	--	0.0000718	0
Tin	0.00926	Eph In-Stream	2.79	Eph ISCO	0.00497	0.00481
Uranium	0.00848	Down B2	0.000162	Down S1	0.00349	0.00295
Vanadium	0.0276	Eph In-Stream	0.00181	Down S1	0.00713	0.00611
Ytterbium	0.00201	Eph In-Stream	<	--	0.00028	0.0000549
Yttrium	0.0264	Eph In-Stream	<	Down B2, Con B2	0.00487	0.00303

< multiple samples below method detection limit

-- multiple samples equal to minimum value

Stream sample $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ are shown in Figure 3 and Table 15. Big Creek stream samples range from -7.59‰ to 9.10‰ $\delta^{15}\text{N-NO}_3$ and -3.41‰ to 6.71‰ $\delta^{18}\text{O-NO}_3$. These ranges are similar to NO_3 values expected from nitrification of nitrogen stored in soils sampled in the watershed. For the upstream, downstream, and confluence sites, the B2 samples exhibited enriched $\delta^{15}\text{N-NO}_3$ compared to B1, S1, and S2 samples.

Table 15. Stream sample $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$.

#	Sample Name	$\delta^{15}\text{N}$ (‰)	$\delta^{18}\text{O}$ (‰)
14	Upstream S1	-0.43	1.85
14D	Upstream S1 Duplicate	0.11	0.28
15	Upstream S2	0.20	9.10
16	Upstream B1	0.17	2.15
17	Upstream B2	3.76	7.07
17D	Upstream B2 Duplicate	3.72	8.38
18	Downstream S1	1.44	1.07
19	Downstream S2	4.01	3.16
19D	Downstream S2 Duplicate	2.89	3.33
20	Downstream B1	4.98	2.25
21	Downstream B2	6.41	-0.62
21D	Downstream B2 Duplicate	7.02	3.75
22	Confluence S1	3.07	2.39
23	Confluence S2	3.42	4.87
23D	Confluence S2 Duplicate	3.29	2.35
23D	Confluence S2 Duplicate	2.66	6.90
24	Confluence B1	3.80	2.95
25	Confluence B2	4.90	-2.21
25D	Confluence B2 Duplicate	5.27	-2.70
25D	Confluence B2 Duplicate	3.84	4.50
26	Ephemeral S1	0.72	-0.68
27	Ephemeral S2	2.07	-0.66
27D	Ephemeral S2 Duplicate	2.02	-0.61
5A	Ephemeral In-Stream 5/2/16	-3.42	2.41
5B	Ephemeral ISCO 5/2/16	0.54	-7.59

D = duplicate

B samples collected during base-flow conditions

S samples collected after rainfall

Wilcoxon Rank Sum Tests were conducted with a 95% confidence interval to compare $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ between stream sampling sites. In Big Creek, $\delta^{15}\text{N-NO}_3$ was found to

be statistically higher (more enriched) at the downstream site compared to the upstream site, downstream $\delta^{15}\text{N-NO}_3$ was statistically higher than ephemeral $\delta^{15}\text{N-NO}_3$, and confluence $\delta^{15}\text{N-NO}_3$ was statistically higher than both upstream $\delta^{15}\text{N-NO}_3$ and ephemeral $\delta^{15}\text{N-NO}_3$. The upstream site had statistically higher $\delta^{18}\text{O-NO}_3$ compared to the ephemeral site.

Stream $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ vs. NO_3 concentration plots were used to determine influence of denitrification and mixing in Big Creek. Linear plots of $\delta^{15}\text{N-NO}_3$ vs. $1/\text{NO}_3$ concentration indicate mixing of two solutions with different $\delta^{15}\text{N-NO}_3$, and linear plots of $\delta^{15}\text{N-NO}_3$ vs. $\ln \text{NO}_3$ concentration denote the occurrence of denitrification. Isotopic ratios were plotted separately for individual stream sites and for all stream samples combined. When the stream sites were plotted together, stream samples showed no evidence of mixing (Figure 5) or denitrification (Figure 6). However, plotted by individual stream sites, both upstream plots were linear. Figure 7 contains a plot of $\delta^{15}\text{N-NO}_3$ vs. $1/\text{NO}_3$ concentration at the upstream site, with a trendline R^2 of 0.9829. A plot of $\delta^{15}\text{N-NO}_3$ vs. $\ln \text{NO}_3$ concentration at the upstream site exhibited a trendline R^2 of 0.9873 (Figure 8). The confluence $\delta^{15}\text{N-NO}_3$ vs. $1/\text{NO}_3$ concentration plot trendline R^2 value was 0.8229 (Figure 9). No other individual stream site plots were linear.

Stream $\delta^{18}\text{O-PO}_4$ values are shown in Figure 4 and Table 16. Stream sample $\delta^{18}\text{O-PO}_4$ ranged from 36.3 to 55.4‰. Many stream samples did not contain sufficient PO_4 to obtain an isotopic ratio. Due to low PO_4 content in most Big Creek stream samples, $\delta^{18}\text{O-PO}_4$ data have a high degree of instrumental uncertainty. These data should be regarded as estimates. Calculated equilibrium $\delta^{18}\text{O-PO}_4$ ranged from -17.75 to -8.44‰. The equilibrium $\delta^{18}\text{O-PO}_4$ for the upstream B2, downstream B1, and ephemeral S1 samples were depleted compared the measured stream $\delta^{18}\text{O-PO}_4$.

Table 16. Stream sample $\delta^{18}\text{O-PO}_4$ of samples containing sufficient phosphate, stream water temperature at time of sampling, and calculated equilibrium $\delta^{18}\text{O-PO}_4$.

#	Sample Name	$\delta^{18}\text{O-PO}_4$ (‰)	Water T (°C)	Equilibrium $\delta^{18}\text{O-PO}_4$ (‰)
16	Upstream B1	-36.3	24.0	-10.6
17	Upstream B2	39.6	28.6	-13.2
20	Downstream B1	22.3	24.3	-17.7
21	Downstream B2	-8.1	24.4	-8.4
26	Ephemeral S1	55.4	14.0	-12.5

B samples collected during base-flow conditions

S samples collected after rainfall

Stream water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are presented in Table 17 and Figure 10. Stream water $\delta^{18}\text{O}$ ranged from -6.68‰ to -4.96‰ and $\delta^2\text{H}$ ranged from -41.82‰ to -26.83‰. The global meteoric water line (GMWL) (Craig, 1961) and local meteoric water line (LMWL) (Knerim, 2015) are plotted with stream water in Figure 10. Figure 10 illustrates that stream water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ lie slightly but consistently above the LMWL, indicating evaporative effects.

Table 17. Water isotopic ratios of stream samples.

#	Sample Name	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
14	Upstream S1	-4.96	-26.8
15	Upstream S2	-5.31	-29.1
16	Upstream B1	-5.18	-30.9
17	Upstream B2	-5.28	-32.4
18	Downstream S1	-5.54	-31.7
19	Downstream S2	-6.52	-39.7
20	Downstream B1	-6.19	-38.0
21	Downstream B2	-5.05	-28.7
22	Confluence S1	-6.68	-41.8
23	Confluence S2	-5.30	-29.7
24	Confluence B1	-5.49	-34.2
25	Confluence B2	-5.65	-36.1
26	Ephemeral S1	-5.75	-35.2
27	Ephemeral S2	-5.48	-33.0

B samples collected during base-flow conditions

S samples collected after rainfall

Field runoff samples were collected in auto-samplers after a large rain event. The ephemeral stream was sampled twice early in the study in order to determine any effects of the

auto-sampler: In the stream channel (in-stream, 5A) and in the automatic sampler present (ISCO, 5B). Neither sample contained sufficient PO_4 to obtain an isotopic ratio. The samples were not analyzed for anion concentrations or water isotopes. Between sample 5A and 5B, $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ varied by 3.96‰ $\delta^{15}\text{N-NO}_3$ and 9.99‰ $\delta^{18}\text{O-NO}_3$. Sample 5B contained larger amounts of calcium, strontium, barium, lutetium, and uranium. The average percent difference between cation concentrations of samples 5A and 5B was 77.8%. These effects could be due to the sampling of the ephemeral stream at different points in the hydrograph. The automatic sample was collected during the rising limb when stream flow consists mostly of overland runoff, while the in-stream sample was collected during the falling limb, in which stream flow consists mainly of groundwater with longer water-rock interaction time.

V. Discussion

A. Potential Nutrient Sources

Geochemical and isotopic data were analyzed to establish a database of potential nutrient source characteristics in the Big Creek watershed. Source samples contained nitrogen largely in the form of $\text{NH}_3\text{-N}$, with little to no $\text{NO}_3\text{-N}$. Such results for relative nitrogen-species concentrations are expected because of the respective redox conditions of these media. Ammonia from various potential sources is nitrified moving from source to stream. By way of example, source sample $\text{NH}_3\text{-N}$ ranged from 0.11-1040.00 mg/L and $\text{NO}_3\text{-N}$ from 0-0.380 mg/L, while the ephemeral S1 sample contained no discernable $\text{NH}_3\text{-N}$ and contained 0.77 mg/L $\text{NO}_3\text{-N}$. Field 1 runoff exhibited the highest $\text{NO}_3\text{-N}$ concentration of all sources. Nutrient transport to Big Creek is likely occurring via overland runoff.

Chicken litter and old cow manure NO_3 is most likely undergoing denitrification in-situ as indicated by increased $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ when compared to referenced manure ranges

(Figure 3; Table 9). The septic system sample plots with a relatively heavy $\delta^{15}\text{N-NO}_3$, indicative of denitrification. Denitrification enriches NO_3 $\delta^{18}\text{O}:\delta^{15}\text{N}$ by a 1:2 ratio (Kendall, 1998). The old cow manure $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ may also indicate nitrification involving waters that have been highly evaporated resulting in relatively enriched $\delta^{18}\text{O-NO}_3$ values available for microbial processing (Kendall and Caldwell, 1998). Two oxygen atoms from water are retained by NO_3 produced during nitrification (Hollocher, 1984). The old Savoy lagoon sample had an unusually enriched $\delta^{18}\text{O-NO}_3$ value of 59.06‰, consistent with values expected of atmospheric NO_3 ; however, either atmospheric deposition of nitrogen or extreme evaporation of lagoon water—enriching the water available to NO_3 -producing microbes—could explain the heavy values. The preferential uptake of the light oxygen isotope during biological processes could also explain the enriched $\delta^{18}\text{O-NO}_3$, leaving an enriched substrate (Kendall, 1998). All runoff samples had elevated $\delta^{18}\text{O-NO}_3$, indicative of potential atmospheric deposition, oxygen-exchange effects, or nitrification using a highly evaporated water source. Potential nutrient source samples exhibited widely variable $\delta^{18}\text{O-PO}_4$ values, ranging from -78.8‰ to 101‰ (Table 11, Figure 4). The range of $\delta^{18}\text{O}$ found in naturally occurring materials is -62.8‰ to 109‰ (Coplen et al., 2002). The minimum and maximum $\delta^{18}\text{O-PO}_4$ values were found in stream-bottom sediment, indicating these samples likely did not contain sufficient PO_4 to obtain a precise isotopic ratio. All sources except the Savoy lagoon and ephemeral stream sediment displayed heavy phosphate oxygen isotopic ratios.

B. Nutrient Dynamics in Big Creek Watershed

The complexity of the interaction between geochemical species in surface-water and groundwater makes source identification difficult using concentration data alone. The lack of spatial and temporal variance combined with the limited number of stream and source

samples gives only a snapshot of nutrient dynamics in Big Creek. Stream chloride-to-bromide ratios indicate a human influence of stream sample chemistry which could arise from any combination of the analyzed sources. Base-flow stream samples had higher specific conductance than storm-flow samples, indicating greater groundwater contribution to stream-flow during base-flow periods. Higher concentrations of $\text{NH}_3\text{-N}$, bromide, SO_4 , PO_4 , lithium, sodium, magnesium, manganese, strontium, barium, and uranium during base-flow periods suggests input of these analytes by groundwater. The lack of a statistically significant difference between the upstream and downstream sites for PO_4 and $\text{NO}_3\text{-N}$ concentrations suggests that either very little processing was occurring or changes in nutrient inputs and removal were roughly balanced.

Stream sample $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ overlapped isotopic ranges documented in other studies of NO_3 in manure and septic waste and NO_3 produced by nitrification of NH_4 in fertilizer and precipitation (Figure 4). Stream $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ also fell within estimated ranges of soil NO_3 and $\delta^{15}\text{N-N}$ of stream sediment. The CAFO solids pond $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values were similar, but not identical, to stream sample $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$. Plots of $\delta^{15}\text{N-NO}_3$ vs. $1/\text{NO}_3$ concentration for the upstream and confluence sites were linear. These plots imply mixing of two distinct sources. However, the lack of measurable concentrations of NO_3 in most potential nutrient source samples and the limited sample size of stream samples makes mixing of sources difficult to confidently assess in this manner.

Wilcoxon Rank Sum Tests for $\delta^{15}\text{N-NO}_3$ suggest input of an enriched nitrogen source along Big Creek. While $\delta^{15}\text{N-NO}_3$ increased downstream, no statistical difference was determined for $\delta^{18}\text{O-NO}_3$: this implies that denitrification is not likely occurring in Big Creek between these sites and a source input with a more enriched $\delta^{15}\text{N}$ is potentially responsible for the elevated $\delta^{15}\text{N}$ between sites. Nitrification of stream sediment nitrogen along the upstream to

downstream reach of Big Creek may explain the decoupling of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ signatures; such nitrification could obfuscate any isotopic indication of denitrification along the reach, making the assessment of denitrification there inconclusive. Coupling of denitrification in the water-sediment interface and growth of algal biomass, causing enrichment of $\delta^{15}\text{N}$ of residual NO_3 , could also be responsible for increased $\delta^{15}\text{N-NO}_3$ (Ford et al., 2015). Plots of $\delta^{15}\text{N-NO}_3$ vs. $\ln \text{NO}_3$ concentration suggest denitrification is occurring at the upstream site and is not occurring at any other stream site. The relatively heavy isotopic signature imposed on NO_3 by denitrification is not apparent in stream samples (Figure 3), indicating little or no influence of in-stream denitrification.

Stream samples show markedly different $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ when compared to potential nutrient sources sampled—chicken litter, cow manure, field runoff, parking-lot runoff, and septic effluent; as such, stream $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ cannot be explained by simple, direct input of any one these potential sources into the stream. If these sources are responsible for a considerable part of the stream NO_3 load, then modification of isotopic composition by mixing or by fractionation/processing must be inferred. The NO_3 isotope data are most consistent with an interpretation of stream NO_3 being derived from NO_3 stored in soils or from manure or septic sources not represented by the limited number of samples collected for this study. Soil NO_3 can arise from any number of sources, including nitrogen-fixing plants, animal waste, applied waste effluent, and artificial fertilizer.

The overlap between potential source $\delta^{18}\text{O-PO}_4$ values and stream $\delta^{18}\text{O-PO}_4$ values complicates discrimination of nutrient source input to the stream using phosphate oxygen isotopes. Any deviation from calculated $\delta^{18}\text{O-PO}_4$ equilibrium values is a reflection of nutrient source input. Equilibrium $\delta^{18}\text{O-PO}_4$ values suggest the influence of an isotopically heavy

phosphate source in the upstream B2, downstream B1, and ephemeral S1 samples. The upstream B1 sample shows evidence of an isotopically light phosphate source contributing to Big Creek. The downstream B2 sample is roughly in equilibrium with stream water—in this case, the stream phosphate is biologically altered. The enriched $\delta^{18}\text{O}$ values seen in all source samples other than ephemeral sediment and the Savoy lagoon obscures the phosphate isotopic signal of any one nutrient source in Big Creek.

VI. Conclusions

Nutrients in a watershed originate from numerous sources, both natural and anthropogenic. An in-depth understanding of nutrient sources, transport pathways from source to stream, and biological processing is crucial to water-resource protection. The recent establishment of a CAFO in the Big Creek watershed has prompted numerous studies on water-quality in the region. The presence of karst terrain with complex groundwater-surface water connection combined with the multitude of potential nutrient sources in the Big Creek watershed complicates the discrimination of nutrient sources and the understanding of nutrient dynamics.

In this study, traditional methods of geochemical analysis were combined with stable isotope geochemistry to characterize nutrient sources and dynamics in Big Creek. The database of compositions of potential nutrient sources developed in this study will assist in characterizing and understanding nutrient enrichment in other watersheds. In transport from source to stream, $\text{NH}_3\text{-N}$ from various potential sources is undergoing nitrification as evidenced by ranges of source $\text{NH}_3\text{-N}$ (0.11-1040.00 mg/L) and $\text{NO}_3\text{-N}$ (0-0.380 mg/L) and stream $\text{NH}_3\text{-N}$ (0-0.06 mg/L) and $\text{NO}_3\text{-N}$ (0.046-0.809 mg/L). Potential nutrient sources are undergoing numerous processes in-situ that affect NO_3 isotopic ratios—nitrification, denitrification, evaporation, and dilution.

Stream chloride-to-bromide ratios over 400 imply an anthropogenic influence in Big Creek. Big Creek samples exhibited different $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ than chicken litter, cow manure, field runoff, parking-lot runoff, and septic effluent, meaning that if these sources were contributing significantly to the stream nutrient load the isotopic composition of these sources was modified by mixing or fractionation. Stream $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ indicate input of an enriched $\delta^{15}\text{N-NO}_3$ source along Big Creek. Measured soil $\delta^{15}\text{N-N}$ and estimated soil $\delta^{18}\text{O-NO}_3$ (3.8‰ to 6.6‰ $\delta^{15}\text{N-NO}_3$ and 3.4‰ to 4.8‰ $\delta^{18}\text{O-NO}_3$) overlap stream $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ (-7.59‰ to 9.10‰ $\delta^{15}\text{N-NO}_3$ and -3.41‰ to 6.71‰ $\delta^{18}\text{O-NO}_3$). Big Creek NO_3 is in part derived from soils in the watershed. Septic or manure sources not represented in this study could also contribute NO_3 to Big Creek. Ranges of stream $\delta^{18}\text{O-PO}_4$ (36.3 to 55.4‰) and potential source $\delta^{18}\text{O-PO}_4$ (-78.8‰ to 101‰) overlap, complicating source discrimination using phosphate oxygen isotopic ratios. Equilibrium $\delta^{18}\text{O-PO}_4$ values in Big Creek indicate the occurrence of biological processing of phosphate and the input of both isotopically enriched and depleted phosphate sources.

Agriculture is critical to the economy of Northwest Arkansas. This study illustrates the importance of considering the impact agriculture has on water-quality—proper nutrient management is essential to protecting the health of our waterways. Further monitoring of Big Creek and incorporation of groundwater studies in the watershed is recommended to ensure no detriment to water-quality. We must continue to exercise due diligence and develop protocols that allow the agricultural industry to thrive while maintaining the integrity of our watersheds.

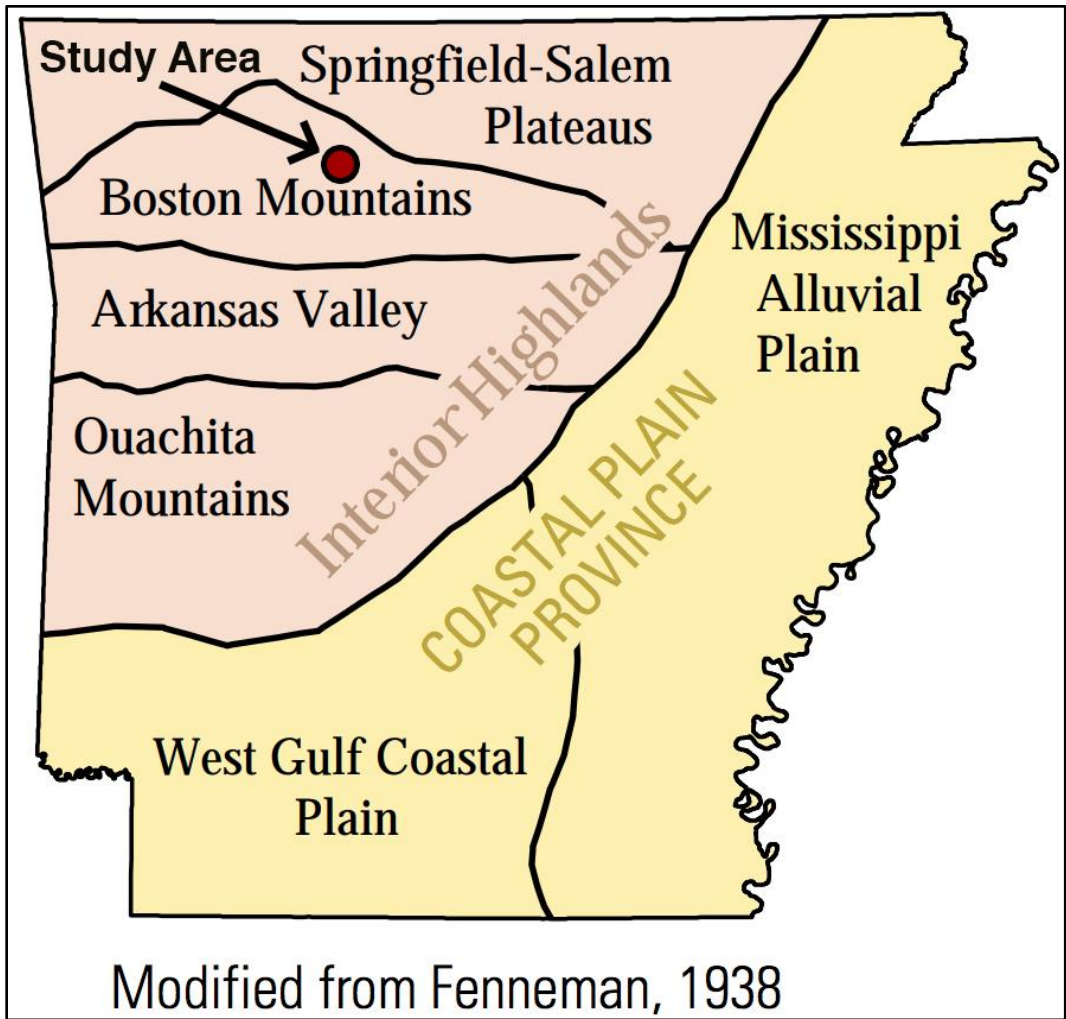


Figure 1. A physiographic map of Arkansas with study area (Mt. Judea) denoted by red circle. Mt. Judea lies on the edge of the Springfield Plateau and the Boston Mountains. Modified from Kresse et. al, 2014.

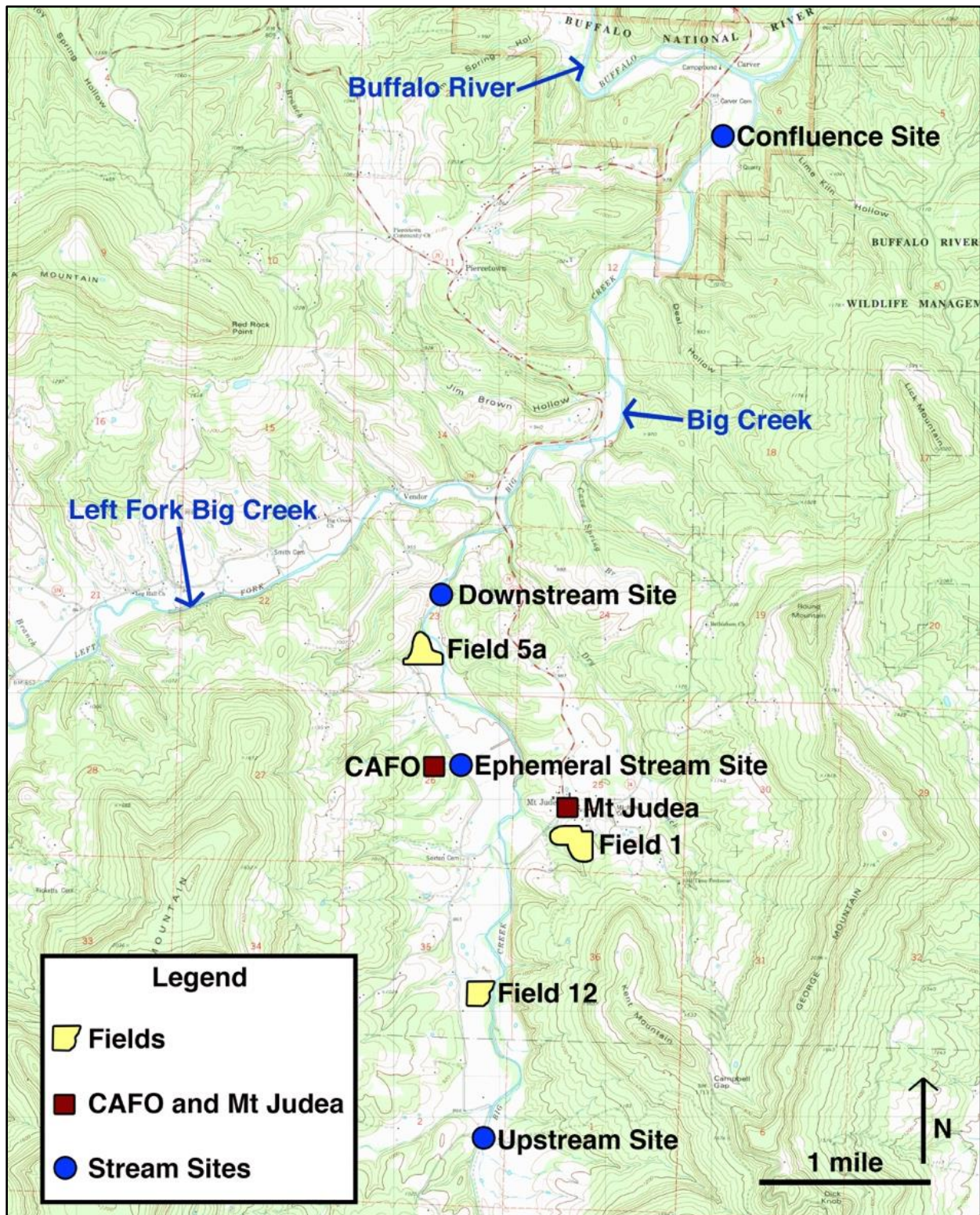


Figure 2. A map of stream sampling sites along Big Creek in Newton County, Arkansas. Storm runoff was collected from BCRET automatic samplers in fields depicted in yellow. Parking lot runoff was collected in Mt. Judea, and the CAFO waste lagoons were sampled. CAFO: Concentrated Animal Feeding Operation. Modified from U.S. Geological Survey, 1980.

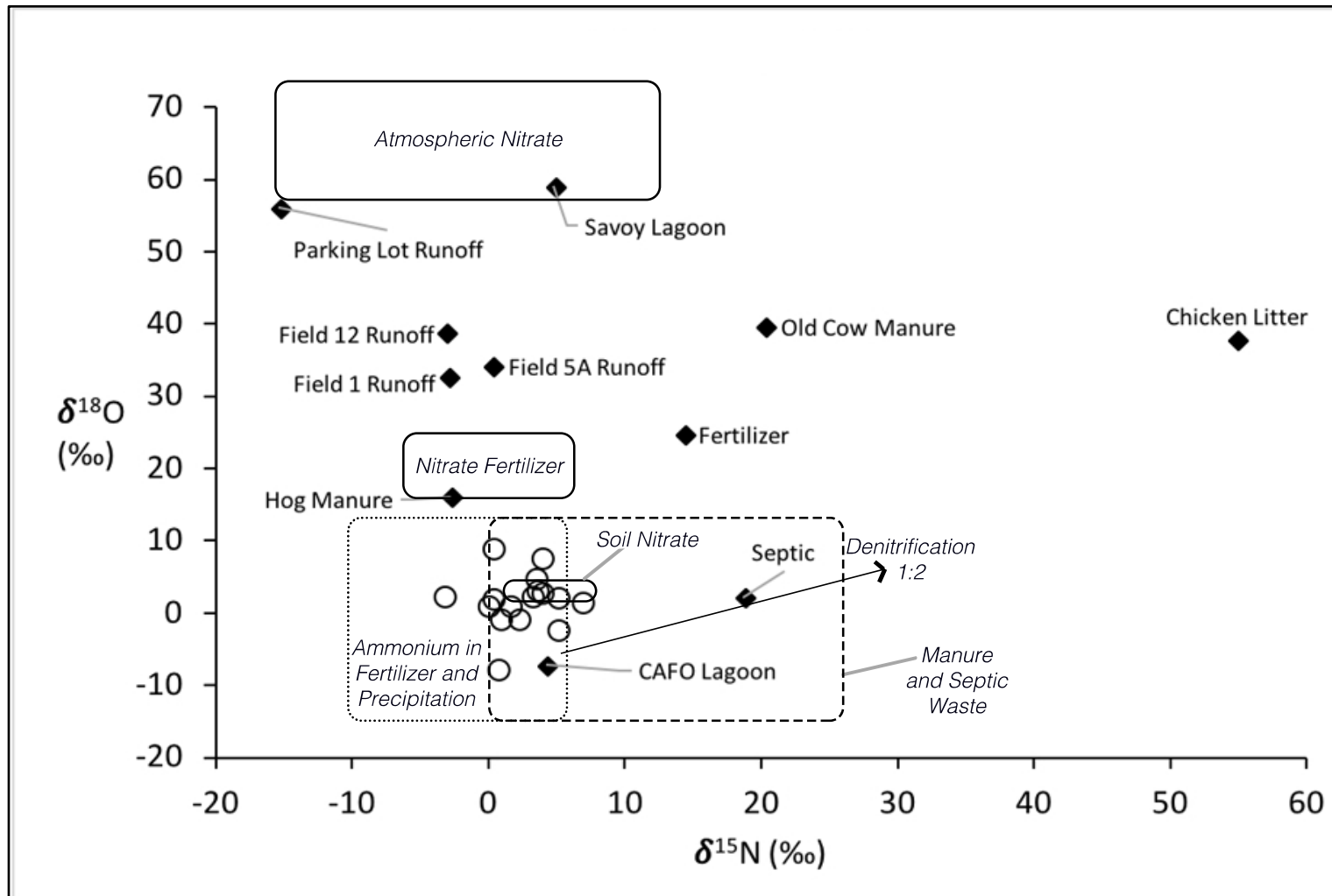


Figure 3. A plot of potential source and stream sample $\delta^{15}\text{N-NO}_3$ vs. $\delta^{18}\text{O-NO}_3$. Potential source samples are represented by diamonds, stream samples by circles. Boxes are representative of indicated nitrogen sources in italics, modified from Kendall, 1998. Soil $\delta^{15}\text{N-NO}_3$ is modified from Fields and Halihan, 2016. Soil $\delta^{18}\text{O-NO}_3$ is derived from stream $\delta^{18}\text{O-NO}_3$ and estimated atmospheric $\delta^{18}\text{O-NO}_3$. Possible $\delta^{15}\text{N-NO}_3$ fractionation in soil is accounted for by adding a 1‰ buffer to the range of $\delta^{15}\text{N}$. CAFO: Concentrated Animal Feeding Operation.

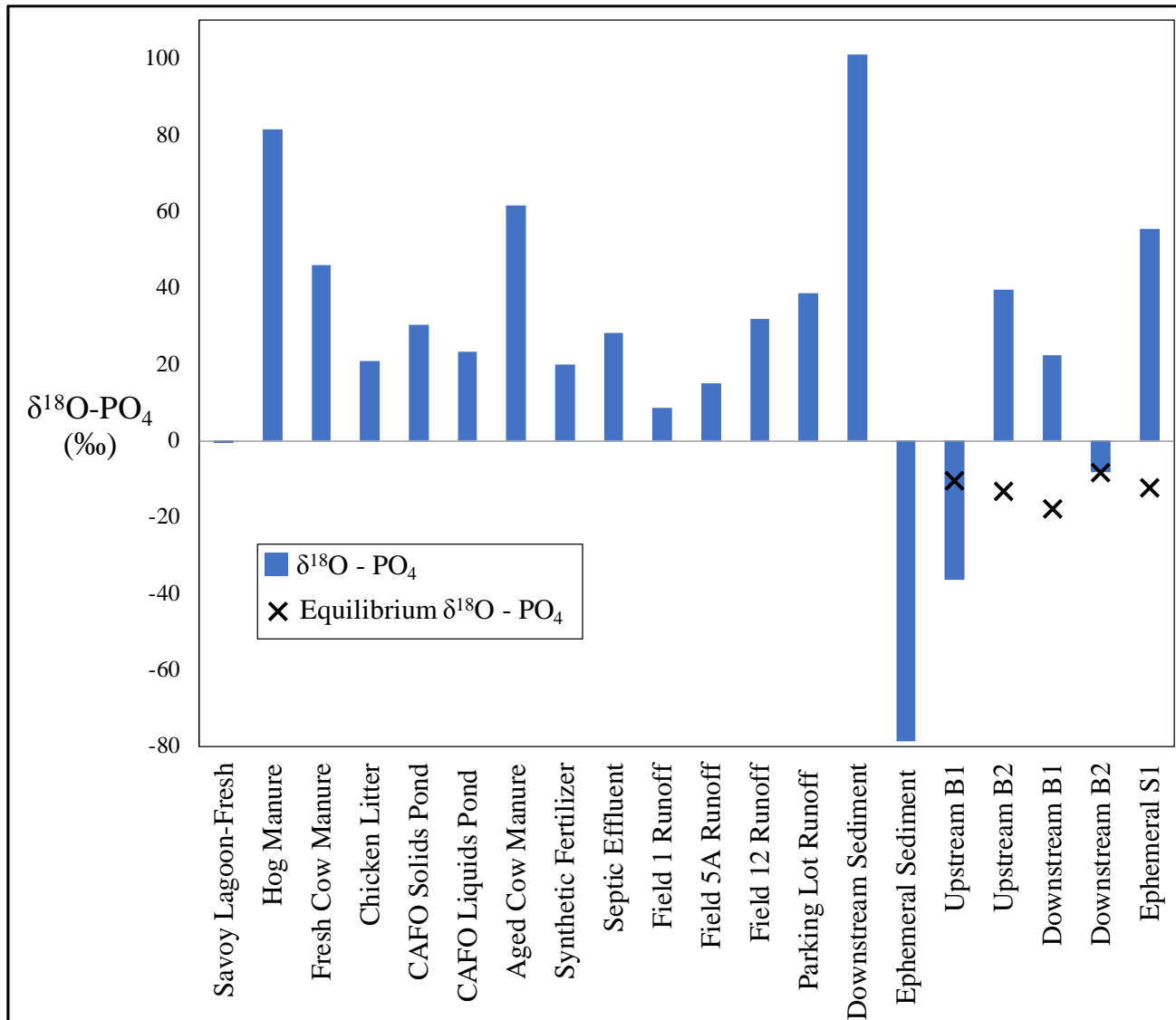


Figure 4. A plot of potential source and stream sample $\delta^{18}\text{O-PO}_4$. Calculated stream equilibrium phosphate oxygen isotopic ratios represented by an X. B: base-flow, S: storm-flow.

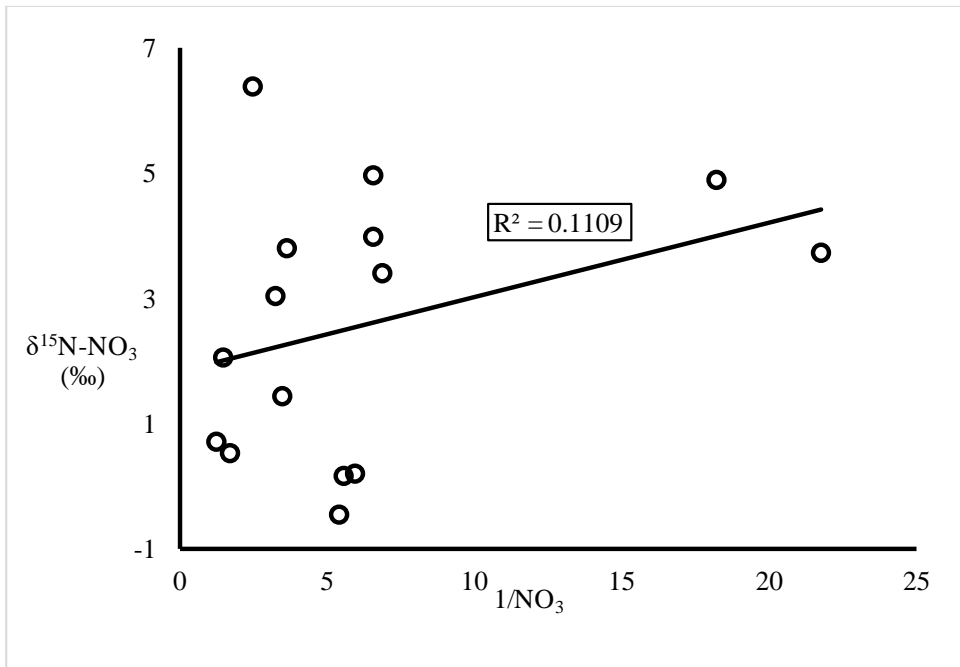


Figure 5. A plot of stream sample $\delta^{15}\text{N-NO}_3$ vs. $1/\text{NO}_3$ concentration from all Big Creek sampling sites.

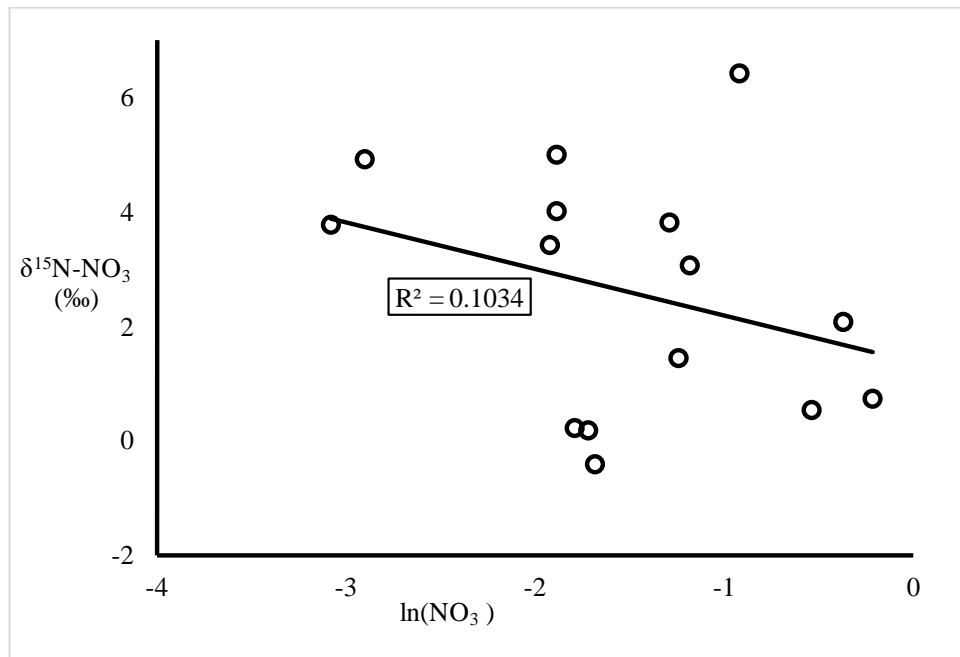


Figure 6. A plot of stream sample $\delta^{15}\text{N-NO}_3$ vs. $\ln(\text{NO}_3)$ concentration from all Big Creek sampling sites.

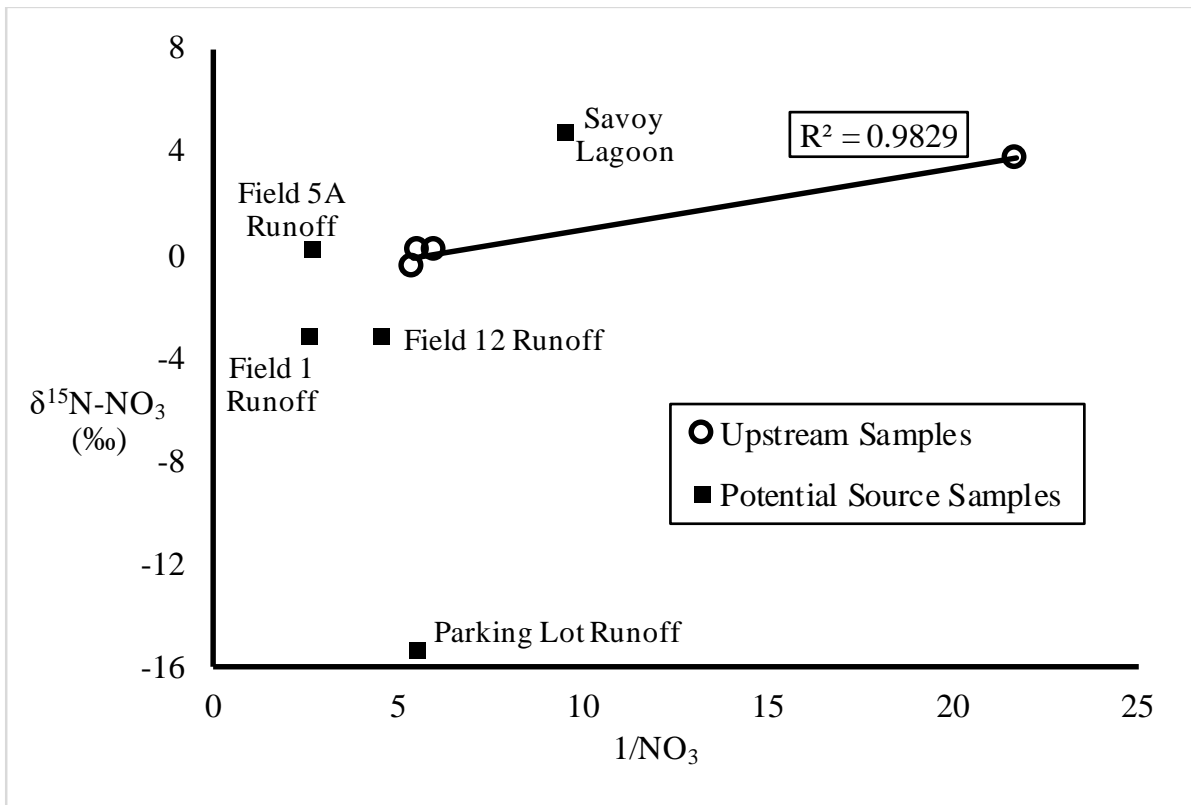


Figure 7. A plot of upstream site sample (circles) and potential source sample (black squares) $\delta^{15}\text{N-NO}_3$ vs. $1/\text{NO}_3$ concentration.

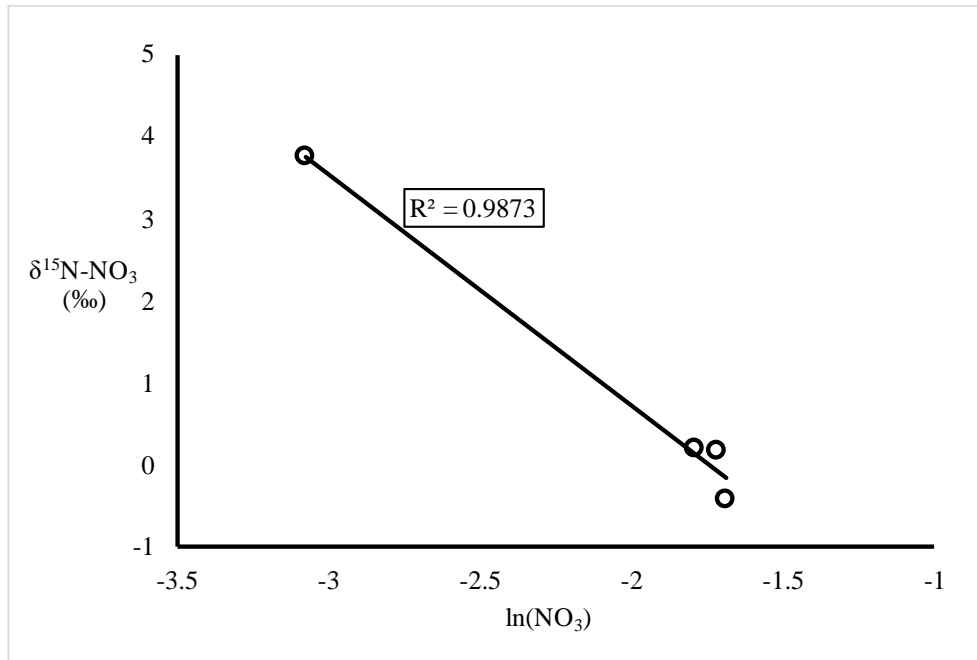


Figure 8. A plot of upstream site sample $\delta^{15}\text{N-NO}_3$ vs. $\ln(\text{NO}_3)$ concentration.

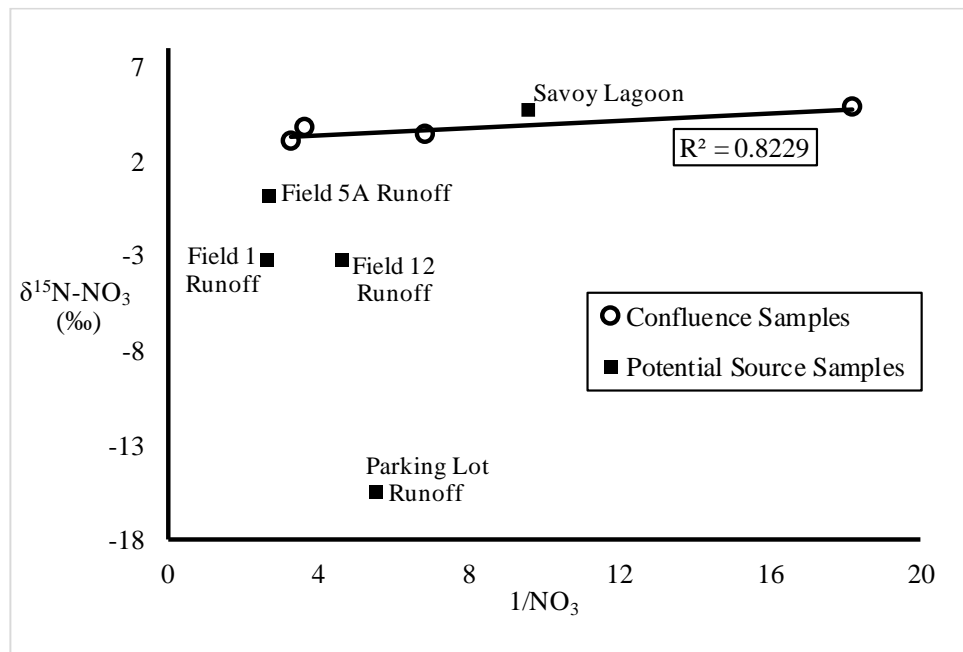


Figure 9. A plot of confluence site sample (circles) and potential source sample (black squares) $\delta^{15}\text{N-NO}_3$ vs. $1/\text{NO}_3$ concentration.

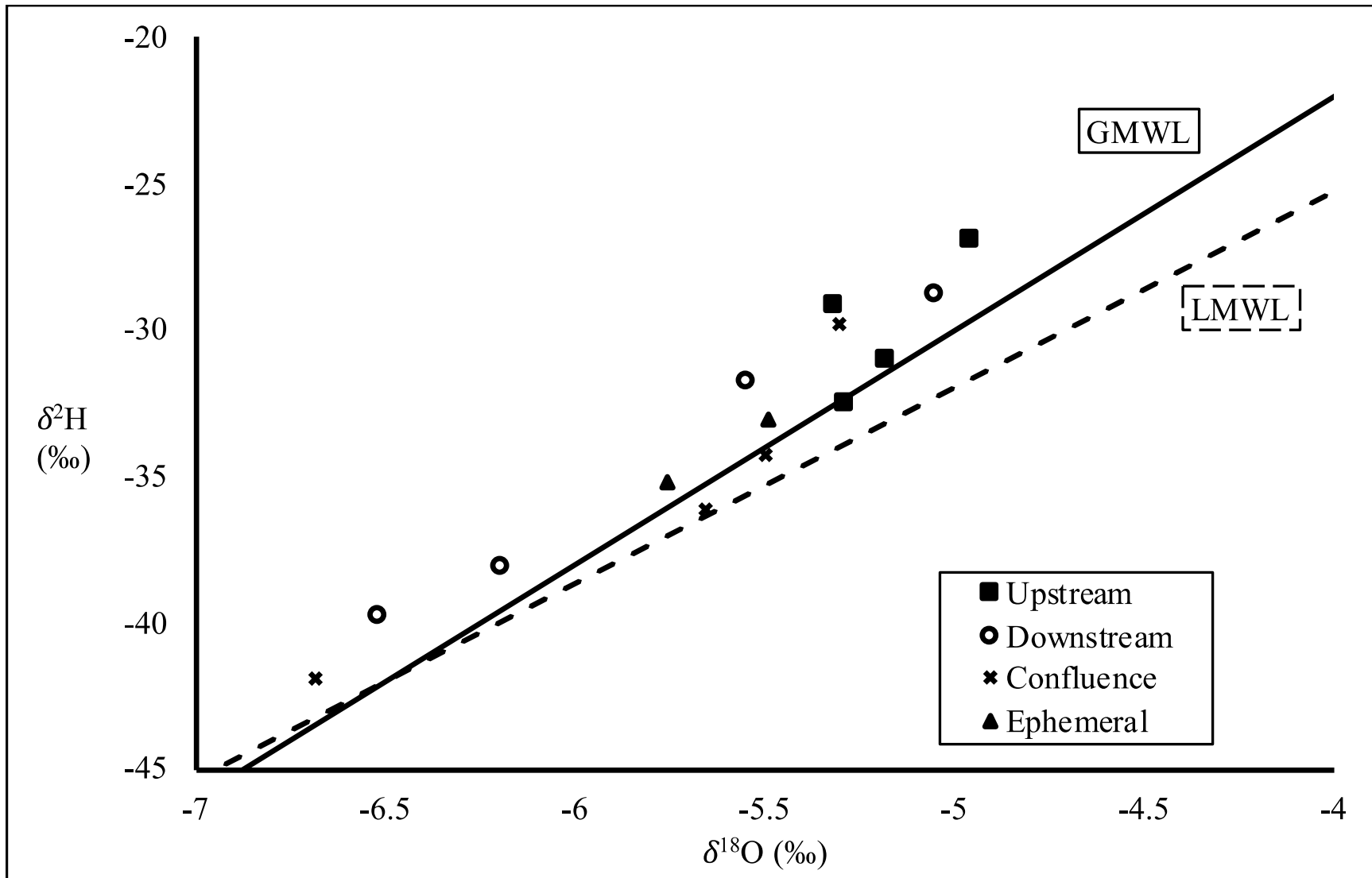


Figure 10. Stream water isotopic ratios. GMWL: Global Meteoric Water Line (Craig, 1961). LMWL: Local Meteoric Water Line (Knerim, 2015)

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IX. Appendix

Table A. Abbreviations seen in text.

‰	Per mille
B	Base-flow
BCRET	Big Creek Research and Extension Team
BNR	Buffalo National River
CF-IRMS	Continuous Flow Isotope Ratio Mass Spectrometer
Con	Confluence
DO	Dissolved Oxygen
Down	Downstream
DP	Dissolved Phosphorus
EPA	Environmental Protection Agency
Eph	Ephemeral
ERI	Electrical Resistivity Imaging
GMWL	Global Meteoric Water Line
HCO₃	Bicarbonate
HNO₃	Nitric Acid
LMWL	Local Meteoric Water Line
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
N₂	Nitrogen Gas
N₂O	Nitrous Oxide
NH₃-N	Ammonia-Nitrogen
NH₄-N	Ammonium-Nitrogen
NO₂-N	Nitrite-Nitrogen
NO₂+NO₃-N	Nitrite+Nitrate-Nitrogen
O₂	Oxygen Gas
S	Storm-flow
SpC	Specific Conductance
TN	Total Nitrogen
TP	Total Phosphorus
Up	Upstream

Table B. List of samples collected and analytes.

	Sample #	Sample Name	pH, SpC, Alkalinity	Anion Suite	Br ⁻	TP	TN, DOC	Cation Suite	NO ₃ Isotopes	PO ₄ Isotopes, Concentration	Water Isotopes	δ ¹⁵ N, %N
Stream Samples	5A	Ephemeral In-Stream						X	X	X		
	5B	Ephemeral ISCO	X	X	X			X	X	X		
	14, 15, 18, 19, 22, 23, 26, 27	Storm-Flow Samples	X	X	X	X	X	X	X	X	X	
	16, 17, 20, 21, 24, 25	Base-Flow Samples	X	X	X	X	X	X	X	X	X	
Source Samples	1A	Savoy Lagoon-Old	X	X				X	X			
	1B	Savoy Lagoon-Fresh		X	X	X	X	X	X	X		
	2	Hog Manure	X	X	X	X	X	X	X	X		
	3	Fresh Cow Manure	X	X	X	X	X	X	X	X		
	4	Chicken Litter	X	X	X	X	X	X	X	X		
	6	CAFO Solids Pond	X	X	X	X	X	X	X	X		
	7	CAFO Liquids Pond	X	X	X	X	X	X	X	X		
	8	Aged Cow Manure	X	X	X	X	X	X	X	X		
	9	Synthetic Fertilizer	X	X	X	X	X	X	X	X		
	10	Septic Effluent	X	X	X	X	X	X	X	X		
	11	Field 1 Runoff	X	X		X	X	X	X	X		
	12	Field 5A Runoff	X	X	X	X	X	X	X	X		
	13	Field 12 Runoff	X	X	X	X	X	X	X	X		
	32	Parking Lot Runoff	X	X	X	X	X	X	X	X		
	28	Upstream Sediment									X	X
	29	Downstream Sediment									X	X
	30	Confluence Sediment									X	X
31	Ephemeral Sediment									X	X	

X: sample was analyzed

SpC: Specific Conductance

Anion suite includes: NH₃-N, Chloride, Fluoride, NO₃+NO₂-N, NO₃-N, and SO₄

Cation suite includes: Lithium, Beryllium, Boron, Sodium, Magnesium, Aluminum, Potassium, Calcium, Scandium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Gallium, Arsenic, Selenium, Rubidium, Strontium, Yttrium, Cadmium, Indium, Tin, Antimony, Cesium, Barium, Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, Lutetium, Rhenium, Thallium, Lead, Bismuth, Thorium, and Uranium

Table C. Potential nutrient source cation concentrations.

PPB	1A - Old Savoy Lagoon	1B - Fresh Savoy Lagoon	2 - Hog Manure	3 - Fresh Cow Manure	4 - Chicken Litter	6 - CAFO Solids Pond	7 - CAFO Liquids Pond	8 - Old Cow Manure	Detection Limit
Aluminum	14.6	2.59	3.7	<	17.7	3.42	27.7	2.68	3.25
Antimony	0.00118	0.00132	0.00375	0.000607	0.00307	0.00214	0.00418	0.00025	0
Arsenic	0.0734	0.086	0.00759	0.0228	1.16	0.567	0.584	0.0506	0.017
Barium	8.17	0.735	1.66	1.99	2.57	1.25	0.928	5.02	0.0863
Beryllium	0	0.0911	0	0.0304	0.0607	0	0	0	0
Bismuth	0.0257	0.0111	<	<	0.000118	<	<	<	0.00281
Boron	43	56.1	7.66	1.71	108	28.1	23.4	2.79	0.605
Cadmium	0.00287	0.0006	<	<	0.0083	<	<	<	0.00174
Calcium	136	75	78.8	192	521	71.1	56.7	143	2.85
Cerium	0.0305	0.0148	0.00153	<	<	<	0.0222	0.0156	0.00239
Cesium	0.0668	0.0543	0.0335	0.0176	0.13	0.0625	0.0462	<	0.00656
Chromium	0.154	0.13	0.308	0.0178	0.437	0.507	0.486	0.0145	0.0192
Cobalt	0.119	0.147	0.159	0.106	1.19	0.212	0.532	0.0899	0.00497
Copper	0.453	0.494	0.574	0.346	225	0.184	0.672	0.203	0.0516
Dysprosium	0.0332	0.0125	0.00449	0.00159	0.00151	0.000529	0.00193	0.00302	0.000931
Erbium	0.0354	0.0151	0.00476	0.0014	0.000994	0.00045	0.00152	0.00178	0.000405
Europium	0.0317	0.0146	0.00396	0.00163	0.000699	0.000233	0.000582	0.000815	0.000662
Gadolinium	0.0326	0.014	0.00493	0.0014	0.00153	0.000425	0.00246	0.00454	0.000726
Gallium	0.0397	0.0168	0.0137	<	0.00611	0.0229	0.0321	0.00305	0
Holmium	0.032	0.0129	0.00397	0.00119	0.000674	0.000333	0.000316	0.000384	0.000107
Indium	0.0368	0.0163	0.00511	0.00163	0.000652	0.000109	<	<	0.00136
Iron	31.2	20.1	199	3.54	212	18	81	6.93	0.379
Lanthanum	0.0316	0.0173	0.00229	0.00148	0.000211	<	0.0153	0.0117	0.00193
Lithium	2.73	4.8	1.07	0.095	0.523	0.855	0.475	0.0238	0
Lutetium	0.0304	0.0132	0.00391	0.00122	0.000539	0.000519	0.000199	0.00014	0.000401
Magnesium	511	671	6547	2183	8710	165	69.9	1323	0.441
Manganese	1.7	1.47	159	7.2	106	0.915	1.55	20.1	0.0387
Neodymium	0.0344	0.0169	0.00411	0.00129	0.00188	<	0.0143	0.0138	0.00374
Nickel	1.29	1.59	4.18	0.688	26.4	2.2	1.78	0.162	0.101
Potassium	16859	21271	14736	6267	86578	35756	31213	1403	5.2
Praseodymium	0.0319	0.0142	0.0041	0.00163	0.000634	<	0.003	0.00241	0.000448
Rhenium	0.03	0.0132	0.00386	0.0012	0.00248	0.00093	0.000809	0.000027	0.000111
Rubidium	14.8	17.2	16.9	12.6	56.9	39.7	32.7	3.07	0.0169
Samarium	0.0326	0.0143	0.00373	0.00167	0.000643	0.000257	0.0027	0.00296	0.00259
Scandium	0.0333	0.0212	0.00303	<	<	<	0.00606	<	0.038
Selenium	0.0126	0.063	<	0.0126	0.0756	<	0.0252	<	0
Sodium	9945	12887	3964	283	37201	9395	7953	79.3	4.84
Strontium	4.69	2.81	10.8	3.27	10.9	1.24	1.29	2.44	0.119
Terbium	0.0326	0.0135	0.00401	0.00152	0.000615	0.000395	0.000266	0.000514	0.000299
Thallium	0.0388	0.0153	0.00264	<	0.000654	<	<	<	0.00129
Thorium	0.0481	0.0183	0.00367	<	<	<	<	<	0.0024
Thulium	0.0331	0.0141	0.00384	0.00147	0.000558	0.000252	0.000159	0.000106	0.000248
Tin	0.00386	0.0062	0.00395	0.00476	0.00863	0.00782	0.00647	0.0044	0
Uranium	0.0362	0.0169	0.0071	0.00139	0.00438	0.0363	0.02	0.000491	0.000421
Vanadium	0.142	0.195	0.117	0.00996	0.479	0.864	1.39	0.0516	0.0048
Ytterbium	0.0334	0.013	0.00439	0.00151	0.00129	0.000604	0.00143	0.000934	0.000625
Yttrium	0.0406	0.016	0.00886	0.00346	0.0117	0.00432	0.022	0.0264	0.00423
Zinc	1.29	<	<	<	284	<	<	<	1.19

< left-censored data

Table D. Potential nutrient source cation concentrations.

PPB	9 – Synthetic Fertilizer	10 - Septic	11 – F1 Runoff	12 - F5A Runoff	13 - F12 Runoff	32 – Parking Lot Runoff	Detection Limit
Aluminum	257.1875	5.82	1.57	1.94	1.66	1.11	3.25
Antimony	5.59375	0.679	0.572	0.679	0.429	1.11	0
Arsenic	0.315625	0.00759	0.0101	0.0152	0.00759	<	0.017
Barium	16.84375	1.45	1.48	0.939	1.18	1.16	0.0863
Beryllium	0	0	0	0	0	0	0
Boron	2.815625	3.34	0.631	0.811	0.631	0.0901	0.605
Cadmium	0.0203125	<	<	<	<	<	0.00174
Calcium	40	94.8	11.3	20.2	20.2	19.2	2.85
Cerium	0.0359375	<	0.00802	0.00431	0.00329	<	0.00239
Cesium	<	0.000605	<	<	<	<	0.00656
Chromium	5.84375	0.0183	<	0.00533	0.193	0.0152	0.0192
Cobalt	0.011625	0.0207	0.00214	<	0.0115	<	0.00497
Copper	<	<	<	<	<	0.108	0.0516
Dysprosium	0.0603125	0.000227	0.00321	0.0023	0.000755	0.000227	0.000931
Erbium	0.044375	<	0.00142	0.000805	0.000379	<	0.000405
Europium	<	<	0.000699	0.0000582	0.000175	<	0.000662
Gadolinium	0.0396875	0.000255	0.00353	0.00149	0.000977	<	0.000726
Gallium	0.1909375	<	0.00763	<	0.00153	0.00305	0
Holmium	0.01171875	<	0.000401	0.000324	<	<	0.000107
Indium	<	<	<	8.69E-10	<	<	0.00136
Iron	245.625	2.9	2.41	2.63	1.8	0.62	0.379
Lanthanum	0.021625	<	0.0155	0.00295	0.00337	<	0.00193
Lithium	0.74375	0	0	0.0238	0	0.0475	0
Lutetium	0.01371875	<	0.0000798	<	<	<	0.000401
Magnesium	321.875	190	34.8	32.5	31.3	4.42	0.441
Manganese	7.875	1.34	0.0488	0.0847	0.0976	0.0398	0.0387
Neodymium	0.06625	0.000118	0.0143	0.00811	0.00482	<	0.00374
Nickel	<	0.055	<	<	0.475	<	0.101
Potassium	9937.5	1020	197	171	99.6	9.23	5.2
Praseodymium	0.01525	<	0.00349	0.00134	0.001	<	0.000448
Rubidium	0.90625	0.971	0.224	0.0642	0.0416	0.00252	0.0169
Samarium	0.0321875	<	0.0027	0.00167	0.00103	<	0.00259
Sodium	<	1740	10.5	15.2	7.33	<	4.84
Strontium	1.909375	2.36	0.223	0.378	0.336	0.227	0.119
Terbium	0.000859375	<	0.000312	0.00022	<	<	0.000299
Thallium	<	<	<	<	0.000619	<	0.00129
Thulium	0.001659375	<	0.0000531	<	<	<	0.000248
Tin	162.8125	4.4	6.56	9.08	11.2	5.3	0
Uranium	3.05	<	<	<	0.000385	<	0.000421
Vanadium	4.84375	0.00543	0.0168	0.0308	0.0177	0.0208	0.0048
Ytterbium	0.0884375	<	0.0011	0.000742	0.00033	0.0000275	0.000625
Yttrium	0.84375	0.00281	0.0223	0.0156	0.00994	0.00389	0.00423

< left-censored data

Table E. Stream sample cation concentrations for upstream and downstream sites on Big Creek.

Sample #	14	15	16	17	18	19	20	21	Detection
Sample Name	Up S1	Up S2	Up B1	Up B2	Down S1	Down S2	Down B1	Down B2	Limit
Aluminum	0.37	0.0924	<	<	<	<	0.0924	0.0924	3.25E-03
Antimony	0.000179	0.000572	0.0005	0.000322	0.000322	0.000572	0.000179	0.000393	0
Arsenic	0	<	0.0101	0	0.00253	0.00506	0	0.00759	1.70E-05
Barium	1.06	1.05	0.963	1.49	0.786	0.922	1.12	1.17	8.63E-05
Boron	0.721	0.27	0.541	0.451	0.721	0.18	0.27	0.361	6.05E-04
Calcium	25.5	31.5	40.1	83	36.2	50.9	64.6	98.2	2.85E-03
Chromium	0.0033	<	0.00127	0.00457	0.0104	<	<	0.00508	1.92E-05
Dysprosium	0.000302	7.55E-05	<	<	<	0.000415	<	1.46E-20	9.31E-07
Gadolinium	0.000637	0.00017	<	<	<	0.00034	4.25E-05	3.40E-10	7.26E-07
Gallium	0.00153	0.00305	0	0.00153	0	0.00153	0	0	0
Iron	0.518	0.0632	0.86	<	<	0.582	<	<	3.79E-04
Lanthanum	0.000301	0.0139	<	<	<	0.000783	<	<	1.93E-06
Lithium	0	0	0.0238	0.0475	0.0238	0.0238	0.0238	0.0713	0
Lutetium	<	3.18E-20	<	<	<	<	<	<	4.01E-07
Magnesium	33.8	40.6	41.3	71.8	36.1	44.6	44.2	56.6	4.41E-04
Manganese	0.0558	0.0259	0.0219	0.0279	0.0259	0.0189	0.00996	0.113	3.87E-05
Neodymium	0.00118	<	<	<	<	0.00165	<	<	3.74E-03
Potassium	64.6	16	24.5	31.5	17.2	18.8	23.6	20.5	5.20E-03
Praseodymium	0.000293	2.44E-05	<	<	<	0.000585	<	<	4.48E-07
Rhenium	<	<	<	<	<	<	<	1.35E-05	1.11E-07
Rubidium	0.00126	<	0.0113	0.0176	0.00252	0.00756	0.00252	0.00756	1.69E-05
Samarium	<	0.000129	<	<	<	0.000129	6.35E-20	<	2.59E-03
Selenium	0	0	0	0	0	0	0	0	0
Sodium	21.7	25.8	26.4	41.3	24	31.9	31	45.2	4.84E-03
Strontium	1.02	1.18	1.4	2.35	1.22	1.6	1.69	2.32	1.19E-04
Terbium	<	<	<	<	<	<	<	<	2.99E-07
Thulium	<	<	<	<	<	<	<	<	2.48E-07
Tin	0.00476	0.00647	0.00395	0.00395	0.00485	0.00413	0.00323	0.00503	0
Uranium	0.000514	0.00063	0.000954	0.00569	0.000162	0.00254	0.00272	0.00848	4.21E-07
Vanadium	0.00725	0.00317	0.00543	0.00634	0.00181	0.00861	0.00679	0.00589	4.80E-06
Ytterbium	2.75E-05	8.24E-05	<	<	2.75E-05	<	<	<	6.25E-07
Yttrium	0.00367	0.00346	0.00476	0.000432	0.000216	0.00173	0.000865	<	4.23E-06

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Table F. Stream sample cation concentrations for the confluence site on Big Creek and the ephemeral stream near Big Creek.

Sample #	22	23	24	25	26	27	5A	5B	
Sample Name	Con S1	Con S2	Con B1	Con B2	Eph S1	Eph S2	Eph In-Stream	Eph ISCO	Detection Limit
Aluminum	0.832	<	<	<	<	<	7.76	0.739	3.25E-03
Antimony	0.00111	0.000179	0.0005	0.000322	0.000143	0.000214	0.000214	0.000214	0
Arsenic	0.00506	0.00759	0.0152	0.0202	0.00253	<	0.0531	1.69E-19	1.70E-05
Barium	1.63	1.19	1.18	0.791	0.961	0.945	1.1	1.22	8.63E-05
Boron	0.541	0.18	0.451	0.721	0.18	0.541	1.17	0.541	6.05E-04
Calcium	52.8	68.5	69.6	82.9	110	136	90.6	129	2.85E-03
Chromium	0.0147	<	<	<	0.0163	0.0483	0.0287	0.0244	1.92E-05
Cobalt	0.00316	<	<	<	<	<	0.00427	<	4.97E-06
Copper	<	<	<	<	<	<	0.218	<	5.16E-05
Dysprosium	0.000604	3.78E-05	3.78E-05	<	0.000113	0.000642	0.00325	0.00121	9.31E-07
Erbium	<	<	<	<	2.37E-05	0.000284	0.0017	0.00118	4.05E-07
Gadolinium	0.00051	4.25E-05	<	<	<	0.000722	0.00336	0.0011	7.26E-07
Gallium	0	0.00153	0	0.00153	0	0.00153	0.00916	0.00305	0
Holmium	<	<	<	<	<	<	0.000989	0.000418	1.07E-07
Iron	0.771	<	0.379	<	<	<	4.7	0.67	3.79E-04
Lanthanum	0.00169	<	<	<	<	<	0.00993	0.000271	1.93E-06
Lithium	0.0475	0	0	0	0	0.0238	0.0475	0.0475	0
Lutetium	<	<	<	<	<	<	0.000559	0.000579	4.01E-07
Magnesium	44.5	54.1	50.2	63.6	27.5	35.8	48.7	31.9	4.41E-04
Manganese	0.0588	<	0.0149	0.291	0.011	0.00697	0.358	0.0508	3.87E-05
Neodymium	0.000823	<	<	<	<	0.000823	0.0162	0.00317	3.74E-03
Potassium	42.1	22.8	26.8	32.2	19	13.1	138	19.5	5.20E-03
Praseodymium	0.000366	<	<	<	<	0.000195	0.00407	0.000902	4.48E-07
Rhenium	<	<	<	<	<	<	0.000472	0.000391	1.11E-07
Rubidium	0.0126	0.00126	0.00756	0.0101	0.0063	0.0063	0.131	0.00882	1.69E-05
Samarium	0.000386	<	6.35E-20	<	<	<	0.00335	0.00103	2.59E-03
Selenium	0.0126	0	0	0.0126	0.0126	0	0	0	0
Sodium	34.7	39.5	38.8	49.8	26.8	35.1	62.1	32.3	4.84E-03
Strontium	1.58	1.98	1.97	2.38	0.993	1.31	0.964	1.12	1.19E-04
Terbium	<	<	<	<	<	<	0.00109	0.000432	2.99E-07
Thulium	<	<	<	<	<	<	0.000777	0.000372	2.48E-07
Tin	0.00593	0.00503	0.00503	0.00422	0.00656	0.00431	0.00926	0.00279	0
Uranium	0.00245	0.00454	0.00439	0.00725	0.00318	0.00602	0.00265	0.00373	4.21E-07
Vanadium	0.00634	0.00362	0.00996	0.00543	0.00725	0.00272	0.0276	0.00589	4.80E-06
Ytterbium	0.000275	5.49E-05	<	<	2.75E-05	0.000247	0.00201	0.000989	6.25E-07
Yttrium	0.00389	0.00259	0.00108	<	0.00303	0.0141	0.0264	0.0128	4.23E-06

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