Image caption: Big Creek, a tributary to the Buffalo National River. Photo courtesy of Tim Glover.

Characterization of Nutrient Sources, Transport Pathways, and Transformations Using Stable Isotope and Geochemical Tools in the Big Creek Watershed of Northwest Arkansas

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Abstract: The establishment of a concentrated animal-feeding operation (CAFO) 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. This study establishes an isotopic and geochemical reference library of potential nutrient sources in the Big Creek watershed by direct sampling of representative possible sources, including septic-system effluent, poultry, swine, and cattle manure, and CAFO waste lagoons. Representative nutrient sources and Big Creek stream samples were analyzed for δ15N-NO_3, δ18O-NO_3, and δ18O-PO_4, as well as a cation and anion suite. Big Creek stream samples were also analyzed for δ18O-H_2O and δ2H-H_2O. Similar chloride-bromide ratios for fresh cow manure, septic-system effluent, and Big Creek samples may indicate an influence on Big Creek water quality. Samples taken from the CAFO waste lagoon, a septic system, field and parking-lot runoff, fertilizer, and hog manure exhibit different δ15N and δ18O as compared to stream samples. Big Creek NO_3 isotope values are similar to NO_3 values expected from nitrification of N stored in soils sampled in the watershed. Discrimination of nutrient source input to Big Creek using δ18O-PO_4 is complicated by overlap between potential source δ18O and stream δ18O. Stream equilibrium δ18O-PO_4 values indicate the biological processing of stream 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.

Key Points:

- Samples taken from the CAFO waste lagoon, a septic system, field and parking-lot runoff, fertilizer, and hog manure exhibit different δ15N-NO_3 and δ18O-NO_3 as compared to stream samples. The isotope data are most consistent with an interpretation of stream nitrate being derived from N stored in soils, or from manure or septic sources not represented by the limited number of samples collected for this study.
- Chloride to bromide ratios indicate human influence and may indicate an input to Big Creek from septic systems and cow manure.

Introduction

The Big Creek watershed has a history of mixed agricultural, "urban" (Mount Judea), and residential land use, and the recent establishment of a Concentrated Animal-Feeding Operation (CAFO) near Mt. Judea in Newton County, AR, has raised concerns over the potential for nutrient enrichment and degradation of water quality in Big Creek and the Buffalo National River (Figure 1). The complex distribution of land use and nutrient sources in the watershed, 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 watershed contamination. Stable isotope geochemical tools can augment traditional methods and improve our understanding of nutrient enrichment in aquatic environments and enable development of more effective management practices.

This project has applied a combined approach of traditional water-quality analysis and novel geochemical tools in characterizing nutrient dynamics in the Big Creek watershed. An isotopic reference database of representative nutrient sources for the Big Creek watershed was developed by sampling directly from nutrient sources. This database is essential for comparative analysis and characterizing pollutant sources in this study as well as for future projects. Stream samples were collected from Big Creek and related to nutrient sources using multi-parameter geochemical analysis. The specific objectives of the study are (1) to establish a database on isotopic compositions of potential nutrient sources; (2) to employ nitrate isotopes for characterizing sources, transport, and transformations; (3) to characterize stream phosphate oxygen isotopic compositions and identify potential sources and biological cycling; (4) to characterize water sources and pathways through the application of water isotopes.

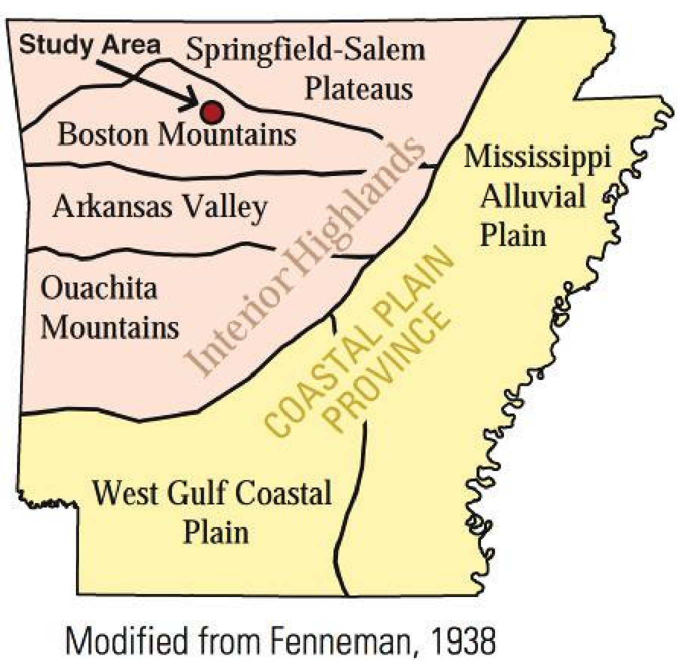

Figure 1. Physiographic map of Arkansas with study area (Mt. Judea) denoted by red circle. Mt Judea lies on the edge of the Springfield Plateau and the Boston Mountains. Modified from Kresse et. al, 2014.

Methods

Field Methods

Samples were taken from sites representative of potential sources based on dominant regional agricultural practices. Waste-holding ponds were sampled at C&H Farms and the University of Arkansas Swine Farm at Savoy, AR. Hog manure was sampled at the University of Arkansas Swine Farm due to sampling restrictions at C&H Farms. The University of Arkansas Broiler Research Unit provided a broiler-litter sample for analysis. Fresh and aged cattle manure samples were taken from a field near Mt. Judea. The manure and litter samples were extracted with deionized water for analysis. A residential septic-system sample was collected near Bella Vista, AR. Runoff samples from three fields (Field 1, Field 5A, and Field 12—all were used for cattle grazing and hay production, and fields 1 and 12 were amended with C&H Farms waste) near Mt. Judea were collected during a rainfall event from Big Creek Research and Extension Team (BCRET) sites (Figure 2). Parking-lot runoff was collected in Mt. Judea. Artificial fertilizer, 13-13-13 (13% nitrogen, 13% phosphorus, and 13% potassium), was dissolved and analyzed.

Four stream sites were chosen for base-flow and high-flow water and stream-bottom sediment sample collection (Tables 1 and 2, Figure 2). Table 3 depicts the samples collected and the analytes measured for individual samples.

Analytical Methods

Sample pH and conductivity values were measured in the field. Alkalinity titrations were performed using a Hach digital titrator, and alkalinity was calculated using the inflection point method (Rounds, 2006). Total nitrogen (TN), dissolved organic carbon (DOC), and cations were analyzed for all samples at the University of Arkansas Stable Isotope Laboratory (UASIL). Cations were analyzed using a Thermo Fisher iCapQ Quadrupole Mass Spectrometer with a CETAC ASX-560 Autosampler.

Samples were sent to the Arkansas Water Resources Center Water Quality Lab (AWRC) for analysis of anions, total phosphorous (TP), ammonia (NH_3), and nitrate+nitrite (NO_3+NO_2). Anions were measured with a Dionex ion chromatograph ICS-1600. Ammonia, TP, and NO_3+NO_2 were analyzed using a Lachat QuickChem 8500. Orthophosphate (PO_4) concentration was measured on a Seal AQ3 autoanalyzer at the University of Nebraska Water Sciences Laboratory (UNWSL) (Table 4).

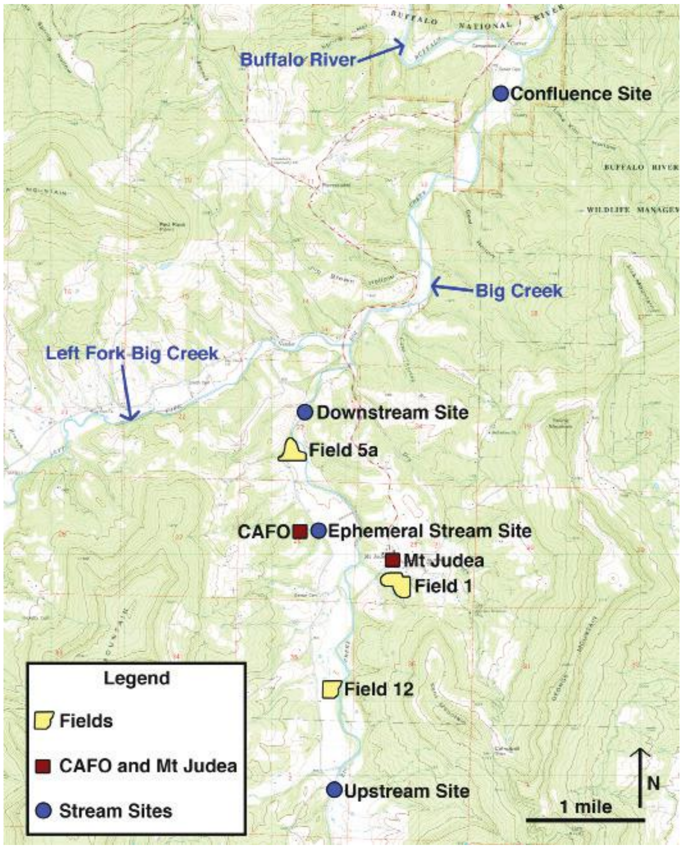

Figure 2. Map of stream sampling sites along Big Creek in Newton County, Arkansas. Storm runoff was collected from BCRET automatic samplers in fields depicted in yellow. Parking lot runoff was collected in Mt. Judea, and the CAFO waste lagoons were sampled. Modified from U.S. Geological Survey, 1980.

Table 1. Latitude and longitude of Big Creek stream sampling sites.

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

Table 2. Hydrologic conditions and sampling dates for stream and run-off samples. Rainfall data is from the National Weather Service Harrison station. Rainfall values are totaled from the date of sampling plus the previous two days. Sample 5A was collected from the ephemeral stream site. Sample 5B was collected from a BCRET automatic sampler located at the ephemeral stream site.

	Date Sampled	Hydrologic Conditions
B1 Samples	7/17/2017	No rain for 7 days, discharge at base-flow conditions
B2 Samples	9/23/2017	No rain for 7 days, discharge at base-flow conditions
S1 Samples	3/30/2017	2.134 cm rainfall
S2 Samples	4/17/2017	1.778 cm rainfall
Samples 5A and 5B	5/2/2016	2.184 cm rainfall
Field Runoff Samples	5/1/2017	10.262 cm rainfall
Parking Lot Runoff	11/15/2017	1.473 cm rainfall

* B = baseflow; S = stormflow

The nitrogen and oxygen isotopic ratios of nitrate were measured at the UASIL. Nitrate δ15N and δ18O were analyzed simultaneously using the microbial denitrifier method (Sigman et al., 2001). After conversion to nitrous oxide, δ15N and δ18O were measured on a continuous flow Thermo Delta plus isotope ratio mass spectrometer (IRMS).

Phosphate oxygen isotopic ratios were prepared and measured at the UNWSL using the methods of McLaughlin et al. (2004) and McLaughlin et al. (2006). The δ18O of resultant silver phosphate was analyzed using high temperature pyrolysis on a Eurovector EA Isoprime continuous IRMS.

Hydrogen and oxygen stable isotope ratios of stream water were measured using a high temperature reduction unit interfaced to a continuous flow Thermo Delta plus XP IRMS at the UASIL. Nitrogen isotope ratios and %N of sediment were analyzed simultaneously at the UASIL on an EA IsoLink IRMS.

Results and Discussion

Geochemical Parameters

Data are presented in Table 4, and summary statistics are presented in Tables 5 and 6. The TN, DOC, and cation analyses contain 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.

Source sample NH_3 ranged from 0.11-1040 mg/L with little to no NO_3 (range: 0-0.38 mg/L), while stream samples contained little NH_3 (range: 0-0.06 mg/L) but slightly more NO_3 (range: 0.046-0.809 mg/L). Such results for relative N-species concentrations are expected because of the respective redox conditions of these media. The nitrogen in the possible nutrient sources is largely in the NH_3 (or NH_4^+) form. The NH_3 from various potential sources is being nitrified moving from source to stream. By way of example, the ephemeral S1 sample contained no discernable NH_3 and contained 0.77 mg/L NO_3. A Wilcoxon Rank Sum Test was conducted with a 95% confidence interval for nitrate and phosphate concentrations between the upstream and downstream sites. No statistically significant difference was observed, indicating that in-stream processes were not changing concentrations considerably—either very little processing was occurring or changes in nutrient inputs and removal were roughly balanced. Conductivity was consistently low in runoff samples. Base-flow stream samples

Table 3. List of samples collected and analytes. 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 standard 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. These two Savoy samples were used for comparison and to support the viability of the samples from the C&H holding ponds.

	Sample #	Sample Name	pH, Cond., Alk.	Anion Suite	Br	TP	TN, DOC	Cation Suite	$\delta^{15}N$ and $\delta^{18}O$ NO_3	$\delta^{18}O$ Phosphate and Ortho-phosphate Concentration	$\delta^{2}H$, $\delta^{18}O$ Water	$\delta^{15}N$, %N
Stream Samples	**5A**	**Ephemeral In-Stream 5/2/16**						X	X	X		
	5B	**Ephemeral ISCO 5/2/16**	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	
Possible 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

had higher conductance than storm-flow samples, indicating greater groundwater contribution to stream-flow during base-flow periods.

Chloride to bromide ratios were analyzed to determine potential anthropogenic influences in Big Creek (Table 7). A Cl/Br ratio of 400 is the theoretical maximum Cl/Br for natural waters; Cl/Br ratios of over 400 are indicative human-influenced waters (Thomas, 2000). The Cl/Br ratio of fresh cow manure was 827.04, and septic effluent had a Cl/Br ratio of 540.52. The stream samples that contained a Cl/Br ratio over 400 include upstream S1 (464.67), downstream S1 (747.5), and confluence S2 (449.8). Stream Cl/Br ratios indicate a human influence of stream sample chemistry which could arise from any combination of the analyzed sources. Table 8 contains data from the analysis of cations.

Isotopic Parameters

Samples taken from the CAFO waste lagoon, a septic system, field and parking-lot runoff, fertilizer, and hog manure exhibit distinctly different δ15N and δ18O (Figure 3 and Table 8), and each of these sources is different as compared to stream samples. Big Creek NO_3 isotope values (δ15N range: -7.59 to 9.10‰; δ18O range: -3.41 to 6.71‰) are similar to NO_3 values expected from nitrification of N stored in soils sampled in the watershed (δ15N range: 3.8 to 6.6; δ18O range: 3.4 to 4.8‰). Chicken litter and old cow

Table 4. Concentrations of anions, NO_3+NO_2, TN, DOC, TP, pH, conductivity, and alkalinity.

	Sample #	Sample Name	NH_3 (mg/L)	Br (mg/L)	Cl (mg/L)	Fl (mg/L)	N+N (mg/L)	NO_3 (mg/L)	SO_4 (mg/L)	TN (mg/L)	DOC (mg/L)	TP (mg/L)	SRP (mg/L)	pH	Cond. (µS/cm)	Alk. (mg/L as $CaCO_3$)
Possible Source Samples	1A	Savoy Lagoon-Old	354	--	444.149	0*	0.16	0.105	24.704	--	--	--	--	7.77	6770	1187.8
	1B	Savoy Lagoon-Fresh	227	0*	542.874	0*	0.17	0*	43.057	<1	<2.14	52.95	16.8	--	--	--
	2	Hog Manure	491	0*	92.773	428.34	0.27	0*	61.951	219.66	819.57	455	319	6.08	5260	101.1
	3	Fresh Cow Manure	307	0.119	98.418	3.353	0.14	0*	0*	0.21*	<2.14	38.2	14.1	7.19	1732	490.3
	4	Chicken Litter	716	0*	1196.99	905.61	1.45	0*	4103.68	<1	<2.14	86.2	347	6.28	7310	535.8
	6	CAFO Solids Pond	1040	0*	586.68	0*	0.22	0*	43.622	<1	<2.14	75.2	122	8.16	4581	4134.5
	7	CAFO Liquids Pond	448	0*	472.332	0.627	0.12	0.108	6.175	<1	<2.14	110.4	91.3	7.96	3314	2987.2
	8	Aged Cow Manure	7.93	0*	16.248	0.242	0.05	0*	0*	<1	<2.14	37.9	21.4	7.06	297.7	272.9
	9	Synthetic Fertilizer	4.34	0.032	5.797	0.102	E 0.02	0*	2.807	9.79	3.45	5.079	6.15	6.95	63.6	--
	10	Septic Effluent	83.9	0.097	52.43	0*	0.06	0*	20.458	79.4	43.89	7.662	7.66	6.55	1313	278
	11	Field 1 Runoff	0.51	--	2.678	0.154	0.34	0.38	2.524	<1	<2.14	0.712	0.571	7.5	51	--
	12	Field 5A Runoff	0.39	0*	2.116	0.147	0.8	0.372	2.294	1.19	7.26	0.868	0.834	7.28	68	45.5
	13	Field 12 Runoff	0.14	0*	1.243	0.138	0.19	0.218	2.038	0.26*	4.69	0.368	0.248	7.35	60	15.2
	32	Parking Lot Runoff	0.11	0.006*	E 0.341	0*	0.08	0.181	1.416	<1	3.59	0.033	0.825	6.62	51.7	--
Stream Samples	14	Upstream S1	0*	0.006*	2.788	0.153	0.17	0.185	3.182	<1	1.46*	0.03	0.015*	7.82	84.7	53.6
	15	Upstream 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	Upstream B1	E 0.04	0.01*	1.196	0*	0.2	0.18	3.876	<1	1.06*	0.024	0.439	8.05	119.1	25.3
	17	Upstream B2	E 0.02	0.011*	2.007	0.021*	0.09	0.046	4.261	<1	1.52*	E 0.01	6.29	7.64	235	55.6
	18	Downstream S1	E 0.01	0.002*	1.495	0.157	0.25	0.288	3.706	<1	1.90*	0.076	0.01*	7.63	114.5	23.3
	19	Downstream S2	0.06	0*	1.83	0.158	0.14	0.152	5.321	<1	1.49*	0.026	0*	7.75	162.9	53.6
	20	Downstream B1	E 0.02	0*	1.623	0.002*	0.18	0.152	4.295	<1	1.81*	0.02	0.157	7.57	180.7	65.7
	21	Downstream B2	E 0.02	0.019	2.595	0.007*	0.45	0.398	4.82	<1	2.53	0.004*	0.703	7.54	276	96
	22	Confluence S1	0.06	0*	1.919	0.155	0.29	0.305	4.852	<1	2.10*	0.03	0.01*	7.87	147.9	94
	23	Confluence S2	0*	0.005*	2.249	0.169	0.12	0.146	6.787	<1	1.37*	0.028	0.022*	8.1	200.7	69.8
	24	Confluence B1	E 0.04	0.008*	1.95	0.206	0.31	0.277	4.723	<1	1.14*	0*	0.185	8	217.7	65.7
	25	Confluence B2	0*	0.019	2.845	0.335	0.08	0.055	5.006	<1	1.63*	0*	0.031	7.44	263	85.9
	26	Ephemeral 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	131.4
	27	Ephemeral S2	0*	0.015	3.93	0.146	0.65	0.692	3.127	0.10*	0.53*	0.03	0.016*	7.48	394	166.8
	5B	Ephemeral ISCO 5/2/16	E 0.03	0*	3.015	0.907	0.51	0.586	2.561	--	--	--	0	7.79	339	--

* = below method detection limit, should be viewed as an estimate

E = below reporting limit and above method detection limit, should be viewed as an estimate

-- = no data available

B = samples collected at base-flow conditions

S = samples collected after rainfall (storm-flow conditions)

< = censored data

EPA = Environmental Protection Agency

APHA = American Public Health Association

Samples 9, 32, and 5B were analyzed for alkalinity but did not yield any data

manure are most likely undergoing denitrification in-situ as indicated by their increased δ15N and δ18O compared to referenced manure and fertilizer ranges. Denitrification increases δ15N and δ18O by a 1:2 ratio. The chicken litter and old cow manure samples may also indicate nitrification involving waters that have been highly evaporated, resulting in relatively high δ18O values. All runoff samples and the Savoy lagoon sample have elevated δ18O, indicative of ei-

Table 5. Minimum and maximum of analytes for possible nutrient source samples.

Possible Nutrient Source Statistics	Minimum	Maximum
Ammonia (mg/L)	0.110	1040
Bromide (mg/L)	0.000	0.120
Chloride (mg/L)	0.340	197
Fluoride (mg/L)	0.000	906
Nitrate+Nitrite (mg/L)	0.020	1.450
Nitrate(mg/L)	0.000	0.380
Sulfate(mg/L)	0.000	4104
Dissolved Organic Carbon (ppm)	*	820
TN (ppm)	*	220
Total Phosphorous (ppm)	0.033	455
Orthophosphate (mg/L)	0.248	347
pH	6.1	8.2
Conductivity (µS/cm)	51	7310
Alkalinity (as $CaCO_3$) (mg/L)	15	4135
δ^{18}O Phosphate (‰)	-78.8	101.0
δ^{15}N Nitrate	-15.4	54.8
δ^{18}O Nitrate	-7.1	59.1
Lithium (ppm)	0.000	0.108
Boron (ppm)	0.004	8.710
Magnesium (ppm)	0.009	86.578
Potassium (ppm)	0.001	0.521
Calcium (ppm)	0.000	0.001
Gallium (ppm)	0.000	0.000
Vanadium (ppm)	0.000	0.000
Selenium (ppm)	0.000	0.011
Strontium (ppm)	0.000	0.000
Tin (ppm)	0.000	0.000
Antimony (ppm)	0.001	0.008
Barium (ppm)	0.000	0.159
Manganese (ppm)	0.001	0.212
Iron (ppm)	0.000	0.057
Rubidium (ppm)	0.000	0.000
Yttrium (ppm)	0.000	0.000
Dysprosium (ppm)	*	37.201
Sodium (ppm)	*	0.028
Aluminum (ppm)	*	0.001
Chromium (ppm)	*	0.001
Cobalt (ppm)	*	0.026
Nickel (ppm)	*	0.225
Copper (ppm)	*	0.001
Arsenic (ppm)	*	0.000

* = left-censored data

Table 6. Minimum, maximum, mean, and median of analytes for stream sources.

Stream Sample Statistics	Minimum	Maximum	Mean	Median
Ammonia (mg/L)	0.000	0.060	0.020	0.020
Bromide (mg/L)	0.000	0.019	0.007	0.006
Chloride (mg/L)	1.196	3.930	2.232	2.007
Fluoride (mg/L)	0.000	0.907	0.181	0.153
Nitrate+Nitrite (mg/L)	0.030	0.770	0.283	0.200
Nitrate(mg/L)	0.046	0.809	0.296	0.185
Sulfate(mg/L)	2.168	6.787	4.170	4.261
Dissolved Organic Carbon (ppm)	0.530	2.530	1.458	1.475
TN (ppm)	*	0.280	0.027	0.000
Total Phosphorous (ppm)	0.000	0.076	0.028	0.027
Orthophosphate (mg/L)	0.000	6.290	0.053	0.016
pH	7.160	8.100	7.720	7.750
Conductivity (µS/cm)	85	394	210	201
Alkalinity (as $CaCO_3$) (mg/L)	23	167	74	66
δ^{18}O Phosphate (‰)	-36.3	55.4	14.6	22.3
δ^{15}N Nitrate	-7.6	9.1	1.9	2.2
δ^{18}O Nitrate	-3.4	6.7	2.2	2.6
δ^{18}O Water	-6.7	-5.0	-5.6	-5.5
δ^{2}H Water	-41.8	-26.8	-33.4	-32.7
Lithium (ppm)	0.000	0.000	0.000	0.000
Boron (ppm)	0.000	0.001	0.000	0.000
Magnesium (ppm)	0.028	0.072	0.045	0.044
Potassium (ppm)	0.013	0.138	0.033	0.023
Calcium (ppm)	0.025	0.136	0.073	0.069
Gallium (ppm)	0.000	0.000	0.000	0.000
Vanadium (ppm)	0.000	0.000	0.000	0.000
Selenium (ppm)	0.000	0.000	0.000	0.000
Strontium (ppm)	0.001	0.002	0.002	0.001
Tin (ppm)	0.000	0.000	0.000	0.000
Antimony (ppm)	0.000	0.000	0.000	0.000
Barium (ppm)	0.001	0.002	0.001	0.001
Sodium (ppm)	0.022	0.062	0.035	0.033
Uranium (ppm)	0.000	0.000	0.000	0.000
Aluminum (ppm)	*	0.008	0.001	0.000
Chromium (ppm)	*	0.000	0.000	0.000
Manganese (ppm)	*	0.000	0.000	0.000
Iron (ppm)	*	0.005	0.001	0.000
Cobalt (ppm)	*	0.000	0.000	0.000
Arsenic (ppm)	*	0.000	0.000	0.000

* = left-censored data

Table 7. Chloride to bromide ratios of samples that contained bromide.

	Sample #	Sample Name	Br (mg/L)	Cl (mg/L)	Cl:Br
Possible Source Samples	3	Fresh Cow Manure	0.119	98.418	827.04
	9	Synthetic Fertilizer	0.032	5.797	181.16
	10	Septic Effluent	0.097	52.43	540.52
Stream Samples	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
	21	Downstream B2	0.019	2.595	136.58
	23	Confluence S2	0.005	2.249	449.80
	24	Confluence B1	0.008	1.95	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	3.93	262.00

ther potential atmospheric deposition or oxygen-exchange effects. The hog manure exhibits a slightly elevated δ18O. The septic system sample plots with a relatively heavy δ15N, indicative of denitrification. Stream sample δ15N and δ18O overlap isotopic ranges documented in other studies for NO_3 in fertilizer and precipitation, soil NO_3, and manure and septic waste.

Stream samples show markedly different isotopic compositions as compared to potential local sources sampled—chicken litter, cow manure, field runoff, parking-lot runoff, and septic effluent; as such, stream NO_3 isotopic composition 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 isotope data are most consistent with an interpretation of stream nitrate being derived from nitrate stored in soils or from manure or septic sources not represented by the limited number of samples collected for this study. The relatively heavy isotopic signature imposed on nitrate by denitrification is not apparent in stream samples (Figure 3), indicating little or no influence of in-stream denitrification and little direct input from these sources to Big Creek. A Wilcoxon Rank Sum Test was conducted with a 95% confidence interval for nitrate δ15N and δ18O: δ15N was found to be statistically higher at the downstream site compared to the upstream site, while no difference was found between the sites for δ18O. This implies that denitrification is not likely occurring in Big Creek between these sites and a source input with a more enriched δ15N is responsible for the elevated δ15N between sites. Sediment organic δ15N ranged from -2.26 to 5.07‰ (Table 9), which overlaps the range for δ15N of stream samples. Nitrification of stream sediment N along the upstream to downstream reach of Big Creek may explain the decoupling of δ15N and δ18O signatures; such nitrification could obfuscate any isotopic indication of denitrification along the reach, making the assessment of denitrification there inconclusive.

Phosphate oxygen isotope ratios are shown in Figure 4 and documented in Table 10. Source δ18O-PO_4 values were extremely variable: Sediment δ18O – -78.8 and 101‰, cow manure δ18O – 45.9 and 61.7‰, CAFO waste-holding ponds δ18O – 30.5 and 23.3‰, chicken litter δ18O – 21‰, septic effluent δ18O – 28.1‰, fertilizer δ18O – 19.9‰, runoff sample δ18O ranged from 8.47 to 38.6‰, and stream δ18O ranged from 36.3 to 55.4‰. This overlap between potential source δ18O values and stream δ18O values complicates discrimination of nutrient source input to the stream using phosphate oxygen isotopes. In addition, phosphate oxygen isotopic composition can be modified through biological mediation (Longinelli et al., 1976). Therefore, δ18O-PO_4 values can indicate mixing of sources or biological oxygen exchange. Theoretical isotopic equilibrium values for δ18O-PO_4 in stream samples were calculated by applying the following equation derived from Longinelli and Nuti, 1973:

$$\delta 18O\text{-}PO_4 = [(T(°C)-111.4)/-4.3] + \delta 18O\text{-}H_2O$$

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

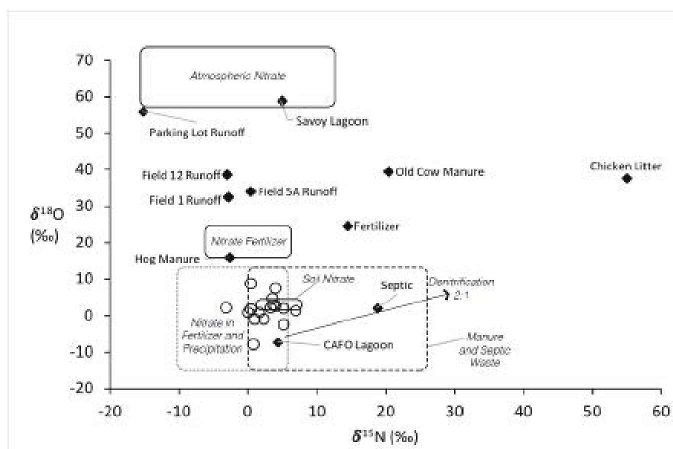

Figure 3. Nitrate isotope ratios. Possible source samples represented by diamonds, stream samples by circles. Boxes are representative of indicated nitrogen sources in italics, modified from Kendall and McDonnell, 1998. The range of δ15N and δ18O for the soil nitrate box is modified from Fields and Halihan, 2016. The range of δ18O for soil nitrate was derived from stream nitrate δ18O and estimated atmospheric nitrate δ18O. Nitrate in soil is biologically nitrified from ammonia: during this process, one oxygen atom is taken from atmospheric O2, while two come from water (Hollocher, 1984). Possible δ15N fractionation in soil was accounted for by adding a 1‰ buffer to the range of δ15N.

Table 8. Nitrate isotope ratios of possible source samples and stream samples. All values in permille (‰) notation.

	Sample #	Sample Name	$\delta^{15}N$ - Nitrate	$\delta^{18}O$ - Nitrate
Possible Source Samples	1A	Savoy Lagoon-Old	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	15.39	18.73
	10	Septic Effluent	18.66	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
Stream Samples	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

The following samples were tested with no result: 1B Savoy Lagoon-Fresh, 3 Fresh Cow Manure, 7 CAFO Liquids Pond

Table 9. Nitrogen isotope ratios and %Nitrogen of sediment samples.

Sample Number	Sample Name	$\delta^{15}N$	%N
28	Upstream Sediment	4.572	0.023
28_d	Upstream Sediment Duplicate	2.612	0.025
29	Downstream Sediment	5.071	0.286
30	Confluence Sediment	2.180	0.154
31	Ephemeral Sediment	-2.258	0.053

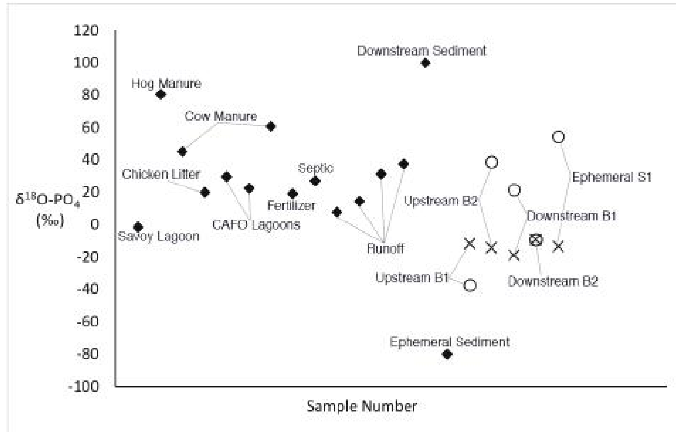

Figure 4. Phosphate oxygen isotope ratios. Possible source samples represented by diamonds, stream samples by circles. Stream equilibrium phosphate oxygen isotope ratios represented by an X.

δ18O ranged from -17.75 to -8.44‰. The equilibrium δ18O-PO_4 for the upstream B2, downstream B1, and ephemeral S1 samples was depleted compared the measured stream δ18O. Phosphate sorbed onto sediment in the ephemeral stream (-78.8‰) is likely influencing δ18O in the ephemeral stream. The enriched δ18O values seen in all source samples other than ephemeral sediment may imply a source input to Big Creek is influencing δ18O. Stream water δ18O and δ2H are presented in Table 11. Figure 5 illustrates that stream water δ18O and δ2H lie slightly but consistently above the local meteoric water line.

Conclusions

Big Creek water quality and isotopic data show the CAFO waste lagoon, a septic system, field and parking-lot runoff, fertilizer, and hog manure exhibit different δ15N and δ18O as compared to stream samples. Big Creek NO_3 isotope values are similar to NO_3 values expected from nitrification of N stored in soils sampled in the watershed. Similar chloride-bromide ratios for fresh cow manure, septic-system effluent, and Big Creek samples may indicate an influence on Big Creek water quality. We recommend that monitoring continues on Big Creek to ensure potential future effects on water quality are recognized. The database of compositions

Table 10. Phosphate oxygen isotope ratios for possible source samples and stream samples, along with water temperature and phosphate oxygen isotope equilibrium ratios for stream samples.

	Sample #	Sample Name	δ18O - Phosphate (‰)	Water Temp (°C)	Equilibrium δ18O - Phosphate (‰)
Possible Source Samples	1B	Savoy Lagoon-Fresh	-0.652	--	
	2	Hog Manure	81.6	--	
	3	Fresh Cow Manure	45.9	--	
	4	Chicken Litter	21	--	
	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	8.47	--	
	12	Field 5A Runoff	15.2	--	
	13	Field 12 Runoff	32	--	
	32	Parking Lot Runoff	38.6	--	
	29	Downstream Sediment	101	--	
	31	Ephemeral Sediment	-78.8	--	
Stream Samples	16	Upstream B1	-36.3	24	-10.6
	17	Upstream B2	39.6	28.6	-13.2
	20	Downstream B1	22.3	24.3	-17.7
	21	Downstream B2	-8.08	24.4	-8.4
	26	Ephemeral S1	55.4	14	-12.5

-- = No Data

The following samples did not contain enough phosphate to measure the oxygen isotope ratio: Upstream S1 and S2 (14 and 15), Downstream S1 and S2 (18 and 19), All Confluence Samples (22, 23, 24, 25), Ephemeral S2 (27), Ephemeral 5/2/16 (5A and 5B), Upstream Sediment, Confluence Sediment.

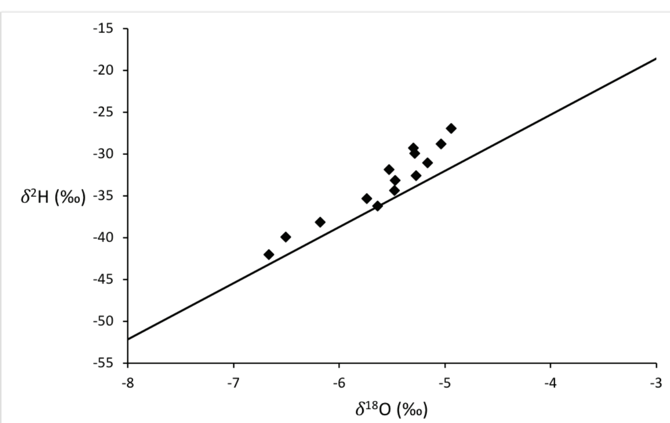

Figure 5. Stream water isotope ratios. Stream samples are represented by diamonds. Black line is a local meteoric water line modified from Knierim, 2015.

Table 11. Hydrogen and oxygen isotope ratios of stream water samples. All values in permille (‰) notation.

Sample #	Sample Name	δ18O - Water	δ2H - Water
14	Upstream S1	-4.96	-26.83
15	Upstream S2	-5.31	-29.11
16	Upstream B1	-5.18	-30.93
17	Upstream B2	-5.28	-32.44
18	Downstream S1	-5.54	-31.71
19	Downstream S2	-6.52	-39.73
20	Downstream B1	-6.19	-38.00
21	Downstream B2	-5.05	-28.68
22	Confluence S1	-6.68	-41.82
23	Confluence S2	-5.30	-29.74
24	Confluence B1	-5.49	-34.18
25	Confluence B2	-5.65	-36.06
26	Ephemeral S1	-5.75	-35.16
27	Ephemeral S2	-5.48	-33.03

of potential nutrient sources developed in this study will assist in addressing nutrient enrichment in other watersheds. The results of this study highlight the importance of effective agricultural, residential, and urban best management practices in protecting the quality of our waterways.

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