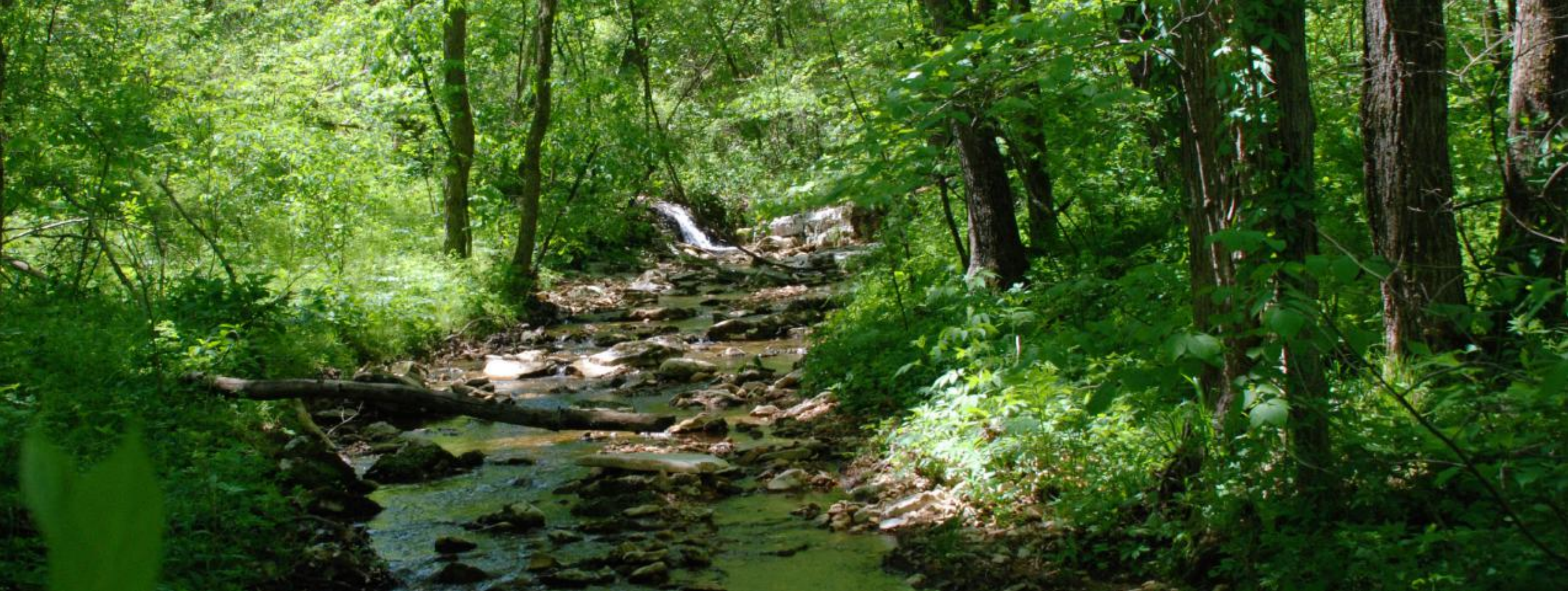

Image caption: A forested stream in the Ozarks of Arkansas. Photo from bioimages.vanderbilt.edu.

Quantifying Flow Sources and Their Impacts on Water Quality in Forested Ozark Streams

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Abstract: Stream water sources play a key role in nutrient and water budgets. Current hydrologic models predict two dominant flow regimes in northern Arkansas, each characterized by differing dominant flow sources: groundwater and runoff from precipitation. Current model estimates of groundwater input were generated at catchment- and kilometer-level scales using probability estimates. Direct measurements of water chemistry from flow sources (i.e. groundwater and precipitation) provide more refined estimates of instream source apportionment, especially in small headwater systems. Water samples were collected in three, primarily-forested Runoff and three Groundwater streams twelve times from March 2018 to November 2018. Nine samples were taken at base or near-base flow while three samples were taken during storm flow. In addition to determining discharge, nutrient concentrations, and conductivity, hydrochemical tracers and end-member mixing analysis (EMMA) were used to apportion streamflow originating from precipitation or groundwater. Results showed that all Runoff streams were driven primarily by rain, which accounted for approximately 89% of channel flow across sites and sampling dates. Median Groundwater stream flow was comprised of 79% groundwater over the study period. Total phosphorus (TP) and nitrogen (TN) concentrations were both greater in Groundwater streams. However, Runoff stream TN was driven by groundwater nitrogen addition and discharge, while no such relationships were found in Groundwater streams. This study validates hydrologic model prediction of flow regime sources while revealing an important yet overlooked source of nitrogen in precipitation-driven streams. Given that this work took place in forested streams, further work is needed in agricultural systems, as Runoff streams may be more susceptible to nitrogen enrichment from nutrient migration through soils to groundwater.

Key Points:

- Groundwater streams were driven primarily by groundwater inputs, except during storm events, when precipitation became the dominant flow source.
- Runoff streams were driven by precipitation inputs during base and storm flows.
- Nitrogen concentrations in Runoff streams increased with groundwater contributions high in nitrogen.
- Runoff stream nitrogen decreased with discharge.
- Groundwater inputs were important nutrient sources in forested precipitation-driven systems.

Introduction

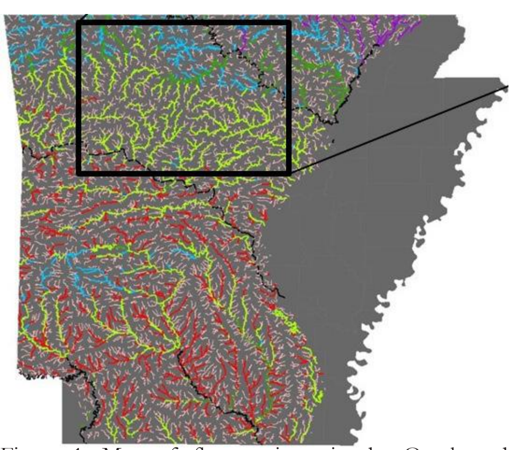
The relative input of groundwater versus surface water varies temporally and spatially across lotic systems. These waters have differing chemistries and nutrient dynamics; however, data quantifying the source and amounts of water entering headwater streams are lacking, even though such data would provide critical insight into potential impacts of nutrient pollution, particularly in streams with low nutrient buffering. Importantly, data revealing the relative contributions of various water sources to headwater streams and how these sources may vary in time and space also provides a decision-making tool for managers to address nutrient mitigation measures across ecoregions and flow classifications. Several natural flow categories exist for streams within the Ozark and Ouachita Interior Highlands (Leasure et al., 2016). Previous work has shown that these classifications influence variation in ecosystem function, discharge, conductivity, and nutrient concentrations, even among minimally-impacted forested systems (Dodd et al., unpublished data). One possible mechanism for these differences in function and water quality is the dominant channel flow source. Further, Leasure et al. (2016) revealed distinct hydroecological areas defined by two dominant flow classifications in the Ozark Highlands and Boston Mountains ecoregions that are likely differentially impacted by pollutants due to differing nutrient buffering capacities and other water quality parameters. These two dominant flow classifications are Runoff Flashy (hereafter Runoff) systems, which dominate the Boston Mountains ecoregion, and Groundwater Flashy (hereafter Groundwater) streams, which dominate the Ozark Highlands.

Currently, little information is available to address the influence of flow regime on the spatial and temporal extent that pollutants may be mitigated by dilution with groundwater inputs. This is critical for freshwater conservation, as understanding the nutrient buffering capacity of streams and variation in water quality lays the foundation for better water resource management (Jarvie et al., 2014). It is especially important to determine these parameters in streams that experience high traffic by the public for recreation, such as forested streams, as pollution in these areas can lead to the closing of campgrounds and swimming areas during the summer months. Source-related nutrient enrichment in forested streams would signal a need for additional focused efforts in agricultural systems. Differences in flow sources and, in turn, potential avenues for enrichment allow managers to focus on streams that are most susceptible to water quality degradation.

Our study objective was to use water chemistry and hydrologic field data to confirm distinctions between groundwater and surface water-dominated modeled flow regime classifications. We investigated whether actual stream water sources align with predicted flow types and how nutrient concentration in source waters affected instream nutrients. We also examined conductivity, gross primary production, and community respiration. We predicted that groundwater would contribute 70 to 95% of the flow in Groundwater streams and less than 50% of flow in Runoff streams based on previous studies in this region (Jarvie et al., 2014).

Methods

This study took place in six minimally-impacted forested streams (Figure 1). Three streams classified as Runoff systems were located in the Boston Mountains ecoregion, while three Groundwater streams were nested within the Ozark Highlands ecoregion. All streams were nested with-



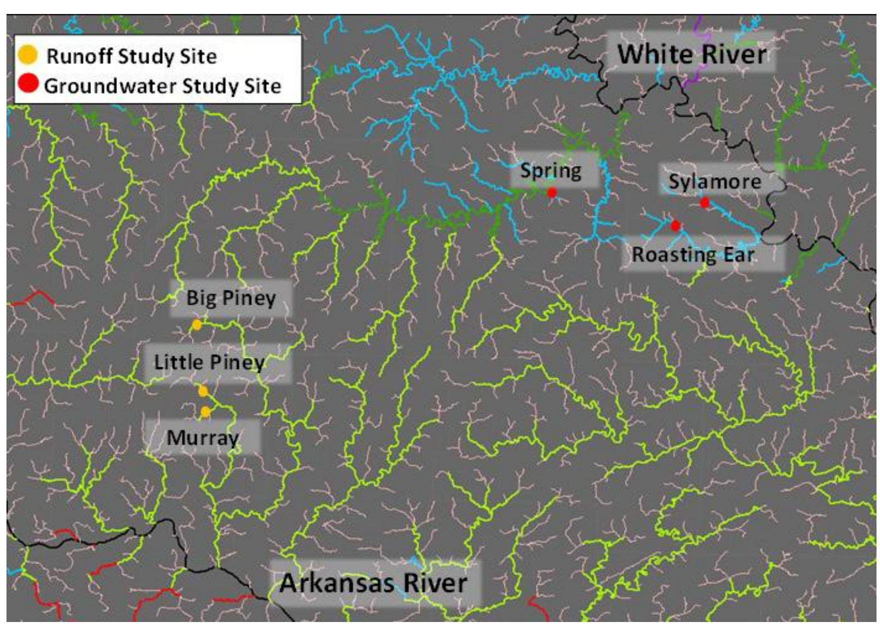


Figure 1. Map of flow regimes in the Ozark and Ouachita Interior Highlands based on Leasure et al. (2016). Highlighted area shows individual study sites sampled from 2018 to 2019 across northern Arkansas. Teal streams in map represent groundwater streams. Light green streams in map represent runoff streams.

in watersheds that consisted of 84-97% forested land cover and 1-8% pastoral land use, with existing datasets showing strong relationships with downstream USGS gage discharges (R^2 values from 0.70 to 0.94).

Water samples were taken roughly every two weeks as well as during storm flow for total nitrogen (TN), total phosphorus (TP), conductivity, and trace and rare earth elements from March 27th to May 19th, then from July 31st to November 2nd, 2018. Flow in study reaches was monitored using established relationships between discharge in the reach and discharge at a downstream USGS gage or a nearby proxy gage within the watershed. Groundwater sources were directly sampled from a well at least monthly and deposition samples were collected directly after precipitation events using a rain sampler placed near the stream in an area of little to no canopy cover. Nutrient concentrations of source waters (rain and groundwater) were measured on the six sampling dates from August 1st to October 30th.

Persulfate digests of unfiltered water samples followed by colorimetric benchtop SRP analyses using the ascorbic acid method yielded TP concentrations. TN was determined using a Shimadzu TOC-L analyzer (Shimadzu Corporation, Kyoto, Japan). Samples for trace elements and metals (aluminum, arsenic, barium, beryllium, boron, cadmium, cesium, cobalt, chromium, copper, iron, potassium, lithium, lutetium, manganese, mercury, molybdenum, phosphorus, nickel, lead, samarium, selenium, titanium, uranium, vanadium, and zinc) were measured on an inductively-coupled plasma mass spectrometer (Thermo Fisher Scientific, Waltham, MA) on source (groundwater and precipitation) and stream water samples to estimate relative surfacewater:groundwater contributions.

End-member mixing analysis (EMMA) was employed to apportion water sources. Conservative tracers were identified and confirmed using pairwise comparisons of all tracer combinations (Hooper 2003). Mixing ratios (m) were determined according to the equation

$$m = \frac{[\text{Tracer}]_{\text{sample}} - [\text{Tracer}]_{\text{groundwater}}}{[\text{Tracer}]_{\text{precipitation}} - [\text{Tracer}]_{\text{groundwater}}}$$

(Rueedi et al., 2005)

Nutrient concentrations, conductivity, discharge, and mixing fractions were compared across flow regimes and sampling dates using repeated-measures ANOVA (RM-ANOVA). Linear regressions were used to investigate relationships between mixing fractions and discharge as well as nutrient concentrations and discharge. Unless otherwise specified, data are reported as median ± standard error of the median.

Results and Discussion

Groundwater accounted for 70% or more of channel flow in Groundwater streams on eight out of twelve (67%) of sampling events. During base flow, median groundwater contribution to channel flow in Groundwater streams was 82 (±3.4)%. Groundwater made up 35 (±14.3)% of channel flow during storm events. Two out of three Groundwater streams were not diluted by precipitation inputs during one storm event in late August, which accounted for the high variation in storm sample groundwater fractions.

In Runoff streams, groundwater contributed less than 25% of channel flow on all but one sampling date (Figure 2). On April 6th, 2018, Runoff streams consisted of 60 (±17.0)% groundwater. Median base flow groundwater contribution was 10 (±6.0)%, while median storm flow contribution was 14 (±3.9)%. These findings align with model-predicted flow sources, though these data reveal a degree of temporal variation in dominant sources, especially in Groundwater streams when inundated by storm runoff.

Discharge differed between flow regimes on three sampling dates, two of which were storm events (Flow: $F(1,25)= 0.17$, $p=0.68$; Date: $F(11,25)$: 11.62, $p<0.0001$; Flow*Date: $F(11,25)$: 2.20, $p=0.05$). Groundwater site discharge increased with percent flow derived from precipitation ($R^2= 0.48$, $p=0.01$). However, Runoff sites did not exhibit any relationship between mixing fractions and discharge ($R^2= 0.08$, $p=0.38$). Median base flow in Runoff streams was 0.40 (±0.38) m^3/s, while discharge in Groundwater streams was 0.66 (±0.76) m^3/s. Storm flow in Runoff streams was 6.48 (±3.14) m^3/s, while median storm flow in Groundwater streams was 4.52 (±2.63) m^3/s. Hydrographs showing median flows within each flow regime are shown in Figure 3.

Conductivity was greater in Groundwater streams (Flow: $F(1,25)=926.77$, $p<0.0001$) and was greatest during the summer/early fall when discharge was low (Date: $F(11,25)$: 5.33, $p<0.0001$; Flow*Date: $F(11,25)$: 0.92, $p=0.52$). Con-

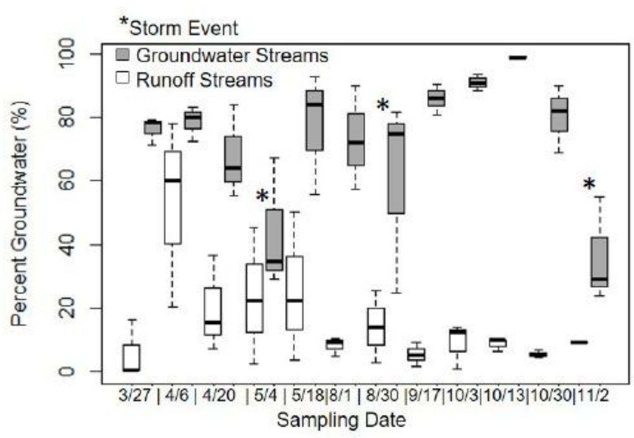


Figure 2. Median groundwater contribution to Runoff and Groundwater streams on each sampling date. Whiskers represent ± 1 SE of median.

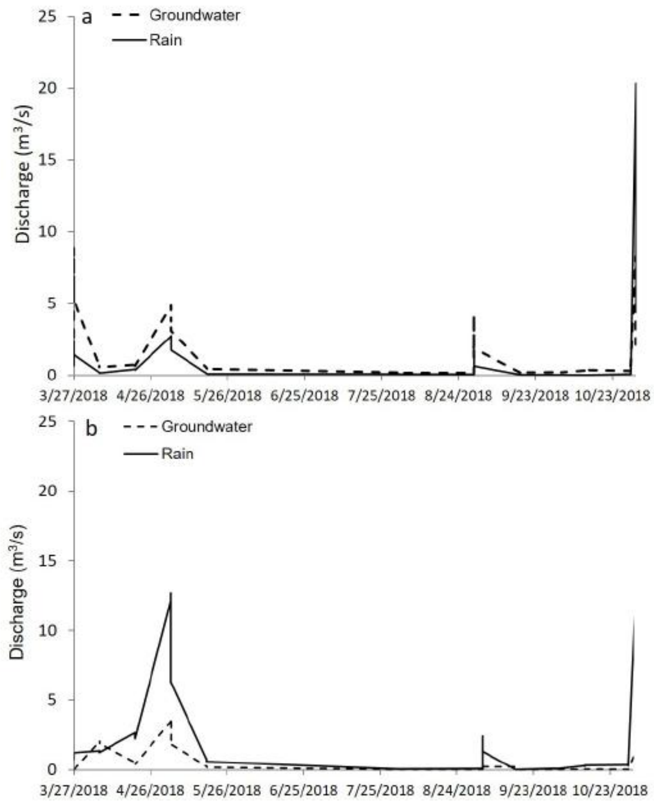


Figure 3. Median hydrographs for (a) Groundwater and (b) Runoff streams, illustrating groundwater and precipitation contributions to channel flow over the study period.

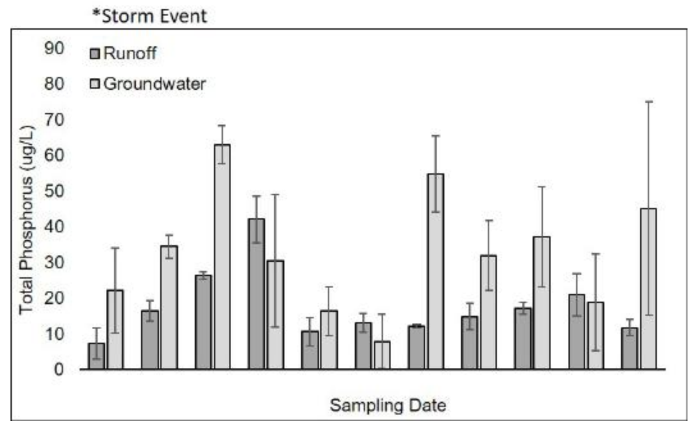


Figure 4. Median instream total phosphorus concentrations on each sampling date. Whiskers= 25th and 75th percentiles.

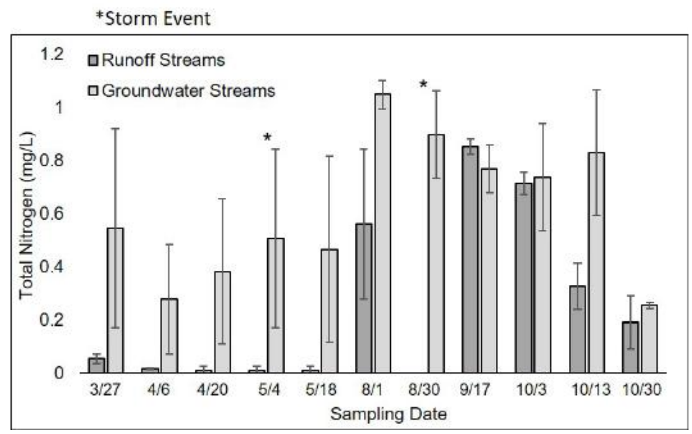


Figure 5. Median instream total nitrogen concentrations on each sampling date. Whiskers= 25th and 75th percentiles.

ductivity varied from 123 to 294 μS/cm in Groundwater streams, while conductivity in Runoff streams ranged from 11 to 47 μS/cm. Runoff stream conductivity was not related to discharge or source mixing fractions; however, Groundwater stream conductivity increased with greater groundwater contributions (R^2=0.64, p=0.03). Groundwater sources across flow regimes exhibited high conductivity (Groundwater=183±81 μS/cm, Runoff=199±33 μS/cm), while precipitation samples had low conductivity across flow regimes (Groundwater=14±6 μS/cm, Runoff=3±0.89 μS/cm).

Total phosphorus concentrations differed by flow regime on four out of twelve sampling dates (RM-ANOVA; Flow: F(1,25)=10.61; p=0.003; Date: F(11,25): 3.34, p= 0.002; Flow*Date: F(11,25): 48.0, p<0.0001) (Figure 4). Specifically, Groundwater streams held greater phosphorus concentrations on three sampling dates (April 6, April 20, and August 30), while Runoff streams exhibited greater P during the final storm sampling event on November 1. Runoff stream P concentrations ranged from 7.33 to 26.38 μg/L P under base flow conditions, while Groundwater stream P ranged from 7.9 to 63 μg/L P. Storm event P levels ranged from 12.19 to 42.09 μg/L P in Runoff streams and 0.94 to 54.81 μg/L P in Groundwater streams. Rain and groundwater P concentrations were not related to instream P concentrations in either flow regime (Table 1). We observed greater variation in Groundwater stream P, which may be due to pastoral land use in the surrounding area around Roasting Ear Creek. Regardless, P from groundwater and precipitation inputs did not drive instream P concentrations.

Total nitrogen concentrations were greater in Groundwater streams (RM-ANOVA: Flow: F(1,21)=9.43; p=0.004) (Figure 5). Nitrogen did not differ significantly across sampling dates (Date: F(11,21): 1.73, p=0.10; Flow*Date: F(11,21): 0.90, p=0.54). However, we observed that nitrogen levels across flow regimes were consistently low during the spring, reached their maximum levels between August 30th and October 3rd, then declined to their lowest concentrations at the end of the study. Runoff stream nitrogen levels ranged from below detection (<0.01) to 0.85 mg/L N, while Groundwater stream nitrogen varied from 0.25 to 1.05 mg/L N. We found a strong positive relationship between Runoff stream nitrogen and groundwater source N concentrations (R^2=0.93, p=0.007) (Figure 6), though no other relationships between instream and source nitrogen concentrations were observed (Table 1). Additionally, instream nitrogen levels decreased with greater discharge (R^2=

Table 1. Results of linear regression analyses between stream and source water nutrient values. Asterisks denote significant relationships.

Total Phosphorus	**R^2**	**p-value**
Runoff		
Stream v. Groundwater	0.05	0.92
Stream v. Rain	0.49	0.32
Groundwater		
Stream v. Groundwater	0.88	0.08
Stream v. Rain	0.4	0.45
Total Nitrogen	**R^2**	**p-value**
Runoff		
Stream v. Groundwater	0.93	0.007**
Stream v. Rain	0.54	0.26
Groundwater		
Stream v. Groundwater	0.51	0.3
Stream v. Rain	0.27	0.61
Total Organic Carbon	**R^2**	**p-value**
Runoff		
Stream v. Groundwater	0.37	0.47
Stream v. Rain	0.51	0.3
Groundwater		
Stream v. Groundwater	0.44	0.38
Stream v. Rain	0.36	0.48

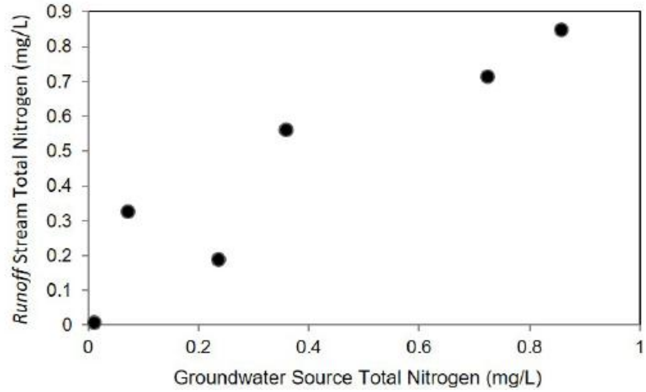


Figure 6. Runoff stream total nitrogen versus groundwater source nitrogen concentrations.

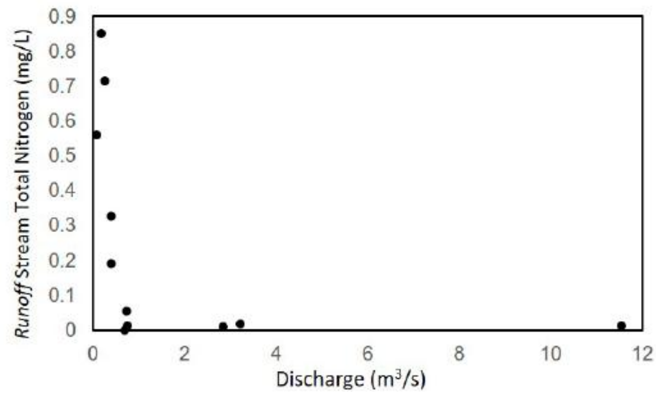


Figure 7. Relationship between Runoff stream discharge and total nitrogen concentrations.

0.86, p=0.03) (Figure 7). These data suggests that groundwater rather than runoff from precipitation is the primary source of instream nitrogen in Runoff systems. Further, precipitation events that increase stream discharge may be diluting nitrogen inputs from groundwater sources. This is of interest given that other Runoff streams in the ecoregion experience greater pressure from anthropogenic activities, and groundwater enrichment exerts a greater influence on instream nitrogen regimes than previously expected.

Total organic carbon (TOC) tended to be greater in Groundwater streams, though TOC levels were not significantly different between flow regimes across sampling dates (Flow: F(1,25)=0.07; p=0.79; Date: F(11,25): 1.23, p=0.30; Flow*Date: F(11,25): 0.32, p=0.97). Additionally, instream TOC concentrations were not related to groundwater or rain source TOC in either flow regime (Table 1).

Gross primary production did not differ across flow regimes and sampling dates (Flow: F(1,16)=0.38; p=0.55; Date: F(3,16): 1.73, p=0.20; Flow*Date: F(3,16): 0.09, p=0.96). However, ecosystem respiration was greater in Groundwater streams (Flow: F(1,16)=4.48; p=0.05), though respiration was similar across sampling dates (Date: F(3,16): 1.05, p=0.40; Flow*Date: F(3,16): 0.19, p=0.90). Stream metabolism was measured only in the late summer and fall

Table 2. Gross primary production (GPP) and ecosystem respiration (ER) estimates on four days during summer/fall portion of the study. All values reported in g $O_2/m^2/d$.

	Runoff		*Groundwater*	
Date	GPP	ER	GPP	ER
8/31/2018	1.47	-7.53	2.14	-7.85
10/2/2018	0.52	-1.62	1.35	-5.85
10/18/2018	0.52	-1.67	1.06	-5.12
10/30/2018	1.67	-1.95	1.93	-3.61

portion of the study; three out of four sampling days took place in September and October, which may account for the similarity in production and respiration across dates. Groundwater stream primary production and respiration were both greatest during late August; Runoff stream respiration was also greatest in August, though primary production was similar between August and late October. Stream temperature peaked in August, which likely drove higher rates of production and respiration on that sampling date. Table 2 contains metabolism values for each flow regime across the four days sampled.

Chloride concentrations were consistently greater in Runoff streams (Flow: F(1,16)=1.67; p=0.04; Date: F(3,16): 0.72, p=0.25; Flow*Date: F(3,16): 0.12, p=0.60), though chloride concentrations were low across all stream on all sampling dates. Chloride concentrations in Runoff streams averaged 2.83 (±0.25) mg/L Cl, while chloride in Groundwater streams averaged 2.05 (±0.27) mg/L Cl.

Sulfate concentrations were also greater in Runoff streams (Flow: F(1,16)=1.01; p=0.05; Date: F(3,16): 0.24, p=0.62; Flow*Date: F(3,16): 0.12, p=0.64). However, similar to chloride, concentrations were low across flow regimes and sampling dates. Sulfate in Runoff streams ranged from 1.03 to 4.67 mg/L SO_4^{2-}, while Groundwater streams exhibited sulfate concentrations of 1.36 to 6.31 mg/L SO_4^{2-}.

Conclusions

This study confirms previous probability models of primary water sources in the two dominant flow classifications across northern Arkansas while revealing temporal variation in rain and groundwater contributions. Even during base flow, streams occasionally exhibited source contributions that departed from predictions- further work to determine the cause of these events would provide greater insight into drivers of channel flow in these systems. Importantly, we discovered a significant link between Runoff stream and groundwater source nitrogen. In the forested, nutrient-limited systems we sampled, this nitrogen provides a subsidy; however, in other areas of the Boston Mountains, encroachment by pastoral and urban land use will necessitate focused attention on potential effects of groundwater enrichment given that streams in this ecoregion are more influenced by groundwater than previously considered.

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