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ORIGINAL ARTICLE

Base flow hydrology and water quality of an Ozarks spring and associated recharge area, southern Missouri, USA

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Abstract Human activities in the karst Ozark Plateaus can impact water quality of springs where surface water is rapidly transferred to subsurface conduits. Bennett Spring, in southern Missouri, is the fourth largest spring in the state and supports local tourism activities. Questions regarding poorly functioning on-site wastewater systems (OWS) have raised concerns over the long-term water quality of the spring. This study reports the results of a surface water quality monitoring program in the recharge area where monthly samples were collected at base flow to identify potential pollution sources to the spring. Base flow hydrology of the recharge area was highly variable over the study period, which was drier than normal, causing an incomplete sampling record due to no flow conditions at some sites. For most of the year, nutrient levels were less than the eutrophic threshold (ET) of 0.075 mg/l total phosphorus (TP) and 1.5 mg/l total nitrogen (TN). Sites that consistently displayed concentrations of TP and TN higher than the ET were influenced by wastewater treatment plants (WTP) or OWS. Sites with nutrient concentrations above the ET were likely influenced by the re-release of nonpoint source related TP and TN delivered to streams during storm events. Water quality and discharge at the spring outlet remained consistent over the sampling period suggesting diffuse recharge from a deep aquifer source is able to dilute shallow ground water sources carrying nonpoint pollutants at base flow. Historical and regional data comparisons show these trends have been consistent over at least the last two decades.

Keywords Karst · Spring · Water quality · Nutrients · Ozarks

Introduction

Karst environments are known to be highly susceptible to ground water pollution when surface runoff is transferred through subsurface conduits to spring outlets with little interaction with the aquifer matrix (White 1988). Sinkholes and losing streams can rapidly transfer water, sediment, and contaminants from upland recharge areas to negatively influence the water quality at spring outlets (Boyer and Pasquarell 1999; Lerch et al. 2005; Hasenmueller et al. 2006). Surface-to-spring contamination has been well documented for areas affected by both point and nonpoint pollution sources located in karst regions around the United States (Hallberg 1986; Boyer and Pasquarell 1995, 1996; Stueber and Criss 2005). Previous studies usually relate spring water quality to broad-scale land use activities and rarely to specific sources within the recharge area. The exception being a study by Younos et al. (2001) that identified pollution sources in a southwest Virginia karst system by collecting water quality data from the recharge area and spring outfalls to assess potential sources of water quality impairment.

How surface water enters the groundwater system is important for both water quality and quantity. The most common mechanism for groundwater recharge occurs by the relatively slow downward movement of water through soil and rock over a large area known as diffuse recharge,

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which maintains a high storage volume providing a consistent supply of water to springs (White 1988). In addition to diffuse recharge, aquifers in karst terrain receive the relatively rapid transfer of water through sinkholes or losing streams connected by subsurface conduits (White 2006). Surface water entering the aquifer in this fashion has very little contact with soil or rock and consequently the chemical nature of the water changes little in route (Bullard et al. 2001; Lerch et al. 2005).

Pollution sources change when stream flow is dominated by either storm events or base flow. During storm events, nonpoint pollution from runoff water moving over the landscape washes into nearby streams or karst openings (Novotny and Chesters 1989; White 2006). During base flow conditions, when there is less dilution by runoff, point sources are the main contributor of pollution (USEPA 2008). While this conventional approach to pollution sources is widely understood, studies show that nonpoint sources can impact base flow water quality depending on the source and nature of the constituent. For instance, storm events can transport sediment-bound pollutants such as phosphorus into aquatic ecosystems that can equilibrate with the surrounding waters and can become biologically available (Correll 1999). In addition, failing or improperly sited and constructed on-site wastewater systems (OWS) can contribute to poor base flow water quality, and can go undetected for decades (Greene County 2003; Kelly et al. 2009).

In the Missouri Ozarks, regional ground water quality assessments were conducted in the early 1990s by the United States Geological Survey (USGS) to analyze nutrients and pesticides in both wells and springs. They concluded that agricultural land uses were responsible for the variability in the concentrations of nutrients and occurrence of pesticides in the regional ground water supply (Adamski and Pugh 1996; Adamski 1997). Ground water quality and surface water quality in the Ozarks tend to be linked by karst networks so that one is always affecting the other (Petersen et al. 1998). Dye-tracing studies can be used to map potential source areas, however, there have been few successful studies that were able to directly link surface contamination with spring water quality at the watershed-scale.

Bennett Spring is the fourth largest spring in the state and is the centerpiece of a long standing trout hatchery and associated tourism industry (Vineyard and Feder 1974). The hydrogeology of the Bennett Spring area has been studied extensively by the Geology Division of the Missouri Department of Natural Resources (MDNR), and the karst connections between the recharge area and the series of smaller springs and losing stream sections have been extensively mapped (Vandike 1992). Dye tracing of losing sections has identified recharge contributions from watersheds that contain point sources, such as municipal wastewater treatment plants (WTP) and non-municipal industrial discharges, as well as nonpoint sources from urban development and agricultural activities. However, the impact of these potential sources on water quality is presently unknown.

The purpose of this study is to establish a baseline dataset for evaluation of current water quality conditions throughout the Bennett Spring Recharge Area (BSRA) and to assess the potential impacts of pollution sources within the BSRA on the spring during base flow conditions. The specific objectives of this study follow: (1) establish a sampling network within the BSRA using the most up-to-date estimates of ground water flow direction; (2) collect water samples monthly for 1 year and analyze for discharge, water chemistry, and nutrients at base flow; and (3) interpret water quality trends and assess the spatial variability of water quality within the recharge area.

Study area

The Bennett Spring Branch Watershed (BSBW) drains 111 km^2 of eastern Dallas County and western Laclede County and is located in the Niangua River Basin (2,665 km^2). The BSBW represents the topographic drainage area that generates surface flow above Bennett Spring. Bennett Spring is located 2.5 km upstream of the confluence with the Niangua River, has an average daily flow of 4.7 cubic meters per second (cms), and provides nearly all of the flow from the BSBW during base flow conditions (Vandike 1992). The BSRA, much larger than the BSBW, has an estimated area of nearly 674 km^2 that crosses the topographic drainage divide into the Gasconade River Basin in southern Laclede County (Fig. 1). The underlying geology is predominately horizontally bedded dolomite with layers of shale and sandstone also present (Sturdevant et al. 2001).

The surface landscape of the BSRA is typical of the Ozark Plateaus Province. The broad flat uplands of the Lebanon Plain near Interstate 44 are underlain by an interbedded dolomite/sandstone formation and contain numerous sinkholes (Harvey et al. 1983). Soils in the area feature thin (<1 m) deposits of loess over cherty residuum derived from limestone and dolomite bedrock (Sturdevant et al. 2001). Land use within the BSBW is mostly forest (54%) with grass/pasture representing the second highest land use (41%) (Table 1). Land use within the larger BSRA is similar, but grass/pasture is the highest land use category (55%) followed by forest (34%). High intensity land uses, such as cropland (4.5%) and urban area (4.9%), are also represented in the BSRA.

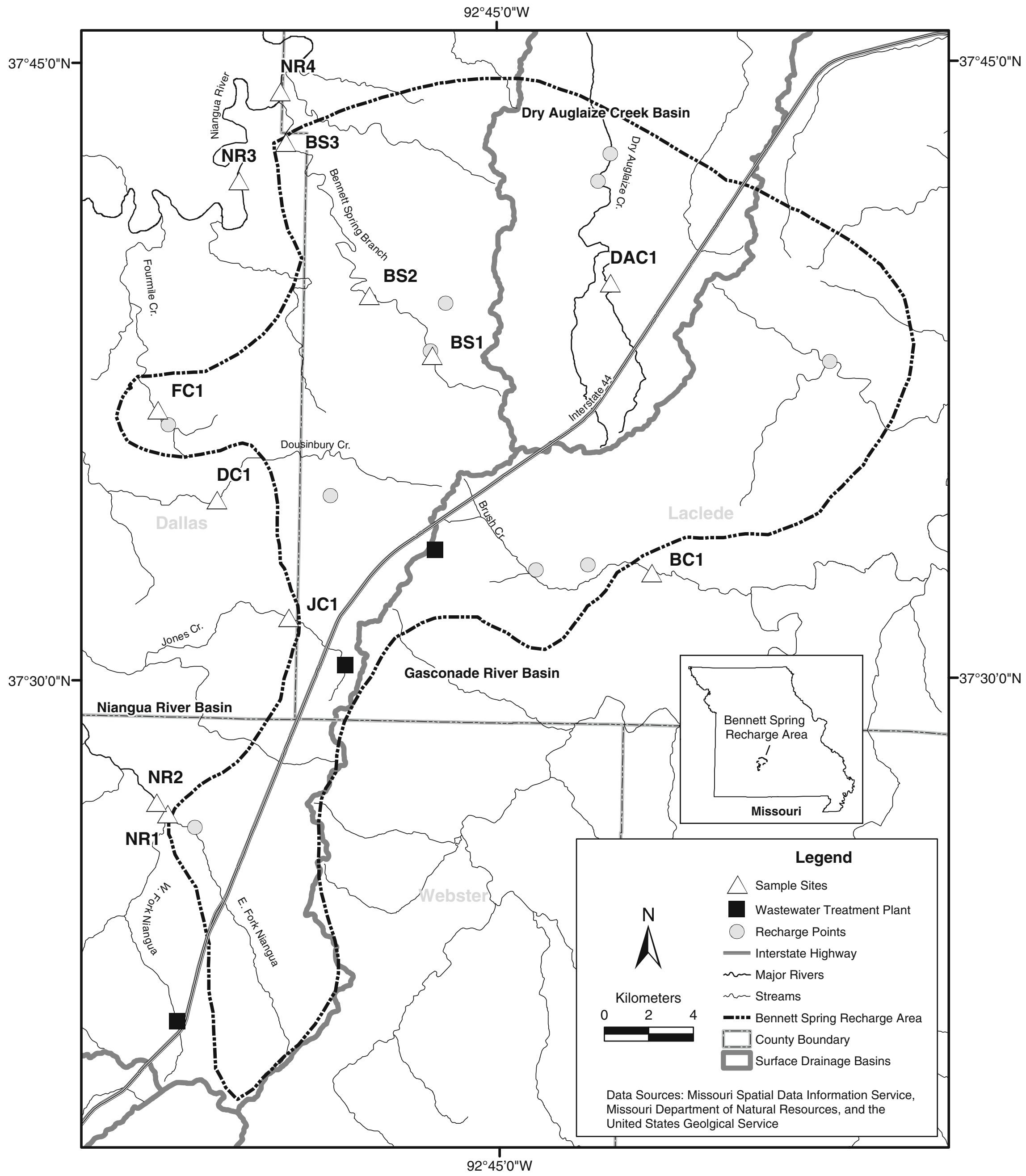


Fig. 1 Sample site map of study area

Methods

Site selection and watershed analysis

Monthly sampling of water quality and discharge occurred at 12 sites for a 1 year period from March 2007 through February 2008. Sampling sites were selected based on two criteria. First, sites had to be within the BSRA boundaries based on a series of dye-tracing experiments by the MDNR in 1992, or along the Niangua River upstream and downstream of the spring tributary confluence (Fig. 1). Second, sites were located in areas where the drainage network was adjacent to public land, typically the right-of-way along public roads at bridge crossings, or at parks and public river access points.

The distribution of the 12 sites chosen for this project included sites at Bennett Spring, within the BSRA, and along the Niangua River at locations above and below the confluence with the spring. The outfall of Bennett Spring is in Bennett Spring State Park near a historical USGS gaging

Table 1 Sample sites with upstream drainage area and land use data

Site #	Stream name	Ad[a] (km^2)	% in BSRA	Urban (%)	Crop-land (%)	Grass/pasture (%)	Forest (%)
Bennett Spring							
BS3	Bennett Spring Outflow	110	100	1	3.2	41	54
Niangua River							
NR3	Upstream of Bennett Spring	998	19	2	5.8	52	38
NR4	Downstream of Bennett Spring	1,141	27	1.8	5.6	50	40
BSRA tributaries with no WTP							
BS1	Bennett Spring Branch	11	100	1.7	2.5	38	57
FC1	Fourmile Creek	11	82	1	9.8	78	10
DAC1	Dry Auglaize Creek	20	100	6.9	2.6	73	15
BS2	Bennett Spring Branch	52	100	1	4.7	48	45
DC1	Dousinbury Creek	55	85	1.6	7.1	61	30
NR1	East Fork Niangua	66	92	5.1	4.5	45	43
BSRA tributaries with WTP							
JC1	Jones Creek	15	93	7.1	7.9	56	26
BC1	Brush Creek	79	89	1.5	4.4	63	30
NR2	Niangua River	144	47	6.3	4.4	50	37

[a] Surface drainage area

station that has been in operation since 1916. The Niangua River sampling sites are located upstream and downstream of the confluence with the Bennett Spring Branch to understand how the spring affects the larger river system. The remaining nine sites are within the BSRA. Only two sites are located within the topographic watershed boundary of the BSBW upstream of the spring. The other seven sites are located along streams in the BSRA near known losing sections verified by previous dye-tracing studies.

Topographic watershed areas above each of the selected sites were delineated from a 30-m digital elevation model (DEM). This area was used to “clip” a simplified 2005 land use dataset published by the Missouri Resource Assessment Program (MoRAP). Land use categories were converted into percentage of total land use for each watershed area. Watershed polygons were also used to locate WTP locations within the topographic watershed above each sampling location. Table 1 summarizes the sample sites selected for this project including major land use categories and drainage area details along with the amount of the recharge that is within the topographic watershed above each sampling location by percentage.

Sample collection and discharge

Grab samples were collected monthly by hand during shallow, integrated base flow at each site in 500 ml plastic bottles, preserved, and cooled in the field. A field duplicate was also collected twice during the day, once in the morning and once in the afternoon, to assess variability due to sample collection technique. A total of 134 samples were collected, including 24 duplicate samples, which yielded from 5 to 12 individual monthly samples per site. During part of the sampling period some sites experienced no flow conditions resulting in less than 12 samples being collected. If water was present in stagnate pools and not hydraulically connected, samples were not analyzed.

Physical water parameters were measured at each site by a Horbia U22 multi-probe meter. Parameters measured include temperature, specific conductivity (SC), and pH. A duplicate measurement was also collected twice a day at the site of the field duplicate for nutrients to assess site variability of the instrument measurements. Median relative percent difference (RPD) for field duplicates over the sampling period were <5% for all parameters.

Discharge was estimated either by direct measurement of velocity in the field with a flow meter, from USGS gaging stations, or by estimation of discharge for reaches located immediately up or downstream of a USGS gage (OEWRI 2006a). Due to the karst characteristics, very low and non-persistent flow during the sampling period made it difficult to sample at each location consistently.

Laboratory analysis

Water samples were analyzed at Missouri State University’s OEWRI Laboratory using USEPA approved Standard Operating Procedures (SOP) in the MDNR approved Quality Assurance Project Plan (QAPP) (OEWRI 2006b, 2007a, b (SOP and QAPP can be accessed at oewri.missouristate.edu)). The QAPP describes in detail the sampling, preservation, and analytical procedures, along with the quality assurance and quality control protocol used for this project. Nutrient concentrations were determined through acid digestion and spectrophotometer analysis. Average detection limits for this method are 0.2 mg/l total nitrogen (TN) and 0.003 mg/l total phosphorus (TP) with a precision and accuracy of less than or equal to 20%. The median RPD of the field duplicate for the sampling period was 9.1% for TP and 5.4% for TN. The 25th and 75th percentile rank for the RPD of the field blanks for the entire study was 3.3 and 23% for TP and 2.3 and 9.4% for TN.

Data analysis

Flow characteristics during sample collection were recorded when feasible. Four different conditions were observed over the sampling period; (i) presence of measurable flow, (ii) flow observed moving through gravel deposits, but was too low to measure, (iii) water standing in disconnected pools and no flow observed, or (iv) as dry conditions during sampling. Monthly mean Q over the sampling period is compared to monthly mean Q trends at sites with USGS gaging stations to understand how the relative hydrological conditions from the study period relate to long-term trends. In addition, mean sample Q at each site is compared to long-term Q statistics from 39 USGS gaging stations in the western Ozarks by drainage area to understand how Q from this study relates to the regional hydrological record.

Individual monthly water chemistry and nutrient concentrations at each site are compared over the sampling period to assess variability among sites and to identify sites that do not follow overall trends. Monthly discharge and nutrient data are compared at selected sites to highlight how the source-to-spring linkage varies throughout the year. The variability in nutrient concentrations within a single site is also compared to published water quality criteria to classify the impairment status of each site. Eutrophic threshold (ET) criteria were used to evaluate nutrient impairment status for each site. While the EPA has set reference conditions for nutrients in Ozarks streams very low (0.0066 mg/l TP, 0.38 mg/l TN), Dodds et al. (1998) used data from lakes and reservoirs to set an ET that could be used to determine trophic state (USEPA 2000). These data have been used to set total maximum daily load (TMDL) limits for watersheds in the Ozarks that are influenced by WTPs where nutrient concentrations are predicted to reach the ET at 0.075 mg/l for TP and 1.5 mg/l for TN (MDNR 2001).

Finally, data collected for this study are compared to historical water quality and discharge data collected by the USGS in the early 1990s at Bennett Spring in order to evaluate the long-term water quality trends at the spring. Comparisons to similar base flow water quality and discharge data collected in the Ozarks region using similar field and laboratory protocol were also evaluated.

Results and discussion

Watershed characteristics

The BSRA is mainly an agricultural area. The major land use category for 10 of the 12 watersheds above the sampling locations is grass/pasture type agriculture with 8 of these 10 watersheds having this land use category covering at least 50% of the area (Table 1). The dominant ground cover for this land use category would be fescue or other cool-season grasses used mainly as forage for beef and dairy cattle. Forest land cover is mostly second growth oak–hickory timber and is the major land use category above 2 of the 12 sites with grass/pasture being the second highest category for both. Cropland, typically corn or soybeans, is found in >5% of the total watershed area at 5 of the 12 sites. Urban land use ranges from 1 to 7.1% above sites within the BSRA and is >5% of the total watershed area above 3 of the 12 sites.

Municipal WTPs are located above three of the sampling sites in the spring recharge area. Not including the spring sampling site, there are no permitted point sources within the watershed above 6 of the 12 sites. Three sites on the Niangua River have WTPs located upstream, but NR3 and NR4 are located above and below the Bennett Spring branch to see how the spring influences the larger Niangua River. For most of the sites, the percentage of the BSRA within the topographic watershed area was >80% suggesting characteristics of the samples collected at these sites are representative of the BSRA. The exception to this is the site at NR2 where less than half of the upstream watershed area is within the BSRA.

Base flow hydrology and sampling

Base flow conditions were variable throughout the sampling period, despite efforts to select field sites with permanent flow. Discharge variability over the course of the 1 year sampling period caused an incomplete sampling record for 8 of the 12 sites within the study area (Table 2). Discharge variability does not seem to be controlled by drainage area, but rather the conduit capacity of losing stream sections that can transport the entire volume of base flow during dry periods in the year. Only 4 of the 12 sites had flow throughout the year with one site being the spring and the other two being the larger Niangua River sites upstream and downstream of the Bennett Spring Branch. Again, only samples collected when flow was present at a

Table 2 Discharge variability over the 1 year sampling period

Site (sample *n*)	Ad[a] (km^2)	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.
BS1 (6)	11	×	×	×	×							•	×
FC1 (7)	11	×	×	×	×	•						×	×
JC1 (10)	15	×	×	×	×	×	•	•	○	○	×	×	×
DAC1 (8)	20	×	×	×	×	×	○	×	○	○	○	×	×
BS2 (6)	52	•	•	•	•	○	○	○			○	•	×
DC1 (11)	55	×	×	×	×	×	×	×	•	○	•	×	×
NR1 (5)	66	×	×	×							×		×
BC1 (12)	79	×	×	×	×	×	×	×	×	×	×	×	×
BS3 (12)	110	×	×	×	×	×	×	×	×	×	×	×	×
NR2 (9)	144	×	×	×	×	×	○	•	○	○	×	×	×
NR3 (12)	998	×	×	×	×	×	×	×	×	×	×	×	×
NR4 (12)	1,141	×	×	×	×	×	×	×	×	×	×	×	×

×, flow; ○, standing pools; •, flow too low to measure; blank, no water

[a] Surface drainage area

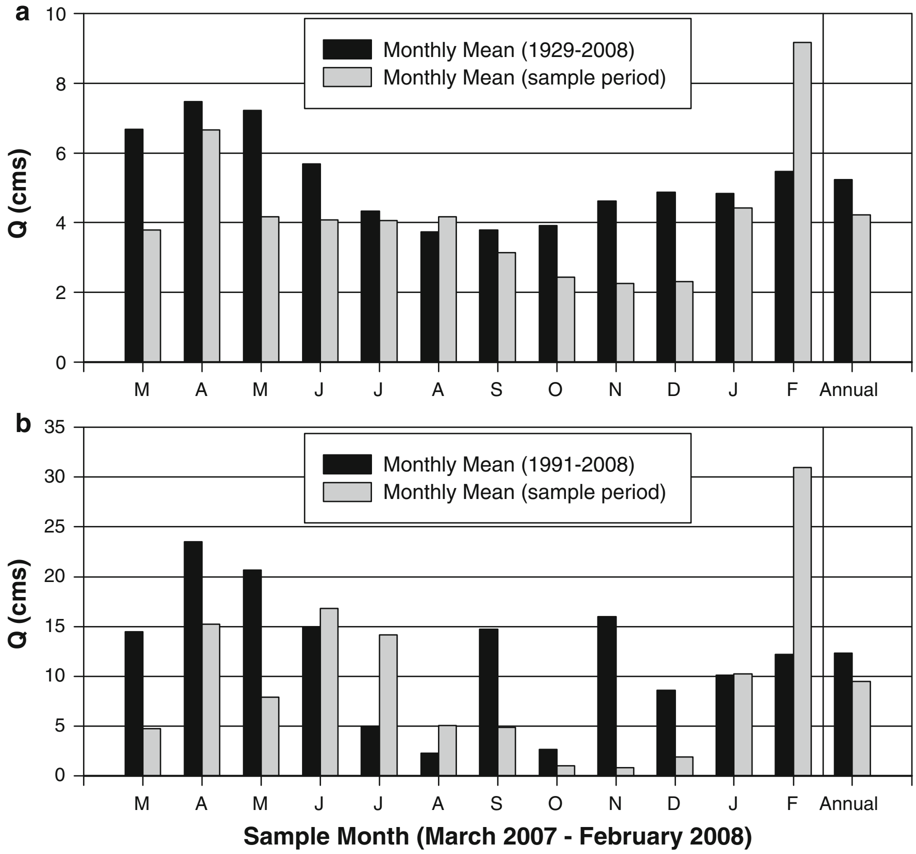


Fig. 2 Mean monthly *Q* for the sampling period at USGS gaging stations. Historic monthly mean *Q* versus month mean *Q* of the sampling period at USGS gaging stations at **a** Bennett Spring (USGS gage 06923500) and **b** Niangua River at Windyville (USGS gage 06923250)

site were analyzed. Water from disconnected standing pools was not analyzed.

Comparing monthly mean *Q* for the sampling period to the historical monthly mean at two USGS gaging sites within the study area showed the sampling period was relatively dry compared to the historical average (Fig. 2). The Bennett Spring record is longer and more consistent over the sampling period than the Niangua record, which shows greater flow variability. Still, a significant dry period beginning in the summer and lasting through the late fall was able to affect the hydrology of the spring. Even with all of the variability experienced over the sampling period,

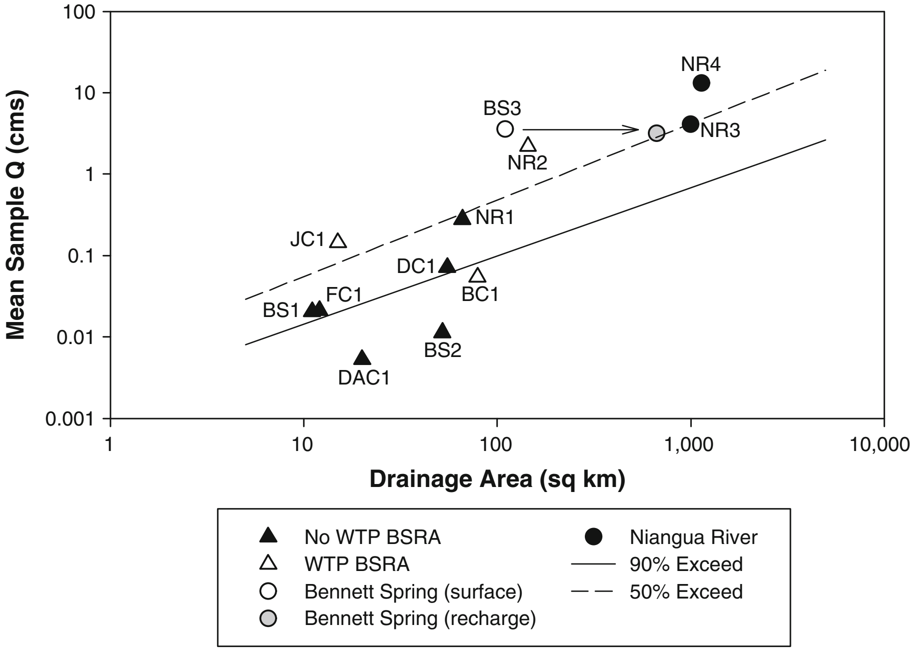


Fig. 3 Mean discharge comparison to regional flow frequency curves. Mean sample *Q* versus drainage area compared to best-fit line representing median flow ($R^2 = 0.97$) and 90% ($R^2 = 0.73$) of all flows exceeded for discharge statistics at 39 USGS gaging stations in the western Ozarks

average *Q* over that time was lower than the historical average at both gages.

High variability in base flow *Q* over the sampling period shows the impact of karst in the form of losing and gaining stream sections within the BSRA. When comparing mean sample *Q* by drainage area from this study to regional USGS gage data, the majority of the BSRA sample *Q* fall near or well below median flow (the 50% exceed line on Fig. 3). The dramatic difference between the mean base flow sample *Q* among sites illustrates the impact of karst on losing and gaining stream sections at sites within the study area. Mean sample *Q* ranges from near the median flow to well below the 90% exceedance for the region for similar watershed drainage areas. Sites with lower mean sample *Q* are reflecting the losing sections among sites while the sites with higher mean sample *Q* are reflecting the gaining, or neutral, stream sections among sites.

The site at Bennett Spring (BS3) shows how the recharge area and surface drainage area compare to *Q* at similar watershed areas in the region. Mean sample *Q* at this site was much higher than the regions median *Q* for a similar size watershed using the surface drainage area to compare. However, using the recharge area for the drainage area comparison, the mean sample *Q* is close to the region median values. This is also reflected in the Niangua River sites where sample *Q* is impacted by the inputs from the spring. The mean sample *Q* at site NR4 is well above the NR3 sample *Q*, which is near the median regional *Q*, with a relatively small increase in drainage area. This is because the BSRA, supplying water to NR4, falls beyond the Niangua River surface drainage boundary and is not reflected in the comparison.

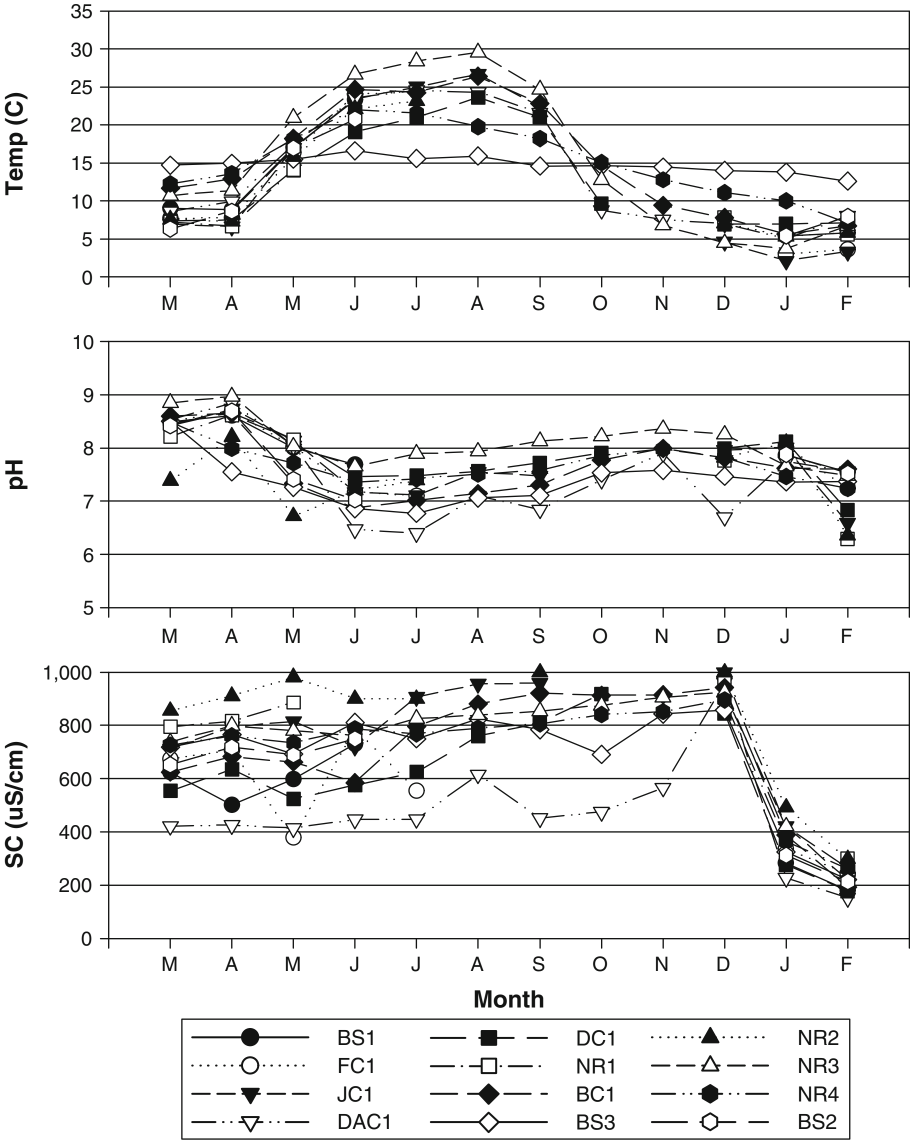
These types of data might prove useful when trying to estimate recharge area size for springs. Analysis such as this may be used in conjunction with dye-tracing studies as supporting evidence for the size of recharge area boundaries. Dye tracing has proven extremely valuable when trying to link observations of water pollution to sources of contamination in karst terrain (Aley and Thomson 2002). Further study is needed to understand both the fluctuations in *Q* and precipitation over long and short-term climate variations and how they relate to the large, deep aquifer fed streams in the Ozarks.

These findings also have implications for water quality monitoring in karst systems such as the Ozarks. In these types of systems the rapid subsurface transfer of water can bypass typical surface drainage routing making the line between base flow and storm flows unclear. Understanding the hydrological variability of the watershed is critical to assigning proper load calculations to annual discharge estimates used to establish nutrient criteria for anticipated uses or TMDL limits required by the Clean Water Act (USEPA 2008).

Physical water parameters

Physical water parameters fluctuated seasonally over the sampling period both at sites and among sites. Temperature followed seasonal trends over the sampling period, with the exception of the site located at the spring (BS3) (Fig. 4). Temperature readings at the spring (BS3) varied little throughout the sampling period staying within a few degrees of 15°C throughout the year. Water temperatures for the remaining sites were relatively low in the early

Fig. 4 Monthly temperature, pH, and SC data by site



spring, begin rising in the summer and into the early fall, before dropping again in the fall and winter months. With the exception of BS3, temperature readings did not vary more than 10°C among sites over any given month over the sampling period.

The pH of the water over the sampling period remained buffered to slightly alkaline over the sampling period, rarely dropping below 7 (Fig. 4). Seasonally pH readings were highest in the spring and then dropped in the summer before rising in the fall and early winter and then dropping again at the end of the sampling period. Variability among sites was <2 standard pH units over the sampling period. DAC1 and NR2 had isolated drops in pH at various times over the sampling period.

Over the majority of the sampling period SC was highly variable among sites ranging from 400 μS/cm to over 900 μS/cm (Fig. 4). Starting in December, variability decreased as all SC measurements became consistently high (>800 μS/cm) among sites and then dropped dramatically (<500 μS/cm) in January and February remaining consistent among all sites. The December increase probably signifies the first pulse of water moving through the system and flushing of accumulated soluble weathering products after the long drought period, with the wet winter causing a dilution effect in January and February.

Total phosphorus

Concentrations of TP showed moderate variability over the sampling period. For the majority of the sites, TP concentrations remained below 0.05 mg/l over most of the sampling period (Fig. 5). Sites NR2, JC1, and DAC1 remained above the ET over the sampling period when flow was available to sample with the exception of the dry

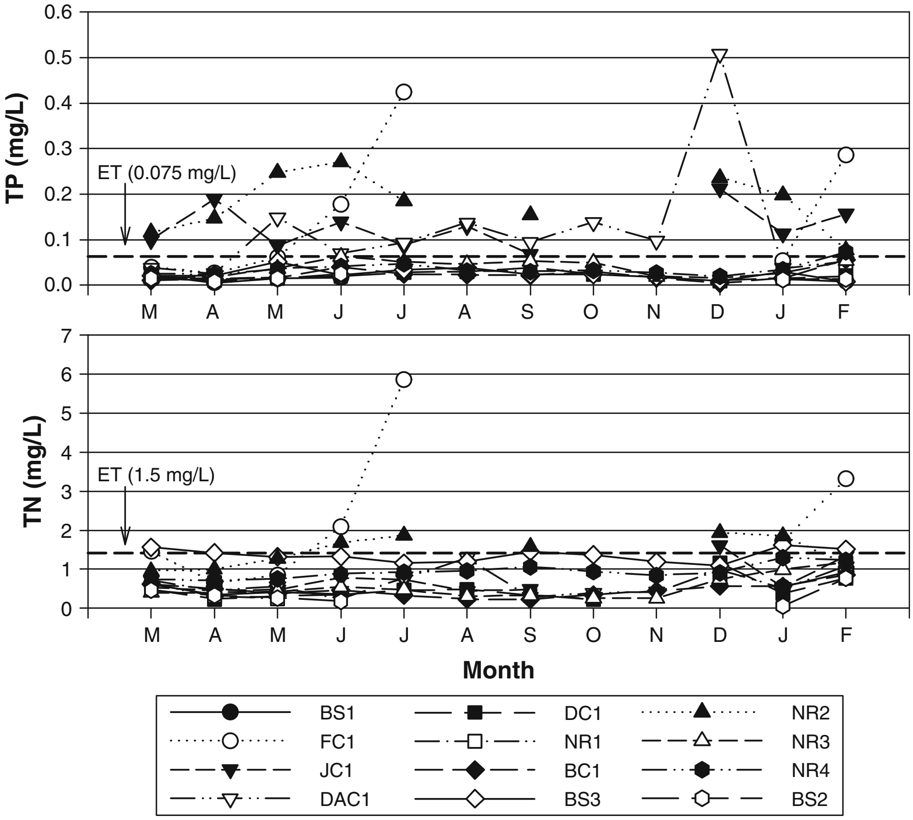


Fig. 5 Monthly TP and TN data by site

period experienced in the fall when there was no water at NR2 and JC1. Site FC1 had isolated high concentrations in June and July and again in February.

Concentrations of TP are influenced to some degree by WTPs in the BSRA. Of the three sites influenced by a WTP, two (JC1 and NR2) are consistently higher than the ET of 0.075 mg/l TP when water is available to sample. Because these sites are influenced by WTP, a consistent source of TP and *Q* is available to these streams. The fact that these streams can go dry shows that water high in TP from these WTP facilities is entering the groundwater system through losing stream sections within the BSRA. Site BC1 is also influenced by a WTP, but TP concentrations here remained below the ET. The WTP facility located upstream of BC1 is the smallest in the study area with a design flow of 121 m^3/d, compared to 312 m^3/d (JC1) and 5,678 m^3/d (NR2) (MDNR 2010). Due to the relatively small size of the WTP and the distance from the sampling point, effluent could be diluted downstream.

Sites without WTP are also high in TP at certain times of the year. FC1 and DAC1 have TP concentrations higher than the ET over most of the sampling period. Concentrations at FC1 are highly variable when water was available to sample. The high variability in sample concentrations at FC1 suggests remobilization of nonpoint sources of TP rather than a consistent source, such as poorly functioning on-site wastewater treatment systems. Storm flows may be responsible for transporting pollutants to the stream system, but seasonal hydrologic conditions may cause the re-release of TP to the system during base flow conditions suggesting temporary storage in karst conduits.

Concentrations of TP collected at DAC1 show a different pattern. Concentrations of TP remain consistently high between May and November. The low variability in concentrations over that time span suggest a consistent supply of TP to the system regardless of rainfall and growing season influence. Inadequately sited or constructed OWS have the potential to impact springs at base flow when septic tank effluent bypassing soil treatment is less dilute and can enter the ground water system through fractures in bedrock (Aley and Thomson 2002; Kelly et al. 2009). Then, in much the same manner as SC, TP spikes in December as *Q* picks up after the fall dry period. January and February samples, during the relatively wet winter period, fall well below the ET suggesting dilution of the consistent source in that watershed.

While sources of TP and direct links to streams with high TP concentrations within the BSRA can be made, they do not seem to influence the spring during base flow conditions. The site at Bennett Spring (BS3) displayed very consistent TP concentrations staying <0.05 mg/l over the sampling period. Surface water with potentially high concentrations of TP entering the aquifer through losing streams appears to be only a small portion of the total discharge of the spring and is effectively diluted by relatively clean water from its apparent main source, diffuse ground water recharge.

Total nitrogen

Concentrations of TN showed less variability over the sampling period when compared to TP concentrations. For the majority of the sampling period, TN concentrations at all sites were less than the ET of 1.5 mg/l (Fig. 5). Similar to TP, variability to that trend is seen at WTP sites NR2 and JC1, and at the site FC1 without WTP influence. At all three sites, TN concentrations were slightly elevated during June and July and again from December through February, both times where short-term rainfall was higher than normal. Site FC1 has the highest percentage (about 90%) of agricultural land use of all basins. In agricultural watersheds, nitrates from fertilizers are known to move through the shallow ground water system and enter streams (Sharpley et al. 1987).

Bennett Spring (BS3) had fairly consistent TN concentrations over the majority of the sampling period. Concentrations of TN ranged from 1 to 1.5 mg/l until the winter months, where they were slightly higher. Overall, TN concentrations at BS3 were elevated when compared to the other sites in this study. Nitrogen, unlike phosphorus, tends to stay in its dissolved form and could migrate through porous bedrock with water and re-emerge at the spring through ground water recharge even in diffuse recharge areas.

Results of this study show that Bennett Spring is a nitrogen source to the Niangua River system. Concentrations of TN increase from above to below the Bennett Spring Branch tributary at the Niangua River sites. These data suggest springs are a significant source of nitrogen loading to Ozarks stream systems during base flow conditions. However, the Niangua River sites did not exceed the ET limit over the sampling period. Again, these findings are important when accessing potential pollution sources for water quality monitoring studies in the Ozarks where understanding N:P ratios is important for limiting eutrophic conditions (MDNR 2001).

Seasonal variability in discharge and water quality

Comparison of monthly temperature and discharge measurements collected over the sampling period at four selected sites show differences in seasonal variability associated with the stream's source water (Fig. 6). These sites represent different hydrologic source situations. Site DC1 (55 km^2) is within the BSRA and is not influenced by a WTP. Site BC1 (79 km^2) is also within the BSRA and is influenced by a WTP. The sites within the BSRA were chosen based on similar drainage areas and consistent flow throughout the sampling period. Site BS3 (110 km^2) is the spring with a very small topographic drainage area compared to the amount of discharge it produces. Site NR3 (998 km^2) is along the Niangua River above the confluence with the spring and is influenced by a WTP.

Discharge was least variable at the spring (BS3) throughout the sampling period. This observation again suggests a connection to the deep aquifer as the water supply to base flow discharge at Bennett Spring. Discharge decreased slightly over the sampling period at BS3 until February 2008 when base flow was high after a series of large storm events that winter. For sites DC1 and BC1, Q decreases from March to November and rebounds in the later part of the sampling period. The Q at NR3 actually increases from March to June and then decreases to November, showing that the larger river lags behind the smaller streams, which are more sensitive to short-term precipitation fluctuations.

Consistent temperature readings at the spring (BS3) help verify that water emerging at the spring is from a different source than the other selected sites. Temperature trends were similar among the other sites throughout the sampling period, rising in the spring and summer and falling in the fall and winter. Site NR3 on the Niangua River had the highest fluctuation in temperature among selected sites. The non-WTP impacted site DC1 had lower temperature than the WTP site BC1 over the sampling period indicting treatment plant effluent was affecting the water at this site and not simply leaving the stream through a losing section upstream of the sampling site.

While the data presented here is limited, pollution source water seems to impact seasonal variability in nutrient concentrations within the BSRA. Concentrations of TP in non-WTP (DC1) watersheds versus watersheds containing a WTP (BC1) both peak near 0.04 mg/l, but DC1 peaks in the early fall while BC1 peaks in the early summer (Fig. 7). Concentrations of TN remain low through the majority of the sampling period for the sites within the BSRA until the winter months when they begin to rise. The spike in TN concentrations in December at DC1 is not seen at BC1. This suggests TN concentrations in WTP influenced sites could be less susceptible to seasonal precipitation cycles at base flow reflecting the influence of a consistent source. Again, high nutrient concentrations are reflected at base flow following a relatively wet period in the final month of the sampling period. This is not only due to the attenuation of storm-event related nonpoint pollution through the karst system, but also to the decrease in nutrient uptake by dormant vegetation within the watershed.

Nutrient concentrations at the spring (BS3) do not follow the same pattern as the other sites. Concentrations of

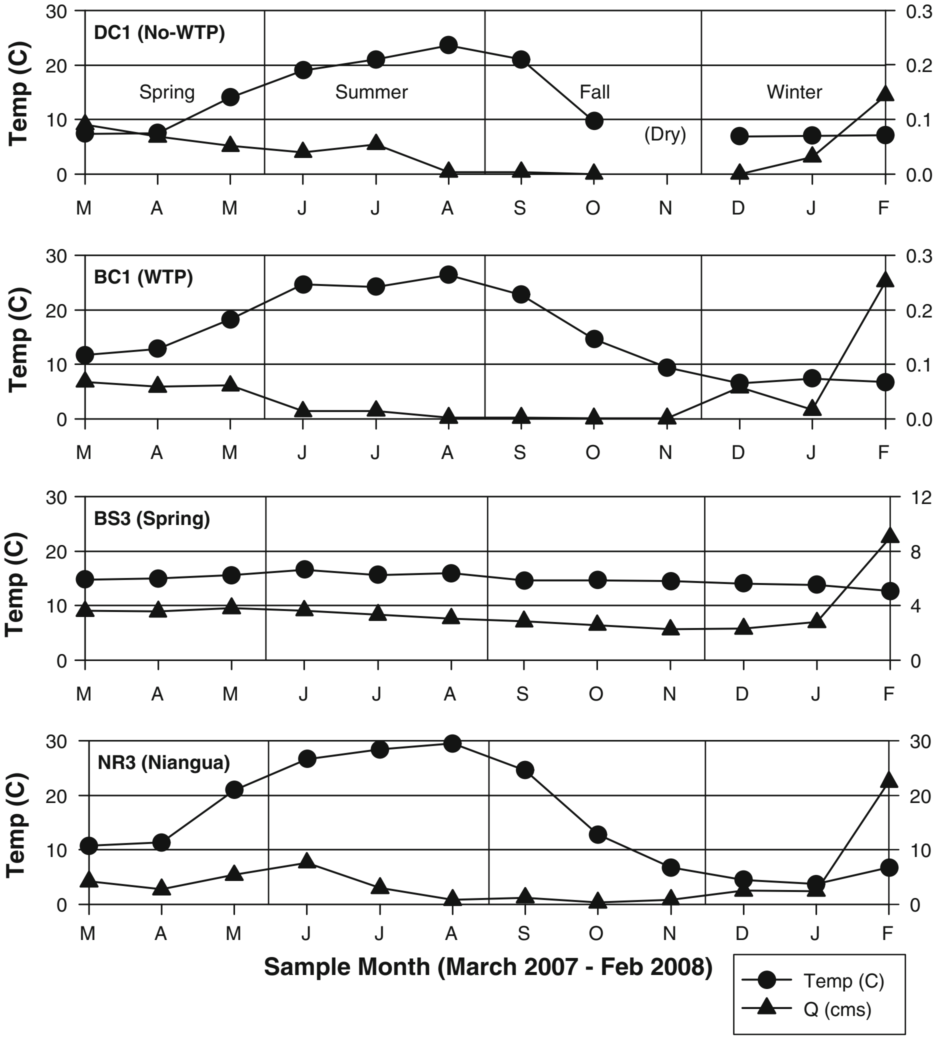


Fig. 6 Seasonal temperature and *Q* variability at selected sites

TP peak near 0.05 mg/l in the late spring and show a steady decrease for the remainder of the sampling period. This trend stays true for the final sampling month when TP concentrations increase for the sites within the BSRA and site NR3 located upstream of the spring branch. The spring site has consistently higher concentrations of TN among sites and displays the same winter increase as the other sites, peaking sooner and lasting longer than the others. Again, these data suggest that while the upland sites are connected to the spring via karst conduits, characteristics of waters in the BSRA are not reflected in the springs water quality at base flow. The site at NR3 along the Niangua River has the highest variability in seasonal TP concentration, ranging over 0.04 mg/l from the spring to the summer and having a secondary peak again from the fall to the winter months. Concentrations of TN at NR3 also follow a similar trend to the BSRA sites with relatively low concentrations for the majority of the sampling period and rising in the winter months.

Historical and regional water quality trends

Historical data from the USGS station at Bennett Spring (USGS Gage 06923500) is compared to data from this study to understand the relationship of base flow water quality to high flows and to compare data over time. The USGS collected water quality data at Bennett Spring between 1991 and 1995 at several different intervals, from weekly to monthly, over the 4 year sampling period. Types of water data compared are; discharge, TP, TN, SC, pH, and temperature. In this dataset USGS detection limits ranged from 0.01 to 0.02 mg/l TP while detection limits for the current study were 0.003 mg/l for TP.

Data for this study were collected at much lower discharges than the USGS dataset. Sample discharges at the 75th percentile for this study are less than the 25th percentile sample discharge for the USGS dataset (Table 3). Again, this study emphasized collecting data at base flow conditions and not a range of flows. The emphasis on base

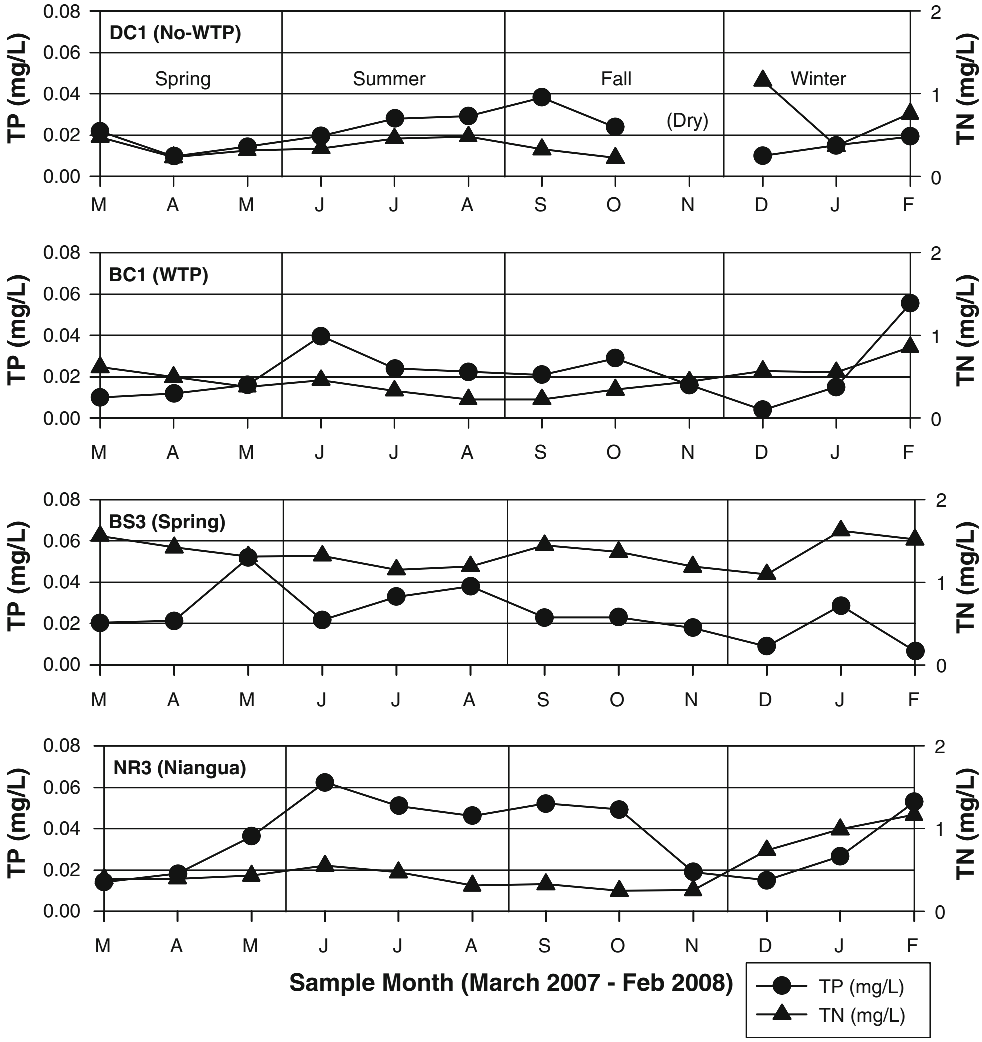


Fig. 7 Seasonal TP and TN variability at selected sites

flow and drier than normal conditions experienced over the sampling period likely accounts for the lower pH levels and higher SC and temperature data collected during this study compared to the USGS. When comparing the sample discharge from both datasets to the mean daily discharge for the gage, the majority of the USGS samples were collected above the 50% exceedance for that station (Fig. 8). The majority of sample discharges for this study fall between 90 and 50% exceedance flows for this gage, with some data collected during flows less than the 90% exceedance. Data from this study extends the low flow water quality record at this site that can be used to more accurately assess and model annual loads and understand contamination dynamics during drought conditions.

Data reported by the USGS and the present study at Bennett Spring show TP and TN concentrations follow similar trends given the analytical limitations of the higher detection limit used in the USGS study. Nutrient concentrations at the spring are consistent regardless of discharge variability due to groundwater controls. This study targeted base flow conditions as opposed to the USGS sampling design which sampled a range of flows over a set interval of time. Given this flow disparity, these trends suggest present nutrient concentrations at this site are similar to levels collected in the early and middle 1990s. Accounting for the higher detection limits for the USGS it is evident that ambient nutrient concentrations have probably remained at similar levels over the last two decades.

Recent water quality studies in the Ozarks that include base flow sampling show that water quality at Bennett Spring and the BSRA is similar to regional trends. Regional data include sites from a range of land use types including urban, agricultural, and forested watersheds. Studies that include sites with similar drainage areas and mean sample *Q* as this study yield similar ranges of nutrient concentrations (Table 4). Site specific mean concentrations of TP for this study range from 0.013 to 0.181 mg/l TP, while regionally TP concentrations range from 0.006 to 2.03 mg/l TP. Mean concentrations of TN for this study range from 0.34 to 1.68 mg/l TN, while TN

Table 3 Historical nutrient data comparison (USGS gage 06923500)

Parameter	n	USGS			n	MSU (OEWRI)		
		25th Percentile	50th Percentile	75th Percentile		25th Percentile	50th Percentile	75th Percentile
Q (cms)	54	4.1	4.7	6.1	12	2.7	3.2	3.6
TP (mg/l)	57	0.02	0.02	0.03	12	0.02	0.022	0.03
TN (mg/l)	8	1.48	1.55	1.73	12	1.19	1.34	1.47
SC (μS/cm)	52	315	365	392	12	692	757	814
pH	52	7.4	7.6	7.6	12	7.1	7.4	7.5
Temp (°C)	59	7.7	8	8.5	12	14.3	14.7	15.5

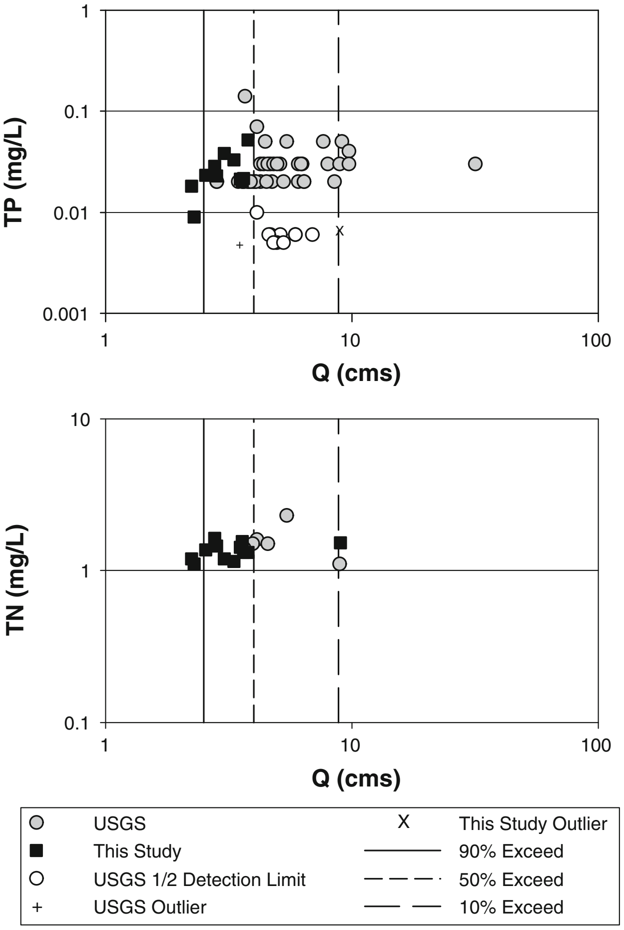


Fig. 8 Comparison of TP and TN concentrations versus sample discharge to historical USGS data at Bennett Spring (USGS gage 06923500). *Note*: USGS 1/2 Detection Limit data is plotted to show that low concentrations were sampled, but reported as less than the method detection limit

concentrations range from 0.38 to as high as 11.7 mg/l TN in waters impacted by WTPs across the region.

Conclusions

Results of this study show the variability in Q and nutrient concentrations in a small karst system at base flow. While data from this study are limited, some correlations do exist between higher nutrient concentrations and sites that drain areas with both point and nonpoint pollution sources. However, the variability in the recharge area did not correlate to similar variability in nutrients and Q at the spring. This trend appears to be consistent over time and throughout the region. The eight main conclusions of this study are described in detail below:

1. *Monitoring network established.* Recharge maps and field reconnaissance were used to develop monitoring network of nine sites within the BSRA using previous research and taking to account road access, proximity to known dye-trace locations, distribution of monitoring sites throughout the BSRA, and having permanent year-round flow. Sites within the study area were mostly grass/pasture type agriculture with WTPs located upstream of three of the sites.
2. *Base flow discharge is highly variable in the BSRA.* High discharge variability in the BSRA over the sampling period made sampling in this area difficult. Hydrological conditions experienced over the sampling period were dryer than normal, including a very dry period in late summer that lasted through the fall. Seasonal temperature and discharge fluctuate greatly throughout the year due to losing stream sections, seasonally high evapotranspiration rates, and a perched water table, all factors that are controlling flow conditions over the sampling period. The Niangua River also varies seasonally, but lags slightly behind the BSRA system. Meanwhile, temperature and discharge are very consistent at Bennett Spring indicating diffuse flow from the deep aquifer can maintain consistent discharge at the spring despite seasonal drought conditions. These data also show that the diffuse deep aquifer source can dilute potentially high concentrations of pollutants from the BSRA at the spring.
3. *Recharge area hydrology is important for water quality monitoring and dye-tracing programs.* Regional drainage area to Q relationships shows that the spring discharge and BSRA are similar to the regional

Table 4 Comparison of base flow water quality data from karst systems in the Ozarks

Study	# of sites	# of samples per site	Ad[a] (km^2)	Mean Q (cm)	Mean TP (mg/l)	Mean TN (mg/l)
Borchelt (2007)	**19**	**12**	**51–2,567**	**0.21–11.9**	**0.006–0.178**	**0.38–11.7**
Miller (2006)	10	17	7.2–50	0.02–0.54	0.028–0.176	0.77–2.98
Bowen (2004)	2	3–11	0.5–12.7	0.34–0.47	0.038–0.065	2.3–2.8
Richards and Johnson (2002)	**4**	**2**	**3.3–151**	**0.02–0.37**	**<0.05–2.03**	0.79–8.29[b]
This Study (2009)	**12**	**5–12**	**11–1,141**	**0.01–13**	**0.013–0.181**	**0.34–1.68**

Bold values, WTP influence at some sites

[a] Area drained

[b] Reported as nitrate, but reflects nitrate plus nitrite (Richards and Johnson 2002)

trend. These data might prove useful when trying to estimate recharge area size for springs when used in conjunction with dye-tracing studies as supporting evidence of recharge area boundaries. Furthermore, these data can enhance water quality models where the line between base flow and storm flows can be unclear and load allocations are important for understanding impairment criteria.

4. *Concentrations of TP had moderate monthly variability*. Watersheds influenced by a WTP had the highest concentrations of TP and were generally higher than established ET levels. For sites not influenced by WTP, concentration variability can be used to isolate sources. High variability suggests storm-event nonpoint transport and release at base flow, while low variability suggests consistent source inputs such as OWS. All samples collected at Bennett Spring were below the ET. Concentrations of TP were higher during the summer months in the BSRA and Niangua River, while TP concentrations stayed consistent at Bennett Spring throughout the sampling period due to dilution from deep aquifer sources.
5. *Concentrations of TN are relatively consistent*. Of the sites that exceeded the ET for TN, one was influenced by a WTP and one was an agricultural watershed. Bennett Spring had high TN concentrations compared to the other sites, but 75% of the samples were below the ET limit. Since the majority of TN is found in dissolved form, nonpoint sources from fertilizers or OWS are able to move into the aquifer. Data from this study show Bennett Spring is a TN source to the Niangua River during base flow conditions. Seasonally, TN concentrations did not vary until the winter months.
6. *Historical water quality trends remain similar over last two decades*. Water quality sampling for this study occurred at much lower flows than the USGS samples collected in the early 1990s. Data from this study helps complete the low flow water quality records for this gage and laboratory methods used to analyze TP quantify low concentration data that were unavailable in the USGS records. Trends show that the nutrient concentrations have remained relatively consistent over the last decade due to little land use change and clean deep aquifer sources at the spring.
7. *Diffuse base flow dilutes water from pollution sources within the BSRA*. Overall, the majority of the discharge at Bennett Spring is fed through diffuse recharge during base flow conditions and the sources of pollution, including point sources, within the BSRA have little or no effect on the water quality at the spring.
8. *Nutrient concentrations from this study appear similar to recent studies of karst systems in the Ozarks region.* Nutrient concentrations reported here are within the range of concentrations reported by other base flow studies in karst areas of the Ozarks at similar drainage areas over a range of land uses.

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