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Tributary contribution to the Spring River, AR as determined by water quality analyses

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Abstract

Tributaries often play an important role in the chemical properties, productivity and species diversity in a river channel. The objective of this study was to analyze the effect of tributaries on the water quality of the Spring River, AR. The Spring River has an approximate length of 92 km and has been divided into four zones according to the water source(s) that feed that segment of river. In this study approximately 30 km of the upstream river segment were sampled, which included nine tributaries contributing to the main river channel and incorporated the upper three previously defined zones. Samples were collected from the headwaters located at Mammoth Spring, AR, as well as within the tributaries and above and below the confluence of each tributary with the Spring River. Water-quality parameters analyzed included pH, conductivity, alkalinity, total suspended solids, fecal coliforms, nutrients (orthophosphate, nitrate, nitrite), and total dissolved ions. Results of total dissolved ions indicated a slight shift in the defined zones. Seven of the nine tributaries indicated chemical contributions ranging from 3.5 to 66.7% to the main stream. Results from this study demonstrate the extent of tributary contribution to the Spring River systems.

Introduction

Tributaries may significantly alter the main stream into which they flow. The River Continuum Concept (RCC) predicts gradual change in biota as a waterway transitions from headwaters to a larger system (Vannote et al. 1980). Minshall et al. (1985) stated that additions from tributaries may play significant role on the typical pattern of the continuum by altering the expected trophic and community patterns described by Vannote et al (1980). Others have stated that tributaries cause discontinuities in lotic ecosystems and play a much more influential role than stated in the RCC (Perry and Schaeffer 1987, Rice et al. 2001).

Tributaries may affect water quality of the receiving waterway. This influence is dependent upon the properties of the tributary catchments (Rice et al. 2001). Previous studies have reported that the junctions between tributaries and main stream have high biodiversity (Benda et al. 2004, Kiffney et al. 2006). It is clear that tributaries have the potential to effect the waterways into which they feed.

The Spring River, located in north central AR, originates from Mammoth Spring, AR. Mammoth Spring is fed from the Ozark Plateau Aquifer and is recharged from rainwater infiltration (Vineyard and Feder 1982).

The drainage area that recharges this aquifer is located in south central MO. Research suggests that fecal coliform and nutrient loading are threats to surface waters in this agriculturally dominated area (Wilkerson 2000). The portion of the Spring River catchment located in Missouri is approximately 1244 km² and land use consist primarily of grassland/cropland (49.1%) and forest/woodland (48.3%) (Wilkerson 2000). The portion of the catchment located in Arkansas is approximately 1992 km² and land use consist primarily of forest (65.7%) and grassland (26.2%) (ArkansasWater.org 2010). Hannigan and Bickford (2003) noted that the Spring River and its tributaries are largely unpolluted and any potential contamination would be from agricultural run-off in the north and western tributaries.

The Spring River is unique when compared to traditional first order-second order streams as described in the RCC (Vannote et al. 1980) due to its headwater domination by a single source, Mammoth Spring. The river, with a reach of approximately 92 km, has been divided into four unique zones based upon hydrological differences determined by varying proportions of end-member water types (Hannigan and Bickford 2003).

Hannigan and Bickford (2003) used end-member mixing analysis (EMMA) and binary mixing/mass balance calculations to define three water types that

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dominate the Spring River: groundwater, overland/subsurface flow and bank storage. The mixture of these three water types was found to be responsible for streamwater chemistry of the Spring River. They concluded that further exploration was needed to constrain the hydrochemistry of the river (Hannigan and Bickford 2003).

The Spring River and five related tributaries, Field Creek, Big Creek, English Creek, Myatt Creek and Gut Creek, are designated as Extraordinary Resource Streams (APCEC 2007). The Spring River has additionally been designated as an Ecologically Sensitive Waterbody (APCEC 2007). Its uses include primary contact, person full body (swimming) and secondary contact, person partial contact (wading), recreation and fisheries as well as a water supply for domestic, agriculture and industry (APCEC 2007).

The objective of this study was to determine the chemical and bacteriological influences of tributaries on a stretch of the Spring River. Using a combination of methods, the contribution of each tributary to the river was determined.

Materials and Methods

Study Site

Headwaters of the Spring River are dominated by Mammoth Spring which contributes approximately $3.4 \times 10^5 \text{ m}^3$ water/hour (Hannigan and Bickford 2003). Approximately 30 km of the upstream reach and contributing tributaries were sampled which included three of the defined zones. The headwaters, Mammoth Springs (MS) and nine total tributaries were sampled: Warm Fork (TWF), tributary two (T2), Field Creek (TFC), Big Creek (TBC), English Creek (TEC), Myatt Creek (TMC), Gut Creek (TGC), Scrabble Creek (TSC) and South Fork (TSF) (Figure 1). Samples were collected on June 2-3, 2009, and according to hydrograph records for gage 07069305 located in Hardy, AR, this followed a streamflow peak on May 26-27, 2009 (USGS 2010). This may indicate that sampling occurred during conditions above baseflow. Samples were taken approximately 30 m within the tributary (upstream of the confluence) and approximately 50 m above and below the confluence of each tributary with the Spring River. Samples were collected within the water column in Nalgene™ containers prepped according to American Public Health Association (APHA 2005) protocol. Two separate samples were taken at each location, one with headspace for bacteriological analysis and one without headspace for chemical analyses. When wading was

necessary for sample collection, samples were collected upstream of the disturbed substrate.

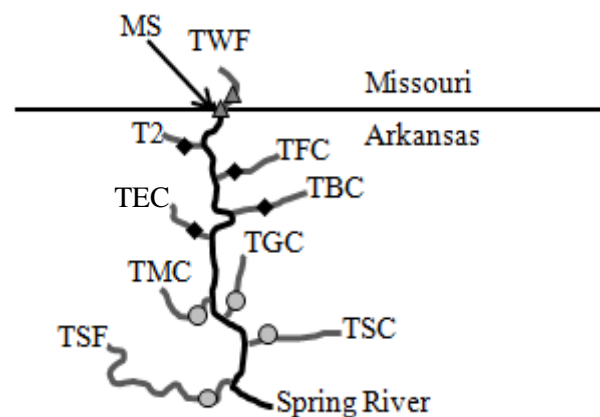


Figure 1: Map showing sampled headwater source, MS and nine contributing tributaries of Spring River AR. Shapes indicate zones defined as defined by ion chemistry and tributary input: triangle (zone 1), diamond (zone 2) and circle (zone 3). Tributaries are not drawn to scale of actual length.

Methodology

Following collection, samples were packed on ice and transported to Arkansas State University Ecotoxicology Research Facility for analysis. Subsamples were filtered and preserved for nutrient and total dissolved ion analysis (TDIs) (APHA 2005). Water quality measurements included pH, conductivity ($\mu\text{S}/\text{cm}$), total suspended solids (TSS) (mg/L), fecal coliform (colony forming units: $\text{CFU}/100\text{mL}$), alkalinity (CaCO_3/L ; mEq), nutrients (NO_2^- , NO_3^- , PO_4^{3-} ; mg/L) and TDIs (mEq). DO, pH, and conductivity were measured using a VWR™ SympHony field meter and conductivity was normalized at 18°C (Smith 1962). All water quality measurements followed the APHA guidelines and holding times (APHA 2005). The evaluation of fecal coliform presence in water samples was accomplished by enumerating the number of blue colonies after a 24h incubation period using rosolic acid as a growth medium. Alkalinity was determined using a potentiometric titration technique, with the pH endpoint of 4.5.

Levels of NO_2^- , NO_3^- and PO_4^{3-} were determined using a LACHET Quikchem 4000 Flow Injection Analysis (FIA) automated nutrient analyzer. The method used for NO_2^- and NO_3^- had a detection limit of $0.1 \text{ mg}/\text{L}$. Method used for PO_4^{3-} had a detection limit of $0.01 \text{ mg}/\text{L}$.

TDIs were determined with a Dionex DX-120 Ion Chromatograph (IC) using established procedures at Arkansas State University (Greenberg et al. 1992). Major ions measured included cations (K^+ , Na^+ , Mg^{2+} , Ca^{2+}) and anions (Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-}). A five point calibration curve was determined using cation and anion aqueous standards. Charge-balance error was calculated for each site to check accuracy of water-quality data (Freeze and Cherry 1979). Ca^{2+} and Mg^{2+} concentrations (mEq) were compared with alkalinity values. These two ions were chosen based on rock formulas for limestone and dolomite. This was done to determine the influence of bedrock lithology on stream chemistry.

Percent contribution for individual tributaries compared to the main stem was calculated by using concentration values of a conservative ion, Cl^- (mEq/L) with the following formula:

$$N_1(x) + N_2(1-x) = N_3$$

where N_1 = Cl^- concentration in the main stem above the tributary

N_2 = tributary Cl^- concentration

N_3 = Cl^- concentration below the confluence of the tributary with the main stem

The determined x value, fraction contribution of main stem, was then multiplied by 100% to calculate the percent contribution of the main stem. This value was subtracted from 100 to determine percent contribution of individual tributaries.

Results

In all water quality measurements, pH ranged from 7.00-8.38, conductivity from 288-544 $\mu S/cm$ at 18°C, and TSS from 1.5-28.5 mg/L. The lowest fecal coliform value was enumerated at 6 CFU/100mL and two sites were above allowable levels determined by the APCEC for the primary contact waters (APCEC 2007) (Table 1). Alkalinity ranged from 4.0-6.4 mEq/L (Table 2).

NO_3^- and PO_4^{3-} indicated a downward trend from the mouth of the river, MS, to the lowest collection point, TSF DN (NO_3^- $R^2=0.77$, PO_4^{3-} $R^2=0.65$) (Figure 2 and 3, respectively). There were no detectable levels of NO_2^- in any of the samples measured. NO_3^- ranged from below detection limit to 4.88 mg/L in water sampled from MS. Three of the nine tributaries contributed detectable levels of NO_3^- : TWF, T2, and TFC. PO_4^{3-} ranged from 0.01-0.11 mg/L with the

greatest value detected in water from TWF DN. All tributaries contributed detectable levels of PO_4^{3-} (Table 1).

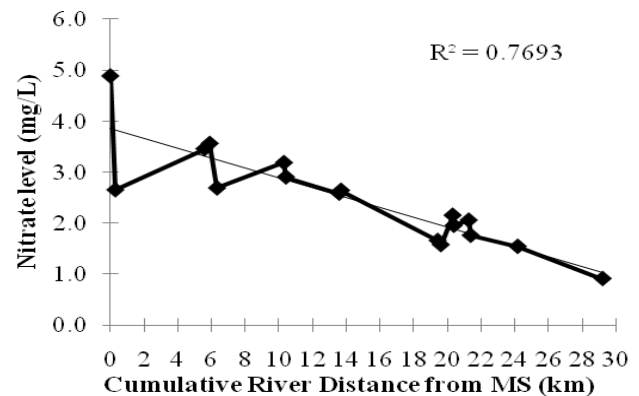


Figure 2: Decreasing trend in NO_3^- in the main stem of the Spring River associated with tributary contribution and distance from source MS.

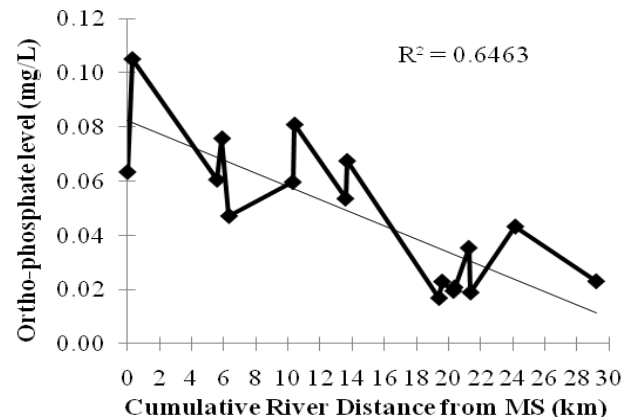


Figure 3: Decreasing trend in PO_4^{3-} in the main stem of the Spring River associated with tributary contribution and distance from source MS.

The cations K^+ , Na^+ , Mg^{2+} and Ca^{2+} ranged from 0.01-0.04 mEq/L, 0.01-0.07 mEq/L, 2.44-3.89 mEq/L and 1.93-3.47 mEq/L, respectively. The anion F^- was consistent at 0.02 mEq/L for all samples. The remaining anions Cl^- and SO_4^{2-} ranged from 0.05-0.12 mEq/L and 0.04-0.12 mEq/L, respectively.

Charge-balance error for all sample sites, with the exception of T2 UP, T2, TGC and TSC, fell within the accepted $\pm 5\%$. All site charge-balance errors fell below 7.8%. Total dissolved ions (TDIs) ranged from 8.72 to 13.97 mEq/L. The highest values were detected in the tributaries with the exception of

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Table 1: Water quality measurements for pH, conductivity, total suspended solids (TSS), fecal coliforms and nutrients measured from the headwaters, tributaries and main channel of the Spring River, AR. Downstream denoted by (DN) and upstream by (UP). Below detection limit (BDL). Cumulative distance (km) is descriptive of the main channel. Cumulative distance for tributaries is the location at which the tributary enters the main channel.

| Cumulative Distance (km) | Sample Site | pH | conductivity ($\mu\text{S}/\text{cm}$)** | fecal coliform (CFU/100mL) | TSS (mg/L) | PO_4^{3-} (mg/L) | NO_3^- (mg/L) |
|--------------------------|--------------|------|--|----------------------------|------------|---------------------------|------------------------|
| 0.0 | MS | 7.00 | 416 | 20 | 4.2 | 0.06 | 4.88 |
| 0.14 | TWF | 8.24 | 483 | 71 | 3.1 | 0.03 | 1.09 |
| 0.30 | TWF DN | 7.69 | 402 | 60 | 8.8 | 0.11 | 2.65 |
| 5.58 | T2 UP | 7.93 | 288 | 109 | 6.6 | 0.06 | 3.45 |
| 5.63 | T2 | 7.85 | 464 | 446* | 7.7 | 0.02 | 0.03 |
| 5.90 | T2 DN/TFC UP | 7.86 | 337 | 80 | 10.3 | 0.08 | 3.56 |
| 6.28 | TFC | 8.38 | 390 | 800* | 7.1 | 0.08 | 0.35 |
| 6.33 | TFC DN | 7.96 | 294 | 109 | 9.3 | 0.05 | 2.68 |
| 10.30 | TBC UP | 8.17 | 306 | 66 | 9.7 | 0.06 | 3.18 |
| 10.38 | TBC | 8.18 | 339 | 103 | 28.5 | 0.03 | BDL |
| 10.42 | TBC DN | 8.17 | 316 | 51 | 9.0 | 0.08 | 2.90 |
| 13.58 | TEC UP | 8.30 | 380 | 71 | 4.9 | 0.05 | 2.58 |
| 13.62 | TEC | 8.29 | 501 | 34 | 4.8 | 0.02 | BDL |
| 13.69 | TEC DN | 8.04 | 334 | 91 | 11.4 | 0.07 | 2.64 |
| 19.42 | TMC UP | 8.41 | 345 | 74 | 11.1 | 0.02 | 1.65 |
| 19.49 | TMC | 8.13 | 390 | 63 | 4.5 | 0.02 | BDL |
| 19.61 | TMC DN | 8.29 | 336 | 43 | 4.7 | 0.02 | 1.57 |
| 20.24 | TGC UP | 8.20 | 375 | 43 | 11.8 | 0.02 | 2.15 |
| 20.31 | TGC | 8.20 | 438 | 74 | 5.9 | 0.01 | BDL |
| 20.38 | TGC DN | 8.28 | 378 | 29 | 10.8 | 0.02 | 1.95 |
| 21.26 | TSC UP | 8.27 | 444 | 40 | 9.8 | 0.04 | 2.05 |
| 21.31 | TSC | 8.20 | 544 | 14 | 1.5 | 0.01 | BDL |
| 21.38 | TSC DN | 8.27 | 422 | 343 | 9.3 | 0.02 | 1.76 |
| 24.17 | TSF UP | 8.20 | 441 | 31 | 7.4 | 0.04 | 1.54 |
| 24.65 | TSF | 8.20 | 433 | 6 | 4.0 | 0.05 | BDL |
| 29.21 | TSF DN | 8.30 | 455 | 20 | 9.4 | 0.02 | 0.91 |

*exceeds maximum allowable level for primary contact recreational designation

**conductivity normalized at 18°C

TSF, which had the lowest value of 8.72 mEq/L (Table 2). Comparison of Ca^{2+} and Mg^{2+} concentrations with measured alkalinity indicated a clustering in tributary contribution based on bedrock lithology and the delineation of three spatially distinct zones (Figure 4).

Seven of the nine tributaries were determined to have a detectable contribution to the Spring River based on the concentration of Cl⁻ (mEq/L) (Table 2).

Discussion

To protect Ecologically Sensitive and Extraordinary Resource Waterbodies, it is important to understand the influence of tributaries on these systems. The Spring River has been designated as a primary and secondary contact waterway, so direct human contact is expected.

The primary contact designation allows a maximum level of fecal coliform at 400 coliforms/100mL (APCEC 2007). In this study, T2 bordered that level while TFC was double the allowable level. It was observed that agricultural grazing land bordered both sides of T2, and construction and clearing of land was occurring at time of collection around TFC. High fecal coliform levels contributed only slightly to the main stream as dilution occurred below the confluence. The size of the river

compared to the contribution from these two tributaries may have been key in keeping the levels of fecal coliforms below the acceptable limit in the main stem of the Spring River.

Minshall et al. (1985) stated that a tributary may dilute mainstream nutrient concentrations. Results of nutrient analysis in this study indicate that tributaries were diluting the river and lowering detected levels as NO_3^- and PO_4^{3-} values followed a decreasing pattern starting at or near the mouth of the river (Mammoth

Table 2: Water measurements including ion, alkalinity, total dissolved ions (TDI) and tributary contribution. Downstream denoted by (DN) and upstream by (UP). Percent tributary contribution is calculated on an individual basis at point of entry to mainstream.

| Cumulative Distance (km) | Sample Site | Cations (mEq/L) | | | | Anions (mEq/L) | | | Alkalinity (mEq/L) | TDIs* (mEq/L) | Tributary Contribution (%) |
|--------------------------|--------------|-----------------|-----------------|------------------|------------------|----------------|-------------------------------|-----------------|--------------------|---------------|----------------------------|
| | | K ⁺ | Na ⁺ | Mg ²⁺ | Ca ²⁺ | F ⁻ | SO ₄ ²⁻ | Cl ⁻ | | | |
| 0.0 | MS | 0.04 | 0.07 | 2.44 | 2.12 | 0.02 | 0.06 | 0.10 | 4.0 | 8.96 | |
| 0.14 | TWF | 0.03 | 0.04 | 2.81 | 1.93 | 0.02 | 0.10 | 0.11 | 4.6 | 9.63 | 47 |
| 0.30 | TWF DN | 0.03 | 0.05 | 2.60 | 2.25 | 0.02 | 0.10 | 0.11 | 4.3 | 9.52 | |
| 5.58 | T2 UP** | 0.03 | 0.05 | 2.59 | 2.25 | 0.02 | 0.05 | 0.11 | 4.1 | 9.32 | |
| 5.63 | T2** | 0.01 | 0.03 | 3.89 | 3.47 | 0.02 | 0.10 | 0.07 | 6.4 | 13.97 | 14 |
| 5.90 | T2 DN/TFC UP | 0.03 | 0.07 | 2.60 | 2.25 | 0.02 | 0.09 | 0.11 | 4.3 | 9.53 | |
| 6.28 | TFC | 0.03 | 0.03 | 3.47 | 3.08 | 0.02 | 0.07 | 0.08 | 5.8 | 12.59 | |
| 6.33 | TFC DN | 0.03 | 0.05 | 2.59 | 2.23 | 0.02 | 0.12 | 0.12 | 4.5 | 9.71 | |
| 10.30 | TBC UP | 0.03 | 0.06 | 2.60 | 2.24 | 0.02 | 0.05 | 0.11 | 4.4 | 9.62 | |
| 10.38 | TBC | 0.02 | 0.02 | 3.03 | 2.76 | 0.02 | 0.04 | 0.06 | 5.4 | 11.32 | 9.5 |
| 10.42 | TBC DN | 0.03 | 0.05 | 2.60 | 2.25 | 0.02 | 0.08 | 0.10 | 4.2 | 9.36 | |
| 13.58 | TEC UP | 0.03 | 0.05 | 2.61 | 2.26 | 0.02 | 0.08 | 0.09 | 4.5 | 9.69 | |
| 13.62 | TEC | 0.02 | 0.02 | 3.67 | 3.08 | 0.02 | 0.10 | 0.08 | 6.3 | 13.27 | 67 |
| 13.69 | TEC DN | 0.03 | 0.05 | 2.64 | 2.30 | 0.02 | 0.05 | 0.09 | 4.6 | 9.85 | |
| 19.42 | TMC UP | 0.03 | 0.05 | 2.71 | 2.35 | 0.02 | 0.05 | 0.09 | 4.6 | 9.95 | |
| 19.49 | TMC | 0.02 | 0.01 | 3.28 | 2.71 | 0.02 | 0.04 | 0.07 | 5.6 | 11.76 | 16 |
| 19.61 | TMC DN | 0.04 | 0.05 | 2.75 | 2.37 | 0.02 | 0.05 | 0.09 | 4.6 | 10.0 | |
| 20.24 | TGC UP | 0.03 | 0.05 | 2.72 | 2.33 | 0.02 | 0.05 | 0.09 | 4.6 | 9.94 | |
| 20.31 | TGC** | 0.02 | 0.01 | 2.49 | 2.81 | 0.02 | 0.08 | 0.05 | 5.2 | 10.74 | |
| 20.38 | TGC DN | 0.03 | 0.05 | 2.76 | 2.38 | 0.02 | 0.07 | 0.10 | 4.2 | 9.65 | |
| 21.26 | TSC UP | 0.03 | 0.04 | 2.76 | 2.37 | 0.02 | 0.08 | 0.09 | 4.9 | 10.32 | |
| 21.31 | TSC** | 0.01 | 0.01 | 3.83 | 3.37 | 0.02 | 0.07 | 0.05 | 6.1 | 13.48 | 3.5 |
| 21.38 | TSC DN | 0.03 | 0.05 | 3.75 | 2.37 | 0.02 | 0.05 | 0.09 | 4.8 | 10.2 | |
| 24.17 | TSF UP | 0.03 | 0.04 | 2.76 | 2.35 | 0.02 | 0.06 | 0.09 | 4.6 | 9.94 | |
| 24.65 | TSF | 0.02 | 0.03 | 2.44 | 2.07 | 0.02 | 0.06 | 0.07 | 4.0 | 8.72 | 10 |
| 29.21 | TSF DN | 0.04 | 0.04 | 2.73 | 2.33 | 0.02 | 0.08 | 0.08 | 4.5 | 9.82 | |

*TDIs includes NO_3^- and PO_4^{3-} values from Table 1. Values were converted to mEq/L prior to summation.

**charge-balance error does not fall within recommended +/- 5% (Freeze and Cherry 1979). T2 UP 5.7%, T2 5.8%, TGC 7.8% and TSC 7.2%.

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Springs; MS). Wilkerson (2000) suggested that nutrient loading may occur in the rural drainage area that recharges the aquifer that feeds MS. This statement is supported in this study as the highest nutrient levels were measured at or near the mouth of the Spring River. This result also indicates the importance of tributary contribution.

The TDIs were higher in the tributaries (with the exception of TWF and TSF) which are smaller than the main stream. The difference in TDIs may be a result of the shallower tributaries having greater water/rock interactions.

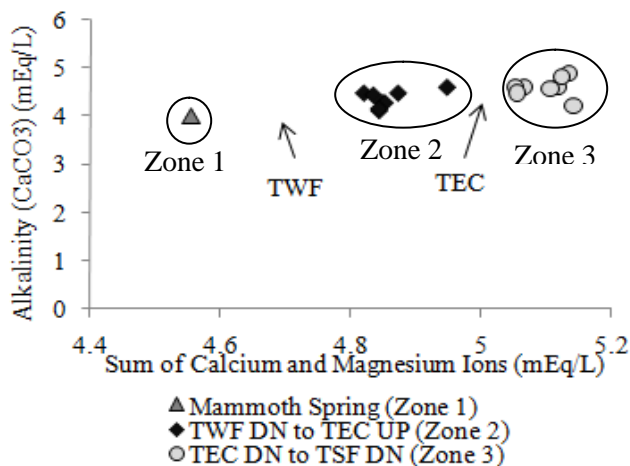


Figure 4: Ratio of alkalinity (CaCO₃, mEq/L) and sum of Ca²⁺ (mEq/L) and Mg²⁺ (mEq/L) for the main stream indicating that spatially distinct zones occur within the Spring River.

The unique zones determined in the present study (Figure 4), MS (Zone 1), TWF DN to TEC UP (Zone 2) and TEC DN to TSF DN (Zone 3), were consistent with the three zones defined for this particular stretch of the river with one exception. Hannigan and Bickford (2003) categorized TWF DN in Zone 1, but our analyses classified it into Zone 2. In their study, in which monthly samples were taken over a 12 month period, zones were based upon two contributing endmembers, groundwater and overland/subsurface. Hannigan and Bickford (2003) also noted that although TWF added warmer water in the summer, the domination of groundwater in this zone quickly diluted any chemical additions. The shift in Zone 2 to include TWF DN may indicate that TWF is playing a larger role the Spring River system than previously thought. This is also supported by the 47% contribution by TWF to the main stream. This present study employed

a single sampling event and, based on ion chemistry and tributary input, closely confirmed the previously defined zones. The unique zoning may indicate that the tributaries in the Spring River system are resulting in discontinuities in the continuum of the river as described by Perry and Schaeffer (1987) and Rice et al. (2001).

Conclusion

Due to the atypically large headwater source of this river system compared to a traditional first order-second order streams as described in the RCC tributary effect may be underestimated compared to more traditional systems (Vannote et al. 1980). In a traditional system the headwaters and contributing tributaries are more comparable in size. With the increase in stream order, the main stream is typically larger than the contributing tributaries. The uniqueness of this river system should be taken into consideration when comparing the results of this study to results obtained for other, more typical streams.

Additional research may help to establish if the tributaries are causing discontinuities in this system. An important investigation would be to determine if differences in biota exist in the various zones of the Spring River, AR.

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