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Relationship Between Land-Use and Water Quality in Spring-Fed Streams of the Ozark National Forest

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Running Title: Land-Use Effects on Spring-Fed Streams of the Ozark National Forest

Abstract

Spring-fed streams are abundant in karst topographic regions such as the Ozarks, providing an important and valuable water resource. Many of these spring-fed streams presently receive agriculture runoff, but few studies have examined the impacts of this runoff on water quality. We examined water quality in Ozark spring-fed streams surrounded by either agricultural (N=3) or primarily forested land (N=3) in the riparian zone. We hypothesized that agricultural sites would have greater dissolved nutrient concentrations and conductivity than forested sites and that water quality would fluctuate with distance from the spring source. Conductivity ($p<0.001$), nitrate ($p<0.001$), total nitrogen (TN; $p<0.001$), soluble reactive phosphorus (SRP; $p=0.014$), calcium ($p=0.046$), chlorine ($p<0.001$), and barium ($p=0.043$)) concentrations were greater in agricultural compared to forested spring-fed streams. Aluminum ($p=0.006$), cadmium ($p<0.001$), magnesium ($p=0.020$), and sulfate ($p=0.001$) concentrations were lower in agricultural compared to forested streams. These water chemistry data reflect land-use differences and could be used to help inform land-use management in these watersheds to improve and maintain high water quality.

Introduction

Human activities at the landscape scale can impact stream water quality (Allan et al. 1997). Rapid human population growth has resulted in worldwide land-use alterations, greatly influencing stream and river ecosystems (Helms et al. 2009).The increased area of impermeable surfaces associated with urbanization changes the water quality of affected streams by reducing infiltration, and thus increasing surface runoff (Paul and Meyer 2001). Further, agricultural activities, such as livestock grazing, can often result in soil compaction which leaves nutrients and other contaminants susceptible to off-site transport (Sauer et al. 1999). In these ways, runoff over a wide land area can result in nonpoint inputs of nutrients from fertilizers, metals, ions, pesticides, and sediments into streams (Cooper 1999; Paul and Meyer 2001). Accordingly, water quality can be impacted as the area of agricultural land within a catchment increases (Sponseller et al. 2001).

The Ozark Plateaus region is a karst system characterized by the presence of caves, springs, sinkholes and losing streams resulting from chemical weathering of, predominantly, dolomite and limestone bedrock. This system underlies much of Northwest Arkansas and stores significant quantities of groundwater, providing a major water resource for the state. Due to rapid infiltration of surface pollutants to groundwater, karst ecosystems are highly susceptible to pollution from anthropogenic sources, such as agriculture (Boyer and Pasquarel 1996). As Northwest Arkansas has grown, so has the conversion of land for urban and agricultural purposes. In addition to effluent from septic systems found prevalently in rural areas (Harden et al. 2008), the application of animal manure to pastures has been identified as a leading non-point source of pollution in Ozark region streams (Popova et al. 2006) leaving local groundwater systems at great risk of contamination.

Surface-to-spring contamination in areas affected by both point and nonpoint pollution have been documented in karst regions throughout the United States (Boyer and Pasquerell 1996, Steuber and Criss 2005), leaving these unique ecosystems at risk. Due to the prevalence of spring fed streams in Northwest Arkansas, and their resource value, careful monitoring and assessment is important to ensure proper and effective management. The main objective of this study was to determine effects of agriculture land use on the water quality in spring-fed streams of the Ozark National forest.

Methods

Six spring-fed streams were chosen from the Ozark National Forest. These included three un-impacted/primarily forested streams (N=3) and three human-impacted/ primarily pasture (N=3) streams. These sites were characterized by observed land-use immediately surrounding the study reaches. For each of the study streams, the source and three downstream reaches were marked at approximately 0 (source), 30 (reach 1), 275 (reach 2), and 520 (reach 3) meters. Each reach was a length of 20 times the width of the stream and the reaches were approximately 200-300 m apart. Water samples and physical measurements were taken between the 3rd and 28th of June, 2011.

Water Sampling

Water samples were collected in the middle of the thalweg for each site in the hypocrenal zone and as near to the source flow as possible in the eucrenal zone. At each location, three unfiltered 50-mL samples were collected directly from the stream. Two additional 50-mL samples were filtered through a syringe, using 1 μm glass fiber filters. At the source, reach 1, and reach 3 a 100-mL and a 40-mL sample were filtered through a syringe, using 0.45 μm membrane filters, for metal and ion analyses. The 40mL sample was acidified in the field with 4 drops of concentrated hydrochloric acid. All water samples were kept on ice and out of direct light until proper storage units were available.

Table 1: Study reach locations and descriptions.

Site	Distance from Source (m)	Land-Use	County	Coordinates	Discharge (m^3/s)
White Oak Source	0	Pasture	Boone, AR	36º16′N, 93º02′W	0.01921
White Oak Reach 1	32				0.01921
White Oak Reach 2	283				0.02908
White Oak Reach 3	530				0.04468
Bullpen Source	0	Pasture	Searcy, AR	36º05′N, 92º55′W	0.00479
Bullpen Reach1	24				0.00479
Bullpen Reach 2	256				0.00216
Bullpen Reach 3	493				0.67282
Bowden Source	0	Pasture	Searcy, AR	36º05′N, 92º55′W	0.33474
Bowden Reach 1	18				0.33474
Bowden Reach 2	249				0.36969
Bowden Reach 3	515				0.23982
Fitton Source	0	Forest	Newton, AR	36º05′N, 93º13′W	0.01561
Fitton Reach 1	30				0.01561
Fitton Reach 2	293				0.01641
Fitton Reach 3	573				0.01466
Carver Source	0	Forest	Newton, AR	35º58′N, 93º02′W	0.00458
Carver Reach 1	21				0.00458
Carver Reach 2	253				0.00473
Carver Reach 3	485				0.00341
Leatherwood Source	0	Forest	Newton, AR	36º01′N, 93º21′W	0.00378
Leatherwood Reach 1	18				0.00378
Leatherwood Reach 2	248				0.00128
Leatherwood Reach 3	482				0.00468

The physico-chemical parameters, with the exception of pH, were also measured at the mid-point of the source and each of the three reaches. The measurements included conductivity (Mettler Toledo FG3, Mettler-Toledo Incorporated, Columbus, OH) and temperature and DO (YSI Model 95; YSI Incorporated, Yellow Springs, OH). A transect of the reach was measured and divided into equal intervals where velocity (Marsh-McBirney Flo-Mate™ Portable Velocity Flow Meter (HACH Company, Frederick, MD) and depth measurements were taken to determine discharge. Measurements of pH in room temperature filtered water samples were taken immediately after returning to the lab (Orion 2-Star, Thermo Fisher Scientific Incorporated, Waltham, MA).

Chemical analyses of filtered water samples for soluble reactive phosphorus (SRP) and ammonium (NH_4^+) were completed within 24 h of returning to the laboratory using ascorbic acid and phenate methods, respectively (APHA 2005). The additional water samples were kept frozen pending further analyses. Water samples were later thawed slowly in a warm water bath. The 1µm GFF filtered water samples were analyzed for nitrite and nitrate N (hereafter NO_3^-) using the cadmium reduction method (APHA 2005) on a Latchat QuickChem 8500 Automated Ion Analyzer (Latchat Instruments, Milwaukee, WI) and unfiltered samples were analyzed for total N (TN) and total P (TP) concentrations using a persulfate digest followed by the standard colorimetric ascorbic acid method and automated analysis using a Shimadzu TNM-1 TOC analyzer (Shimadzu Scientific Instruments, Columbia, MD), respectively. Metal and ion concentrations were measured in the acidified and regular water samples taken using the 0.45 µm membrane filters with inductively coupled plasma optical emissions spectrophotometer by the Arkansas Water Resources Center laboratory.

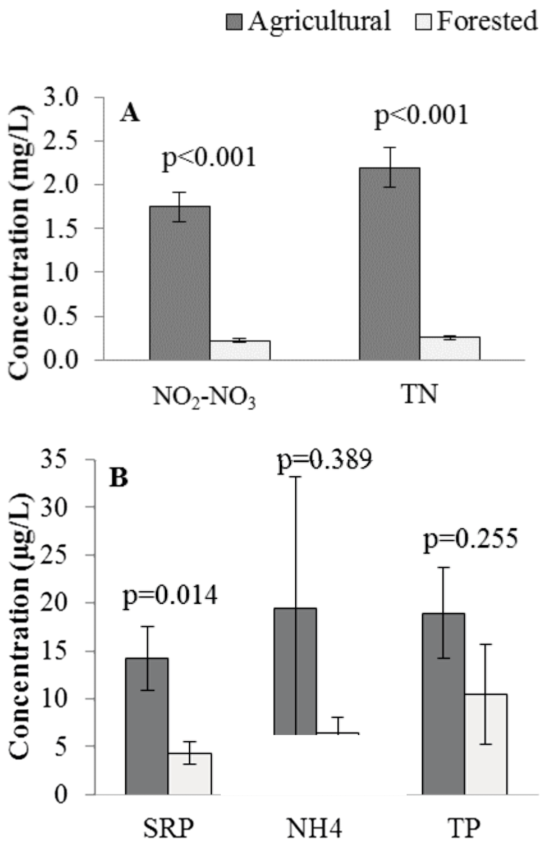

Figure 1: Mean (+1 SE) nutrient concentrations of the agricultural and forested sites. Mean dissolved nitrate (NO_3+NO_2-N) and total N (A) Mean soluble reactive phosphorus (SRP), dissolved ammonium (NH_{4+}-N), and total phosphorous (B).

Statistical Analysis

Statistical analyses were conducted using SAS statistical software (version 9.1, SAS Institute, Cary, NC). Two-way analyses of variance (ANOVA) were used to determine if land use (forested or agricultural) and distance downstream interacted to affect nutrient concentrations, metal and ion concentrations, and physico-chemical parameters. Correlations were examined for relationships between nutrient concentrations, metal and ion concentrations, and physico-chemical parameters and distance in meters from the source in each of the six study streams individually to examine the potential for unique water chemistry patterns in each stream.

Results

Data analysis showed that land use and distance downstream did not interact to affect nutrient, metal, or ion concentrations ($p>0.05$). In addition, no significant differences were found with distance alone. Comparisons of nutrient concentrations between agricultural and forested streams, however, showed that concentrations of NO_3^- (Figure 1A), TN (Figure 1B), and SRP (Figure 1B) were greater in agricultural compared to forested sites. There was no statistically significant difference in NH_4^+ (Figure 1B) and TP (Figure 1B) concentrations when agricultural and forested streams were compared. Concentrations of the ions calcium (Figure 2A), chloride (Figure 2B), and barium (Figure 2C) were significantly greater in agricultural sites when compared to forested sites.

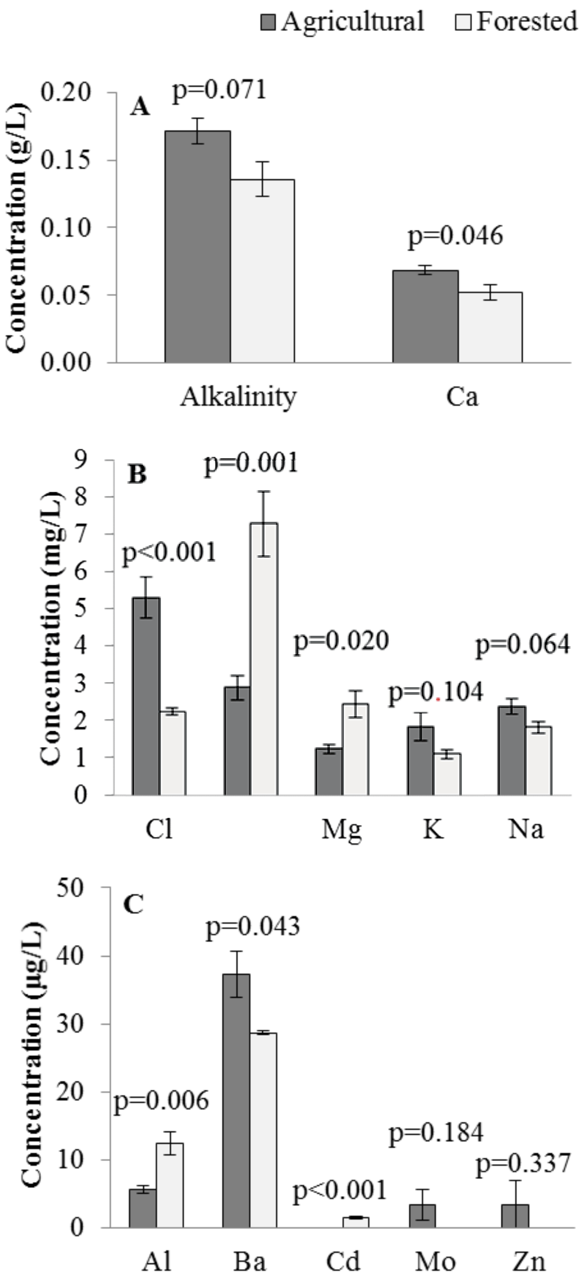

Figure 2: Mean (+1 SE) metal and ion concentrations of the agricultural and forested sites. Mean concentrations of alkalinity and calcium (A); chlorine, sulfate, magnesium, potassium, and sodium (B); and aluminum, barium, cadmium, molybdenum, and zinc (C).

Conversely, concentrations of the metals aluminum (Figure 2C), cadmium (Figure 2C), and magnesium (Figure 2B) were significantly lower in agricultural sites compared to forested sites. Additional metal and ion concentrations, alkalinity (Figure 2A), potassium (Figure 2B), sodium (Figure 2B), molybdenum, and zinc (Figure 2C) were not statistically significantly different between the two land use types.

Conductivity measurements showed no significant difference with land use and distance interaction or with distance alone, but were significantly greater for agricultural streams compared to forested streams. Measurements of pH showed no significant effect of land use and distance interaction or between agricultural and forested streams. However, the source and reach 1 measurements were significantly lower than reach 2 (p=0.001 and 0.024, respectively) and reach 3 (p=0.002 and 0.027, respectively). The source and reach 1, and reach 2 and reach 3 were not significantly different. There were no statistically significant differences seen with land use, distance, or the interaction of the two for DO and temperature.

Statistically significant correlations were found between some nutrient concentrations, metal and ion concentrations, and physico-chemical parameters and distance from the source in each of the six study streams. Correlation data are shown in Tables 2 and 3 with statistically significant values shown as bold and italicized.

Discussion

Data showed statistically significantly greater concentrations of NO_3^- , TN, and SRP in agricultural compared to forested sites. These higher concentrations could be due to nonpoint nutrient inputs associated with manures and fertilizers (Carpenter et al. 1998, Steuber and Criss 2005). Statistically significant negative correlations of TN and nitrates in two of the forested streams could be explained by dilution by groundwater inputs (Table 2). In the agricultural stream Bullpen, the significant negative correlation with distance from the source is likely because the source of the stream was receiving direct input of manure by livestock (personal observation; Table 2). Therefore, concentrations may have decreased via dilution and biological uptake as distance from the source increased. Such demonstrated nutrient enrichment of aquatic ecosystems can lead to deleterious effects in streams. These effects can include decreased water clarity, reduced oxygen levels, negative impacts on aquatic communities, and water treatment problems, such as odor and bad taste, increased filtration costs, and possible risks to human health.

We also found that chloride, calcium, and barium concentrations were greater in agricultural compared to forested sites. Conversely, concentrations of cadmium, aluminum, magnesium, and sulfates were significantly

Table 2: Correlations between distance, and nutrient and physical variables in individual study streams, (correlation coefficient (r), p-value). Listed top to bottom, three agricultural streams followed by three forested streams.

Site	NH_4+ (µg/L)	NO_3/NO_2 (mg/L)	TN (mg/L)	SRP (µg/L)	TP (µg/L)	Temp. (^{0}C)	DO (mg/L)	pH	Conduct. (uS/cm)
Bullpen	***-0.55, 0.049***	***-0.95, 0.049***	-0.93, 0.068	-0.52, 0.476	0.46, 0.536	0.22, 0.780	***0.98, 0.018***	0.85, 0.153	0.33, 0.668
White Oak	---	-0.46, 0.542	-0.63, 0.367	-0.82, 0.178	-0.87, 0.127	***0.96, 0.039***	0.64, 0.357	0.78, 0.218	0.41, 0.592
Bowden	---	-0.22, 0.775	-0.22, 0.780	-0.53, 0.473	0.66, 0.339	0.85, 0.146	***0.98, 0.023***	0.82, 0.184	0.05, 0.946
Fitton	0.20, 0.715	-0.92, 0.082	***-0.99, 0.004***	-0.90, 0.098	-0.69, 0.312	0.82, 0.178	-0.93, 0.066	0.78, 0.220	***0.98, 0.0240***
Carver	0.91, 0.091	-0.91, 0.087	-0.75, 0.255	-0.46, 0.537	0.61, 0.388	***0.99, <0.001***	-0.94, 0.060	***0.96, 0.038***	-0.83, 0.169
Leatherwood	0.63, 0.372	***-0.99, <0.001***	-0.83, 0.168	-0.69, 0.311	---	***0.99, <0.001***	-0.34, 0.656	***0.99, 0.013***	0.87, 0.130

Table 3: Correlations between distance and metal and ion concentrations in individual study streams, (correlation coefficient (r), p-value). Listed top to bottom, three agricultural streams followed by three forested streams.

Site	Alk (g/L)	Al (µg/L)	Ba (µg/L)	Cd (µg/L)	Ca (g/L)	Cl (mg/L)	Mg (mg/L)	Mo (µg/L)	K (mg/L)	Na (mg/L)	SO_4 (mg/L)	Zn (µg/L)
Bullpen	0.50, 0.668	0.28, 0.818	0.25, 0.839	---	0.49, 0.676	***-0.99, 0.009***	0.96, 0.177	---	-0.86, 0.344	-0.99, 0.055	-0.99, 0.058	---
White Oak	***-0.99, 0.034***	-0.45, 0.701	***-0.99, 0.039***	---	-0.90, 0.290	-0.89, 0.295	-0.99, 0.062	0.45, 0.706	0.81, 0.403	-0.95, 0.204	***0.99, 0.019***	---
Bowden	***-0.99, 0.020***	0.53, 0.647	0.99, 0.073	---	-0.97, 0.149	0.90, 0.292	0.99, 0.053	---	0.98, 0.119	-0.97, 0.161	0.82, 0.391	-0.47, 0.687
Fitton	***0.99, 0.030***	***-0.99, 0.030***	***0.99, 0.030***	0.54, 0.637	***0.99, 0.014***	***-0.99, 0.018***	***-0.99, 0.028***	---	***-0.99, 0.043***	***-0.99, 0.049***	***-0.99, 0.033***	---
Carver	0.99, 0.075	***0.99, 0.025***	***-0.99, 0.025***	0.47, 0.692	***0.99, 0.027***	***0.99, 0.038***	***0.99, 0.019***	---	***-0.99, 0.025***	0.88, 0.309	-0.99, 0.063	---
Leatherwood	-0.47, 0.688	---	***-0.99, 0.021***	---	***-0.99, 0.032***	-0.87, 0.323	***-0.99, 0.021***	---	-0.99, 0.063	-0.99, 0.095	***-0.99, 0.005***	---

lower in agricultural streams compared to forested streams. Chloride and calcium have agricultural sources, and elevated concentrations could be due to fertilizer runoff to the agricultural sites (Allan 1995; Steuber and Criss 2005). Calcium is also a constituent of limestone, which is readily soluble in water, implying bedrock dissolution as a source of this element in karst stream water (Allan 1995, Steuber and Criss 2005). The additional differences in metal and ion concentrations between sites may be due to differences in geology in the Ozark Plateau region. The area has diverse lithologies, including both sedimentary and igneous rocks, and diverse mineralogies, including extensive secondary mineralization. Multiple correlations were found between trace element concentrations and distance in individual streams (Table 3). Differences likely demonstrate varying inputs of groundwater throughout the length of the stream and differences in underlying geology.

In addition to nutrient and trace element concentrations, physico-chemical parameters can affect stream ecosystems. This study examined conductivity, temperature, pH, and dissolved oxygen to characterize the streams and determine the effects of land use alteration on the Ozark streams. No statistically significant differences were found between agricultural and forested streams for temperature, pH, or dissolved oxygen. Increased temperature is common in small, unshaded streams due to changes in air temperature and absorption of solar radiation (Allan 1995). Groundwater inputs along the distance of the streams, likely explain the lack of significant difference between agricultural and forested sites (Allan 1995). Correlation data for individual streams, however, indicated positive correlations between temperature and distance from the source in one agricultural and two forested streams. Diel fluctuations, decreased shading, and differences in groundwater inputs, could explain these correlations. Greater conductivity found in agricultural streams compared to forested streams was indicative of higher overall ion concentrations, which coincides with nutrient and trace element data.

The karst topography and increasing area of agriculture in Northwest Arkansas make water quality degradation by agricultural runoff to surface water and groundwater, a concern. (Boyer and Pasquerell 1996, Steuber and Criss 2005, ADEQ 2008) These water chemistry data reflect distinct land-use differences that may become greater as land-use change continues in the region. Continued monitoring of these spring-fed springs is important to ensure proper management efforts and protection of these valuable groundwater systems.

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