LINKING WATERSHED SUBBASIN CHARACTERISTICS TO WATER QUALITY PARAMETERS IN WAR EAGLE CREEK WATERSHED

K. W. Migliaccio, B. E. Haggard, I. Chaubey, M. D. Matlock

ABSTRACT. *A short-term sampling program was conducted to assess watershed-scale influences such as catchment land use, seasonal variability, and catchment size in War Eagle Creek in northwest Arkansas. The objective was to identify strategic subbasin sampling locations in War Eagle Creek watershed that would minimize the number of sampling sites while fully characterizing seasonal water quality. Additionally, we compared result from each sampling station (subbasin) to suggested ecoregion nutrient and sestonic chlorophyll-a criteria. Thirteen subbasins were identified within War Eagle Creek watershed for sampling and assessment. The effects of the WWTP effluent discharge (subbasin 8) were evident, as all constituent concentrations (conductivity, SRP, TP, NO_2-N, NO_3-N, and TN) were significantly greater ($p < 0.10$) downstream from the effluent discharge site compared with the majority of the other subbasins. NO_3-N plus NO_2-N and TN median concentrations for pasture-dominated subbasins 10 and 12 were greater than most other values. Similarly, regression analyses indicated a strong correlation between TN and % pasture cover in the subbasin ($r = 0.912$) and between NO_3-N and % pasture cover in the subbasin ($r = 0.925$). Chlorophyll-a median concentration was greatest for subbasin 11, which was above median ecoregion criteria values. Sites and constituents varied seasonally, with lowest concentrations often measured in the winter-spring season and greatest loads calculated for winter-spring and fall seasons. Results indicated that a reduction of over 50% in the number of sites sampled can be made without losing information on the variability of the selected water quality parameters. By monitoring the reduced set of sampling sites, a more focused and frugal water quality monitoring program can be developed to determine the quality of water in War Eagle Creek for assessing designated uses.*

Keywords. *Nonpoint-source pollution, Nutrients, Point-source pollution, Seasonality, Water quality.*

Stream nutrient concentrations are largely contingent upon watershed-scale influences, including catchment land use (Jordan et al., 1997; Haggard et al., 2003; Buck et al., 2004), seasonal variability (Munn and Prepas, 1986; Mulholland and Hill, 1997), and catchment size (Brainwood et al., 2004; Buck et al, 2004). The very nature of aquatic nutrient dynamics suggests that the threshold concentration or level at which nutrients would be considered a pollutant is variable. Considering the USEPA definition of a pollutant, nutrients would most often be considered a pollutant when the concentration results in "adverse effects" on "the usefulness of a resource" (USEPA, 2007). Typically, nutrients become a concern when elevated concentrations result in increased eutrophication, impacting fisheries, aesthetics, and the quality of drinking water resources (beneficial use criteria). The threshold concentration above which the resource's beneficial uses become impaired would be considered a numeric nutrient limit or water quality criteria that protects the aquatic system from adverse conditions.

Nutrient criteria have been proposed on an ecoregion level (e.g., see USEPA 2000a, 2000b). The basis of having a single criterion per ecoregion relies on the assumption that within the ecoregion, there are similar natural sources of nutrients. Ecoregion-based nutrient criteria development implies that all catchments within an aggregate ecoregion should be held to the same criteria, with little consideration for catchment land use, seasonal variability, or catchment size. The USEPA guidance identifies two methods for evaluating reference stream constituent values for developing nutrient criteria by ecoregion (USEPA, 2000c). (1) One method is to choose the 75th percentile concentrations from minimally impacted or reference streams within an ecoregion as the ambient nutrient criteria (USEPA, 2000b, 2000c; Rohm et al., 2002). For example, the Oklahoma Water Resources Board (OWRB, 2002) selected the 75th percentile of flow-weighted total P (TP) concentrations from Clark et al. (2000) as the numeric TP criteria for Oklahoma's Scenic Rivers. (2) Alternatively, the 25th percentile value of median nutrient concentrations from all streams within an ecoregion may be used to define nutrient criteria. The 25th percentile of all streams is generally used when inadequate or minimum reference stream data are available to determine a 75th percentile value.

Our goal was to assess water quality in the War Eagle Creek watershed by subbasin units in a relatively short amount of time so as to identify a reduced number of sampling sites that would represent water quality within the wa-

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The authors are **Kati W. Migliaccio, ASABE Member Engineer,** Assistant Professor, Tropical Research and Education Center, University of Florida, Homestead, Florida; **Brian E. Haggard,** Associate Professor, Department of Biological and Agricultural Engineering, University of Arkansas, Fayetteville, Arkansas; **Indrajeet Chaubey, ASABE Member,** Associate Professor, Department of Agricultural and Biological Engineering and Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, Indiana; and **Marty D. Matlock,** Associate Professor, Department of Biological and Agricultural Engineering, University of Arkansas, Fayetteville, Arkansas. **Corresponding author:** Kati W. Migliaccio, Tropical Research and Education Center, University of Florida, 18905 SW 280th St., Homestead, FL 33031; phone: 305-246-7000; fax; 305-246-7003; e-mail: klwhite@ufl.edu.

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STUDY SITE

The study catchment was the War Eagle Creek watershed in northwest Arkansas (fig. 1). War Eagle Creek is one of the main tributaries to Beaver Reservoir, which is the primary drinking water supply for northwest Arkansas. The War Eagle Creek watershed encompasses approximately 681 km^2 with land use distributions of 64% forest, 36% pasture, and <1% urban and other (CAST, 2002). Nutrient nonpoint sources in the watershed include land application of animal manure and agricultural production facilities for chickens, turkeys, swine, and cattle; other nonpoint sources include natural background nutrient loading (e.g., forest, geological sources, atmospheric deposition) and those from the small urban-suburban areas. The dominant point source in the watershed is the wastewater treatment plant (WWTP) effluent discharge from the city of Huntsville, Arkansas, located in subbasin 8. The Huntsville WWTP contributed approximately 4,164 m^3 per day (1.1 MGD) of flow, with an average annual load of 8.3 Mg year^{-1} of nitrate (NO_3–N) plus nitrite (NO_2–N) and 5.9 Mg year^{-1} of total phosphorus (TP) during 2003 and 2004. Nutrients from nonpoint and point sources are a concern in War Eagle Creek watershed because of the potential influence on eutrophication rates in the downstream Beaver Reservoir. In addition, War Eagle Creek is a popular spot for fishing, canoeing, swimming, and hiking, and continued recreational use of the stream will depend on its water quality status.

METHODS

WATER QUALITY SAMPLING

The outlet for this study was the U.S. Geological Survey (USGS) gauging station for War Eagle Creek near Hindsville (USGS Station No. 07049000) (fig. 1). Statistical information on flow values for this station was reported by the USGS (Brossett et al., 2004; Schrader et al., 2005) and is presented in table 1. Water quality samples were also collected at the USGS station during 2003 and 2004; average annual nutrient loads were estimated using available water quality samples, daily flows, and LOADEST software (Crawford, 1991, 1996) (table 2).

War Eagle Creek watershed was divided into 13 subbasins using a 30 m digital elevation map (DEM) from the USGS. The portion of land cover contributing surface flow to each subbasin outlet is identified in table 3 using 1999 land use and land cover data (CAST, 2002). The area value presented for each subbasin in table 3 represents the entire area draining to that outlet. For example, the area value reported for subbasin 3 includes subbasins 3, 2, and 1. Our subbasins were selected to identify tributary constituent inputs into War Eagle Creek and constituent concentrations throughout the main branch of War Eagle Creek.

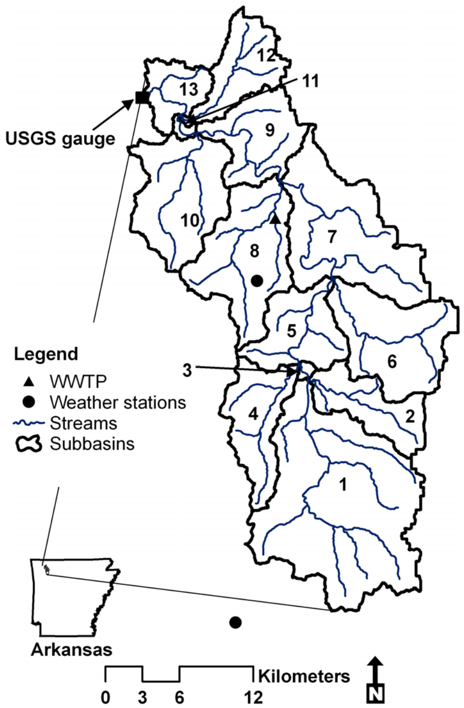

Figure 1. War Eagle Creek catchment with stream segments and subbasins identified.

Table 1. Summary statistics for discharge (or flow) at USGS gauge station 07049000, War Eagle Creek near Hindsville, Arkansas (all units in m^3 s^{-1}) (Brossett et al., 2004; Schrader et al., 2005).

Statistic	Calendar Year 2003	Calendar Year 2004	All Available Data[a]
Annual mean	4.50	10.54	7.90
Highest daily mean	97.73 (May)	450.42 (Apr.)	538.24
Lowest daily mean	0.34 (Aug.)	0.28 (Sep.)	<0.01
10% of values exceed	9.09	20.03	16.23
50% of values exceed	2.29	4.05	2.21
90% of values exceed	0.42	0.42	0.28

[a] All available data include water years 1952-1970 and 1999-2005.

Table 2. Average annual loads and flow from USGS gauge station 07049000 and Huntsville WWTP for 2003 and 2004.

Constituent	USGS Station	WWTP	WWTP Percentage of Loads at the USGS Gauge
NO_3-N + NO_2-N (Mg year^{-1})	214.2	8.3	3.9%
TP (Mg year^{-1})	42.7	5.9	13.8%
Flow (m^3)	1.685 E8	4.164 E4	

Each subbasin was monitored between August 2003 and March 2004 with sampling dates selected to capture each of the three seasons: winter-spring (high flow), summer (low flow), and fall (low flow after leaf abscission). Winter-spring, summer, and fall were considered by months as January through June, July through September, and October through December, respectively. The divisions of months into seasons were made based on two factors: (1) leaf abscission and leaf litter in streams, and (2) previously measured flow conditions. Months in which leaf abscission occurs and leaf litter is present in streams are normally October through December in northwest Arkansas. Hence, these months were selected for a sampling period (or season). Next, the remaining

Table 3. Land use distribution for each subbasin outlet drainage area in War Eagle Creek watershed in km^2 (percentage of subbasin).

Subbasin[a]	Urban	Forest	Pasture	Other	Total
1 - War Eagle Creek	0.0 (0)	136.7 (83)	27.6 (17)	0.3 (<1)	164.6 (0.05)
2 - Henderson Creek	0.1 (<1)	28.7 (79)	7.7 (21)	0.0 (0)	36.5 (0.01)
3 - War Eagle Creek	0.1 (<1)	166.0 (82)	36.2 (18)	0.3 (<1)	202.6 (0.06)
4 - Jackson Creek	0.0 (0)	32.9 (78)	9.1 (22)	0.0 (<1)	42.0 (0.01)
5 - War Eagle Creek	0.2 (<1)	221.1 (77)	63.8 (22)	0.5 (<1)	285.6 (0.09)
6 - Wharton Creek	0.0 (0)	42.7 (65)	22.4 (34)	0.1 (<1)	65.2 (0.02)
7 - War Eagle Creek	0.3 (<1)	319.3 (72)	121.0 (27)	1.0 (<1)	441.6 (0.14)
8 - Holeman Creek	2.5 (4)	36.8 (52)	31.1 (44)	0.2 (<1)	70.6 (0.02)
9 - War Eagle Creek	2.8 (<1)	383.3 (69)	168.0 (30)	1.3 (<1)	555.4 (0.17)
10 - Glade Creek	0.1 (<1)	24.7 (38)	39.8 (62)	0.1 (<1)	64.7 (0.02)
11 - War Eagle Creek	2.8 (<1)	409.4 (66)	208.8 (34)	1.3 (<1)	622.3 (0.19)
12 - Clear Creek	0.0 (0)	14.0 (39)	21.5 (60)	0.1 (5)	35.6 (0.01)
13 - War Eagle Creek	2.8 (<1)	433.7 (64)	242.2 (36)	1.4 (<1)	680.1 (0.21)

[a] Subbasins 1, 3, 5, 7, 9, 11, and 13 are on the main stem of War Eagle Creek; all other subbasins encompass tributaries.

months were divided into low-flow and high-flow periods using USGS data. Measured flow data were collected at USGS gauge station 07049000 starting in mid-1998; average monthly flows for 1999 to 2002 were calculated. A divide in flow conditions was evident in the resulting data set. Low flows, ranging from 0.60 to 5.04 m^3 s^{-1} were present from July to August. High flows, ranging from 6.95 to 17.4 m^3 s^{-1} were present from January to June.

Three sampling events were conducted during each season, in which water samples were collected and physicochemical parameters were measured. Monitoring was conducted during base flow conditions because stream nutrient criteria from USEPA analysis was derived from data largely collected during base flow conditions. Furthermore, stream nutrient criteria should also be targeted toward base flow conditions because it is under sustained base flow that nuisance algal biomass might develop. However, this is not to imply that storm event loads are inconsequential. Storm events may contribute substantial loads into downstream receiving waters and therefore may also influence their long-term trophic status. Quantification of storm event loads was not an objective of our study.

Water samples were collected at each site just upstream or downstream from a riffle, near the thalweg of the channel and just under the surface. Unfiltered water samples were collected for the analyses of TP, total nitrogen (TN), and sestonic chlorophyll-*a*; filtered (0.45 μm membrane) water samples were collected for the analyses of soluble reactive phosphorus (SRP), and NO_3–N plus NO_2–N. In addition, SRP filtered samples were acidified (pH < 2). A known volume of water was filtered through a Whatman (GF/F) glass fiber filter to determine sestonic chlorophyll-*a*. All water samples and sestonic chlorophyll-*a* filters were frozen until analyzed. (By definition, sestonic chlorophyll-*a* is simply an indirect measure of algae abundance in the water column, similar to measuring chlorophyll-*a* in lakes and reservoirs. Sestonic algae in streams represent both sloughed periphytic algae and pseudo or true phytoplankton, which might exist in some streams with minimal flow or velocity.)

Physicochemical parameters were measured in the field and included pH (pH Testr 2 double-junction pH meter, Oakton Instruments, West Caldwell, N.J.), temperature and conductivity (115A plus conductivity meter, Orion, Beverly, Mass.), and dissolved oxygen (model 85, YSI, Yellow Springs, Ohio). Water samples were analyzed for SRP using the automated ascorbic acid reduction method, and NO_3–N and NO_2–N were measured using cadmium-copper reduction and colorimetric analysis (APHA, 1998). Total P and TN were measured on an unfiltered water sample using persulfate, autoclave digestion, and the colorimetric procedures for SRP and NO_3–N (APHA, 1998). Sestonic chlorophyll-*a* concentration in the water samples was determined using the trichromatic method (APHA, 1998).

Water quality sampling was conducted during base flow conditions. Base flow conditions were identified using precipitation data and water level at the USGS gauge. Sampling did not occur immediately following a rainfall event or during peak flows. In addition, War Eagle Creek can be quite dangerous (slippery embankments and strong, fast flows) during storm flows. Stream velocity and depth measurements were taken at equal width increments using a Marsh-McBirney velocity meter when stream conditions permitted. Velocity measurements were not taken when there was no flow in the stream or when stream water height or velocity prevented safe measurement. Stream discharge (or flow) was estimated as a product of stream cross-sectional area and velocity (Hauer and Lamberti, 1996).

STATISTICAL EVALUATIONS

Sample data results were modified using a natural log-transformation to accommodate for the non-normal distribution of concentration data and to minimize outlier influences (Hirsch et al., 1991; Lettenmaier et al., 1991). Variables included in the data analysis were TP, SRP, TN, NO_3–N, NO_2–N, chlorophyll-*a*, and conductivity. For some seasons and subbasin reach sampling sites, sufficient data were not available to complete this analysis, because some sites were intermittent and dry during the summer season.

Sufficient datasets were evaluated statistically using analysis of variance (ANOVA) and were analyzed by (1) comparing the 13 sampling locations (n = 9) and (2) comparing data from all sampling sites by season (i.e., winter-spring, summer, and fall) (n = 3). The null hypothesis for each analysis was that there were no significant differences between subbasin water quality parameters:

$$H_0 : \mu_1 = \mu_2 = \ldots = \mu_k \qquad (1)$$

where the subscripts represent different sample populations, μ represents the mean, and H_0 represents the null hypothesis ($\alpha = 0.10$). Data sets were also evaluated using Tukey's honestly significant different (HSD) test to separate significantly different means (Sheskin, 2004).

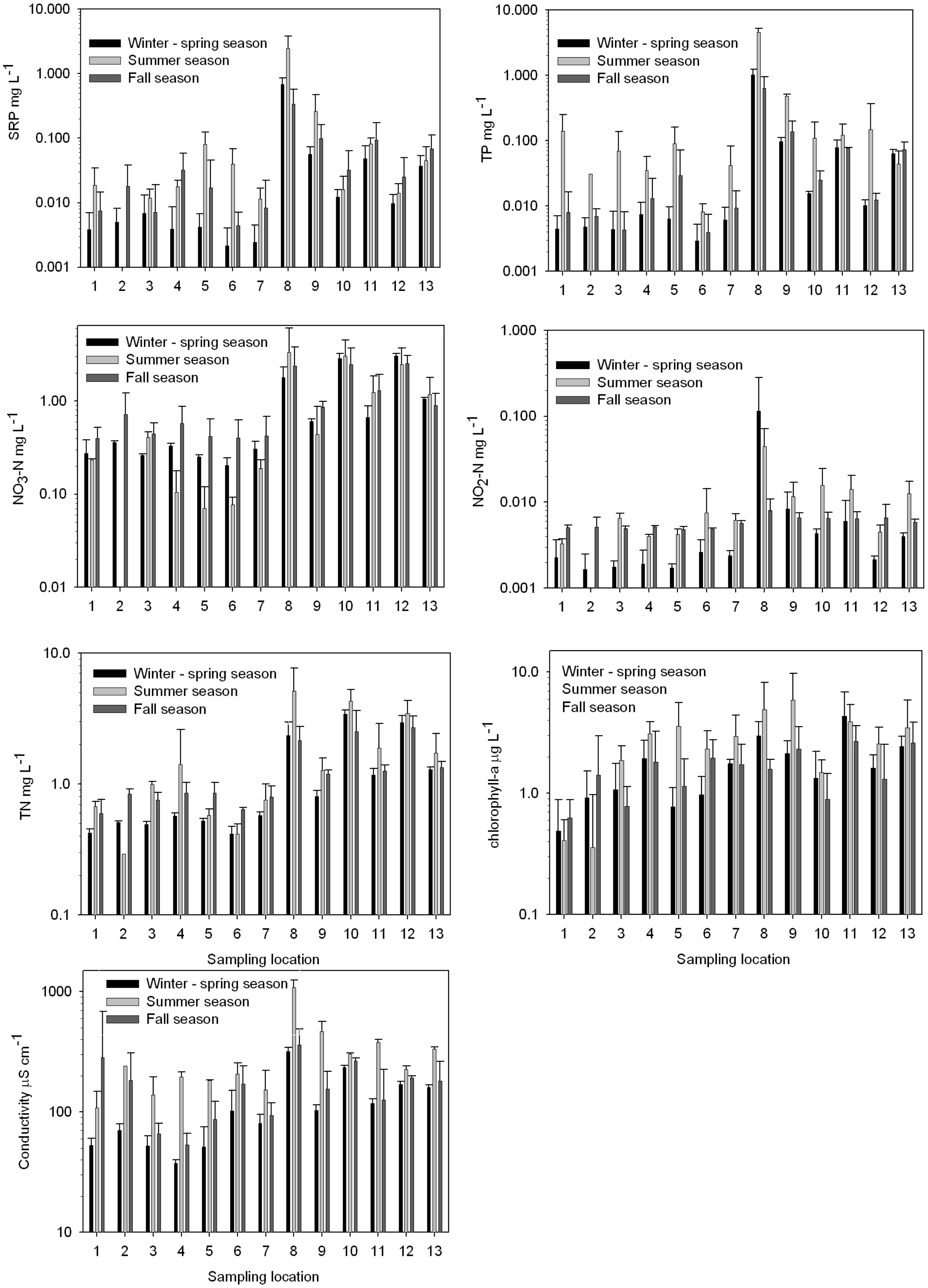

Figure 2. Phosphorus, nitrogen, chlorophyll-*a*, and conductivity mean concentrations and standard deviation bars ($n = 3$) from available data collected in 2003 to 2004 in each defined subbasin of War Eagle Creek.

Linear regression was used to evaluate the effect of land use (table 3) on water chemistry by regressing geometric mean nutrient concentrations against the proportion of a given land use (arcsin square root transformed) (Steel et al., 1997); we used urban, forest, pasture, and subbasin area (size) in the regression analyses. Regression results presented in the text were significant. S-PLUS 7 Insightful software and Statistix 8.0 Analytical software were used for statistical evaluations.

RESULTS AND DISCUSSION

STATISTICAL EVALUATIONS BETWEEN SITES

Several subbasins had significantly different constituent concentrations, and these differences were linked to the distance factors, catchment land use, and an effluent discharge (figs. 2 and 3). The effects of the WWTP effluent discharge were evident on water chemistry; the concentrations of all constituents (conductivity, SRP, TP, NO_2–N, NO_3–N, and TN) evaluated were significantly greater ($p < 0.10$) downstream from the effluent discharge site (subbasin 8) compared with the majority of the other subbasins (figs. 2 and 3). In particular, SRP and TP were greatest downstream from the effluent discharge (subbasin 8), where SRP and TP concentrations were approximately 2.44 and 4.55 mg L^{-1}, respectively. Comparison of estimated annual loads of TP from the WWTP and from the downstream USGS gauging station indicated that the WWTP annual load corresponded to 13.8% of the TP leaving the War Eagle Creek watershed (table 2). Additionally, SRP and TP concentrations were generally less than 0.05 and 0.10 mg L^{-1}, respectively, in subbasins not influenced from effluent discharges, i.e., WWTPs. SRP and TP average daily loads were also tabulated by season using available data (table 4). SRP and TP loads were always greatest from subbasin 8 and sites downstream from subbasin 8. Although elevated SRP and TP concentrations persisted at all sites (subbasins 9, 11, and 13) monitored downstream from the effluent discharge, concentrations did decrease with distance further downstream.

Historically, most WWTPs in northwest Arkansas did not operate with P limits on effluent discharges, and therefore many effluent discharges significantly increased SRP and TP concentrations in the receiving stream. The decreases in stream water SRP and TP concentrations downstream from effluent discharge may be from dilution (Ekka et al., 2006); however, biotic uptake and sediment interactions can also be important. Benthic sediments temporarily store PO_4–P from the water column in effluent-dominated Ozark streams (Ekka et al., 2006). Haggard et al. (2005) showed that stream sediments can release PO_4–P back to the stream water when effluent P concentrations are low.

Although SRP and TP concentrations were greatest downstream from the effluent discharge, some other subbasins (10 and 12) had similar NO_3–N and TN concentrations compared to those downstream from the effluent discharge (figs. 2 and 3). However, NO_2–N concentrations were greatest downstream from the effluent discharge (subbasin 8) and even exceeded 0.1 mg L^{-1} during winter-spring sampling. NO_2–N loads were generally above average for subbasin 8. The greatest NO_3–N concentration was approximately 3 mg L^{-1} in subbasins 8, 10, and 12; whereas NO_3–N concentrations in subbasins 1 through 7 were generally less than 0.5 mg L^{-1}. NO_3–N loads were greatest during the winter-spring and

Chlorophyll-a

	3	4	5	6	8	9	10	11	12
1	Y	Y	Y	Y	Y	Y	Y	Y	Y
3					Y	Y		Y	
4									
5								Y	
6									
8							Y		
9							Y		
10								Y	

Conductivity

	8	9	10	11	12
1	Y		Y		
3	Y	Y	Y		Y
4	Y	Y	Y		Y
5	Y		Y		
6	Y				
8		Y		Y	Y
9					
10					

SRP

	8	9	10	11	12	13
1	Y	Y		Y		Y
3	Y	Y		Y		Y
4	Y	Y		Y		
5	Y	Y		Y		Y
6	Y	Y		Y		Y
7	Y	Y	Y	Y	Y	Y
8			Y	Y	Y	Y
9					Y	

TP

	8	9	10	11	12	13
1	Y	Y		Y		
3	Y	Y		Y		Y
4	Y	Y		Y		
5	Y	Y				
6	Y	Y	Y	Y		Y
7	Y	Y		Y		
8		Y	Y	Y	Y	Y
9					Y	

NO_2-N

	8	9	10	11	12	13
1	Y					
3	Y					
4	Y					
5	Y					
6	Y					
7	Y					
8		Y	Y	Y	Y	Y
9						
10						

NO_3-N

	8	9	10	11	12	13
1	Y		Y	Y	Y	Y
3	Y		Y	Y	Y	Y
4	Y		Y	Y	Y	Y
5	Y	Y	Y	Y	Y	Y
6	Y	Y	Y	Y	Y	Y
7	Y		Y	Y	Y	Y
8		Y				
9			Y		Y	
10				Y		Y

TN

	6	8	9	10	11	12	13
1		Y	Y	Y	Y	Y	Y
3		Y		Y	Y	Y	Y
4	Y	Y		Y	Y	Y	Y
5		Y	Y	Y	Y	Y	Y
6		Y	Y	Y	Y	Y	Y
7		Y		Y	Y	Y	Y
8			Y		Y		Y
9				Y		Y	
10					Y		Y
11						Y	
12							Y

Figure 3. Tukey's honestly significant difference (HSD) test results (significant differences denoted with "Y"). Numbers represent subbasin sampling sites. A significant difference indicates that corresponding sampling sites data were significantly different (α = 0.10, *n* = 9) considering all data for all seasons. Sites with no significant difference from another are not presented.

Table 4. Average daily load of constituents by site and season using water quality data and flow measurements collected on three sampling dates for each season.

Season	Site	Chl-*a* (kg)	SRP (kg)	NO_3-N (kg)	NO_2-N (kg)	TP (kg)	TN (kg)
Winter-spring	1	0.06	0.55	35.97	0.30	0.47	51.65
	2	0.00	0.02	1.23	0.00	0.02	1.75
	3[a]	--	--	--	--	--	--
	4	0.04	0.10	7.07	0.04	0.14	12.24
	5[a]	--	--	--	--	--	--
	6	0.01	0.02	2.19	0.03	0.03	4.53
	7[a]	--	--	--	--	--	--
	8	0.09	20.77	56.37	4.47	31.34	73.34
	9[a]	--	--	--	--	--	--
	10	0.03	0.26	62.18	0.09	0.33	73.78
	11[a]	--	--	--	--	--	--
	12	0.02	0.14	46.82	0.03	0.15	44.68
	13	0.96	13.95	422.70	1.58	25.29	517.18
Summer	1	0	0	0	0	0	0
	2	0	0	0	0	0	0
	3	0	0	0	0	0	0
	4	0	0	0	0	0	0
	5	0	0	0	0	0	0
	6	0	0	0	0	0	0
	7	0.01	0.01	0.68	0.02	0.23	2.78
	8	0.02	15.00	19.53	0.25	22.15	27.65
	9	0.09	6.78	11.12	0.25	8.85	25.53
	10	0.01	0.22	26.44	0.12	1.03	34.79
	11	0.13	3.50	57.05	0.53	5.13	62.93
	12	0.02	0.11	18.24	0.03	1.56	23.90
	13	0.19	5.03	107.51	1.10	4.29	152.98
Fall	1	0.03	0.54	29.12	0.31	0.89	32.26
	2	0.00	0.00	0.21	0.00	0.00	0.13
	3[a]	--	--	--	--	--	--
	4	0.02	0.25	11.60	0.09	0.19	15.57
	5	0.09	0.97	57.60	0.53	2.16	89.57
	6	0.01	0.05	4.01	0.04	0.02	4.94
	7[a]	--	--	--	--	--	--
	8	0.06	9.04	92.26	0.29	24.15	71.30
	9[a]	--	--	--	--	--	--
	10	0.01	0.46	42.40	0.10	0.50	51.08
	11[a]	--	--	--	--	--	--
	12	0.01	0.24	25.04	0.06	0.13	26.72
	13[b]	1.43	15.91	338.99	2.23	28.69	505.22

[a] Stream flow was not measured due to danger related to water height or velocity.

[b] For site 13, values were calculated using USGS station 07049000.

fall seasons, with subbasins 8, 10, and 12 (table 4) contributing the greatest loads to War Eagle Creek. TN concentrations were more variable than NO_3–N concentrations, ranging from 2 to 5 mg TN L^{-1} in subbasins 8, 10, and 12 and generally less than 1 mg L^{-1} in most other subbasins. Seasonal loads of TN were much greater in the winter-spring and fall seasons (>500 kg d^{-1}) as compared to the summer season (152 kg d^{-1}). However, flows were greatly reduced during the summer season (<1.0 m^3 s^{-1}) as compared to other seasons (>4.0 m^3 s^{-1}).

The WWTP effluent discharge was the likely source of elevated N concentrations in subbasin 8, but subbasins 10 and 12 are headwater streams draining subbasins with approximately 60% pasture and 40% forested land. The source of elevated NO_3–N in subbasins 10 and 12 is likely from groundwater contributions, because sampling was targeted at base flow conditions. NO_3–N is a highly mobile ion, and elevated groundwater and stream NO_3–N concentrations are often correlated to increasing fractions of pasture and agricultural land use (Pionke et al., 1996; Petersen et al., 1999; Owens and Bonta, 2004). In fact, Haggard et al. (2003) showed that geometric mean SRP, NO_3–N, and TN concentrations in Ozark streams increased with an increase in the fraction of pasture land use in a subbasin.

Unlike stream nutrient concentrations that showed spatial variation related to an effluent discharge and differing fractions of land use in the drainage areas, sestonic chlorophyll-*a* concentrations did not show this variation in the War Eagle Creek watershed. Sestonic chlorophyll-*a* concentrations varied from less than 0.5 to almost 6 μg L^{-1}. Geometric mean sestonic chlorophyll-*a* concentrations across the sites were positively correlated with subbasin area ($r = 0.64$, $p = 0.02$). Lohman and Jones (1999) reported that the correlation between mean sestonic chlorophyll-*a* and nutrients improved when subbasin area was included (see also Jones et al., 1984; Van Nieuwenhuyse and Jones, 1996). In this study, catchment area and geometric mean SRP concentrations explained more than 66% of the variation observed in geometric mean sestonic chlorophyll-*a* concentrations (from regression analyses). A possible explanation for this is that as catchment area increases, stream width increases, providing more insolation. Algal growth in the War Eagle Creek watershed and other tributaries to Beaver Reservoir has been characterized as P limited (White et al., 2005; Ludwig, 2006), and maximum potential productivity (Matlock et al., 1999) has been correlated to photosynthetic available radiation (PAR) across the Beaver Reservoir watershed (Ludwig, 2006).

Conductivity was greatest at subbasin 8 (fig. 2), likely from the effluent discharge. Land use explained at least 71% of the variability in conductivity (from regression analyses). However, the correlation with urban land use is likely an artifact of the WWTP that is located in subbasin 8.

STATISTICAL EVALUATIONS FOR SEASONS

Statistical evaluation using ANOVA of the dataset for seasonal variability indicated that for all constituents (chlorophyll-*a*, conductivity, SRP, TP, NO_2–N, NO_3–N, and TN), significant differences were present among the seasons when comparing all data for all sites. However, when data were evaluated on a site basis, only some sampling locations were observed as having significant differences among seasons (table 5). The presence of seasonal differences among some sampling locations and not others indicates that seasonality may or may not be detected depending on the site that is sampled. Hence, site selection may determine the ability of a monitoring program to capture seasonal variability in water quality.

Although NO_2–N concentrations are often unreported in the literature, we were able to measure NO_2–N concentrations above our detection limit (0.005 mg L^{-1}) and to identify a seasonal pattern within the War Eagle Creek watershed. NO_3–N concentrations were generally greatest during the summer season, except downstream from the WWTP effluent discharge (subbasin 8). The variations in subbasin 8 were likely from incomplete nitrification at the WWTP during winter-spring; the observation that NO_2–N concentrations were greatest when NO_3–N concentrations were lowest provides some circumstantial evidence. NO_3–N and TN showed some seasonal variation as well, although no conclusive pattern was observed, possibly due to the number of water sam–

Table 5. Results from ANOVA statistical evaluations for War Eagle Creek subbasins considering seasonal variability in measured constituents.

Variable	Sampling Sites with Significant Difference among Seasons (p-value)	Sites with Insufficient Data for Analysis
Chlorophyll-*a*	5 (0.03), 6 (0.07), 8 (0.08)	2, 13
Conductivity	3 (0.03), 4 (<0.01), 5 (0.02), 8 (<0.01), 9 (<0.01), 10 (<0.01), 12 (<0.01)	2, 7, 13
SRP	6 (0.03), 8 (<0.01), 9 (0.01)	2
TP	1 (0.05), 8 (<0.01) 9 (<0.01), 10 (0.03)	2
NO_3-N	4 (0.03), 5 (0.03), 6 (<0.01)	2
NO_2-N	1 (0.09), 3 (<0.01), 4 (<0.01), 5 (<0.01), 7 (<0.01), 10 (0.01), 12 (<0.01), 13 (<0.01)	2
TN	1 (0.03), 3 (<0.01), 5 (<0.01), 6 (0.01), 8 (0.10), 9 (0.03)	2

ples collected. SRP and TP varied seasonally at a few sites, but this variation was most likely from variations in the proportion of the WWTP effluent discharge that composes base flow (table 2). Therefore, differences in seasonal nutrient concentration presented no distinct pattern based on the samples collected.

Monitoring results for sestonic chlorophyll-*a* concentrations in the stream water indicated a greater seasonal variability than nutrients in the War Eagle Creek watershed. Many sites (greater than 75%) showed that sestonic chlorophyll-*a* concentrations were greater during the summer season compared to the other seasons sampled. The periphyton and sestonic algae would likely be greatest during the summer season due to sustained periods of low flow conditions (Bernhardt and Likens, 2004), which facilitate algal growth by providing a constant supply of nutrients and minimal shearing stress. Lesser sestonic chlorophyll-*a* concentrations during the winter-spring sampling is likely a result of episodic storm events and increased stream base flow inhibiting the abundance of sestonic algae.

Conductivity was seasonally variable through the War Eagle Creek watershed. The greatest conductivity was generally measured during the summer, whereas the lowest conductivity was often observed during the winter-spring sampling. This could be attributed to increased evapotranspiration within the riparian corridor of groundwater-fed streams that occurs in the summer with warmer temperatures. The increased evapotranspiration results in the concentration of dissolved ions in groundwater potentially increasing conductivity. Alternatively, the riparian corridor and upland vegetation have lower transpirations rates (due to dormant vegetation and milder weather) and greater groundwater contributions during the winter-spring season.

WATER QUALITY MONITORING AT WAR EAGLE CREEK

As of yet, numerical nutrient criteria have not been designated for War Eagle Creek nor in the state of Arkansas. Hence, USEPA and other available guidance on nutrient criteria recommendations were used as a guide for evaluating our measured values. The USEPA ecoregion criteria recommendations relevant to War Eagle Creek and northwest Arkansas are those presented for aggregate ecoregion XI (Central and Eastern Forested Uplands Ecoregion). Within aggregate ecoregion XI, further division is presented by USEPA so that ecoregion XI is divided into level III ecoregions. The specific level III ecoregions for northwest Arkansas are level III ecoregions 38 and 39 (USEPA, 2000b). In the current documentation from USEPA (2000b), only the 25th percentile values are provided (accumulated from all relevant data from within the specified region), and no 75th percentile values from reference streams are presented. However, Clark et al. (2000) presented 75th percentile values of nutrient concentrations in potential reference streams (fig. 4).

The plots of PO_4–P, TP, NO_3–N plus NO_2–N, and TN indicated that median values for subbasins 1 through 7 were similar to USEPA (2000b) 25th percentile and Clark et al. (2000) 75th percentile values. Alternatively, an increase in median concentrations for all N and P constituents was measured starting with subbasin 8, which is influenced by an effluent discharge. Farther downstream (subbasins 9, 11, and 13), median P concentrations decreased and were similar to the USEPA ecoregion and Clark et al. (2000) values (fig. 4).

NO_3–N plus NO_2–N and TN median concentrations for subbasins 10 and 12 were greater than the USEPA (2000b) 25th percentile and Clark et al. (2000) 75th percentile values. These two subbasins, which are characterized by pasture-dominated land cover, were the only two sampling sites that resulted in N concentration medians above the presented ecoregion references. Similarly, regression analyses indicated a strong correlation between TN and % pasture cover in the subbasin ($r = 0.912$) and between NO_3–N and % pasture cover in the subbasin ($r = 0.925$).

Median chlorophyll-*a* concentrations for the 13 sites within War Eagle Creek were generally similar in range to the 25th percentile USEPA ecoregion values. However, some median concentrations were greater than the 25th percentile values, particularly at subbasins 4, 9, and 11. These subbasins were 1.6, 1.6, and 2.2 times greater than the aggregate chlorophyll-*a* ecoregion value (1.6 $\mu g\ L^{-1}$), respectively. While these sampling sites were measured with greater chlorophyll-*a* median concentrations, the values were still fairly low, with the greatest value at 3.5 $\mu g\ L^{-1}$.

Hence, if USEPA (2000b) nutrient values were used as a water quality goal for War Eagle Creek and its tributaries, we would have identified two different interesting watershed characteristics. The first would be the WWTP effluent discharge and its influence on water quality in subbasin 8, and our second concern would be the N concentrations from the pasture-dominated subbasins. However, if the outlet sampling location for the entire watershed (subbasin 13) was measured for nutrient concentrations, it would be found to be within the ranges of the USEPA ecoregion values and the Clark et al. (2000) values. This implies that the location for sampling water to meet a quality goal will influence conclusions regarding the status of a water body or waters within its watershed. Hence, selection of the monitoring location should reflect the overall goal of the monitoring program. Our seasonal sampling program goal was to evaluate seasonal differences and land use correlations among the subbasins so that tributaries to War Eagle Creek and locations along the main stream of the creek that were potential water quality concerns could be identified. Once locations of water quality concern were identified, these locations would then be suggested as sites required for a sufficient, future monitoring program.

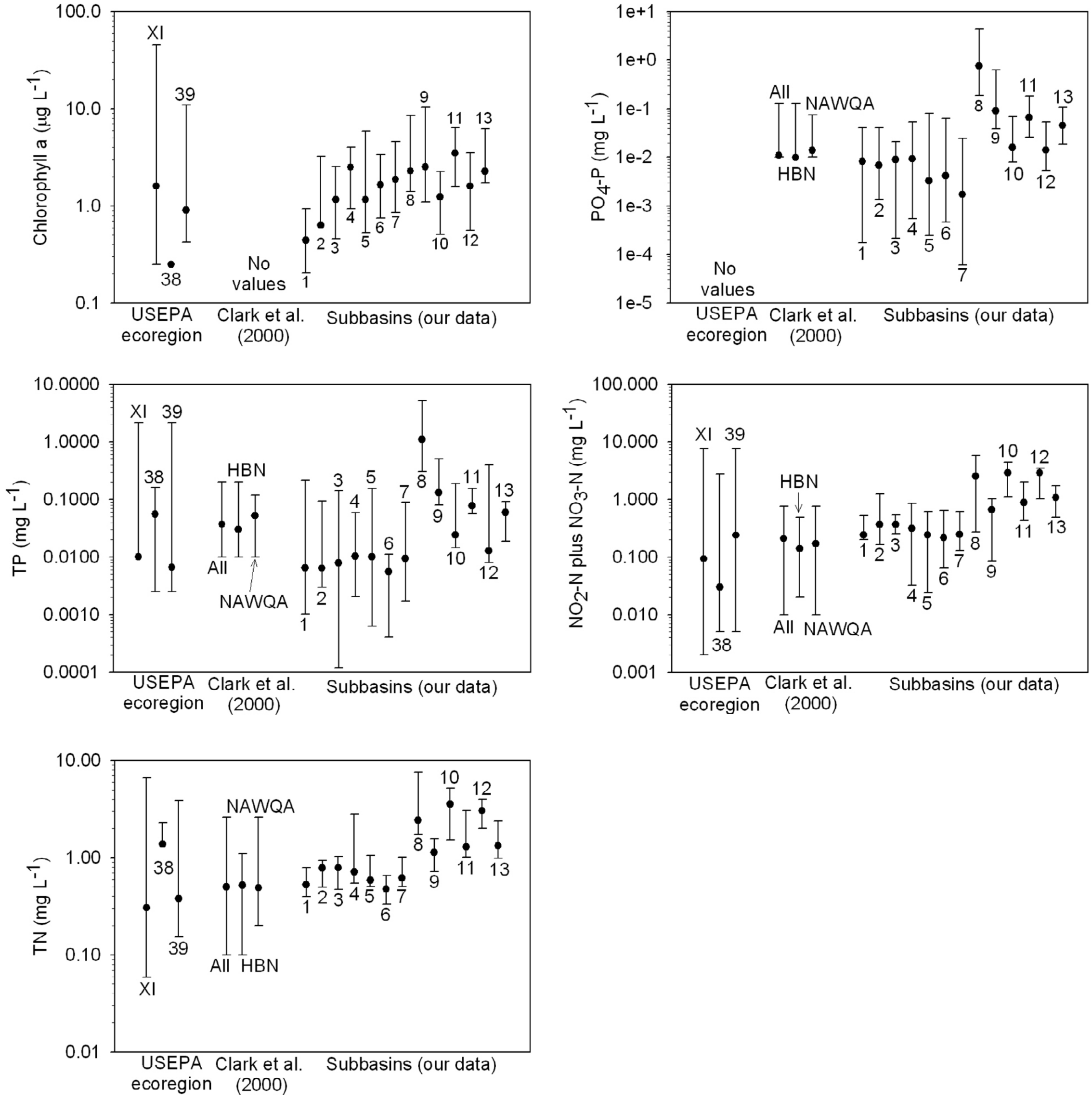

Figure 4. USEPA aggregate ecoregion XI and level III ecoregions 38 and 39 (USEPA, 2000b) 25th percentile data (dark circles); data presented by Clark et al. (2000) as all data, Hydrologic Benchmark Network (HBN), and National Water Quality Assessment (NAWQA) 75th percentile data (dark circles); and median values (dark circles) for each subbasin are presented by constituent. For each value, minimum (dash below dark circle) and maximum (dash above dark circle) are denoted.

Results suggest that land use and point source contributions are dominant factors influencing N and P inputs into the watershed. Hence, sampling sites should consider subbasins 8, 10, and 13. Subbasin 8 should be included in a monitoring program because of the influence that the WWTP located in the subbasin has on water quality, as previously detailed. Subbasin 10 should be monitored because of the dominant pasture land use, which is linked to its greater N concentrations. Subbasin 13 should also be sampled since this subbasin represents the entire watershed and a land use dominated by forest. In addition, water quality values for the selected parameters are most likely to vary seasonally. Hence, the monitoring strategy should include seasonal sampling.

In addition to seasonal and land use considerations, results indicate that chlorophyll-*a* median concentration was greatest for subbasin 11 and that subbasin 11 median chlorophyll-*a* concentration was above the USEPA and Clark et al. (2000) recommendations (fig. 4). Subbasin 11 should therefore be included in our monitoring program. It would also be advantageous to include a reference stream. A reference subbasin would be one that is predominantly forest with no significant effluent discharges (such as from a WWTP). Reference subbasin monitoring is essential for adjusting or verifying ecoregion level or other suggested nutrient criteria (for ensuring their appropriateness for the watershed). Without reference subbasin monitoring, nutrient goals for water quality may be unrealistic and may result in misguidance in watershed management strategies. The subbasins identified in our watershed as potential reference monitoring locations were subbasins 1 and 3. Monitoring of the subbasins previously suggested (1, 8, 10, 11, and 13) from the 13 originally sampled would result in a reduction of >50% in the number of sites sampled while not losing information on the variability of the selected water quality parameters.

Results suggested that implementation of a high-density subbasin sampling protocol for one year that includes seasonal sampling would provide an indication of the variability in water quality throughout a selected watershed. Sampling results could be used to identify a minimal set of sampling locations that represent the water quality variability in the watershed for a long-term monitoring program. By monitoring the minimal set of sampling locations and implementing appropriate Best Management Practices (BMPs), a logical watershed management program could be developed to meet designated nutrient criteria. The nutrient concentrations of reference subbasins (1 and 3) in War Eagle Creek watershed were similar to the USEPA ecoregion and Clark et al. (2000) recommended nutrient concentrations (fig. 4), suggesting that these recommended criteria are a reasonable starting point for evaluating water quality in this watershed.

CONCLUSIONS

Water quality was evaluated in the War Eagle Creek watershed by subbasin unit during 2003 and 2004. The effects of the WWTP effluent discharge were evident, as concentrations of all constituents evaluated (conductivity, SRP, TP, NO_2-N, NO_3-N, and TN) were greater downstream from the effluent discharge site (subbasin 8) compared with the majority of the other subbasins. Comparison of estimated annual loads of TP from the WWTP and from the downstream USGS gauging station indicated that the WWTP annual load corresponded to 13.8% of the TP leaving the War Eagle Creek watershed.

Constituent concentrations varied among seasons; however, no clear trend was evident. Thus, we recommend that all seasons be represented in a water quality data monitoring program.

Regression analyses indicated a strong correlation between TN and % pasture cover in the subbasin (r = 0.912) and between NO_3-N and % pasture cover in the subbasin (r = 0.925) (corresponding to subbasins 10 and 12). Alternatively, geometric mean sestonic chlorophyll-*a* concentrations across the sites were positively correlated with subbasin area (r = 0.64, p = 0.02).

Comparison of results from each sampling station (subbasin) with ecoregion nutrient and sestonic chlorophyll-*a* criteria (from USEPA, 2000b) indicated that: (1) PO_4-P, TP, NO_3-N plus NO_2-N, and TN median values for subbasins 1 through 7 were similar to USEPA 25th percentile and Clark et al. (2000) 75th percentile values, while median concentrations for all N and P constituents measured starting with subbasin 8 (which is influenced by an effluent discharge) were greater; (2) NO_3-N plus NO_2-N and TN median concentrations for subbasins 10 and 12 were greater than the USEPA 25th percentile and Clark et al. (2000) 75th percentile values; and (3) chlorophyll-*a* median concentration was greatest for subbasin 11 and was above the USEPA and Clark et al. (2000) recommendations.

Hence, water quality variability in War Eagle Creek watershed could be assessed by monitoring five subbasin sites (subbasins 1, 8, 10, 11, and 13) of the original 13. Subbasins 1 and 13 were included as the reference stream monitoring site and the watershed outlet monitoring site, respectively. By monitoring the reduced set of sampling sites, a more focused and frugal water quality monitoring program can be developed to determine the quality of water in War Eagle Creek for assessing designated uses.

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NOMENCLATURE

ANOVA = analysis of variance
NH_4-N = ammonium-nitrogen
DEM = digital elevation map
HSD = honestly significant difference
N = nitrogen
NO_2-N = nitrite-nitrogen
NO_3-N = nitrate-nitrogen
OWRB = Oklahoma Water Resources Board
P = phosphorus
SRP = soluble reactive phosphorus
TN = total nitrogen
TP = total phosphorus
USEPA = U.S. Environmental Protection Agency
USGS = U.S. Geological Survey
WWTP = wastewater treatment plant