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Controls on Nutrients Across a Prairie Stream Watershed: Land Use and Riparian Cover Effects

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ABSTRACT / Nutrient inputs generally are increased by human-induced land use changes and can lead to eutrophication and impairment of surface waters. Understanding the scale at which land use influences nutrient loading is necessary for the development of management practices and policies that improve water quality. The authors assessed the relationships between land use and stream nutrients in a prairie watershed dominated by intermittent stream flow in the first-order higher elevation reaches. Total nitrogen, nitrate, and phosphorus concentrations were greater in tributaries occupying the lower portions of the watershed, closely mirroring the increased density of row crop agriculture from headwaters to lower-elevation alluvial areas. Land cover classified at three spatial scales in each sub-basin above sampling sites (riparian in the entire catchment, catchment land cover, and riparian across the 2 km upstream) was highly correlated with variation in both total nitrogen (r^2 = 53%, 52%, and 49%, respectively) and nitrate (r^2 = 69%, 65%, and 56%, respectively) concentrations among sites. However, phosphorus concentrations were not significantly associated with riparian or catchment land cover classes at any spatial scale. Separating land use from riparian cover in the entire watershed was difficult, but riparian cover was most closely correlated with in-stream nutrient concentrations. By controlling for land cover, a significant correlation of riparian cover for the 2 km above the sampling site with in-stream nutrient concentrations could be established. Surprisingly, land use in the entire watershed, including small intermittent streams, had a large influence on average downstream water quality although the headwater streams were not flowing for a substantial portion of the year. This suggests that nutrient criteria may not be met only by managing permanently flowing streams.

Land use drives nutrient loadings throughout the United States (U.S. Environmental Protection Agency [USEPA] 2000) and elsewhere. Excessive inputs of nitrogen and phosphorus often result in eutrophication (Carpenter and others 1998; Dodds and others 2002), impairing both the physical and biologic integrity of surface waters. Within watersheds, changing land use patterns may be reflected by a longitudinal gradient of in-stream conditions. The negative influences of land use conversion on both physiochemical (Buck and others 2004; Johnson and others 1997) and biotic (Allan 2004; Harding and others 1999; Storey and Cowley 1997; Whiles and others 2000) water quality metrics within agricultural catchments are well documented.

Prairie streams are not well studied relative to temperate forested systems (Dodds 1997). Only a moderate number of studies have investigated nutrient conditions (Harding and others 1999; Kemp and Dodds 2001). Grassland streams are abundant worldwide (Dodds 1997). Highly endangered at present, such streams once characterized a large portion of the North American continent (Dodds and others 2004). Intermittence is a characteristic feature of such streams, and intermittent streams are only just beginning to receive attention with regard to factors other than macroinvertebrates and fish (Boulton and Lake 1990). The relationship of water quality to intermittence has yet to be well described.

Areas formerly dominated by tallgrass prairie but now converted to cropland, such as the Corn Belt ecoregion of Iowa, have substantially greater nutrient concentrations in rivers and streams than they did under the reference condition, as indicated by broad-scale analyses of human land use effects (Dodds and Oakes 2004). Areas formerly in tallgrass prairie now contribute substantially to eutrophication problems in the Gulf of Mexico (Alexander and others 2000). An understanding of factors that may mitigate human influences on nutrients in streams has taken on added urgency (Dodds and Welch 2000).

KEY WORDS: Nitrogen; Phosphorus; Prairie watershed; Riparian; Water quality

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Particular emphasis has been placed on water quality as related to stream riparian zones, which serve an important role as interfaces between terrestrial and aquatic ecosystems. The protection or restoration of riparian zones has been widely promoted as a management practice to improve water quality (Natural Resources Conservation Service [NRCS] 1996). Land use in the riparian ecotone is highly correlated with surface nutrient concentrations at both field (Karr and Schlosser 1978; Lowrance and others 1984; Peterjohn and Correll 1984) and landscape (Johnson and others 1997; Osborne and Wiley 1988; Sliva and Williams 2001) scales across a wide range of geologic and climatic conditions (Sabater and others 2003). In some instances, riparian land use (Johnson and others 1997) or sewage inputs (Osborne and Wiley 1988) are better predictors of in-stream nutrient concentrations than land cover in the entire catchment, although contrasting reports from other investigators (Hunsaker and Levine 1995; Sliva and Williams 2001) indicate that the strength of these relationships may vary. It is not well established where riparian protection has the greatest influence on water quality. Is protection a few kilometers above a sensitive site adequate, or are whole-watershed approaches necessary? The answer may depend on the ecosystem attribute of concern (Johnson and Covich 1997). Additionally, little is known about the function of riparian zones in watersheds containing intact, moderately impacted grasslands.

Nutrient loading and retention often are regulated at spatial scales larger than the reach scale (Allan and others 1997). Thus, investigation into land use–nutrient dynamics requires the examination of these processes at the scale of entire watersheds. The development of remote sensing and geographic information systems technologies has facilitated the examination of landscape influences (Johnson and Gage 1997) by enabling watershed-scale studies of nutrient dynamics. The strength of land use influences may decrease with catchment size (Buck and others 2004), and may reflect the scale of the study design (Allan and others 1997). Therefore, it may be necessary to conduct analyses that encompass a diversity of catchment sizes and spatial scales for an accurate assessment of land use impacts.

The objectives of our study were to assess land use–nutrient relationships within a Midwestern United States prairie watershed, and to examine the influence of longitudinal changes in land use intensity on in-stream nutrient concentrations. We used remote sensing and geographic information systems technologies to examine relationships between nutrient concentrations and land cover at three spatial scales: riparian land cover above sites, catchment land cover above sites, and riparian land cover for the entire 2 km above sampling sites. Because riparian zones regulate allochthonous inputs to surface waters (Karr and Schlosser 1978; Peterjohn and Correll 1984), we hypothesized that land use conditions in the riparian ecotone would be highly correlated with in-stream nutrient concentrations. Gradients of land use intensity within the watershed were investigated by comparing nutrient concentrations sampled in relatively pristine headwater areas with those sampled in more agriculturally impacted lowland tributaries. Seasonal nutrient concentrations were related to land use intensity by examination of long-term datasets obtained from the nearby Konza Prairie Biological Station (Kansas). Similarly, the flow of small streams was characterized using the long-term hydrologic datasets from Konza Prairie Biological Station.

Methods

Study Sites

For this study, 28 sampling sites were selected within the Mill Creek watershed, a fifth-order stream with a 1,010-km^2 drainage basin located in the Flint Hills region of Kansas, USA (Figure 1, Table 1). Higher-elevation (upland) headwaters of the basin are characterized by rolling hills, shallow coarse soils, and tallgrass prairie predominantly used as cattle pasture. These pastures, typically burned annually, experience a high density of cattle for only the first few months of summer. Reduced topography, alluvium soils, and a mixture of tallgrass prairie and row crop agriculture characterize the lower elevation reaches of the drainage. Largely because of steep topography and unfavorable soils, a low proportion (mainly the unconsolidated soils near larger streams) of the upper reaches of Mill Creek have been converted to cropland agriculture, and are used primarily as rangeland for cattle. This has resulted in a gradient of increasing land use intensity moving from upstream to downstream. Sites were selected to capture this gradient as well as the diversity of stream sizes, and to encompass all major subcatchments of Mill Creek. Sampling was conducted primarily upstream of public-access bridge crossings because public access is not allowed at most other points in the basin. No confined livestock operations or other point sources were observed in close proximity to the sampling locations, and large licensed operations (more than 200 animals) did not occur above sampling sites.

Seasonal nutrient concentrations in pristine headwaters and agriculturally impacted downstream sites were examined in Kings Creek (Kansas) located on the Konza Prairie Biological Station approximately 30 km

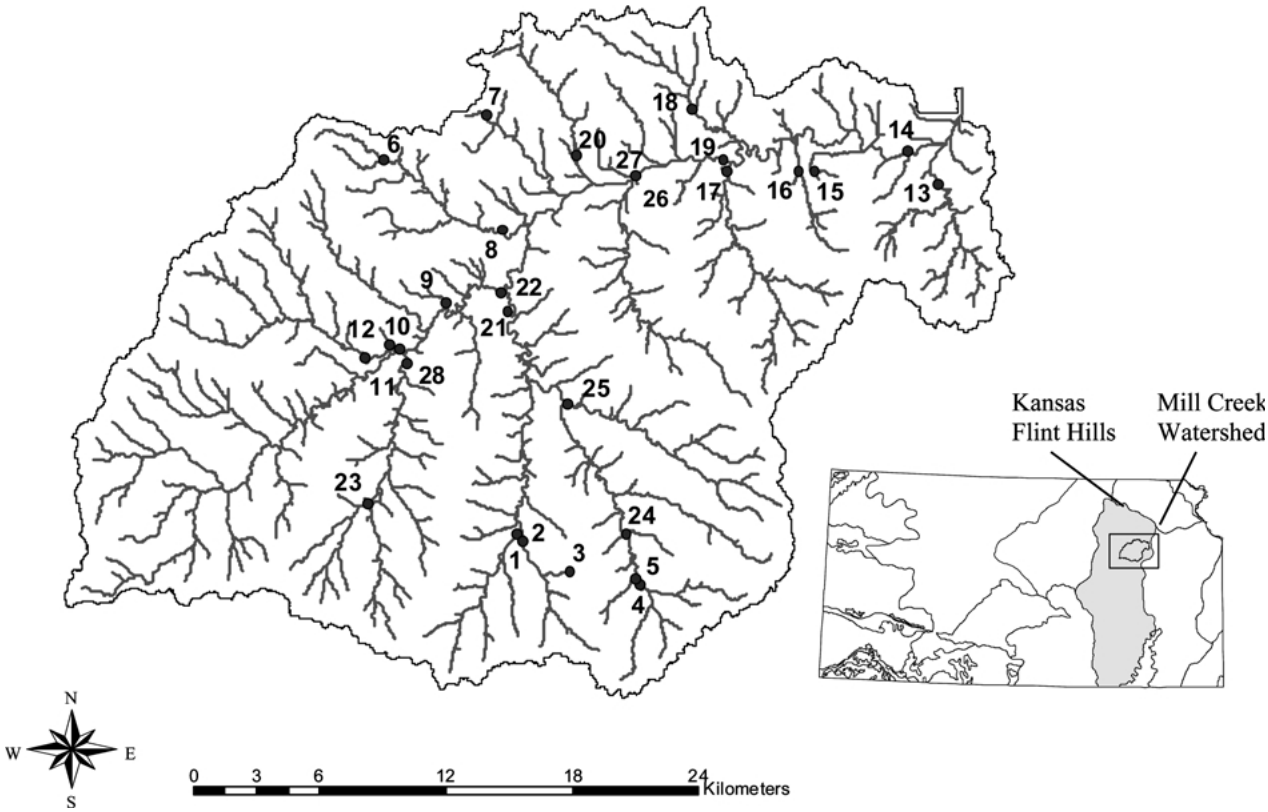

Figure 1. Location of sampling sites in the Mill Creek watershed, Kansas.

from Mill Creek, as were patterns of hydrology in small streams. Detailed descriptions of the location (Kemp and Dodds 2001), geology (Oviatt 1998), hydrology, chemistry (Gray and others 1998), and biology (Gray and Dodds 1998) of these sites have been published previously.

Two sites on Kings Creek were examined. The first, N01B, is located on a first-order intermittent tributary with a relatively pristine upland watershed consisting entirely of native tallgrass prairie grazed by bison stocked at 0.7 animal units/ha. The second site (nature trail) is located on a second-order perennial downstream reach of Kings Creek. The nature trail site is located below 0.2 km^2 of fertilized cropland, and thus is moderately impacted by agriculture. Because Mill Creek and Kings Creek are located near each other, there is little variation in geology, soils, or climatic conditions between the two watersheds. Therefore, the long-term datasets collected at Kings Creek could be used to investigate temporal trends in the Flint Hills region of Kansas under relatively pristine conditions.

Water Chemistry Sampling and Analysis

Water chemistry data were collected at Mill Creek on 15 May 2002, 14 June 2002, 23 October 2002, 7 February 2003, 26 March 2003, 16 May 2003, 15 June 2003, and 8 September 2003. Sampling was conducted throughout the year to encompass the hydrologic variation characteristics of Mill Creek (Figure 2). Each site was sampled for total nitrogen (TN), nitrate (NO_3^-), and total phosphorus (TP). Water samples were taken from the thalweg of each stream in acid-washed bottles. Samples were frozen and stored in the dark before analysis.

Nitrate samples were filtered through Whatman GF/F glass microfiber filters (effective retention, 0.7 μm) and analyzed by Cd reduction followed by diazo dye formation. Total nitrogen and TP samples were digested by a perchlorate-autoclave method (Ameel and others 1993). Digested TN samples were analyzed for NO_3^-, as described earlier, and TP samples were analyzed for soluble reactive phosphorus by the ammonium-phosphomolybdate method (American Public Health Association [APHA] 1992). Efficiency of digestion was assessed using urea and adenosine triphosphate spikes for nitrogen and phosphorus internal standards, respectively. External standards and internal spikes assessed reliability and recovery efficiencies of the assays. Detection limits of the assays were 0.7 μg/l for NO_3^- and 3 μg/l for TN and TP.

Table 1. Name, location, catchment size (area), percentage cropland, mean nutrient concentrations, number of sampling periods (n), and discharge data for selected sampling sites within the Mill Creek watershed. Site 13 was not included in analyses (see Methods)

Site	Name	Longitude	Latitude	Area (km^2)	Cropland (%)	TN (μg/l)	NO_3^-N (μg/l)	TP (μg/l)	N (μg/l)	Discharge-May 2003 (m^3/s)
1	South Branch Mill Creek headwaters	−96.273	38.890	34	1.89	331	94	13	7	
2	South Branch Mill Creek headwaters	−96.270	38.887	21	1.45	261	46	13	7	0.027
3	South Branch Mill Creek tributary	−96.242	38.873	3	0.70	463	142	15	7	
4	East Branch Mill Creek below dam	−96.199	38.867	30	0.67	361	16	11	7	0.020
5	East Branch Mill Creek tributary	−96.202	38.870	7	0.07	256	104	9	6	
6	Hendricks Cr. headwaters	−96.354	39.063	12	3.19	959	178	33	7	
7	Pretty Creek	−96.293	39.083	4	26.43	907	534	30	6	
8	Hendricks Creek main stem	−96.283	39.031	48	5.41	360	123	18	6	
9	West Branch Mill Creek tributary	−96.317	38.997	4	0.99	273	38	8	3	
10	West Branch Mill Creek tributary	−96.350	38.978	2	5.46	334	170	15	3	
11	West Branch Mill Creek	−96.344	38.976	224	9.65	464	55	24	7	0.750
12	Spring Creek	−96.365	38.971	63	3.99	294	104	15	7	
13	Dry Creek	−96.020	39.052	42	11.97	1787	858	9	2	
14	Mill Creek at Maple Hill	−96.039	39.067	1010	9.84	697	92	39	7	
15	Stuckey's Creek	−96.095	39.058	7	27.20	530	207	27	6	
16	Dog Creek	−96.105	39.058	15	17.37	1222	276	43	6	0.019
17	Snokomo Creek	−96.147	39.058	67	6.27	400	160	12	7	0.101
18	Mulberry Creek	−96.169	39.086	23	16.84	1911	806	84	6	
19	Mill Creek at Paxico	−96.150	39.063	848	8.26	590	202	28	7	
20	Paw Paw Creek	−96.238	39.065	20	15.05	1899	644	234	6	
21	South Branch Mill Creek	−96.279	38.993	270	4.73	462	196	20	7	1.783
22	West Branch Mill Creek	−96.284	39.001	373	7.58	490	59	28	7	0.779
23	Illinois Creek headwaters	−96.363	38.904	23	5.00	322	50	23	7	
24	East Branch Mill Creek	−96.208	38.891	42	0.89	426	111	12	7	
25	Nehring Creek	−96.243	38.951	48	4.07	533	115	16	7	0.055
26	Kuenzli Creek	−96.202	39.056	357	4.48	515	69	26	6	
27	Mill Creek at Michaelis ranch	−96.203	39.056	823	7.73	501	139	26	7	
28	Illinois Creek main stem	−96.340	38.969	91	3.62	319	61	37	6	0.334

TN, total nitrogen concentration; NO_3^-N, nitrate concentration; TP, total phosphorus concentration; N, nitrogen.

Mean concentrations across sampling periods were calculated for TN, NO_3^-, and TP, with the following exceptions: site 13 was inaccessible during five of the seven sampling periods because of highway construction, and thus was not included in the analyses. Sites located on smaller tributaries exhibited periodic drying, or were frozen in the winter (Table 1). In these instances, mean nutrient concentrations were calculated from fewer than seven samples. There were not sufficient sampling periods to analyze temporal trends in nutrient concentrations using the data collected from Mill Creek. Therefore, only mean nutrient concentrations were used in statistical analyses comparing water chemistry values with riparian and catchment land cover data.

Samples from Kings Creek were taken approximately three times per week from 1994 to 2001, and mean monthly nutrient concentrations used in analyses were

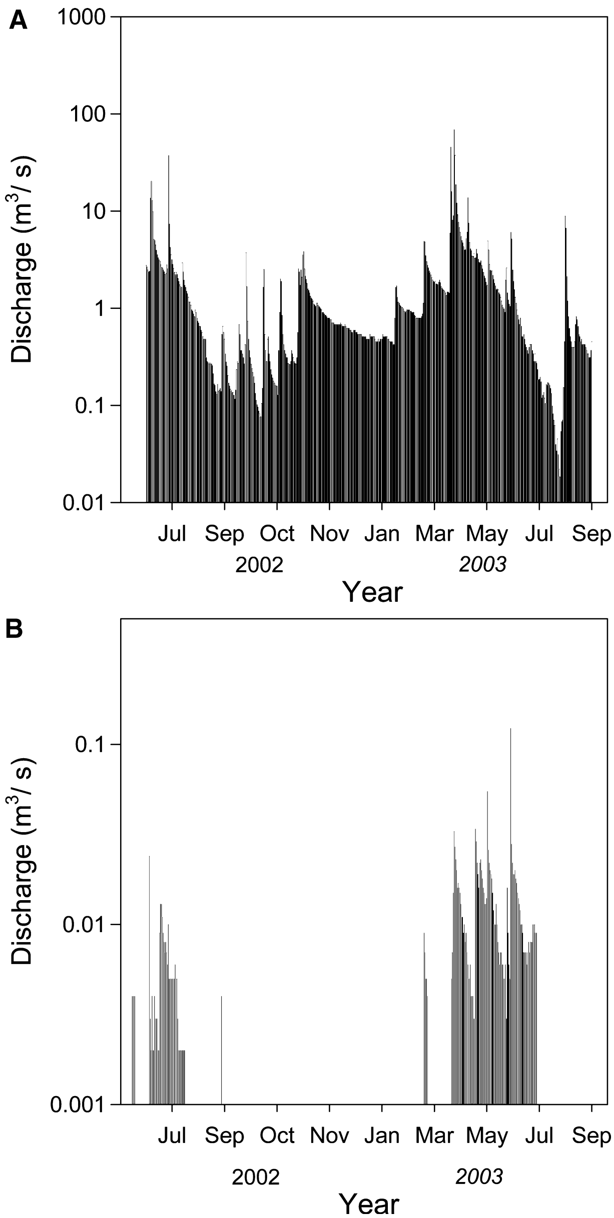

Figure 2. Mean daily discharge (m^3/s) at the lower part of the Mill Creek watershed (A, sampling station 14, Table 1) taken from U.S. Geological Survey discharge data collected from May 2002 through September 2003, and of a nearby first-order prairie stream, Kings Creek, watershed N04D (B).

quantified from a total of 528 and 1,163 samples taken on the N01B and nature trail sites, respectively. Hydrology is reported for a first-order sub-basin of Kings Creek (station N04D) as an indicator of typical conditions.

Digital and Land Cover Data

Land cover was assessed at three spatial scales: catchment and riparian land cover in the entire subcatchment above each sampling site and riparian land cover over the 2 km immediately upstream of each sampling site. Digital stream networks were derived for the Mill Creek watershed using a 30-m digital elevation model, ARCGIS (Arcview ver. 8.2 2002), and ArcHydro (Maidment 2002) software. The catchment area of Mill Creek and the subcatchment above each sampling site were delineated using catchment-processing tools in ArcHydro software. By overlaying subcatchment layers with digitized riparian and catchment land cover data, we quantified catchment and riparian land cover above each sampling site.

Local riparian influence was examined by quantifying riparian land cover 2 km upstream of each sampling site using geoprocessing tools in ARCGIS software. To examine spatial patterns of soil characteristics within the basin, soil types were classified from the state soil geographic database (STATSGO; NRCS 1994). Cropland and alluvial soils were almost completely coincident, except in some small residential areas. Therefore, it was not possible to test statistically for the effect of soils because crops are grown in essentially all areas where alluvial soils have accumulated.

Riparian land cover was classified from the Kansas Riparian Areas Inventory dataset (NRCS 2001). The riparian ecotone in this dataset was defined as the 33 m adjacent to the stream and digitized at a 1:24,000 scale from USGS Digital Orthophotograph Quarter Quadrangles that reflected land cover conditions in 1991. This dataset contained 11 land cover classes (animal production area, barren land, cropland, crop/tree mix, forest, grassland, grass/tree mix, shrub/scrub land, urban land, urban/tree mix, water), and riparian areas were classified by the land cover type occurring in 51% or more of the 33-m ecotone. Three of the 11 land cover classes (shrub/scrub land, barren land, and animal production area) did not account for more than 1% of the riparian land cover in the subcatchment above any sampling site, and thus were not included in analyses. The remaining eight classes were aggregated into four classes (cropland, forest, grassland, and urban land) according to the classification scheme developed by Anderson and others (1976).

Catchment land cover was classified from the Kansas Land Cover dataset (Kansas Applied Remote Sensing [KARS] 1993). This dataset was digitized at a 1:100,000 scale from Landsat Thematic Mapper imagery classes that reflect land cover conditions in 1991. The KARS dataset also contained 11 land cover classes, and was reclassified in the same way as the riparian dataset. Comparison of the riparian dataset with a 33-m "buffer" clipped from the catchment dataset showed similar classifications (Kendall's Tau correlation coefficient, 0.93). Differences are likely attributable to the higher spatial resolution of the riparian dataset. Catchment land cover at the 1:24,000 scale was not available for Mill Creek at the time of this study. Because this study emphasized the influence of riparian land uses, we chose to use the highest-resolution riparian dataset available. Because land cover was expressed as percentages, the spatial mismatch of the two datasets was not problematic. Strong correlations between the two datasets allowed for comparison of catchment land cover with riparian land cover.

Statistical Analyses

Mixed linear models were used to identify land cover classes (cropland, forest, grassland, urban land) that exhibited significant relationships with in-stream nutrient concentrations. Because the watersheds of many of the sites were nested within each other (Figure 1), spatial autocorrelation prevented us from examining all sites independently. We accounted for spatial autocorrelation by using a mixed linear model with an unequal covariance matrix, in which uncorrelated sites were treated independently, and the degree of correlation for nested sites was assumed to be proportional to the distance between them. A Satterthwaite approximation (Satterthwaite 1941) was used to compute the denominator degrees of freedom, and distances between nested sites were calculated from their geographic positioning (latitude and longitude coordinates) along the stream channel. Separate analyses were conducted to assess relationships between nutrient concentrations and land cover at the three spatial scales.

After significant land cover classes were identified using mixed linear models, multiple linear regression analyses were run to examine the strength of correlations between land cover classes identified as significant and nutrient concentrations at all three spatial scales. As stated earlier, the spatial autocorrelation in this sampling design violated independence assumptions. Thus, the use of regression here was intended to be descriptive (Roth and others 1996), and correlations (R^2 values) simply reflected the strength of land use–nutrient relationships. To investigate the influence of riparian land cover independent of catchment effects, we examined partial correlations (r) between riparian land cover classes that were significant in mixed linear models and nutrient concentrations, controlling for catchment land cover classes that were significant in the mixed linear models.

Results

Hydrology and Water Chemistry Data

Hydrology was variable throughout the sampling time in the lower part of Mill Creek, with discharge varying over three orders of magnitude (Figure 2). Kings Creek, with an area of 1 km^2, is comparable with the smaller sampling sites on Mill Creek and had sporadic flow over the sampling period. These data suggest that most of the smaller tributaries were not flowing during summer and winter, and thus could be classified as intermittent.

Nutrient assays showed considerable variation in TN, NO_3^-, and TP concentrations among sites (Figure 3). Upland (higher elevation) headwater sites were characterized by low nutrient concentrations, with mean TN concentrations generally less than 500 μg/l, mean NO_3^--N concentrations generally less than 150 μg/l, and mean TP concentrations generally not exceeding 30 μg/l (Table 1). Lowland tributaries exhibited higher nutrient concentrations, with mean TN concentrations at some sites approaching 2,000 μg/l, mean NO_3^--N concentrations approaching 800 μg/l, and mean TP concentrations at some lowland sites exceeding 200 μg/l. Samples taken at main stem sites showed intermediate TN, NO_3^-, and TP concentrations relative to upland and lowland tributaries. Elevated nutrient concentrations in lowland tributaries closely mirrored the presence of alluvium soils, and consequently row-crop agriculture, within the basin.

Nutrient concentrations in Mill Creek also were highly variable with respect to the sampling period (Figure 4). Across sites, nutrient concentrations were typically lowest during the winter and early spring sampling periods, and highest in mid and late summer. Upland headwater sites exhibited comparatively less variability in TN, NO_3^-, and TP concentrations among sampling periods than either lowland tributary sites or main stem sites. Sites on lowland tributaries showed the largest nutrient concentrations, with TN, NO_3^-, and TP concentrations more than doubling in the summer months.

In Kings Creek, TN and NO_3^- concentrations at the agriculturally impacted nature trail site also were higher than the concentrations at the upland, higher-elevation N01B site, particularly in the mid and late summer months, when base flow is most heavily influenced by groundwater (Figure 5). However, TP concentrations and seasonal fluctuations were very similar at both Kings Creek sites. The N01B data required the entire period of record, not just the range of sampling dates used at Mill Creek. In small Flint Hills streams, any month can have a discharge of zero or flow.

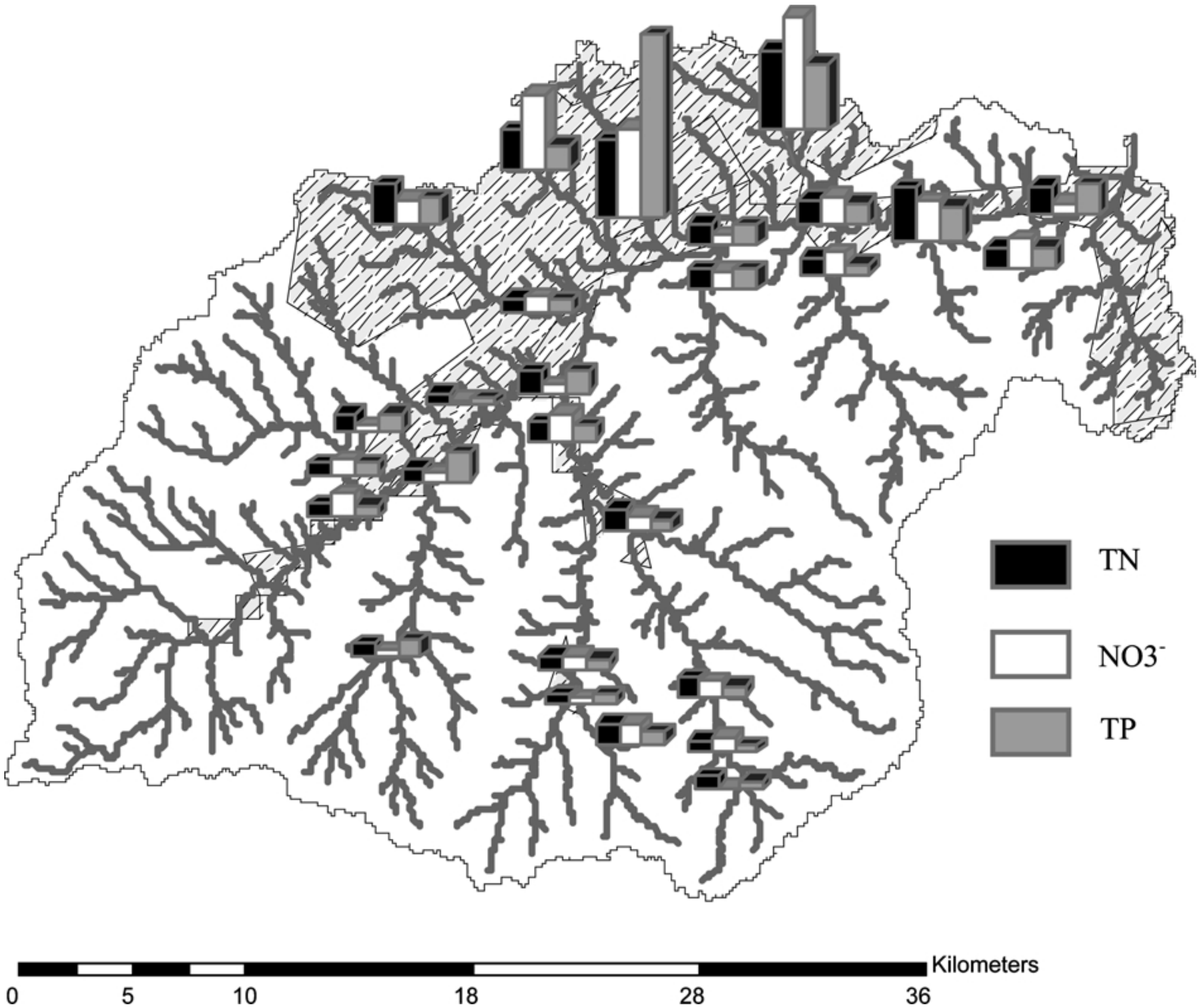

Figure 3. Nutrient concentrations at sites within the Mill Creek watershed. Total nitrogen (TN), nitrate (NO3−), and total phosphorus (TP) concentrations are presented as a proportion of mean nutrient concentrations from each site over mean concentrations across sites. Mean concentrations across sites were 638 μg/l for TN, 202 μg/l for NO3−, and 31 μg/l for TP. Shading indicates the presence of alluvium soils, which closely mirrored agricultural activity in the catchment and elevated nutrient concentrations in the lower elevations of the watershed.

Land Use–Nutrient Relationships

Land use in the watershed and the riparian zones of the watersheds were correlated, but not strongly in many cases (Table 2). Many of the correlations were driven by the fact that most of the upland areas were grassland and had few trees, whereas alluvial areas tended to be converted to cropland, but also had tree-lined riparian areas near to the larger stream channels. Larger streams are more likely to have substantial alluvial soils, and the northern part of the watershed lies within the alluvial influence of the larger Kansas River. These topographic relationships are reflected in the negative correlation between cropland and grassland land use, whereas there was little relationship between forest and grassland or forest and cropland. Likewise, riparian cropland and grassland were negatively correlated, but neither was related to the degree of riparian forest. Riparian cover 2 km upstream was poorly related to riparian cover in the whole watershed above (Table 2).

Mixed linear models indicated that riparian land cover at both subcatchment and local scales as well as catchment land cover was significantly associated with TN and NO_3^- concentrations, but not TP concentra-

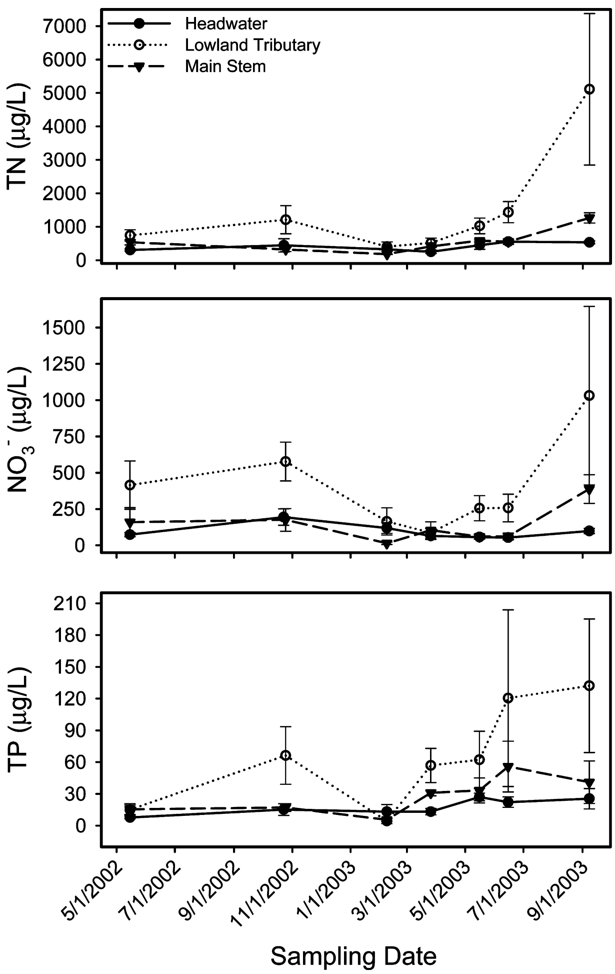

Figure 4. Spatial and temporal variation in nutrient concentrations in the Mill Creek watershed. Mean values for upland (sites 1–6, 8–12, 23–25, 28), lowland tributary (sites 7, 15–18, 20), and main stem (sites 14, 19, 21, 22, 27) sites are presented to illustrate intrasite and intersite variation in nutrient concentrations. Error bars represent one standard error.

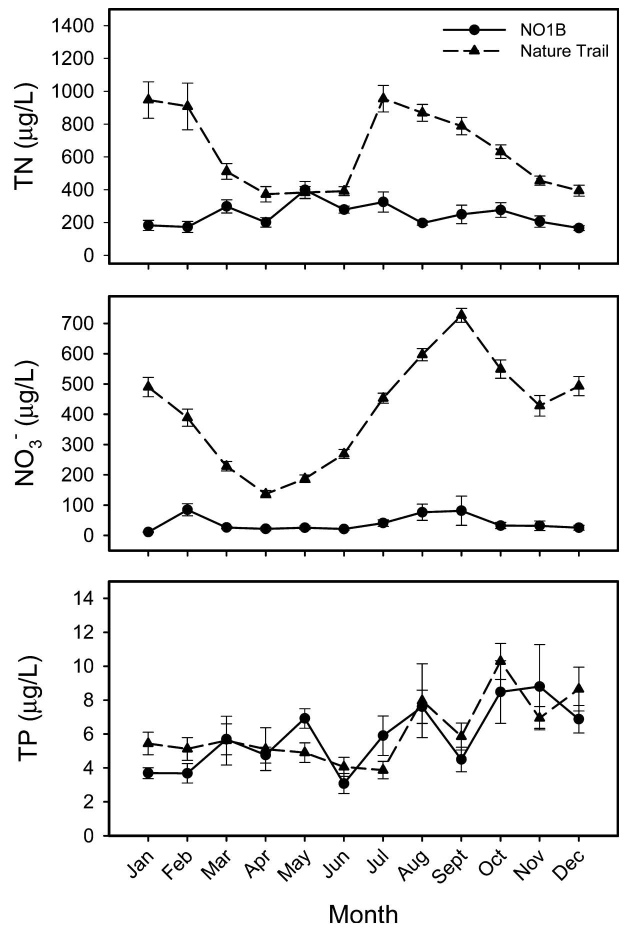

Figure 5. Mean monthly nutrient concentrations (1994–2001) in Kings Creek, located on the Konza Prairie Biological Station. The data presented were collected at a relatively pristine headwater site (N01B) as well as at a downstream site moderately impacted by agriculture (Nature Trail), and illustrate the temporal and spatial variation in nutrient concentrations in Kings Creek. Error bars represent one standard error.

tions (Table 3). The percentages of cropland, forested land, and urban land in the riparian ecotone of each subcatchment were significantly ($P < 0.05$) related to both TN and NO_3^- concentrations. Cropland and forest land cover classes were significantly associated with TN and NO_3^- at the catchment scale. At the local riparian scale, the percentage of cropland in the riparian ecotone 2 km upstream of the sampling site also was significantly related to TN and NO_3^- concentrations.

Land cover classes that were significant in the mixed linear models correlated highly with TN and NO_3^- concentrations in multiple regression analyses across spatial scales (Figure 6). Riparian land cover in the subcatchment above each site was most correlated with in-stream NO_3^- concentrations, explaining almost 70% of the variance among sites. Catchment and local riparian land cover also explained high percentages of variance in NO_3^- concentrations among sites. Land cover classes exhibited higher correlations with NO_3^- than TN, with the most pronounced differences occurring at the riparian subcatchment scale. Land cover at all three spatial scales showed similar degrees of correlation with TN concentrations.

Partial correlations indicated that the percentage of riparian cropland in the 2 km upstream of the sampling site was significantly ($P < 0.05$) correlated with TN and NO_3^-, even after control was used for variance explained by catchment land cover classes that were

Table 2. Correlations among land-use variables. L_= land use, r_ = riparian, r_ 2k = riparian averaged across the 2 km above the site of sample collection. Only significant correlations as determined by the nonparametric Kendall tau test at $P < 0.05$ are given.

	L_crop	L_grass	L_forest	L_urban	r_crop	r_forest	r_grass	r_urban	r_c2k	r_f2k	r_g2k	r_u2k
L_crop	1.00	−0.87			0.46		−0.34		0.33		−0.32	0.37
L_grass	−0.87	1.00			−0.42		0.40		−0.36		0.35	−0.33
L_forest			1.00	0.39		0.31				0.50		
L_urban			0.39	1.00						0.39		
r_crop	0.46	−0.42			1.00		−0.44					0.30
r_forest			0.31		−0.44	1.00	−0.34			0.31		
r_grass	−0.34	0.40				−0.34	1.00	−0.33				
r_urban							−0.33	1.00				
r_c2k	0.33	−0.36							1.00		−0.30	0.29
r_f2k			0.50	0.39		0.31				1.00		
r_g2k	−0.32	0.35							−0.30	−0.50	1.00	
r_u2k	0.37	−0.33			0.30				0.29			1.00

Table 3. Results of mixed linear models used to identify land cover classes that exhibited significant relationships with nutrient concentrations sampled in Mill Creek. Relationships between total nitrogen (TN, µg/l), nitrate (NO_3-N, µg/l), total phosphorus (TP, µg/l), catchment land cover above sites (catchment, %), riparian land cover above sites (riparian, %), and local riparian land cover 2 km above sites (2K riparian, %) are presented.

Comparison	Classification	Parameter estimate	*t* Value	*P* Value
TN riparian				
	Intercept	868.18	4.15	0.0005
	Crop	18.18	2.67	0.0156
	Forest	−116.66	−3.71	0.0018
	Urban	−17.16	−2.54	0.0193
TN catchment				
	Intercept	647.24	3.78	0.0014
	Crop	34.83	3.15	0.0074
	Forest	−100.12	−2.56	0.0177
TN-2K riparian				
	Intercept	612.33	4.92	0.0002
	Crop	2.87	2.41	0.0441
NO_3-N riparian				
	Intercept	260.74	3.49	0.0021
	Crop	11.27	4.54	0.0002
	Forest	−8.75	−3.92	0.0008
	Urban	−43.81	−4.39	0.0003
NO_3-N catchment				
	Intercept	219.27	3.79	0.0019
	Crop	17.64	4.98	0.0002
	Forest	−58.31	−3.82	0.0010
NO_3-N-2K riparian				
	Intercept	36.37	1.01	0.3232
	Crop	5.21	5.62	<0.0001
TP riparian				
	Intercept	41.93	2.82	0.0133
	Crop	−0.08	−0.65	0.5294
TP catchment				
	Intercept	31.51	1.92	0.0699
	Crop	0.93	1.09	0.2920
TP-2K riparian				
	Intercept	39.99	2.75	0.0157
	Crop	0.02	0.49	0.6364

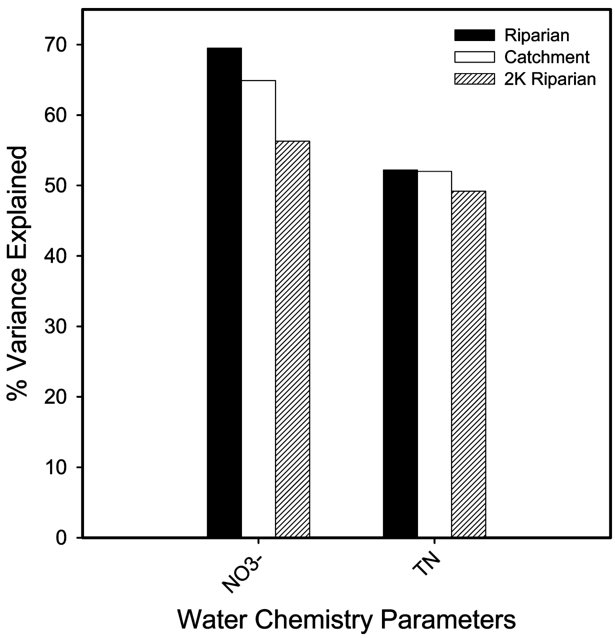

Figure 6. Results of descriptive regression models relating total nitrogen (TN) and nitrate (NO_3^-) concentrations to riparian land cover (riparian) and catchment land cover (catchment) above each site, and local riparian land cover (2K riparian) 2 km upstream of each site in the Mill Creek watershed. Variance (R^2 values) in nutrient concentrations accounted for by land cover at the three spatial scales is presented. All values reported as significant at $P < 0.05$.

significant in the mixed linear models (Table 4). Riparian land cover at the subcatchment scale was not significantly correlated with TN or NO_3^- after catchment effects had been taken into account.

Discussion

Water Chemistry Data

Nutrient concentrations and fluctuations closely mirrored the increasing degree of agricultural intensity from the headwaters to the lower reaches of Mill Creek. In lowland tributaries, elevated TN, NO_3^-, and TP concentrations in mid and late summer probably resulted from seasonal changes in the hydrologic regime. Total nitrogen and NO_3^- concentrations in Kings Creek showed similar seasonal fluctuations at the nature trail site, which have been attributed to the increased influence of row crop–impacted groundwater inputs of NO_3^- during low-discharge periods (Kemp and Dodds 2001). During periods of higher discharge, the receiving capacities of streams often are greater because pollutants can be diluted upon entering surface waters (Novotny and Olem 1994). At Mill Creek, high flow events occurring in lower reaches derived a large portion of their discharge from low-nutrient headwater streams surrounded by relatively pristine grasslands, which often were dry during base flow periods.

Total phosphorus concentrations from the downstream nature trail site at Kings Creek did not exhibit the high concentrations and drastic fluctuations observed in the lowland tributaries of Mill Creek. The high concentrations and fluctuations may reflect the greater extent of agricultural land at Mill Creek, or the influence of unidentified point sources near some Mill Creek sites.

Our study supports previous investigations (Buck and others 2004; Harding and others 1999) that documented degraded physiochemical conditions in relation to increasing agricultural intensity in grassland watersheds. Increasing nutrient loading within watersheds often leads to eutrophication (Dodds and Welch 2000; Dodds and others 2002), impairing surface waters for their designated uses such as drinking and the support of aquatic life. Although biologic data were not collected in this study, Harding and others (1999) have documented increased periphyton levels in the agriculturally impacted lowland tributaries of a grassland watershed in New Zealand. This effect is supported by strong empirical relationships linking nitrogen and phosphorus to periphyton biomass (Dodds and others 2002), although nitrate may not be as strongly related to periphyton biomass as TN (Dodds 2003).

The presence of agriculture on Mill Creek was associated with fertile alluvium soils in the lower reaches of the drainage. Whereas row crop agriculture and alluvial soils were not examined independently at Mill Creek, Kemp and Dodds (2001) demonstrated that groundwater flowing under alluvial grassland had 10-fold lower dissolved nitrogen concentrations than groundwater flowing beneath fertilized cropland at Kings Creek. Because the dominant mode of nitrogen transport to surface water is via subsurface flow as NO_3^- (Hill 1996), NO_3^- inputs drove spatial and temporal patterns in TN concentrations in Kings Creek (Kemp and Dodds 2001), and also likely structured TN dynamics in the geologically similar Mill Creek.

Land Use–Nutrient Relationships

Land cover classes were highly correlated with TN and NO_3^- concentrations, but not TP concentrations. Mixed linear model results indicating a significant association of agricultural, forest, and urban lands with variation in TN and NO_3^- concentrations among sites were consistent with the results of previous studies (Johnson and others 1997; Jones and others 2001; Osborne and Wiley 1988; Sliva and Williams 2001).

Table 4. Partial correlations among nutrient concentrations and riparian land cover classes in the Mill Creek watershed. Correlations controlled for catchment land cover classes that were significant in mixed linear models, and were used to partition additional variance explained by riparian land cover from variance explained by catchment land cover. Partial correlations (*r*) for which subcatchment riparian cropland (crop), forest, and urban land (urban), and riparian cropland 2 km above sites (2K crop) were significantly associated with total nitrogen (TN) and nitrate (NO_3^-) concentrations in mixed linear models (Table 3) are presented

Water chemistry parameter	Catchment land cover variables controlled for	Riparian land cover	*r*	*P* Value
TN	Crop, forest	Crop, urban	Crop = 0.18	0.396
			Urban = −0.33	0.109
		2K crop	2K Crop = 0.43	0.033
NO_3^-	Crop, forest	Crop, forest, urban	Crop = 0.33	0.111
			Forest = −0.23	0.272
			Urban = −0.24	0.246
		2K crop	Crop = 0.49	0.014

Interestingly, urban land uses were negatively associated with elevated nutrient concentrations. However, the only sizeable "urban" center in the Mill Creek watershed (the town of Alma, with a population of 760) occurred downstream from the headwater areas in grassland and upstream from the most extensive areas of cropland in the basin.

Total nitrogen and NO_3^- concentrations exhibited similar relationships with land use. Both TN and NO_3^- were significantly related to the same land cover classes across spatial scales, and both showed comparable degrees of correlation with land cover in multiple regression analyses. These similarities likely occurred because NO_3^- often is the dominant form of nitrogen entering surface waters from the adjacent landscape (Hill 1996; Novotny and Olem 1994). Likewise, correlations with land cover were stronger for NO_3^- than for TN across spatial scales, likely because commercial fertilizer in the form of NO_3^- often dominates nitrogen loading to aquatic ecosystems (Allan and Flecker 1993; Carpenter and others 1998).

The finding that TP concentrations in Mill Creek were not significantly related to catchment or riparian land cover contradicts some previous studies (Hunsaker and Levine 1995; Jones and others 2001; Osborne and Wiley 1988; Sliva and Williams 2001) that reported strong landscape influences on phosphorus dynamics, but agrees with the results of Johnson and others (1997), who found no significant relationships between catchment and riparian land cover and TP concentrations in 63 subcatchments of the Saginaw Bay (Michigan) watershed. However, these studies were conducted in widely varying biophysical settings. The current study provides information for prairie streams that was previously lacking. Because phosphorus inputs to surface waters can be largely dependent on precipitation events, perhaps entering streams via "pulses" of sediment-bound nutrients from the landscape (Novotny and Olem 1994) or originating from point sources, TP concentrations may have been more difficult to relate to watershed land uses (Johnson and others 1997). Our sampling regimen was not temporally fine enough to pick out such effects.

Total nitrogen and NO_3^- concentrations were most strongly related to riparian land cover in the subcatchment above each sampling site, which is consistent with previous work (Dillaha and others 1989; Karr and Schlosser 1978; Lowrance and others 1997) identifying riparian zones as key regulators of nitrogen inputs to surface waters. Distinguishing the impacts of land uses in the riparian ecotone from those in the entire catchment often is difficult because they are highly correlated. In many watersheds impacted by anthropogenic land use conversion, riparian land cover may simply reflect dominant catchment land cover types (Hunsaker and Levine 1995). However, partial correlations indicated that riparian land cover from the sampling site to 2 km upstream added information regarding TN and NO_3^- concentrations even after catchment influences had been taken into account, which suggests that riparian conditions were important determinants of water quality at Mill Creek. In instances of NO_3^- entering surface water via groundwater that flows below the rooting zones of riparian vegetation, riparian zones in this region of the United States may not completely control nitrogen inputs from adjacent cropland (Kemp and Dodds 2001). However, these inputs would likely be greater in the absence of intact riparian vegetation, which still may mitigate nutrients entering from overland flow.

It could be that the width of the riparian zone alters land–nutrient relationships. The high-quality data available for riparian land cover were digitized only for 33-m width. Thus, this is the width of the buffer zone we were able to assess.

The strength of the observed land cover–nutrient relationships may have been influenced by the study design and spatial scales of analysis. Although strong relationships between nitrogen and land cover were expected at the subcatchment scale, riparian cropland 2 km upstream of sites also was highly correlated with TN and NO_3^- concentrations. This may reflect the size-dependent nature of relationships between local land use and in-stream conditions, which are strongest in small catchments, and subsequently decrease as catchment size increases (Buck and others 2004). Thus, because the majority of sampling sites were located on small (third-order or less) tributaries, the design of this study may have been best suited for detecting local influences, and possibly was less able to detect larger-scale spatial effects (Allan and others 1997). Also, because riparian land uses adjacent to small headwater streams may exert a large impact on in-stream nutrient concentrations (Oakes 2003), the strength of local riparian correlations may have reflected the importance of headwater areas in regulating water quality. In either instance, riparian land cover appears to be a strong indicator of water quality conditions in the Mill Creek watershed, suggesting that protected riparian zones may help to ameliorate land use impacts at Mill Creek and other watersheds in the Midwestern United States.

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