Biogeochemistry **53:** 125–141, 2001.

Spatial and temporal patterns of nitrogen concentrations in pristine and agriculturally-influenced prairie streams

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Key words: ammonium, groundwater, nitrate, nutrient cycling, riparian buffer zones, streams

Abstract. Long-term data on nitrogen chemistry of streams draining Konza Prairie Biological Station (Konza), Kansas were analyzed to assess spatial and temporal patterns and examine the influence of agricultural activity on these patterns. Upland watersheds of Konza are predominantly tallgrass prairies, but agricultural fields and riparian forests border the lower reaches of the streams. We have up to 11 years of data in the relatively pristine upland reaches and 4 years of data on wells and downstream reaches influenced by fertilized croplands. Seasonal and spatial patterns in total nitrogen (TN) concentrations were driven largely by changes in the nitrate (NO_3^-) concentrations. A gradient of increasing NO_3^- concentrations occurred from pristine upland stream reaches to the more agriculturally-influenced lowland reaches. Nitrate concentrations varied seasonally and were negatively correlated with discharge in areas influenced by row-crop agriculture ($p = 0.007$). The NO_3^- concentrations of stream water in lowland reaches were lowest during times of high precipitation, when the relative influence of groundwater drainage is minimal and water in the channel is primarily derived from upland prairie reaches. The groundwater from cropland increased stream NO_3^- concentrations about four-fold during low-discharge periods, even though significant riparian forest corridors existed along most of the lower stream channel. The minimum NO_3^- concentrations in the agriculturally influenced reaches were greater than at any time in prairie reaches. Analysis of data before and after introduction of bison to four prairie watersheds revealed a 35% increase of TN concentrations ($p < 0.05$) in the stream water channels after the introduction of bison. These data suggest that natural processes such as bison grazing, variable discharge, and localized input of groundwater lead to variation in NO_3^- concentrations less than 100-fold in prairie streams. Row-crop agriculture can increase NO_3^- concentrations well over 100-fold relative to pristine systems, and the influence of this land use process over space and time overrides natural processes.

Introduction

Nitrogen (N) concentrations in surface waters draining the midwestern United States are among the highest in the country and average 0.3 to 0.5 mg N/L with the greatest N concentrations found in watersheds predominantly used for urban and agricultural purposes (Omernik 1977; McArthur et al. 1985). Agricultural activities can increase nitrate (NO_3^-) concentrations in streams, leading to possible health problems and eutrophication of water bodies. Excessive N and phosphorous from fertilizer and animal wastes can leach through the soil and be incorporated into groundwater (Schlesinger 1997). Because groundwater is frequently a major component of stream flow, higher in-stream concentrations of these nutrients can also result. Maintenance of buffer strips and natural riparian vegetation may mitigate NO_3^- pollution from croplands (Cooper et al. 1995; Hill 1990; Muscutt et al. 1993).

Water quality can also be a function of the natural watershed. Native prairie has some of the lowest documented rates of N export by streams for any ecosystem, with N export driven primarily by precipitation (Dodds et al. 1996a). Processes controlling nutrient cycling in tallgrass prairie prior to European settlement include fire and bison grazing (Knapp et al. 1999). These processes may alter stream water chemistry by interacting seasonally with the amount and movement of groundwater and soil water, with changes in prairie vegetation, with soil microbes, and especially in response to changes in surface water discharge. McArthur et al. (1985) documented that annual hydrographs on a prairie stream varied considerably from year to year in terms of duration of flow period and the number, magnitude, and timing of major storm flows. This highly variable flow regime characteristic of tallgrass prairie streams means relatively long-term data sets are needed to describe N dynamics (Dodds et al. 1996a).

Grasslands and wooded grasslands cover 28% of terrestrial ecosystems globally (Dodds 1997). Tallgrass prairies once covered greater than 67.6 million hectares of the United States, and were exceeded in total area only by eastern deciduous forests. Most of the landscape once represented by tallgrass prairie has been converted to agricultural land throughout the midwestern United States. The quality of water from native landscapes is the baseline against which the impact of pollutants on surface water resources must be evaluated, but little research has been done on grassland streams relative to temperate forest streams (Dodds 1997). The purpose of this study was to extend previous analyses of the long-term patterns of N chemistry in prairie streams by considering the chemistry of groundwater, the effects of bison, and the impacts of agriculture on these streams.

Methods

Study site description

The Konza Prairie Biological Station (Konza) is located in the Flint Hills region of the Great Plains about 10 km Southeast of Manhattan, Kansas. This area encompasses one of the largest representative tracts of tallgrass prairie. Less than 2 percent of the Konza has ever been plowed, and the land is managed to provide a range of conditions encompassing those of tallgrass prairie prior to European settlement. The 1,060 ha Kings Creek watershed is located entirely within the Konza boundaries. This watershed has been an U.S. Geological Survey benchmark site since 1979. Detailed descriptions of the geology (Oviatt 1998), hydrology, chemistry (Gray et al. 1998) and biology (Gray & Dodds 1998) of this site have been published previously. Long-term data on the streams within Konza have been collected since 1986 with consistent techniques.

Downstream sites and agricultural wells occur in colluvial areas in which the groundwater is flowing directly to the stream. The elevation of the groundwater in the wells installed in colluvium is known to be higher than that of the stream and the colluvium is continuous from the wells to the stream channels. Thus, water is flowing from the wells to the stream at these downstream sites. Upstream sites are located in bedrock limestone resulting in heterogeneous groundwater flow paths that do not necessarily follow the topography of the land. Numerous springs are located in the upstream reaches that allow water to flow in short stream segments during dryer times of the year and serve as the primary source of flow during wetter periods when water flows down the length of the stream channel.

Stream discharge and N chemistry were measured in four relatively pristine upland watersheds on different branches of Kings Creek as well as at various downstream stations that are more influenced by agriculture (Figures 1 and 2, Table 1). The upland streams are second- or third-order intermittent streams, while the lower reaches are permanent streams of fourth- or fifth-order. Individual watersheds are on separate frequencies of controlled burns occurring in spring (mid-April to early May). Watershed designations, N01b, N02b, N04d and N20b, indicate target fire frequencies of 1, 2, 4 and 20 years, respectively. Mean slope, area, and maximal elevation loss are similar among the smaller watersheds. Stream measurements on N04d started in 1986 and in 1987 on the other three watersheds. Bison were introduced to the four watersheds in May 1992. More detailed spatial sampling on Kings Creek has occurred since 1994 including wells, prairie groundwater, and lower reach stream segments influenced by fertilized croplands (Table 1). The Shane Creek watershed, mostly encompassed by Konza, is similar in morpho-

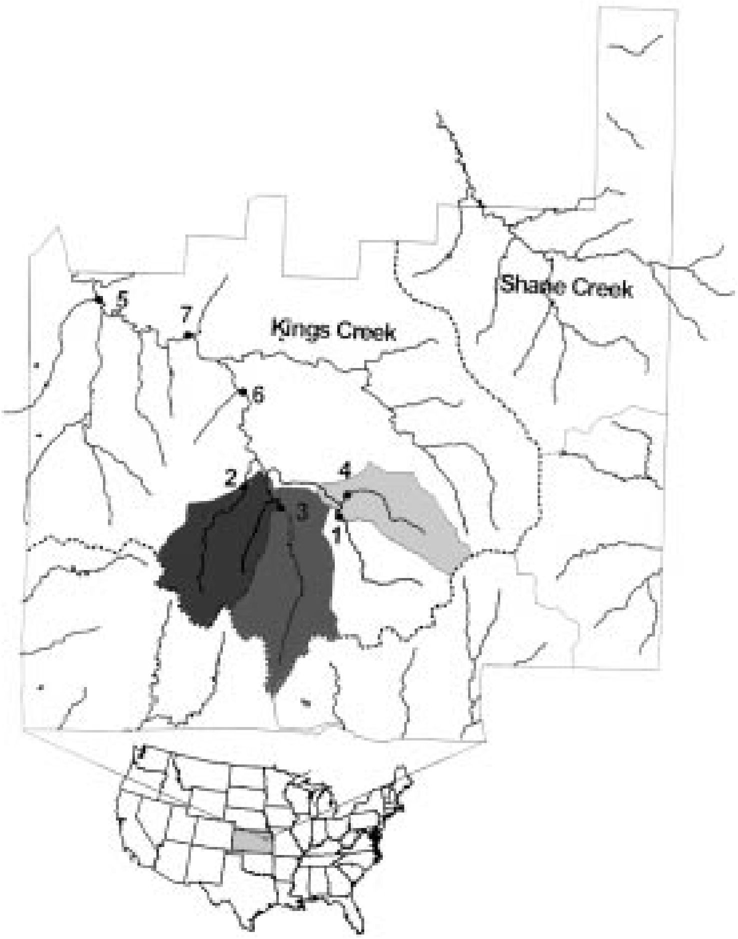

Figure 1. Watersheds and sampling locations used in this study. Numbers correspond to sample site numbers in Table 1. Sites 1, 2, 3 and 4 are found in the smallest individual watershed units nested within successively larger watershed units (Sites 5, 6 and 7). North is at the top of the map and from the east to west boundaries of Konza is 6.75 kilometers.

logy and land use to Kings Creek watershed, and a N chemistry transect was measured in this watershed from lowland to upland reaches in addition to transects in Kings Creek (Figures 1 and 2).

Sample collection & analysis

Stream flow was measured using a V-notch concrete flume equipped with a data-logger for measurement of discharge at each of the watershed sites (N01b, N02b, N04d and N20b) (Dodds 1996a). Downstream collection sites

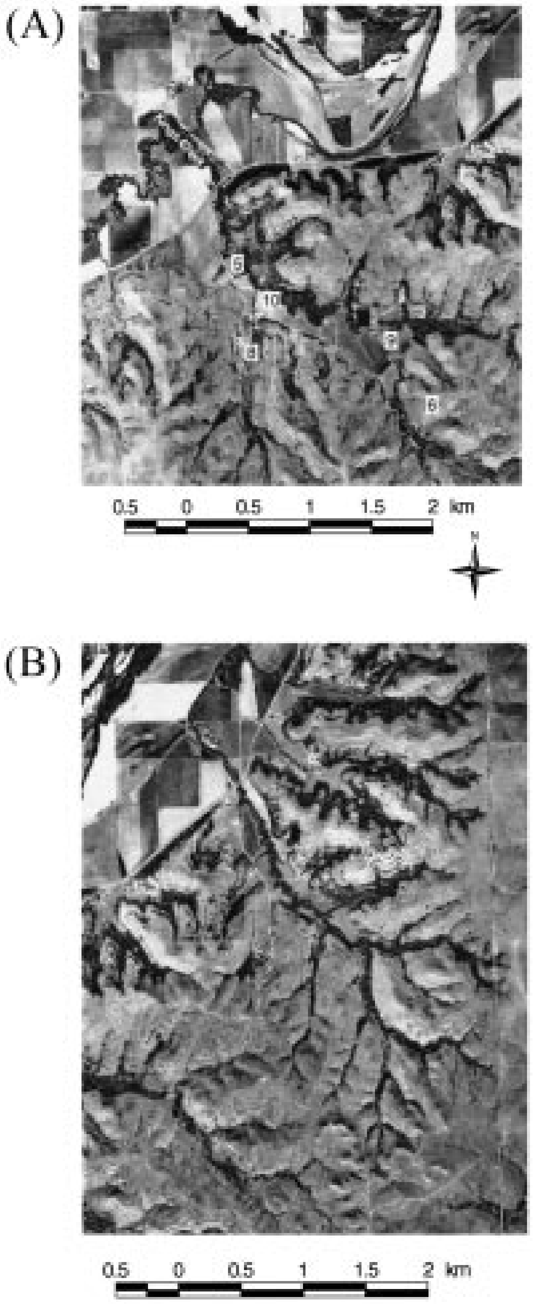

Figure 2. Aerial photographs of the lower reaches of Kings Creek (A) and Shane Creek (B) watersheds. Extensive riparian vegetation (gallery forest) occurs throughout the lower portions of both watersheds. Fertilized cropland occurs to the southwest of the stream channel between sites 7 and 5 in Kings Creek. Numbers correspond to sample site numbers in Table 1. Fertilized cropland in Shane Creek occurs on both sides of the stream channel downstream from the uppermost dirt road that crosses the channel.

Table 1. Characteristics of sample sites; locations are indicated in Figures 1 and 2.

Sample site	Number	Type	Burn frequency	Watershed area	% in agriculture
weir N01b	1	surface water	every year	121	0
weir N02b	2	surface water	every 2 years	119	0
weir N04d	3	surface water	every 4 years	135	0
weir N20b	4	surface water	every 20 years	84	0
Below fertilized cropland	5	surface water	variable	1524	1
Above fertilized cropland	6	surface water	variable	560	0
Below restored cropland	7	surface water	variable	1114	0*
Edler Springs	8	groundwater	nk**	nk	0
Prairie well	9	groundwater	every year	nk	nk
Agricultural well	10	groundwater	never	nk	nk

*Possible crops in riparian zone historically.
**nk = not known.

on Kings Creek are not equipped with data-loggers; thus, U.S. Geological Survey (USGS) data were used for discharge at these sites. The USGS site is located downstream from the upland prairie sites, between sites 6 and 7, and discharge is representative of that at sites 5, 6 and 7.

Grab samples of stream water were collected for chemical analyses three times per week in acid-washed bottles from the center of each stream above the concrete flume and several centimeters below the surface. Groundwater well samples were collected with bailers after three volumes of water were withdrawn.

Filtered water samples were refrigerated immediately and analyzed within 48 hours on a Technicon AutoAnalyzer II for NO_3^- concentrations (NO_3^-+NO_2^-) by diazo dye formation following cadmium reduction, and ammonium (NH_4^+) concentrations (NH_4^++NH_3) by the indo-phenol blue method. Ammonia is not found in significant concentrations (<5%) because the limestone buffering maintains the pH of the streams at 7–8. Therefore, we report concentration of NH_4^++NH_3 as NH_4^+. Likewise, nitrite (NO_2^-) concentrations are low and NO_3^-+NO_2^- is reported as NO_3^-. Unfiltered samples were stored frozen before analysis of total nitrogen (TN) concentrations. Total nitrogen was determined as NO_3^- after an alkaline persulfate digestion (Ameel et al. 1993). The limit of detection was 1 μg/L for NO_3^- and NH_4^+ and 5 μg/L for TN. The detection limit for TN is higher because the procedure requires a 5-fold dilution with digestion reagent.

Statistics

Correlation analyses were performed using the non-parametric Kendall's tau-b test to determine what factors influenced the concentration of NO_3^- in the stream. Analysis of Variance (ANOVA) was used to analyze the NO_3^- concentrations of surface waters and groundwater sites at Konza and pairwise comparisons were made using the non-parametric Student-Newman-Keuls test comparison. To analyze the effect of bison on stream N concentrations, paired t-tests were performed for each watershed using the mean concentration of NO_3^-, NH_4^+, and organic N for each year before and after the bison introduction. This accounted for individual differences among the watersheds. Since four tests were made, the Bonferroni correction was used and alpha was set to 0.0125. Changes in N export with the presence of bison were also tested using paired t-tests.

Results

Spatial and temporal patterns of NO_3^- concentrations

Total nitrogen concentrations were divided into individual components to determine the relative proportion of different forms of N (Figure 3). Nitrate concentrations drove changes in TN across the watersheds (i.e., NO_3^- and TN were significantly positively correlated across all sampling sites and at each individual sampling site, Table 2). Ammonium and organic N were not significantly correlated with TN across the sites ($p > 0.10$). Thus we report NO_3^- concentrations to describe temporal and spatial patterns. Surface and groundwater sites influenced by agriculture had higher NO_3^- concentrations (Figure 3). The highest NO_3^- concentrations, over 1400 μg/L on average, were found in wells beneath agricultural fields (Figure 3). The lowest NO_3^- concentrations, often below detection limits, were found in pristine surface waters of upland prairie streams. On average, surface water increased in NO_3^- concentration over 10 fold when flowing through cultivated land relative to the pristine upland sites (Figure 3).

Transects of NO_3^- concentrations were sampled during different seasons and in different watersheds of similar riparian cover and agricultural activity on Konza. These transects indicated a gradient of increasing NO_3^- concentrations as streams flowed from pristine areas to agricultural lands (Figure 4). This pattern was consistent across seasons and in different watersheds. Samples taken upstream on Konza generally had NO_3^- concentrations that approached detection limits. A large increase in stream NO_3^- concentrations occurred when agricultural fields were first encountered, and the concentra-

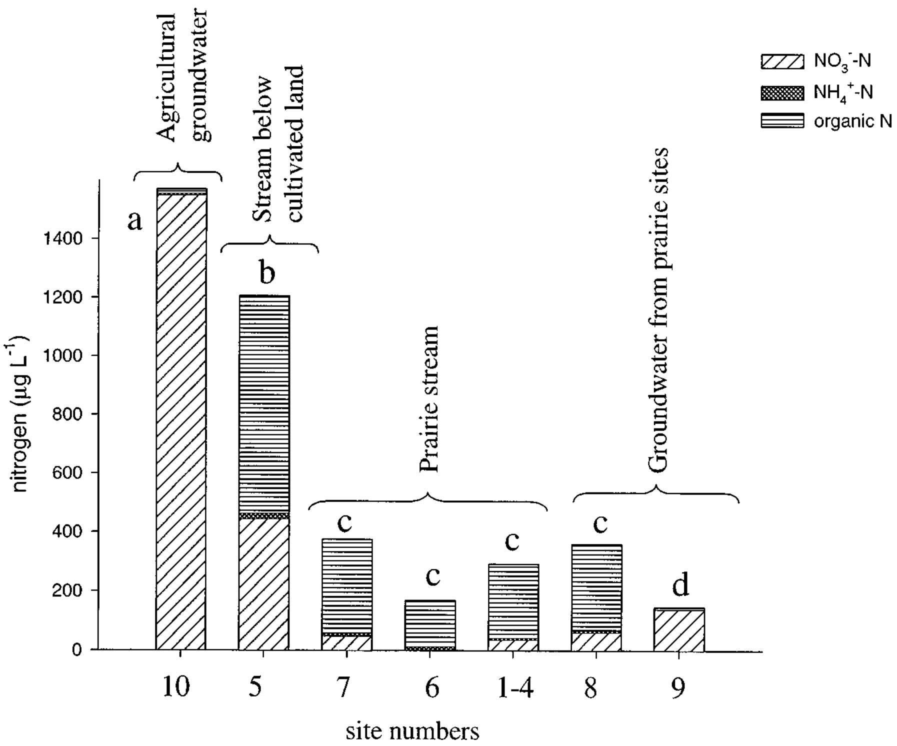

Figure 3. Nitrogen components of surface and groundwater within the Kings Creek watershed. Bars with different letters indicate sites that had significantly different NO_3^- concentrations ($\alpha = 0.05$, Student-Newman-Keuls multiple comparison, overall ANOVA was significant at $p < 0.0001$). Numbers for each bar correspond to sample site numbers in Table 1. n ranged from 36 to 543 per bar.

tion progressively increased, as agricultural fields became more prominent in the downstream landscape. This pattern was consistent during two seasons on Kings Creek (Figure 4(a) and (b)). Shane Creek also had greater NO_3^- concentrations as the stream flowed into agricultural areas from more pristine areas (Figure 4(c)). In the upper Kings Creek transect, groundwater influx increased NO_3^- concentration in the stream which then decreased downstream (Figure 4(d)). Maximum NO_3^- concentrations in the prairie portion of Kings Creek were lower than minimum concentrations in streams adjacent to agricultural fields (Figure 4(a) and (d)).

Correlations of NO_3^- concentration, discharge, NH_4^+ concentration, and TN concentration indicate several factors influenced N concentration (Table 2). A weak negative correlation occurred between NO_3^- concentration and discharge when data from all sites were analyzed simultaneously.

Table 2. Factors correlated with NO_3^- concentration at stream sites
Boldface values are significant at $p < 0.05$.

Site number*	Discharge	NH_4^+	Total nitrogen
All			
tau-b**	**–0.09129**	**0.2391**	**0.72906**
P	**0.002**	**0.006**	**0.0001**
n	**1436**	**1325**	**1412**
1			
tau-b	–0.01189	**0.22116**	**0.2599**
P	0.8781	**0.0015**	**0.001**
n	169	**203**	**288**
2			
tau-b	0.07928	**0.86321**	**0.15396**
P	0.3041	**0.002**	**0.0179**
n	170	**275**	**236**
3			
tau-b	0.00601	0.1026	**0.74652**
P	0.9184	0.6310	**0.0001**
n	293	300	**371**
4			
tau-b	0.16785	**0.53305**	**0.6469**
P	0.2541	**0.002**	**0.0001**
n	48	**43**	**56**
5			
tau-b	**–0.2036**	–0.01794	**0.75103**
P	**0.0007**	0.9353	**0.001**
n	**578**	230	**257**
6			
tau-b	**0.21336**	0.11435	**0.11435**
P	**0.004**	0.5332	**0.0002**
n	**93**	32	**32**
7			
tau-b	**0.19908**	**0.36873**	**0.4675**
P	**0.0067**	**0.0001**	**0.0001**
n	**85**	**242**	**172**

*Site numbers correspond to the numbers on Table 1.
**Kendall's tau-b correlation coefficient.

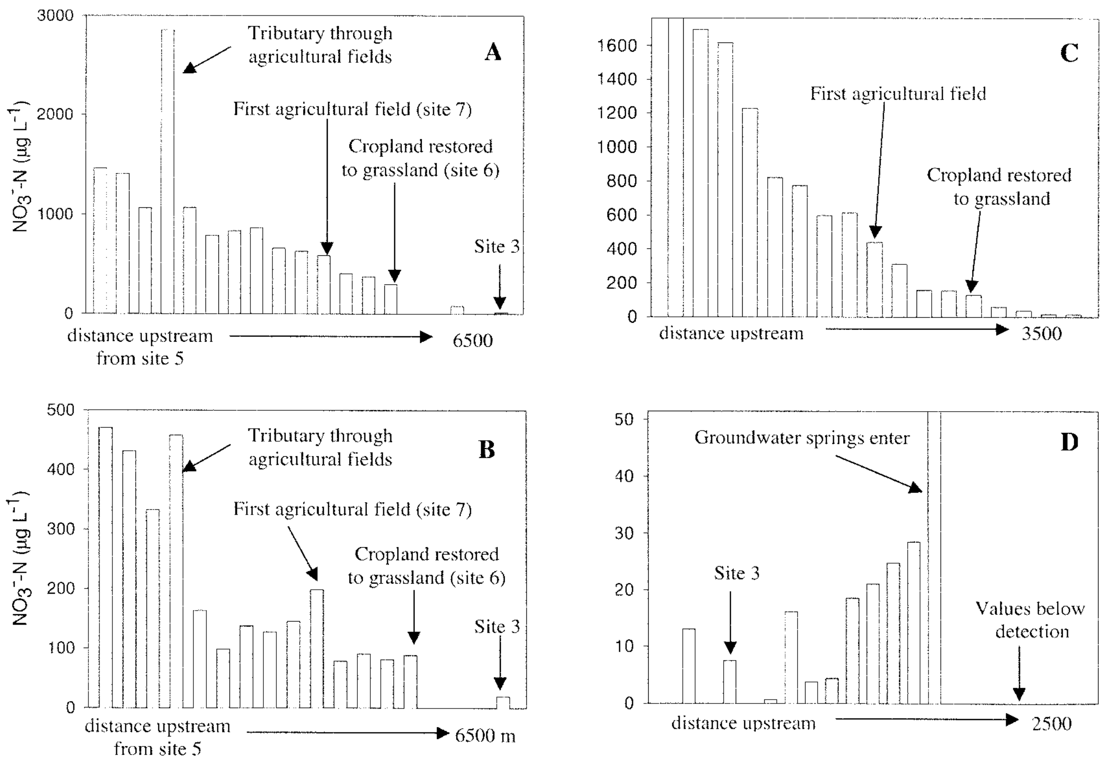

Figure 4. Temporal and spatial variations in NO_3^- concentrations on linear stream transects. Lower Kings Creek watershed in summer 1995 (A) and in winter 1998 (B). Shane Creek watershed in summer 1995 (C) and Upper Kings Creek watershed in summer 1995 (D). Data in Graph A were previously published in Gray et al., 1998.

This relationship was driven by the relatively low NO_3^- concentrations during times of high discharge at the lowest site (Table 2, site 5) where the negative correlation between discharge and NO_3^- was stronger than across all sites. The correlation was positive immediately above active cropland (sites 6 & 7) and not significant in the upland prairie sites upstream from this site. This change in influence of discharge indicates the effect of fertilized cropland because it occurs at the site below the cropland. When all sites were combined, a significant positive correlation between NO_3^- concentration and NH_4^+ concentration occurred but this was not consistent when considering individual sites, suggesting the same processes do not control NH_4^+ and NO_3^- concentrations. Many of these correlations are weak but significant because of the large sample size (n was relatively large for all correlations).

The influence of discharge on NO_3^- concentrations

Prairie groundwater had relatively low NO_3^- concentrations with sharp decreases in concentration associated with large rainfall events as indicated by stream flooding (Figure 5). The prairie groundwater always exhibited lower concentrations than the agriculturally-influenced stream site (Figure 5). During times of low discharge, the agriculturally-influenced downstream site had high NO_3^- concentrations. During high discharge, NO_3^- concentrations decreased (Figure 5), consistent with the negative correlation between NO_3^- and discharge at this site (Table 2). When the water was flowing through the stream channel from upstream prairie reaches (during periods of high discharge), the high-nitrate groundwater from agricultural regions was diluted by low-nitrate water from unfertilized grasslands.

Introduction of bison

Total nitrogen concentration data collected from 1986 until 1996 were analyzed to assess the effect of the bison introduction on N concentration in the stream. Total nitrogen concentrations prior to bison introduction May 1992 were significantly lower than after May 1992 in all four watersheds (t-test, $p < 0.0125$, Figure 6). Unlike changes in TN due to anthropogenic inputs (Figure 3), the increase in TN after the introduction of bison was due to an increase in organic N rather than NO_3^- (Figure 6). All watersheds sampled in the range of the bison showed similar increases in TN concentration. However, the TN export did not exhibit a statistically significant increase after the introduction of bison in all four watersheds analyzed (t-test, $p > 0.05$, Figure 7).

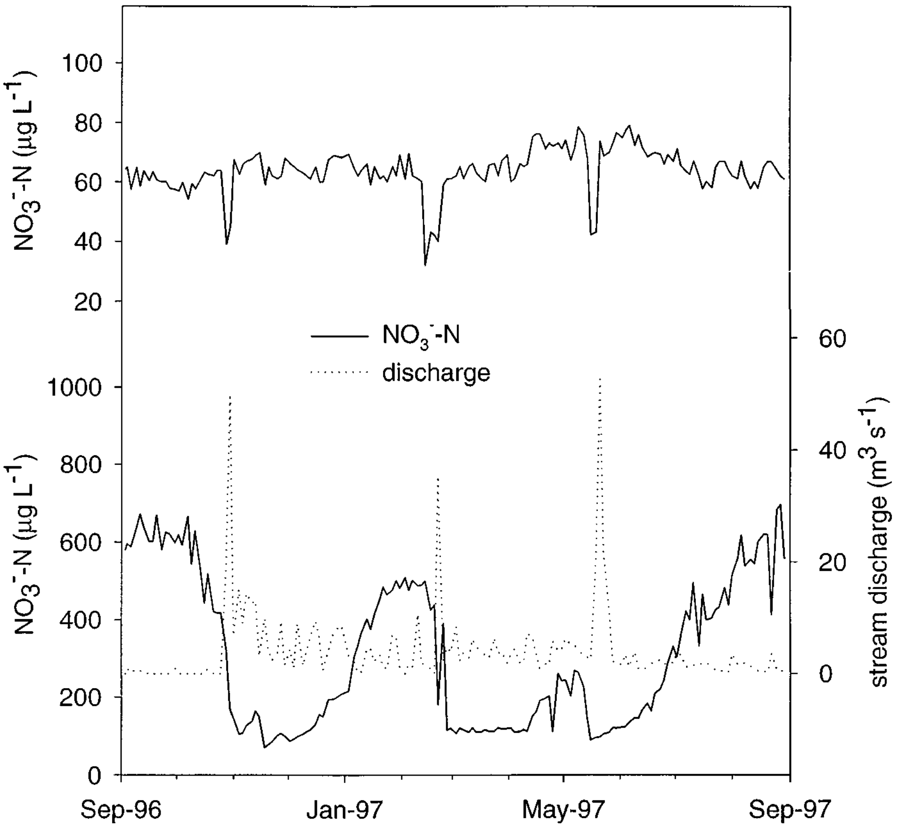

Figure 5. Changes in NO_3^- concentration and stream discharge over time. Groundwater from under prairie (site 9) is the top solid line and surface water below row-crop agriculture is the bottom solid line (site 5).

Discussion

Our results demonstrate increases in NO_3^- concentrations from pristine upland stream reaches to more agriculturally-influenced lowland reaches. A previous study demonstrated NO_3^- concentrations increased with high precipitation upstream (Dodds et al. 1996a), but this did not hold downstream. The NO_3^- concentrations of lowland reaches in this study were greatest during times of low discharge when groundwater from fertilized cropland was a main component of stream flow. In contrast, the NO_3^- concentrations of pristine upland prairie reaches were not strongly influenced by discharge. Photoautotrophic activity is high in our upland streams (Dodds et al. 1996b) and N uptake by photoautotrophs may explain why NO_3^- decreased below sites of groundwater input in pristine reaches of Kings Creek (Figure 4(d)).

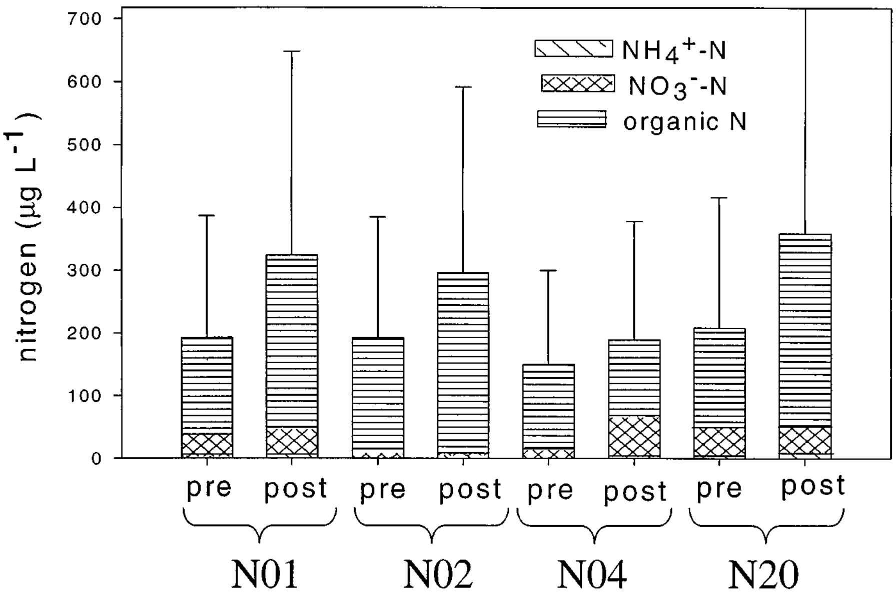

Figure 6. Total N, NH_4^+, NO_3^-, and organic N concentrations at four sites before and after the introduction of bison. Error bars = 1 standard error of TN concentration.

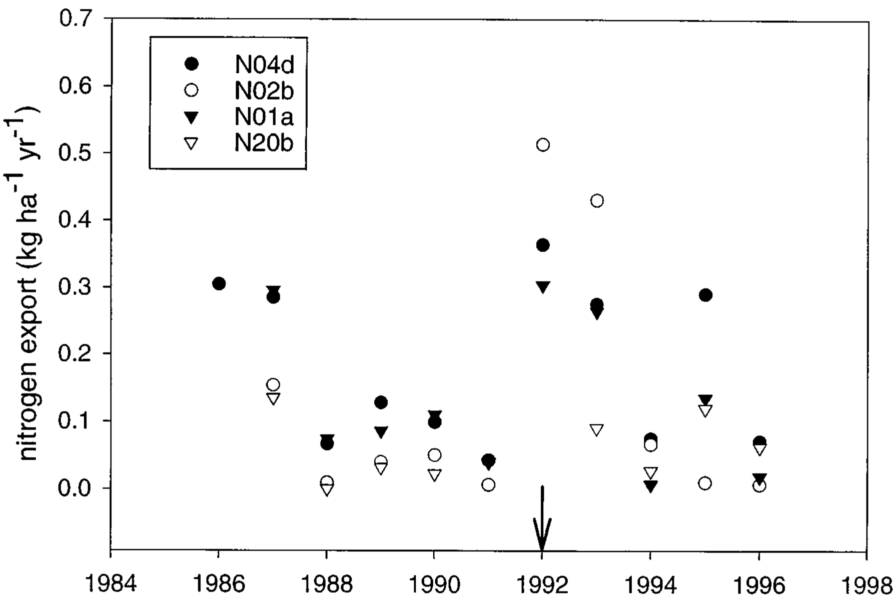

Figure 7. Nitrogen export over time for four watersheds. Arrow indicates the year in which bison were introduced onto the watersheds. See Table 1 for description of sites.

Input of NO_3^- downstream by agriculturally-influenced groundwater probably exceeded the uptake capacity of the biofilms in the stream channel allowing for increased NO_3^- concentrations in the stream when there was a large N-rich baseflow component.

Triska et al. (1989) found NO_3^- concentrations increased as water flowed downstream in a third-order forested stream not influenced by agriculture. They interpreted this increase to mean the reach was a source of dissolved inorganic N to downstream communities under background, low-flow conditions, despite uptake by photoautotrophs. Thus, like our downstream reaches, their stream was probably saturated with N. Meyer et al. (1988) indicated NO_3^- concentrations increase, decrease, or remain constant as discharge changes depending on the stream being sampled, further indication that controls over NO_3^- concentration in stream channels may vary across sites. Based on our data, in streams with similar topography and agricultural influence in the lower reaches, the greatest anthropogenic impacts on NO_3^- should occur downstream during low-discharge periods.

Riparian zones are integral components in shaping stream ecosystems, serving as links between the terrestrial and aquatic systems by influencing nutrient, water, and energy flows (Cooper et al. 1995; Tate 1990). The riparian zone can serve as a buffer zone that absorbs pollution from non-point sources (Griffiths et al. 1997). Forested riparian zones, in some systems, help alleviate N contamination by decreasing sediment and nutrient losses in runoff and below-ground flow (Muscutt et al. 1993). Groundwater movement near streams is generally characterized by subsurface lateral flow from upland areas toward the stream. Riparian zones can remove NO_3^- from this lateral flow by stimulating denitrifying bacteria, microbial immobilization, or vegetative uptake (Griffiths et al. 1997).

In our study, the groundwater from cropland had a negative impact on streamwater quality, even though significant riparian forest corridors occurred along most of the lower stream channel. The inability of the riparian zone to completely control N flux from cropland of limited areas may be due to the fact that much of the groundwater flows to the stream below the rooting zones of the trees or because the forested riparian zones are saturated with N. Observations of the steeply cut banks common in the downstream reaches indicate numerous locations where the groundwater can enter the stream from below the rooting zone of the vegetation. Our results only indicate riparian vegetation does not completely mitigate N contamination from fertilized croplands; such inputs might be greater without intact riparian vegetation.

Dodds et al. (1996b) suggested lower surface water NO_3^- concentrations in larger pristine watersheds were due to the longer flow paths. They hypothesized that in larger watersheds more of the N was immobilized by biota before exiting the watershed. At larger spatial scales this pattern was reversed, apparently by agricultural influences. However, we can not test this explanation statistically because we are not aware of any replicate larger watersheds with no agriculture.

Bison increased the TN concentration but we could not detect this as a significant increase in N export by the streams. However, if N concentration increases overall, N export per unit discharge must also increase. The lack of a statistically significant increase in N export across years in our study was because the effect of variable precipitation exceeded the increase in concentration resulting from the presence of bison. These data indicate the value of long-term data sets. The export of N was higher for the first two years following bison introduction. However, these two years had high annual discharge, which increased N export. Analysis using the two years after bison introduction did not demonstrate a significant effect on TN concentration (Dodds et al. 1996a), whereas the longer-term data did.

Olness et al. (1980) found that TN concentrations in surface runoff from continuously cattle-grazed watersheds were significantly greater than those in runoff from rotation-grazed or ungrazed watersheds. These demonstrated an average of 2–3 ppm N increases in continuously grazed watersheds, a greater effect than bison had in our study. However, this effect of large grazing ungulates is consistent with our finding of increased TN concentrations with the presence of bison. Knapp et al. (1999) stated bison grazing increases rates of N cycling, and the heterogeneity of N availability on land, so bison have a clear influence on terrestrial N cycling. Bison effects apparently extend to the aquatic ecosystems, but the mechanism is not clear. Possible mechanisms include alterations in runoff, N excretion in and near the stream, and removal of plants that immobilize N. Regardless, N export rates in the stream, even with the presence of bison (Figure 7), still fall on the low end of those documented for terrestrial systems in general (Dodds et al. 1996a) and are many times less than similar grasslands that are continuously grazed by cattle (Olness et al. 1980).

Ideally, our experimental design would include an upland watershed with agricultural inputs and a control watershed lacking the presence of bison. However, for logistical reasons such a design is not available. We are fortunate to have tallgrass prairie watersheds as large as 100 ha area. Furthermore, suspended and dissolved organic N are measured together, making interpretations of the changes in total N more difficult. These limitations are offset by the use of a unique long-term data set, which provides information on how robust our results are in the face of temporal (hydrological) and spatial variability.

In conclusion, we found anthropogenic inputs of N from row-crop agriculture dominated all other factors influencing N concentration. This occurred in spite of the fact that only 1% of the watershed was fertilized cropland. This effect was most evident during times of low discharge when groundwater under cropland dominated stream flow inputs. Riparian buffer zones did not remove the effects of fertilized cropland on stream N concentrations. Factors characteristic of tallgrass prairie prior to European settlement such as fire, bison grazing, flooding, and pristine groundwater inflows do not increase concentrations of stream NO_3^- and N runoff nearly as strongly as the presence of fertilized cropland.

Acknowledgements

We thank Rosemary Ramundo, Amanda Kuhl, and Drew Clark's Manhattan High School Stream Team for collecting and processing samples; Michelle Evans, Brent Brock, Dolly Gudder, Greg Hoch, Jeff Pontius, and John Blair for assistance with analysis and earlier versions of the manuscript, as well as three anonymous reviewers. This research was supported by the Long-Term Ecological Research (LTER) grants provided to Konza by the National Science Foundation. This is contribution no. 99-340-J from the Kansas Agricultural Experiment Station.

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