Water Nutrient Flux Across Lower Order Streams in Watersheds with Diverse Land Uses and Variable Saturation Levels

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<u>Abstract</u>

Changes in natural and anthropogenic factors can have a major impact on water quality and streamflow. These factors can have differing levels of influence based on land use area and saturation levels of watersheds. Research has shown a significant correlation between land use area and water quality. However, previous research has focused on interactions of land use, water quality, and streamflow in higher order streams, while significant water pollutants could originate in lower order streams. We collected water quality, precipitation, and streamflow data from three watersheds in Northeast Kansas, USA with different, distinct land uses at variable saturation rates. We used analysis of variance to determine interactions between water quality parameters and different land uses at variable saturation rates, observing a significant correlation between land cover and the concentration of total nitrogen and nitrate nitrogen. The urban land use area showed the highest concentrations of total nitrogen and nitrate, while the grassland land use area showed the lowest concentration. Rainfall events had the largest impact on nutrient concentrations in land use areas with more exposed soil, like agriculture, likely due to the mobilization of sediment carrying nutrients into waterways. These findings support the hypothesis that grassland ecosystems have lower rates of nutrient pollution in surface water than urban and agricultural systems, which are contributing more polluting nutrients, and have higher rates of nutrient mobilization in surface water.



Figure 1: Conceptual model of experiment structure displaying total nitrogen and total phosphorus concentrations in first and second order streams in varying watersheds under different saturation levels.

Keywords

Land Use, Water Quality, Precipitation, Nutrient, Streamflow

1. Introduction

Streamflow and water chemistry are controlled by various natural and anthropogenic factors. The changes these factors cause can be harmful to the environments they are in and the organisms that inhabit them. Changes in natural and anthropogenic factors such as precipitation and land use cause many point source and nonpoint source pollution issues (Brion, G. et al. 2011; Dodds, W et al. 2007; Lin, H. et al. 2001). The United States Environmental Protection Agency defines point source pollution as a "single identifiable source of pollution" (National Oceanic and Atmospheric Administration, n.d.) and nonpoint source pollution as "pollution from many diffused sources" (US EPA, 2022). Nonpoint source pollution runoff inputs of nitrogen and phosphorus due to precipitation can cause eutrophication and damaging changes in the trophic state of many lakes, reservoirs, and streams (Dodds, W et al. 2007; Lin, H. et al. 2001). Researchers also presume point source pollution shows degradation of water chemistry based on

the different types of land uses they come from (Brion, G. et al. 2011). The influences precipitation and land use have on nutrient mobilization, transportation, and deposition show many concerns in first and second-order streams (Tran, C et al. 2010; Brion, G. et al. 2011; Davis, N. et al. 2003)

To prevent the transport of nutrients into surface water, evaluation must begin at the source of pollution. Researchers have compared nutrient runoff from different catchments with distinct, dominant land uses (Brion et al., 2011; Oyarzun et al., 2007; Verheyen et al., 2015; Yazdi et al., 2021). Across many of the analyzed studies, nutrient concentrations in streams correlate directly to or are associated with land use upstream (Clune et al., 2020; Shu et al., 2022; Wang et al., 2014). Of land uses evaluated, croplands and developed areas were considered the most harmful to water quality. Total nitrogen (TN) and total phosphorus (TP) concentrations were higher in agricultural and developed land areas than in undeveloped areas (Clune et al., 2020). These increased levels of nitrogen and phosphorus are the result of elevated nutrient inputs, agriculture practices like tillage and tile drainage, and urban challenges like wastewater and low infiltration, which may result in higher flow (Clune et al., 2020). Contrastingly, undeveloped, vegetated land tended to have lower concentrations of nutrients in stream water (Shu et al., 2022).

While many studies show that land use is directly correlated to water quality, Shu et al. (2022) explains that it could be the proximity of the land use to the surface water that has the greatest impact on water quality. "RDA showed that land cover type in the 500- and 1000-m buffer zones better explained variations in water quality than land cover at the sub-basin scale" (Shu et al., 2022). This indicates that riparian buffer strips could be an effective means of controlling pollution from high-loss land-use areas.

Annual precipitation is an integral part of international Kansas and other midwestern states' environments and economies and global environments. Precipitation events have been monitored in Kansas using NOAA's automated surface observing systems along with satellite imaging, and volunteer community reporting (Bitew et al., 2012; Garbrecht et al., 2004). Many of the researchers working on precipitation effects are evaluating agricultural yield while focusing on higher order stream flows. Additionally, much of the recent analysis is being conducted by simulated modeling using massive online databases from equipment collecting data every hour (Bitew et al., 2012; Garbrecht et al., 2004; Hatley et al., 2023). These studies have found that there is a gradual increase in the overall amount of precipitation yearly (Bitew et al., 2012; Garbrecht et al., 2004). However, this may be due to storms with increasing intensity over shorter periods which does not allow for the previous standard of water absorption by ground infiltration. This leads to increased rates of nutrient runoff, longer droughts, and streams with lower flow throughout the year (Putman et al., 2019; Rahmani et al., 2015).

Increasing nutrient levels in streams and waterways have become of growing concern, and these concentrations can vary based on land uses and precipitation. With the spread of agriculture and urban cover, native ecosystems have become more fragmented resulting in increased nutrient and

sediment concentrations in streams (Spahr et al., 2024). Increasing nutrient concentrations, especially nitrogen and phosphorus from point and nonpoint sources, has led to intensified eutrophication in lakes and streams, which has large cascading effects on the surrounding ecosystem function (Ross et al., 2023). Deforestation of riparian vegetation along streams can also enhance nutrient and sediment loading in stream systems, increasing levels of nitrate 100fold, as well as impacting food webs and organization of the aquatic community (Dodds et al., 2023; Zhang et al., 2024). Modeling attempts have focused on categorizing and tracking nutrient loading in streams across land covers, especially in rural and urban areas resulting in a better understanding of the dynamics that exist between land cover, stream flow, and water chemistry (Guo et al., 2019; Ross et al., 2023; Jatko et al., 2024). Historically, studies that track changes in nutrient concentrations across land cover and precipitation gradients have been limited to larger third or fourth order streams, but new evidence suggests that smaller headwater streams play large roles in determining overall water chemistry of the system (Dodds and Oakes, 2007; Morgan et al., 2013; Seybold and McGlynn, 2018). However, there is little knowledge about the impact of land use and precipitation on nitrogen and phosphorus concentrations in small first order streams (Brion et al., 2011; Seybold and McGlynn, 2018).

This study aims to determine the differences in water chemistry that exist in stream flow and water chemistry across three different land uses: agricultural, urban, and grassland, before and after a precipitation event. Specifically, we intend to identify nitrogen and phosphorus concentrations in small first and second order streams across different land use areas. We will also investigate the effect of precipitation on nutrient concentrations in stream water. We hypothesize that grassland areas will have lower relative concentrations of TN and TP in stormwater runoff in streams. Through this research, we hope to decrease deposition of nitrogen and phosphorus into first and second order streams. To do this, we intend to use our hypothesis to promote the use of grassland buffer areas in agricultural and urban areas to decrease nutrient runoff and promote infiltration of nutrient rich water.

2. Methods

2.1 Study Area



Figure 2. Map of all study sites and locations in Kansas (A) and the individual watershed areas and stream sampling sites for Konza (grassland) (B), Little Bull (agriculture) (C), and Indian Creek (urban) (D). Each sampling site is indicated with its corresponding sample label (ex. K1, L1, or I1), and the network of sampled streams within each watershed.

For this study, watersheds were selected based on land use category (grassland, agricultural, and urban) across the state of Kansas (Figure 2A.). Watersheds were identified using the USGS StreamStat website, and were selected for similar watershed size, weather/precipitation patterns, and one of the three dominant land use categories. This search resulted in three distinct watersheds, ranging from $10 - 40 \text{ km}^2$, which are the Konza Prairie watershed (grassland), Little Bull Creek watershed (agriculture), and Indian Creek watershed (urban) (Figure 2B, C, D).

The Konza Prairie Biological Station (KPBS) is a 3,478–ha native grassland in northeastern Kansas in the Flint Hills region, the largest remaining area of unplowed tallgrass prairie in the U.S. (Samson and Knopf, 1994). King's Creek, an intermittent stream that runs through KPBS, is dominated by shallow groundwater flow through limestone and runs through fine, smectic, mesic, Udertic Paleustols (Dodds et al., 2023). The King's Creek watershed covers 10.62 km² of KPBS and is dominated by grassland cover, with less than 10% urban and agricultural cover

(USGS, 2024). Little Bull Creek watershed is at the southern edge of Gardner, Kansas and expands southeast for most of the 13.16 km². This watershed encompasses 62.6 percent agriculture with 31.6 percent urban area, but all samples taken from this study area were taken from the agricultural portion. Little Bull Creek is a perennial stream that flows throughout the watershed. Nursery crops, greenhouses, sod, grain, and oilseed crops dominate the agriculture in the area. Additionally, cattle, pigs, sheep, and goats are also raised in the area (National Ag Statistics Survey, 2017). Indian Creek watershed is an area inside Overland Park on the Kansas side of Kansas City with 42.74 km² draining into the Missouri river. The land use coverage for the Indian Creek watershed is 94.7 percent urban with small amounts of agriculture and other green spaces. Indian Creek is a perennial stream flowing through the area near residential areas, parks, golf courses, and industrial areas. Key characteristics of watersheds sampled throughout this research are also analyzed (Table 1).

Table 1: Key watershed characteristics, including watershed area, land cover percentage, annual precipitation (*Kansas Office of the State Climatologist · Kansas Climate*, 2024), median streamflow, dominant soil type, and geologic structure.

	Konza (grassland)	Little Bull Creek	Indian Creek (urban)
Watershed area:	10.62 km^2	13.16 km^2	42.74 km^2
Land cover (%):	97.34%	62.60%	94.70%
Annual precipitation (mm):	838 – 914 mm	990 – 1,117 mm	990 – 1,117 mm
Median flow (m^3/s) :	$0 \text{ m}^{3}/\text{s}$	0.146355543 m ³ /s	1.004147903 m ³ /s
Dominant Soil type:	Mollisol	Mollisol	Mollisol
Geological System:	Permian	Pennsylvanian	Pennsylvanian

2.2 Data Collection, Sampling, and Analysis

Historical streamflow data for all three catchments were obtained from United States Geological Survey (USGS) monitoring stations USGS 06879650 (grassland), USGS 06893300 (urban), and USGS 06914990 (agricultural) (USGS, 2024). The data encompasses daily flow measurements from 2014 to present for all three sampling watersheds. Historical precipitation data was collected from the National Centers for Environmental Information (NCEI) database (National Centers for Environmental Information, n.d.). The data consists of precipitation amounts recorded daily from January 1st, 2014, to present for all three sampling watersheds.

Dry sample collection took place on March 19, 2024 (Figure 3). The area received no rain for 6 days before sampling and only 28 mm of rain in the prior 14 days in the grassland watershed and less than 0.5 mm of rain in the agricultural and urban watersheds. Wet sample collection took place on April 16, 2024 (Figure 3), the day following 21.3 mm of precipitation in the grassland watershed and 6.35 mm of precipitation in the agricultural and urban watersheds (*Kansas*)

Mesonet · *Historical Weather*, 2024). Sampling bottles 30mL in size were washed with 5% hydrochloric acid and rinsed with deionized water before use. These sample bottles were used to collect unfiltered samples from the center of the thalweg, representing the sampling location. Upon returning, samples were stored in the dark at 3°C until submitted to the laboratory for testing. Samples were analyzed for nitrate (NO³⁻), orthophosphate (PO₄³⁻), and TN and TP using potassium persulfate digestion.



Figure 3: Graphs display precipitation and streamflow discharge over three months in three different land use watersheds. Dry sample timing is indicated with the green rectangle. Wet sample timing is indicated with the purple rectangle.

2.3 Data Analysis

Stream water quality data and nutrient concentrations were analyzed using a two-way analysis of variance (ANOVA), a multi-variate statistical test to determine the interaction between nutrient concentration, land use, and treatment (dry vs. wet sampling) across the three sampled watersheds. Data was coded and graphed using R (version 4.2.1) and the ggplot2 package (version 3.3.6; Wickham, 2016).

3. Results

3.1 Hydrology: Streamflow Response to Land Cover and Precipitation



Figure 4: Graphs A, B, and C display streamflow discharge and annual precipitation over the past ten years for three distinct land use areas. Graphs D, E, and F display streamflow discharge normalized by watershed areas and annual precipitation over the past ten years for three distinct land use areas.

The urban and agricultural watersheds had higher levels of standardized discharge compared to the grassland watershed. This is likely due to the higher levels of annual precipitation and Hortonian overland flow. Hortonian overland flow occurs when rainfall exceeds the infiltration rate into the ground in a watershed. Hortonian flow contributes to increased nonpoint source runoff and is more common compared to groundwater infiltration in the urban and agriculture watersheds. Interflow, the infiltration of precipitation into the ground, is much higher in the grassland watershed compared to the agriculture and urban watersheds. Urban and agricultural land uses have greater soil compaction, less permanent vegetation, and increased anthropogenic cover, causing lower rates of groundwater infiltration compared to grasslands.

3.2 Water Quality: Nutrient Concentration Response to Land Cover and Precipitation



Figure 5: Graphs display the changes in nutrient concentrations in each sampling location within the three watersheds (grassland (K), agriculture (LB), and urban (IC)) for both wet and dry sampling events. Total nitrogen, total phosphorus, and nitrate are displayed in mg/L. Orthophosphate is displayed in 0.001 mg/L.



Figure 6: Graphs display changes in nutrient concentrations across land cover (red = urban, green = grassland, and yellow = agriculture) before and after a rain event. A. The change in total nitrogen concentrations for all watersheds for dry and wet sampling. B. The change in total phosphorus for all watersheds for dry and wet sampling. C. The change in nitrate concentrations for all watersheds for dry and wet sampling. D. The change in orthophosphate for all watersheds for dry and wet sampling.

Total nitrogen concentration is significantly correlated to land cover in watersheds sampled (p = 0.02597, $R^2 = 0.2616$), but not to saturation levels (p = 0.83111) (Table 2). The elevated levels of

total nitrogen in the urban watershed could be the result of point source pollution or overapplication of lawn fertilizer (Figure 6A). The elevated levels of total nitrogen in the agricultural land use area could be a result of synthetic nitrogen fertilizer. The grassland watershed receives no synthetic nitrogen fertilizer, which could be the result of the lower total nitrogen concentrations.

Low total phosphorus concentrations for all land cover areas were observed, with lower concentrations of total phosphorus in the grassland and agricultural watershed at low saturation (Figure 6B). These concentrations were not significantly correlated to land cover (p = 0.5507, $R^2 = 0.1127$) or saturation levels (p = 0.3059) in watersheds sampled (Table 2). Total phosphorus was especially low in the grassland watershed, likely because the area receives no synthetic fertilizer, and has little to no point source pollution. Total phosphorus was higher in the urban and agricultural areas possibly because of point source pollution or synthetic phosphorus fertilizer additions. Rainfall events increased total phosphorus concentrations likely due to the mobilization of sediment carrying the nutrient into waterways. Rainfall events could have had a lower impact on total phosphorus concentrations in the urban areas because there is less exposed soil that can be eroded and translocated in this watershed.

Nitrate concentrations are significantly correlated to land cover in watersheds sampled (p = 0.0372, $R^2 = 0.265$), but not to saturation levels (p = 0.4002) (Table 2). Concentrations were the highest in the urban watershed, followed by the agricultural watershed, and then grassland, like the observed pattern of total nitrogen (Figure 6C). While these concentrations are still below the allowable amount of nitrate for drinkable water in the U.S., this increase in concentrations in urban areas is still concerning. It is possible that these increases in nitrate nitrogen concentrations are a result of excessive spring fertilizer applications on lawns and golf courses in urban areas. Elevated nitrate in agricultural areas is likely a result of spring fertilizer application before planting crops. The grassland watershed occurs in a nutrient limited system, where high infiltration locks nutrients in the soil, which could be the result of the lower total nitrogen concentrations in stream water.

Orthophosphate concentrations were low in all watersheds at all sampling times (Figure 6D). These concentrations were not significantly correlated to the landcover (p=0.578, $R^2 = 0.114$) or saturation rate (p = 0.544) of sampled watersheds (Table 2). The grassland watershed consistently showed higher concentrations of orthophosphate than hypothesized, likely because orthophosphate is a test for organic phosphorus, which is a common form of plant available phosphorus. Elevated levels of orthophosphate could also be the result of grazing animals in the agricultural and grassland watersheds.

Table 2: Summary statistics table for nutrient concentrations for analysis of variance (ANOVA). Significance is identified with an asterisk (*). Only total nitrogen and nitrate were significantly correlated with watershed. No correlation exists between watershed for total phosphorus and orthophosphate, and for treatment and watershed:treatment for all nutrient analysis.

Anova Association (p-value)	Total Nitrogen	Total Phosphorus	Nitrate	Orthophosphate
Watershed	0.0257*	0.551	0.0372*	0.578
Treatment	0.831	0.306	0.400	0.544
Watershed:Treatement	0.695	0.615	0.569	0.409
R ²	0.262	0.113	0.265	0.114

4. Discussion

Land use, hydrology, and saturation all have large impacts and are interconnected with the flux of nutrients, specifically nitrogen and phosphorus, in first and second order streams. A significant correlation was found between total nitrogen and nitrate nitrogen across land use. Grasslands overall had the lowest rates of nitrogen and phosphorus compared to the agriculture and urban watershed, except for KNZ 4 during wet sampling (Figure 5). This decrease in nutrient concentration is due to the stream not flowing; the water sample was taken from a stagnant pool, which likely concentrated more nitrogen and phosphorus compared to the flowing stream. In addition, the elevated levels of nitrate and total phosphorus at location IC3 (Figure 5) were likely due to the proximity of the sampling location downstream from the Overland Park wastewater treatment plant. This point-source pollution likely caused the increase in the level of nitrogen and phosphorus in both our dry and wet samples from the location.

Other studies have shown similar results, with agricultural land uses having higher concentrations of nitrate compared to grassland (Brion et al., 2011). The heightened levels of both nitrogen and phosphorus in the urban watershed found in this study is comparable to past studies which have found that urban areas have higher point and nonpoint sources of pollution, resulting in increased nitrogen and phosphorus in stream water (Tremblay et al., 2020). Our findings that land use influences concentrations of nutrient pollution further addresses the need for water quality monitoring and reduction of pollution in first and second order streams, which are typically ignored (Seybold and McGlynn, 2018).

Limitations of this research include the short time period of sampling, which did not capture seasonal variability of this data. We were unable to capture the absolute high and low points of precipitation during our study period due to logistical challenges (Figure 3). We also only had one replication of our data, with only one watershed per land use type. Only two sampling sets, one wet and one dry, were captured during the research period. We were also unable to identify specific sources of pollution in our research area. Similar explanations for higher nutrient levels at different study area locations could be addressed in a follow-up study.

Future research could address how the evaluated relationships change across ecosystems, temperature gradients, rainfall gradients, or other natural variability. Changes in correlation between water quality, land cover, and saturation level across seasons or over many years could prove significant in some cases. Finally, identifying and accounting for point source pollution

could improve knowledge on how nonpoint source pollution contributes to these water quality parameters in lower order streams.

5. Conclusion

In this study we determined the differences in water quality that exist in stream flow across three different land uses: agricultural, urban, and grassland, before and after a precipitation event. According to the data collected and evaluated in this study, streamflow is a result of precipitation in all three watersheds. Higher levels of Hortonian overland flow and lower levels of interflow in the urban and agricultural watersheds have a direct correlation to the discharge rate. The grassland watershed displayed smaller increases in streamflow with precipitation compared to urban and agricultural watersheds. Total nitrogen and nitrate nitrogen are significantly correlated to land use in watersheds evaluated. Urban and agricultural areas showed higher concentrations of total nitrogen and nitrate nitrogen than was measured in the grassland watersheds. Changes in streamflow, runoff, and nutrient dynamics over land cover display the importance of tracking potential pollutants in small first or second order streams. In the face of global change and increased growth and urbanization, understanding the effect of nutrient pollution in small first and second order streams will be fundamental in conserving and protecting freshwater ecosystems and resources in the future.

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Author's contribution

Matthew Arana did review of literature, field sampling, analyzed data, wrote first draft, and formulated revisions. Ashley Chandler did review of literature, field sampling, graphical abstract, analyzed data, wrote first draft, and formulated revisions. Alex Murphy did review of literature, field sampling, analyzed data, designed graphs, wrote first draft, and formulated revisions. Kalea Nippert did review of literature, field sampling, developed statistical code, analyzed data, designed graphs, wrote first draft, and formulated revisions. Jeeban Panthi served as a mentor, helped with field sampling, and formulated revisions.

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