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Understanding the Combined Effects of Land Cover, Precipitation and Catchment Size on Nitrogen and Discharge—A Case Study of the Mississippi River Basin

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Abstract: Biological processes of rivers are strongly influenced by concentration and fluxes of nitrogen (N) levels. In order to restrain eutrophication, which is typically caused by urbanisation and agricultural expansion, nitrogen levels must be carefully controlled. Data from 2013 to 2017 were gathered from 26 sub-catchments in the Mississippi River basin to assess the effects that catchment size, land cover, and precipitation can have on the discharge and total nitrogen (TN) and how TN yields deviate from a generalised local trend. The findings indicated that land cover and precipitation had a determinative effect on area-weighted discharge (Q_{area}). More specifically, Q_{area} had significant positive (directly proportional) relationships with precipitation, forest, and urbanised land cover, and significant negative (inversely proportional) relationships with grassland/pasture and scrub/shrub land covers. Concurrently, the TN concentration significantly increased in the presence of agricultural land cover, but significantly decreased in forest land cover. The TN yield (TN concentration × Q_{area}) was largely determined by Q_{area} because the latter was observed to fluctuate more dramatically than concentration levels. Consequently, the TN yield exhibited the same relationships that Q_{area} had with precipitation and land covers. The TN yield changed significantly ($p < 0.05$) and positively with instantaneous discharge across all sites. Nevertheless, the rate of TN yield variations with discharge displayed a significant ($p < 0.0001$) negative ($r^2 = 0.80$) relation with the catchment size. Ultimately, this study used discharge readings to facilitate the prediction of TN concentrations and yields across various catchment areas in the Mississippi River basin and provided a robust model for future research in this area.

Keywords: nitrogen; precipitation; land cover; discharge; Mississippi River

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1. Introduction

Human nutrition has considerably improved owing to the use of nitrogen-based fertilisers in agriculture [1,2]. Yet, the overuse of these fertilisers has resulted in unintended health-related and environmental issues [3,4]. For example, the overuse of fertilisers has engendered eutrophication, which can cause more frequent algal blooms, oxygen depletion, water turbidity, and biodiversity loss [5,6]. These consequences have progressively negative effects, for example, oxygen depletion can disband heavy metals that were once precipitated or bound to river sediment particles [7]. These metals are generally associated with harmful effects on water quality and ecosystem wellness [8,9].

Since the Industrial Revolution, nitrogen levels have progressively increased across the globe as a result of human activities [10]. For example, the annual use of commercial nitrogen-based fertilisers increased from 594,000 to 11.5 million tons between 1945 and 1985 in the United States of America [11]. Simultaneously, the concentration of nitrogen in America's water has increased to critical levels [12,13]. Global mobilisable nitrogen levels (N_{mob}) have increased dramatically since industrialisation. Prior to industrialisation, the level was 111 Tg N_{mob}/year, and at present it is 223 Tg N_{mob}/year (Table 1). The pre-industrial nitrogen levels are consistent with estimates made in existing research by [14,15] and cohere with those generated by [16] despite being slightly lower. As a result of increased anthropogenic emissions, such as those produced through industry, the cultivation of crops, and the use of industrial fertilisers, the present N_{mob} levels are high [17].

Table 1. Pre-industrial and contemporary mobilisable nitrogen loadings [17].

	Pre-Industrial N_{mob} (Tg/Year)			Contemporary N_{mob} (Tg/Year)						
	Deposition	Fixation	Total	Deposition	Fixation	Fertiliser	Livestock Load	People Load	Total	World Population Share (%) *
Africa	3.63	31.99	35.61	6.58	25.02	0.94	6.43	2.25	41.22	17.20
Asia	3.29	25.45	28.73	11.21	22.62	20.21	22.41	12.7	89.15	59.54
Australia	0.46	6.99	7.45	0.46	5.7	0.19	1.48	0.09	7.91	0.33
Europe	0.62	3.92	4.54	4.4	3.06	5.48	10.13	3.09	26.16	9.59
North America	1.27	9.81	11.07	6.16	8.76	5.48	5.85	1.95	28.21	7.60
Oceania	0.02	0.34	0.35	0.03	0.17	0.07	0.58	0.02	0.87	0.21
South America	2.75	20.16	22.91	3.51	16.12	1.59	6.63	1.21	29.06	5.53
Totals	12	99	111	32	81	34	54	21	223	100

* [18].

The Mississippi River basin is the third biggest basin in the world, covering approximately 41% of the contiguous United States [19], and is the major source of freshwater and nutrients to the Gulf of Mexico [20]. Ref. [21] approximated the amount of nitrogen delivered to the Gulf of Mexico from the Mississippi River basin. They identified six sources of nitrogen, viz., chemical fertilisers, atmospheric deposition, manure, fixation and other legume sources, urban effluent, and wastewater treatment facilities, which account for 41, 26, 10, 9, 7, and 7%, respectively. The Mississippi River has undergone significant engineering changes throughout the years as a result of human activities, such as urbanization and agricultural growth. These activities have contributed remarkably to the deterioration of water quality in the northern Gulf of Mexico and to the occurrence of seasonal hypoxia (dissolved oxygen less than 2 mg L^{-1}) each summer since the 1980s [22]. This is the world's second biggest human-induced hypoxic zone, ranging in size from 40 km^2 in 1988 owing to drought to 22,730 km^2 in 2017 [23,24]. The Mississippi River/Gulf of Mexico Watershed Nutrient Task Force established a target of lowering the hypoxic zone's size to 5000 km^2 by the year 2035 [25]. However, long-term research has shown that hypoxia has tended to extend over time, posing negative ecological and economic impacts [26,27].

Land cover change is a significant factor influencing N export from the land. The Mississippi River basin is one of the most productive agricultural areas in the United States and has been notably influenced by land cover changes [28,29]. Conversion of natural vegetation to croplands has resulted in a large increase in nitrogen loading beyond baseline levels in the Mississippi River basin prior to the heavy use of synthetic nitrogen fertilisers [30]. On the other hand, climatic change is predicted to also alter nitrogen loadings. Various climate studies predicted certain changes in future climatological conditions, especially for the primary hydrological controller, precipitation [31]. If precipitation alters, the discharge and accumulation of nitrogen will change considerably [32–34]. Existing research contends that the accumulation and discharge of nitrogen will increase in tandem with increased precipitation [35–41]. Similarly, [42] found that the degree of interannual variability in nitrogen loading from the Mississippi basin may vary by a factor of 2.3, with 76% of the variability related to annual precipitation fluctuations. However, the degree to which precipitation fluctuation has an effect on N yield and transport to the Gulf remains unknown. This unpredictability makes identifying and implementing effective N reduction techniques in the case of catastrophic occurrences more difficult [43]. Variation in freshwater nitrogen cycles depends on multiple factors, rather than a single human activity or climate change variable [44]. This is well demonstrated by [45], who observed that N concentrations decrease with forest area ratios and decrease further as levels of precipitation increase. On the other hand, they found that the slope of the concentration and agricultural lands was positive and increased further with precipitation. Likewise [46], concluded that the nitrogen flux from agricultural land is high and increases during periods of heavy rainfall. Consequently, future N fluctuations will result from variations in precipitation and land cover [31]. However, it remains impossible to state whether a trend exists between nitrogen concentrations and yields, with respect to precipitation and/or land cover variations. Existing research typically considers the impacts of land cover and precipitation individually. Limited work has been done to investigate the combined effects of precipitation and land cover on the nitrogen delivery within freshwater, and this research often analyses a particular spatial scale e.g., [45,47,48]. Therefore, further research is needed to understand the behaviour of nitrogen in relation to spatial scale.

Parsons et al. [49,50] detected a relationship between catchment size and erosion rates and hypothesised that a similar relationship may be found between the behaviour of nitrogen and catchment size. Therefore, this hypothesis was investigated in the current study, i.e., catchment area that controls erosion rate could also control nitrogen yield in the Mississippi basin. The present study investigated the combined effects of precipitation and land cover on discharge and nitrogen concentrations within variously sized sub-catchments of the Mississippi basin. Such investigation is important to characterize the relative importance of these drivers (precipitation and land cover) on future changes of the hydrological regime. From the viewpoint of stakeholders or water resources managers, the findings of this research may help watershed stewardship programs within the context of climate and land cover change adaptation. For instance, findings from such studies could be used to help sustain the protection of natural habitat (e.g., wooded regions and wetlands), define long-term impacts on ecological objectives, such as algal blooms, in surface waterways, and identify long-term land cover zoning plans that protect water quality.

2. Materials and Methods

The TN budgets of 26 sub-catchments (hereafter, catchments) in the Mississippi River basin were quantified (Figure 1). Using the United States Geological Survey [51], data pertaining to the monthly nitrogen concentrations and discharges within each catchment between 2013 and 2017 were gathered. The National Water Quality Network (NWQN) contains 110 river sites across the United States monitored by the USGS National Water Quality Program. This network includes monthly TN concentrations and discharge data. The selection of monthly scales was contingent on data availability. The National Land Cover Database was used to collect data about the land cover with a 30 m resolution. Precipitation data for the stations dispersed over each catchment were gathered from the National Oceanic and Atmospheric Administration [52] from 2013 to 2017. The Thiessen polygon technique (Equations (1) and (2)) was used to interpolate the precipitation map for each catchment. In this technique, the precipitation reported at each station is weighted according to the region nearest to the station. The following approach is used to determine the weighing area: The precipitation stations are connected to create a triangular network. To form a polygon around each station, perpendicular bisectors for each of the triangle's sides are created. Thiessen polygons is the name given to these bounding polygons. If P_1, P_2, … , and P_M denote the precipitation magnitudes measured at stations 1, 2, … , and M; and A_1, A_2, … A_M denote the corresponding areas of the Thiessen polygons, then the average precipitation across the catchment P for a catchment area A is given by:

$$\overline{P} = \frac{P_1A_1 + P_2A_2 + \ldots + P_MA_M}{(A_1 + A_2 + \ldots + A_M)} \quad (1)$$

Thus in general for M stations:

$$\overline{P} = \frac{\sum_{i=1}^{M} P_iA_i}{A} = \sum_{i=1}^{M} P_i\frac{A_i}{A} \quad (2)$$

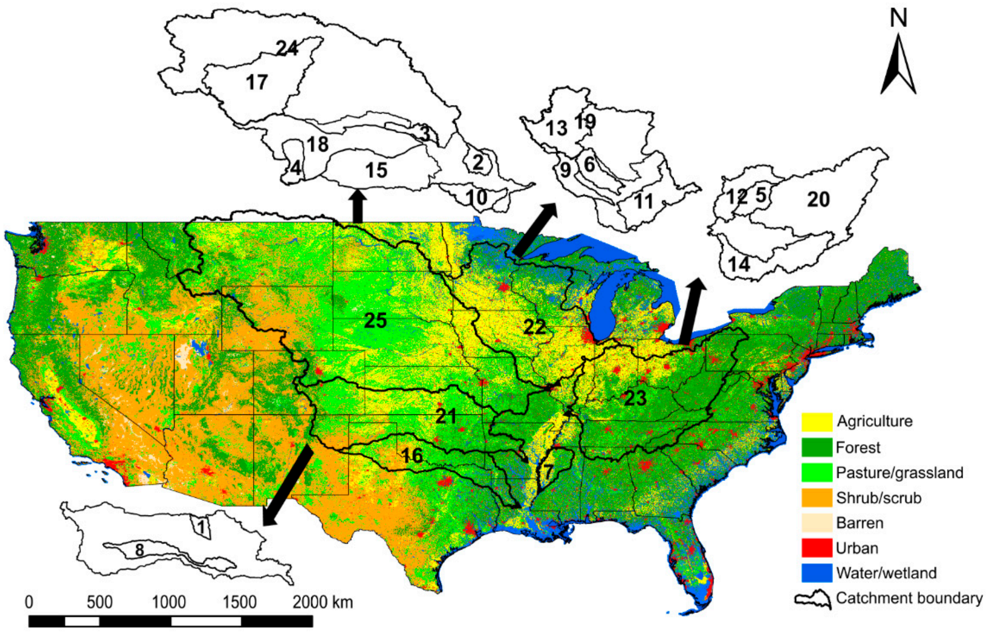


Figure 1. Study sites.

The ratio $\frac{Ai}{A}$ is referred to as the station's weighting factor. The Thiessen polygon approach is preferable to the arithmetic-average method for computing the average precipitation across an area because weighting is applied to the individual stations on a rational basis. Once the weighting parameters are defined, calculating the average P for a set network of stations is quite straightforward [53]. To construct the Thiessen polygons in ArcGIS, we selected Arc Toolbox > Analysis Tools > Proximity > Create Thiessen Polygons. The weighting factor assigned to each station was multiplied by the station's P. The sum of the weightage factor and *p* values for all stations was the catchment's average *p* value. Catchments were selected on the basis of their areas, precipitation levels, and the availability of data relating to the TN concentrations and nitrogen discharge. The catchments under study are geographically widespread, demonstrating diverse levels of areas, land cover, and precipitation (Figure 1). The catchment areas range from approximately 3210 km^2 to 1,848,000 km^2 (Table 2).

The various forms of land cover included pasture/grassland, forest, agricultural land, wetland/water, urbanised land, scrub/shrub lands, and barren lands.

In order to limit the effects of anomalous results among the TN concentration readings, area-weighted discharge values (Q_{area}), and TN yields between catchments, the median measurements of each variable were employed in the regression analysis (Table 3). This meant that the median TN concentration, median Q_{area}, and median TN yield were assessed to determine whether a relationship existed between these variables, and the median monthly precipitation, catchment size, and land cover under study. The TN levels were determined using the following formula:

$$\text{TN yield} = [\text{TN}] \times \text{Q}/\text{A} \quad (3)$$

TN yield describes the total nitrogen yields at the catchment outlet (mg TN m^{-2} min^{-1}); [TN] refers to the total nitrogen concentrations (mg TN L^{-1}); Q indicates the level of discharge at the catchment outlet (L min^{-1}); and A refers to the catchment area (m^2).

Table 2. Study rivers, catchment area (km^2), precipitation (mm), percentage of land cover (%), and the correlations (r^2) of discharge level ($L\ min^{-1}$) with both TN concentrations ($mg\ L^{-1}$) and TN yields ($mg\ m^{-2}\ min^{-1}$).

No.	River	Area (km^2)	Mean Annual Precipitation (m)	Pasture/ Grassland	Forest	Barren	Agriculture	Urban	Water/ Wetland	Shrub/ Scrub	Correlation (r^2) between Q-C	Correlation (r^2) between Q-Y
1	Little Arkansas River near Sedgwick, KS	3210	0.74	23.7	3.7	0.1	61.5	9.4	1.4	0.2	0.02+	**0.96+**
2	Grand River near Sumner, MO	17,820	0.91	47.2	17.7	0.2	26.4	4.7	3.4	0.4	**0.18+**	**0.69+**
3	Elkhorn River at Waterloo, NE	17,869	0.64	31.2	1.6	0.2	57.8	4.2	4.8	0.2	**0.71+**	**0.97+**
4	South Platte River near Kersey, CO	25,019	0.37	30.5	30.8	0.6	4.4	8.9	4.2	20.6	**0.59−**	**0.90+**
5	White River at Hazleton, IN	29,279	0.96	9.5	31.9	0.3	44.1	11.7	2.2	0.3	**0.28+**	**0.92+**
6	Iowa River at Wapello, IA	32,369	0.87	8.6	4.2	0.2	75.9	7.2	3.7	0.2	**0.54+**	**0.94+**
7	Yazoo River below Steele Bayou near Long Lake, MS	34,590	1.22	10.5	26.8	0.2	39.1	5.4	15.9	2.1	**0.09+**	**0.84+**
8	North Canadian River near Harrah, OK	35,680	0.67	48.6	10.4	0.2	24	5.3	1	10.5	**0.31−**	**0.99+**
9	Des Moines River at Keosauqua, IA	36,360	0.85	13.4	9.4	0.2	65.9	7.6	3.2	0.3	**0.61+**	**0.92+**
10	Osage River near St. Thomas, MO	37,769	0.97	45.2	31.4	0.2	12.6	5.8	4.3	0.5	**0.14+**	**0.94+**
11	Illinois River at Valley City, IL	69,259	0.92	4.9	11.7	0.3	64.8	14.2	3.8	0.3	**0.41+**	**0.95+**
12	Wabash River at New Harmony, IN	75,720	0.97	6.3	20.5	0.2	61	9.2	2.5	0.3	**0.24+**	**0.91+**
13	Mississippi River at Hastings, MN	96,090	0.69	9.1	16	0.3	46	7.1	20.8	0.7	**0.51+**	**0.94+**
14	Tennessee River at Highway 60 near Paducah, KY	104,449	1.18	21.9	58.5	0.3	3.4	9.7	4.1	2.1	**0.45+**	**0.93+**
15	Kansas River at DeSoto, KS	154,770	0.64	39.5	2	0.2	53	4	0.9	0.4	**0.58+**	**0.97+**
16	Red River at Alexandria, LA	174,819	0.86	36.6	21.4	0.5	14.5	4.7	6	16.3	**0.26+**	**0.99+**
17	Yellowstone River near Sidney, MT	178,919	0.36	33	12.5	1	3.7	1.3	2.1	46.4	**0.31+**	**0.89+**
18	Platte River at Louisville, NE	221,110	0.41	50.8	8.9	0.3	15.1	3.5	3.4	18	**0.52+**	**0.96+**
19	Mississippi River at Clinton, IA	221,710	0.84	10.7	26.3	0.2	36.5	6.3	19.2	0.8	**0.13+**	**0.83+**
20	Ohio River at Cannelton Dam at Cannelton, IN	251,230	0.99	16.9	59.6	0.5	10.6	9.9	1.6	0.9	**0.58+**	**0.98+**
21	Arkansas River at David D Terry Lock and Dam below Little Rock, AR	410,330	0.65	44.1	15.2	0.3	20.9	4.6	1.7	13.2	**0.29+**	**0.97+**
22	Mississippi River Below Grafton, IL	443,670	0.87	10.6	18.5	0.2	50.4	8.1	11.7	0.5	**0.56+**	**0.93+**
23	Ohio River at Olmsted, IL	525,770	1.05	17.1	53.7	0.4	17.8	7.5	2.5	1	**0.42+**	**0.96+**
24	Missouri River at Omaha, NE	836,050	0.46	42	8.5	0.6	22.3	2.3	3.5	20.8	**0.16+**	**0.37+**
25	Missouri River at Hermann, MO	1,353,370	0.50	43	9.4	0.5	25.8	3.2	3.2	14.9	**0.39+**	**0.88+**
26	Mississippi River at Thebes, IL	1,847,179	0.59	34.4	11.5	0.4	32.7	4.5	5.5	11	**0.62+**	**0.94+**

Note: Bold numbers denote significant correlations ($p < 0.05$). + Positive correlations. − Negative correlations.

Table 3. Catchment area, Q_{area}, TN concentrations, and TN yields of the study sites.

Catchment No.	Area (km^2)	Median Q_{area} ($mm\ min^{-1}$)	Median Concentrations ($mg\ TN\ L^{-1}$)	Median Yields ($mg\ TN\ m^{-2}\ min^{-1}$)
1	3210	3.97×10^5	2.636	8.86×10^5
2	17,820	2.78×10^4	2.551	9.28×10^4
3	17,869	1.62×10^4	7.152	1.30×10^3
4	25,019	6.29×10^5	6.073	3.90×10^4
5	29,279	8.37×10^4	2.834	2.48×10^3
6	32,369	6.01×10^4	8.076	4.84×10^3
7	34,590	7.76×10^4	1.420	1.07×10^3
8	35,680	1.05×10^5	5.394	5.27×10^5
9	36,360	4.24×10^4	9.268	3.66×10^3
10	37,769	3.12×10^4	0.782	2.48×10^4
11	69,259	6.05×10^4	5.168	3.16×10^3
12	75,720	7.49×10^4	4.194	3.13×10^3
13	96,090	3.19×10^4	4.500	1.40×10^3
14	104,449	7.51×10^4	0.663	4.97×10^4
15	154,770	3.11×10^5	2.295	1.62×10^4
16	174,819	1.80×10^4	1.052	1.89×10^4
17	178,919	7.37×10^5	0.845	6.03×10^5
18	221,110	5.79×10^5	3.804	2.17×10^4
19	221,710	4.37×10^4	2.929	1.39×10^3
20	251,230	8.51×10^4	1.906	1.54×10^3
21	410,330	1.12×10^4	0.943	1.04×10^4
22	443,670	4.93×10^4	4.080	2.05×10^3
23	525,770	8.75×10^4	1.822	1.76×10^3
24	836,050	6.76×10^5	2.536	1.71×10^4
25	1,353,370	9.02×10^5	2.959	3.01×10^4
26	1,847,179	2.27×10^4	3.493	8.74×10^4

The relationship between the TN yield and instantaneous discharge were quantified at each catchment. In order to understand the effects of nitrogen discharge on the TN yield, the latter was plotted against discharge for each catchment. A positive correlation between the TN yield and the levels of discharge was expected; however, this was initially tested in accordance with the relationship between nitrogen concentration and discharge. The presence of chemostatic, flushing, or dilution behaviour (i.e., instances in which chemical concentration remains constant, increases, or decreases with discharge respectively) is often assessed by examining the relationship between element concentration and discharge [54]. The TN yield had positive relations with both nitrogen concentrations and discharge levels according to Equation (3). Therefore, if the TN concentrations did not strongly decline with discharge (dilution), constant or ascending concentrations with discharges (chemostatic or flushing) resulted in a positive relationship between yield and discharge. Subsequently, the slope of the relationship between the TN yield and discharge (hereafter, TN yield rate) was quantified for each catchment. The TN yield rate for each catchment was then projected versus its area. A statistical analysis was undertaken using JMP14.2 (SAS Institute, Cary, NC, USA). Within our analysis, the significance level was 0.05. If the p value was found to be less than or equivalent to 0.05, the result was determined to be statistically significant.

3. Results

The analysis found that no significant trend existed between catchment area and precipitation (Table 4), and this indicated that our results were not influenced by the catchment area or climate conditions. The collinearity (r^2) between precipitation and types of land cover reached 78%. Applying variance inflation factors (VIF) to investigate the multicollinearity among catchment area, precipitation, and land cover types showed a significant multicollinearity. Specifically, agriculture land cover exhibited high VIFs (more than 10 *) indicating that this land cover category was highly correlated with at least one of the other parameters in the regression. Excluding this land cover type from the analysis to reduce multicollinearity resulted in low VIFs (less than 10). The ratio of forest and urbanised land cover displayed positive significant ($p < 0.05$) correlations with precipitation, and the percentages of barren, shrub/scrub land, and grassland/pasture had negative correlations with the levels of precipitation (Table 4). Our study found that barren land cover exhibited a significant positive correlation with scrub/shrub land cover. Results also showed a significant positive correlation between forest and urbanised land covers, a significant negative correlation between wetland/water and grassland/pasture cover, a significant positive correlation between grassland/pasture and scrub/shrub land cover, a significant negative correlation between grassland/pasture and urbanised land covers, and a significant negative correlation between scrub/shrub and urbanised land covers (Table 4).

Table 4. Correlation (r) between catchment area (km^2), precipitation (m), and percentage of land cover (%).

	Area (km^2)	Mean Annual Precipitation (m)	Bare Land	Forest	Wetland/Water	Grassland/Pasture	Scrub/Shrub	Urban
Area (km^2)	1.00							
Mean annual precipitation (m)	−0.33	1.00						
Bare land	0.30	**−0.50**	1.00					
Forest	−0.10	**0.58**	0.15	1.00				
Wetland/Water	−0.04	0.19	−0.18	0.05	1.00			
Grassland/Pasture	0.26	**−0.55**	0.22	−0.27	**−0.42**	1.00		
Scrub/Shrub	0.25	**−0.71**	**0.86**	−0.19	−0.21	**0.48**	1.00	
Urban	−0.36	**0.55**	−0.33	**0.41**	−0.01	**−0.70**	**−0.57**	1.00

Note: Bold numbers indicate significant correlations ($p < 0.05$).

3.1. Total Nitrogen, Precipitation, Land Cover, and Catchment Size

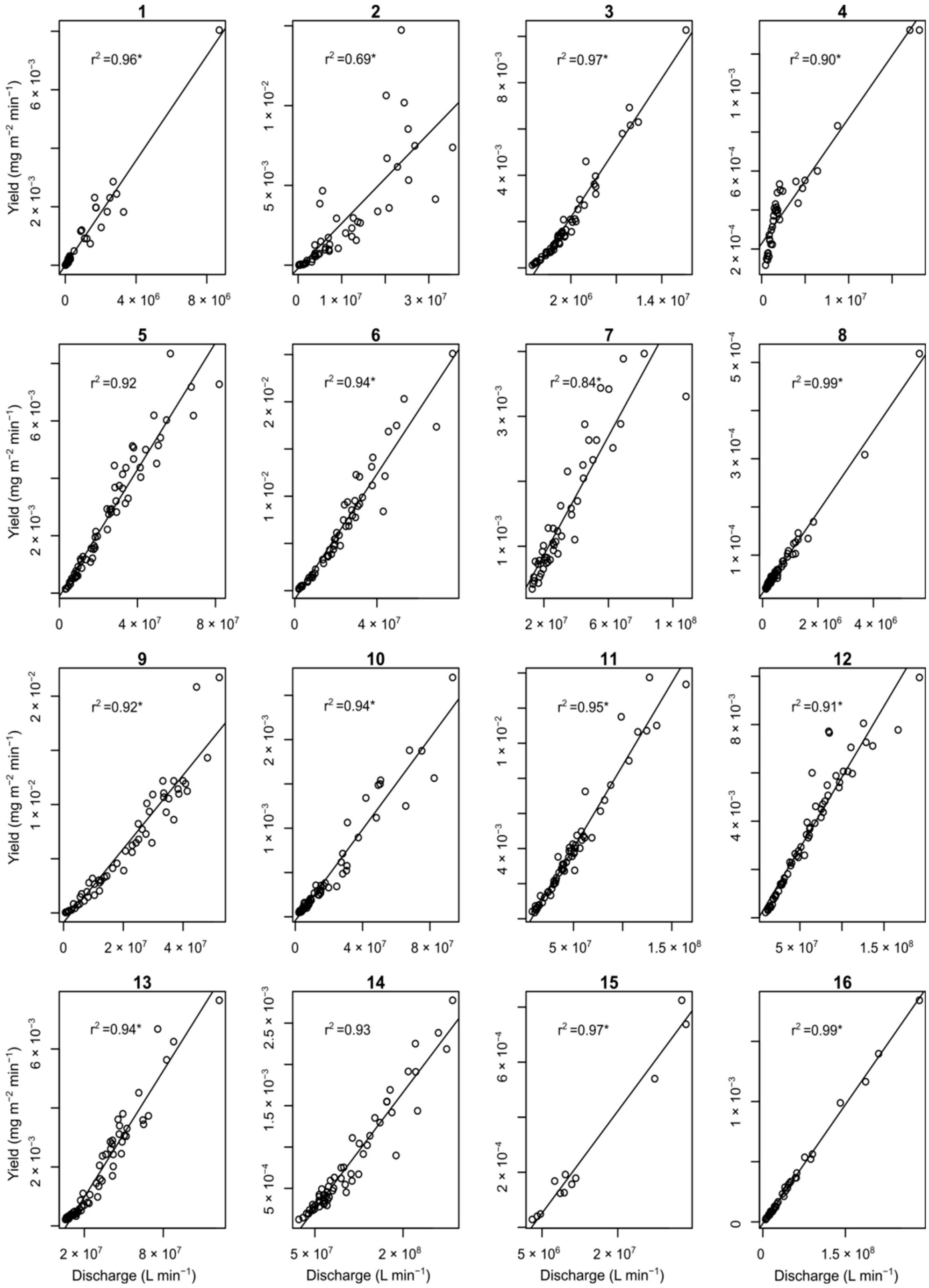
This analysis found that the percentage of agricultural land had a significant positive relationship with the median TN concentration ($p < 0.05$), while the percentage of forest land cover had a negative correlation with the median TN concentration (Table 5).

Table 5. Correlation (r) of Q_{area}, TN concentrations, TN yields with catchment size, precipitation, and land cover types.

	Median Q_{area} (mm min^{-1})	Median TN Concentration (mg L^{-1})	Median TN Yield (mg m^{-2} min^{-1})
Area (km^2)	−0.18	−0.16	−0.20
Mean annual precipitation (m)	**0.83**	−0.18	**0.43**
Barren	−0.21	−0.29	−0.32
Agriculture	0.18	**0.62**	**0.70**
Forest	**0.67**	**−0.44**	−0.01
Wetland/Water	0.16	0.00	0.07
Grassland/Pasture	**−0.75**	−0.29	**−0.76**
Scrub/Shrub	**−0.54**	−0.23	**−0.49**
Urban	**0.64**	0.21	**0.55**

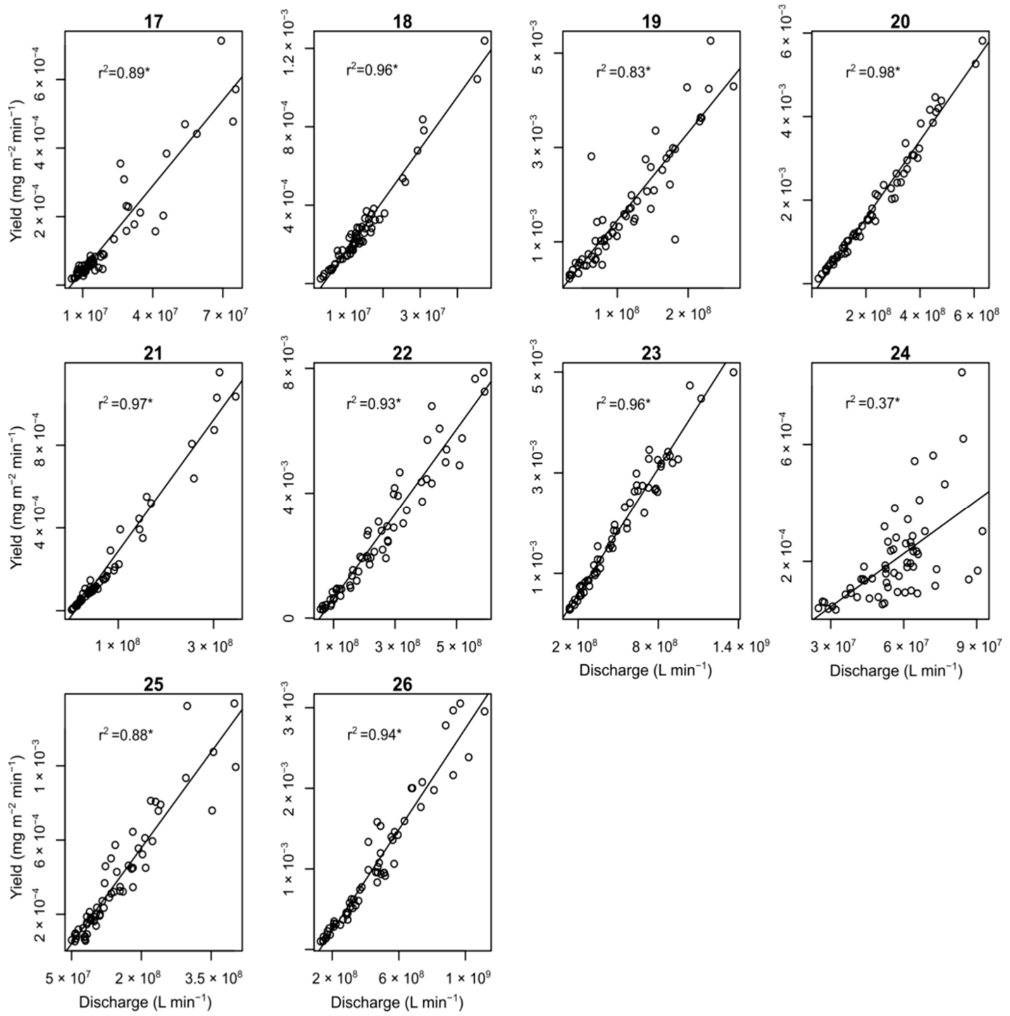
Note: Bold numbers indicate significant correlations ($p < 0.05$).

*A rule of thumb is that if the VIF is more than 10 then multicollinearity exists [55]. In response to precipitation, and ratios of forest and urbanised land cover, the median Q_{area} exhibited a significant positively correlated variation (Table 5). Conversely, the median Q_{area} varied in negative relations with the ratio of grassland/pasture and scrub/shrub lands (Table 5). In addition, a positive correlation existed between the median TN yield and precipitation, agricultural and urbanised land covers, while a negative correlation existed between the median TN yield and grassland/pasture and scrub/shrub land covers (Table 5). The slopes of regression between the TN yield and precipitation and land cover categories were analysed. The slopes of such regression between yield and precipitation, urban, pasture/grassland, shrub/scrub, and agriculture land covers were 0.002324, 0.000235, −0.000063, −0.000059, and 0.000041, respectively. Such regression indicated that the TN yield was more sensitive to precipitation variations followed by urban, pasture/grassland, shrub/scrub, and agriculture land cover variations, respectively. Across the investigated catchments, the relationship between nitrogen concentration and discharge showed a positive correlation in 23 catchments; a negative correlation in 2 catchments, and an insignificant correlation in 1 catchment (Table 2; Figure 2). Finally, across every catchment, a strong positive relation was observed between the TN yield and the discharge (Table 2; Figure 2).



(**a**)

Figure 2. *Cont.*



(**b**)

Figure 2. Instantaneous TN yields (mg TN m^{-2} min^{-1}) versus instantaneous discharge (L min^{-1}) for the studied rivers. (**a**) is for the first panel, and (**b**) for the second panel. * Significant correlations ($p < 0.05$).

3.2. TN Yield Rates

Overall, the TN yields increased with the levels of discharge, though the rate of such increase became smaller with the catchment size. The TN yield rate versus catchment area had a significant negative correlation ($p < 0.0001$; $r^2 = 0.80$) (Figure 3). This can be seen in the following equation:

$$\text{Log Y} = -12.37 - 1.02 \times \text{Log X} \quad (4)$$

where Log indicates the logarithm based 10, Y represents the TN yield rate and X refers to the catchment area.

4. Discussion

Precipitation is documented to be a controlling parameter for the growth and distribution of vegetation e.g., [56–58]. A substantial positive relation was reported between precipitation levels and vegetation density [59]. Likewise, [60] studied the effects of precipitation levels on land cover variation. According to their research, precipitation displayed a gradual increase from barren lands to grasslands to agricultural and forest lands. Simultaneously, land cover itself can affect precipitation levels. Ref. [61] found that highly urbanised environments typically experienced more frequent heavy precipitation. In their studies of Amazonia [62,63], found that precipitation levels declined as a result of deforestation, depending on the variant of land cover that substituted the forested area. They found that replacing forested areas with agricultural land resulted in greater precipitation than replacement with pasture/grassland. Contrastingly [64], found that the conversion of afforestation in the United States increased precipitation levels. Other research found that precipitation significantly enhances with vegetation density [65,66]. This is due to the fact that greater vegetation density quickens the rate of evapotranspiration, and thereby results in a lower vapour pressure deficit, which, in turn, increases the formation of clouds and rainfall [67,68]. The abovementioned explanation can justify the existence of the positive relations between urbanised and forested lands and precipitation levels, and the negative relations between bare lands, grassland/pasture, and scrub/shrub lands with precipitation (Table 4). Q_{area} increased with the level of precipitation (r = 0.87; Table 5), and this could be attributed to the enhanced water availability for runoff [69,70]. Since precipitation drives Q_{area}, the latter followed the same correlations between the former land cover types (i.e., positive relations with urban and forest land cover, and negative relations with grassland/pasture and scrub/shrub land cover) (Tables 4 and 5).

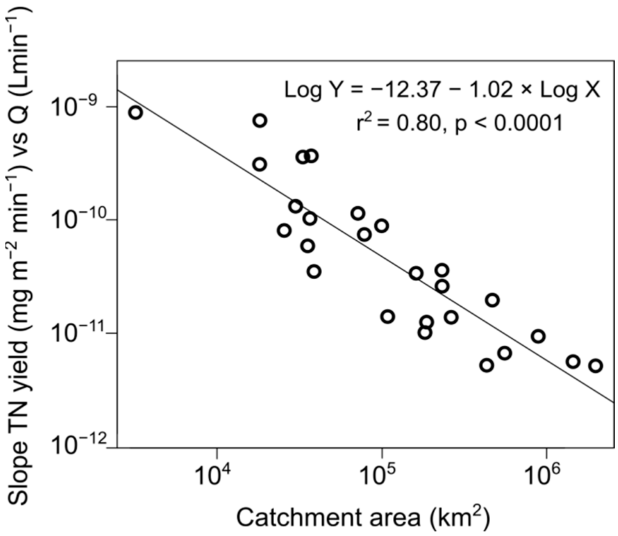


Figure 3. TN yield rates (i.e., the slopes of TN yield—Q regression) versus catchment size.

4.1. Total Nitrogen, Precipitation, Land Cover, and Area

Across the investigated catchments, the TN concentration was found to increase with the ratio of crop land cover (Table 5). The use of agricultural fertiliser generates higher levels of nitrogen in the soil and water runoff [71,72]. Moreover, tillage and other agricultural activities can cause erosion, which also increases the loss of nitrogen. Many studies have found that tillage causes markedly high levels of soil erosion and nitrogen loss [73–75]. On the other hand, TN concentrations are quite low in forested areas due to the limited input of nitrogen, ongoing microbial activities, and dense vegetation within that environment (Table 5). The accumulation of atmospheric nitrogen is the most significant cause of nitrogen build-up in watersheds within areas of high natural vegetation (such as forests). Nevertheless, these levels remain significantly lower than that caused by human activity (such as the use of fertilisers and the production of wastewater) within agricultural and urbanised areas [76]. Without the influence of anthropogenic inputs, the transfer of nitrogen from upland forests into streams can be eliminated by soil-stream interfaces [77–79], microbial absorption assimilation, or the denitrification process [80–82]. In comparison with cropland or grassland, forested land has the lowest levels of microbial nitrogen fixation [83]. In turn, dense vegetation within forested areas limits the incidence of soil erosion and runoff because soils are more stable and the vegetation can absorb precipitation. Therefore, nitrogen loss is limited [84]. Surprisingly, the results of this study did not show a correlation between the ratio of urbanised land cover and the TN concentration (Table 5). Within a previous study that involved mixed land covers such as the watersheds of the Menominee River, Altamaha River, Connecticut River, and Upper Snake River, low TN concentrations were found. Within these large watersheds, the runoff from urbanised and agricultural environments can become diluted in forested and other relatively undeveloped lands [85]. The results of the current analysis cohere with this study, as the nitrogen which had originated from urbanised areas was likely to have been diluted upon reaching undeveloped lands.

A positive correlation was found between TN yields and discharge, which can be explained based on the positive relations between TN concentrations and discharge. The presence of positive relations between the TN concentration and discharge level across the majority of catchments (Table 2) can rationalise the positive relations between TN yields and discharge levels (Table 2; Figure 2). Significantly, within the two catchments that showed a negative correlation between the TN concentrations and discharge, there were higher levels of urbanised land than in other catchments. More specifically, these two catchments had a significant amount of high and medium intensity urbanised land compared to other catchments. This finding was affirmed with reference to data from SPARROW (Spatially Referenced Regression on Watershed attributes) [86], which shows that nitrogen typically emerges as a result of wastewater treatment processes, urbanised land, and the use of agricultural fertiliser and manure. With regard to the two catchments mentioned previously, SPARROW data showed that these catchments had a higher level of nitrogen discharge from wastewater treatment than other catchments. Within these catchments, the presence of a negative correlation between TN concentration and discharge meant a high TN concentration at a low discharge level which could be ascribed to a constant source of nitrogen that is diluted with high discharges (i.e., urban wastewater in the current study). In spite of the negative correlation between the TN concentration and the Q_{area} in these two catchments, a positive correlation still existed between the TN yield and the Q_{area}. This was the result of the rate of variation between the TN concentration levels and the Q_{area}. For example, the South Platte River (near Kersey, Colorado) showed the highest negative correlation between the TN concentration and the Q_{area}. However, within this river, the TN yield still increased in tandem with the levels of Q_{area}. These trends are explained by the fact that the TN concentration declined by a factor of 4.3, whereas the Q_{area} levels increased by a factor of 39.8. Therefore, the results of the present study cohered with the work of [87], which illustrated that streamflow affects nutrient yield variation more than concentration levels. Therefore, this study showed that the N yield follows Q_{area}, in that it shares a positive relation with precipitation and urbanised land and has a negative correlation with grassland/pasture and scrub/shrub land cover (Table 5). Notably, no correlation was found between the TN yield and forested land, even though forested cover maintains reasonably low TN concentration (Table 5). In fact, the TN yield remained consistent within forested areas, as the low TN concentrations were counterbalanced by a heightened Q_{area} (Table 5).

4.2. TN Yield Rate

As mentioned previously, the TN yield increased in tandem with the levels of discharge. However, this rate of increase was contingent on the size of the catchment. Previous research has asserted that the erosion of soil by water contributes significant amounts of nitrogen to various ecosystems [88–91]. In catchments greater than 10 km^2, the level of erosion and, consequently, yield was documented to decrease with catchment size [92,93]. Within these catchments (more than 10 km^2), the sediment sinking potential is typically higher than the sediment sourcing potential, leading to a reduction in sediment yield [94]. This can be ascribed to the fact that large catchments encompass greater floodplain development and more foot slope terrains, in which sediment can be stored [92]. It is also more likely that sediment will be deposited before a catchment's outlet point, as it must travel a greater distance [95,96]. Many research works have found a negative relation between sediment yields and catchment size [97–99], which explains the negative relation between the TN yields and catchment size within this study (Figure 3). This means that smaller catchments experience higher erosion levels and as erosion is a primary controller for nitrogen sourcing, such catchments have higher nitrogen yield rates than larger catchments [100].

Within the present study, a geographically diverse array of catchment areas, various forms of land cover, and differing levels of precipitation were analysed. This study illustrated that the findings presented within Figure 3 can be utilised as a means to predict the TN yield rate throughout the Mississippi basin. By investigating the TN yield rate within a certain catchment area, the TN yields and concentrations levels can be deduced in each instance of discharge.

5. Conclusions

This study found that the TN yield (TN concentration × Q_{area}) was largely determined by Q_{area} because the latter fluctuated more dramatically than nitrogen concentration levels. In addition, the TN concentration and Q_{area} differed according to the level of precipitation and land cover conditions. The TN concentration was found to increase in positive correlations with discharge across most catchments under study except in four catchments. In those four catchments, urban effluent was an important N source, which represented a steady source that was diluted at higher discharges. Variations in precipitation and/or land cover could affect discharge and/or TN concentration and consequently the TN yield. The slopes of regression between the TN yield and precipitation and land cover categories indicated that the N yield was more sensitive to precipitation variations followed by urban, pasture/grassland, shrub/scrub, and agriculture land cover variations, respectively. The TN yields increased in tandem with the levels of discharge, even though the rate of such an increase declined with catchment size. Overall, this study involved the analysis of broad spatial scales, land cover, and precipitation, across several catchments within the Mississippi River basin. Ultimately, the study's findings supported the use of discharge measurements and catchment size as a means to predict TN concentrations and yields.

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