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Combined impact of land cover, precipitation, and catchment area on discharge and phosphorus in the Mississippi basin's subcatchments

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Abstract

Phosphorus (P) supplies (concentrations and fluxes) are essential drivers for biological activities in rivers and should be controlled to prevent eutrophication that usually results from urbanization and agricultural expansion. In this study, data from 26 subcatchments in the Mississippi basin were compiled from 2013 to 2017 to identify how catchment area, precipitation, and land cover affect discharge and total P (TP) and how TP yield diverges from a generalized local response mode. Results revealed that area-weighted discharge (Q_{area}) is controlled by precipitation and land cover (i.e., increases with precipitation and with both urban and forestland covers and decreases with both shrub/scrub and pasture/grassland covers). Total P concentration increases with agricultural land cover and decreases with both forest and water/wetland covers. Total P yield (Q_{area} × concentration) is governed mainly by Q_{area} because the latter changes by a higher order of magnitude compared with concentration in the current study. Hence, TP yield follows the same trends that Q_{area} exhibits with precipitation and land cover. In all catchments, TP yield varied significantly ($p < .05$) and positively with instantaneous discharge. However, the rate of yield variations with discharge exhibited a significant ($p < .0001$) strong negative ($r^2 = -.74$) correlation with catchment area. This study provided a robust model that can predict the TP concentration and yield across different catchment scales in the Mississippi basin by means of discharge readings.

1 | INTRODUCTION

Application of nutrients, such as nitrogen (N) and phosphorus (P), in agriculture has played a significant role in securing the food supply to the growing world population (Stewart & Roberts, 2012). However, excess nutrient use has resulted in water quality problems, including eutrophication, which has negative impacts on human health and environmental quality (Caccia & Boyer, 2005; Carpenter et al., 1998; Howarth et al., 2012). Eutrophication is widely reported to be associated with increased frequency of algal blooms, water turbidity, oxygen depletion, and dominance of specific species and consequently loss of biodiversity (Russell, Weller, Jordan, Sigwart, & Sullivan, 2008; WHO, 2002). For instance, oxygen depletion can mobilize materials such as heavy metals that were formerly precipitated or tied to sediments (Antweiler, Goolsby, & Taylor, 1995). Such metals are linked to detrimental impacts on water quality and ecosystem health (e.g., Ip, Li, Zhang, Wai, & Li, 2007; Jonsson, Johansson, & Worman, 2003; Moore & Ramamoorthy, 1984). Globally, mobilization of N and P into the ecosystems by anthropogenic activities has grown severalfold since the industrial revolution (Schlesinger & Bernhardt, 2013). In the United States, the application of N and P fertilizers rose 10-fold and 4-fold, respectively, between 1950 and the beginning of 1980s (Munn et al., 2018). Such nutrient enrichment that has led to elevated N and P concentrations and loads has adversely affected the water bodies in the United States (Howarth, Sharpley, & Walker, 2002; Litke, 1999; National Research Council, 2000; Turner, Rabalais, & Justic, 2008). Nitrogen is generally the key limiting factor to algal production and eutrophication in coastal marine water (Howarth, 1988). Phosphorus input, on the other hand, usually limits both freshwater primary production (Carlsson et al., 2012; Hecky & Kilham, 1988) and oceanic production in the long term (Myers & Iverson, 1981; Tyrrell, 1999). Although many existing studies (e.g., Howarth & Marino, 2006; Vitousek & Howarth, 1991) have suggested that biota growth response to N is stronger than the response to P in marine environments, Elser et al. (2007) found that P limitation is not trivial in marine ecosystems.

Phosphorus in surface and ground water originates from natural and anthropogenic sources. Natural P sources arise from weathering of certain geologic units (Ator, Brakebill, & Blomquist, 2011) as well as runoff from areas with minimal human effect (Wise & Johnson, 2013). Globally, natural sources contribute to around 10 Mt P yr^{-1} (Smil, 2000). Anthropogenic P effluents stem from point and diffuse sources (Drolc & Koncan, 2002). Urban sewage containing human waste and phosphate detergents represents the main point source of P (Smil, 2000). On the other hand, erosion and runoff caused by land cover conversion represent a significant diffuse source of P. Inorganic fertilizers and animal wastes represent another important diffuse source of P (Table 1) (Smil, 2000).

Phosphorus losses from land to water are influenced by land management practices for food production as well as by climate change (Ockenden et al., 2017). Land cover within a river catchment is an important factor manipulating the concentrations of river nutrients such as P (Ide et al., 2019). For example, agricultural land cover is normally associated with activities such as tillage that significantly contribute to higher erosion and consequently higher P loss (Sharpley & Smith, 1994). Moreover, agricultural land cover is associated the application of fertilizers that are densely applied worldwide even to lands that already hold plentiful P reserves. Considerable amounts of P are also supplied to the farms in the form of manure (Smith, Tilman, & Nekola, 1999). In many regions around the world, P inputs from chemical fertilizers and manure exceed P outputs in farm yields, thus causing surpluses of P that ultimately accumulate in soils (Carpenter et al., 1998; Foy & Withers, 1995; Haygarth, Chapman, Jarvis, & Smith, 1998). Moreover, urban areas can contribute to P pollution because there is a positive correlation reported between P content and urban land use (Brett et al., 2005; Ide et al., 2019). Urbanization is typically associated with modifications of physical and hydrogeological characteristics of basins and creation of nutrient sources. Yard fertilizers, septic tank drainage, domestic animal wastes, and elevated soil erosion in urban areas are commonly linked to high P content and consequently water quality degradation (Carpenter et al., 1998; Soranno, Hubler, Carpenter, & Lathrop, 1996; Tufford, McKellar, & Hussey, 1998). In contrast, Brett et al. (2005) and Ide et al. (2019) found that the average P concentration was negatively correlated with forest area ratio. The loss of forests in humid areas leads to minimizing the recycling of nutrients owing to declining microbial activities and plant processes that immobilize nutrients in the forest canopy, organic matter, and soil (Abelho, 2001; Wahl, McKellar, & Williams, 1997).

Climate, on the other hand, affects the hydrological cycle by altering streamflow (Chang, Evans, & Easterling, 2001), P concentrations (Charlton et al., 2018), and, thus, P loads

Core Ideas

- Total phosphorus (TP) response to land cover and precipitation is defined.
- TP concentration is sensitive to land cover change.
- TP yield is governed by a coupling of precipitation with land cover.
- TP yield vs. discharge correlation (i.e., TP yield rate) is controlled by catchment area.
- TP concentration and yield are predicted based on measurements of discharge.

TABLE 1 Human intensification of the global P cycle

P flows	Natural	Preindustrial 1800	Recent 2000
	Mt P yr^{-1}		
Natural flows intensified by human actions			
Erosion (wind and water)	>10	>15	>30
Anthropogenic flows			
Animal waste	–	>1	>15
Human waste	–	0.5	3
Inorganic fertilizer	–	–	15

Note. Source: Smil (2000).

(Bouraoui, Galbiati, & Bidoglio, 2002). Phosphorus loading in rivers is a function of water quality (P concentration) and discharge (Stow & Borsuk, 2003). Variations in the factors controlling concentration or discharge will, accordingly, result in P loading change. Future climatic changes are expected to alter P loading as many climate models indicate changes in future meteorological conditions, particularly for precipitation, which is the principal hydrological driver (Robertson, Saad, Christiansen, & Lorenz, 2016). Predicted changes in precipitation have considerable impacts on future discharge and P loading. Average discharge and P loading are anticipated to increase as precipitation increases and vice versa (Robertson et al., 2016). In a study by the USEPA (2013), 20 catchments in the United States were tested to evaluate the sensitivity of discharge, nutrient loads, and sediment loads to changes in climate. That study found that when the average annual precipitation changes from −8 to +14%, the average annual discharge changes by −12 to +50%, and the P load changes by −12 to +50%. Similarly, Robertson et al. (2016) concluded that a −5 to +17% change in total annual precipitation results in a −21% to +9% change in total annual discharge and a −29 to +17% change in total annual P loading in the Lake Michigan basin. Bosch, Evans, Scavia, and Allan (2014) found that increases of +3 and +6% in precipitation result in changes in average annual discharge of +6 to +12% and total average annual P loading of +4 to +6%.

Whereas water quality in rivers is documented to be greatly related to land cover (Arnold et al., 2013; Robertson & Saad, 2011), discharge is reported to be strongly linked to precipitation (Miao & Ni, 2009; Yang, Yan, & Liu, 2012). Therefore, in the future, P flux change will be a result of changes in land cover and precipitation (Robertson et al., 2016). Moreover, the impact of land cover and precipitation changes can be coupled; for example, Thompson (2019) found that agricultural lands leach relatively high P amounts, but they do so even more during periods of heavy rains. Likewise, Ockenden et al. (2017) concluded that the increase in P loading due to precipitation increase could be alleviated only by large-scale land cover changes such as a substantial reduction in agricultural land cover. However, it is unclear if a detectable response pattern exists of P concentration and yield with respect to land cover and/or precipitation. Most previous studies focused on either the impact of land cover or the impact of precipitation on streamflow and P delivery to rivers (e.g., Schoonover, Lockaby, & Pan, 2005; Sliva & Williams, 2001; Tu, Xia, Clarke, & Frei, 2007). Although some efforts have been made to understand the coupled impact of land cover and precipitation on streamflow and P budget in rivers, work was limited to a specific spatial scale (e.g., Chang, 2004; El-Khoury et al., 2015). Therefore, the impact of scale on P behavior has not been sufficiently investigated. Parsons, Wainwright, Powell, Kaduk, and Brazier (2004) and Parsons, Brazier, Wainwright, and Powell (2006) established a relation between catchment area and erosion rate and hypothesized that a similar link may exist between catchment area and P dynamics. Therefore, in the current study we examine the hypothesis that catchment scale that drives erosion rates might also drive P yields. Hence, this study has been used to describe the combined impact of land cover and precipitation on discharge and P concentration across various spatial scales.

2 | MATERIALS AND METHODS

Total P (TP) budgets were quantified for 26 subcatchments (catchments, henceforth) in the Mississippi basin, United States (Figure 1). Monthly data of P concentrations and discharges for these catchments from 2013 to 2017 were obtained from the USGS. Monthly scales were selected depending on data availability. Data on catchment land cover were extracted from land cover databases, such as the National Land Cover Database, with a resolution of 30 m. We retrieved data on monthly precipitation from National Oceanic and Atmospheric Administration (https://www.psl.noaa.gov/data/gridded/). The studied sites were chosen based on catchment area, precipitation, and availability of TP concentrations and instantaneous discharge data. The selected catchments are geographically widespread (Figure 1) and have a broad range of size, precipitation, and land cover. The areas of catchments range from about 3,200 to 1,850,000 km^2 (Table 2). Land cover across sites is mixed and may include forest, pasture/grassland, agriculture, barren, water/wetland, urban, and shrub/scrub lands. Correlations (r) between catchment area, precipitation, and land cover were examined (Table 3). To control for differences in TP concentration, area-weighted discharge (Q_{area}), and TP yield between catchments and nonnormality of data arrangement, the median TP concentration, median Q_{area}, and median TP yield (Table 4) were used for each catchment in the regression analysis. The median TP concentration, median Q_{area}, and median TP yield relationships with median monthly precipitation, land cover, and catchment area were investigated (Table 5). Total P yield was computed according to:

$$\text{TP yield} = [\text{TP}] \times \frac{Q}{A} \tag{1}$$

where TP yield is the total P yield at the catchment outlet station (mg TP m^{-2} min^{-1}), [TP] is the total P concentration (mg TP L^{-1}), Q denotes discharge measured at the catchment outlet (L min^{-1}), and A denotes catchment area (m^2). Total P yield relationships with instantaneous discharge were identified for each site. To examine the control of discharge on P yield patterns, we plotted TP yield versus associated discharge across all rivers. The expected positive relationships between TP yield and instantaneous discharge is first tested in light of the relationship between TP concentrations and

TABLE 2 Study sites, catchment area, median monthly precipitation, land cover ratio, and r^2 value between discharge and both total P concentration and total P yield

No.	River	Area	Median monthly precipitation	Forest	Pasture/ grassland	Agriculture	Barren	Water/ wetland	Urban	Shrub/ scrub	r^2 Q-C	r^2 Q-Y
		km²	mm	%	%	%	%	%	%	%		
1	Little Arkansas River near Sedgwick, KS	3,209	55.9	3.2	24.2	62.1	0.0	1.6	8.9	0.0	.10*,a	.99*,a
2	Grand River near Sumner, MO	17,819	63.5	17.2	47.6	27.0	0.1	3.6	4.2	0.2	.21*,a	.62*,a
3	Elkhorn River at Waterloo, NE	17,871	50.8	1.1	31.7	58.4	0.1	5.0	3.7	0.0	.46*,a	.83*,a
4	South Platte River near Kersey, CO	25,022	30.5	30.3	30.9	5.0	0.5	4.4	8.4	20.4	.36*,b	.99*,a
5	White R. at Hazleton, IN	29,280	76.2	31.4	10.1	44.7	0.2	2.4	11.2	0.1	.14*,b	.10*,a
6	Iowa R. at Wapello, IA	32,375	63.5	3.7	9.1	76.5	0.1	3.9	6.7	0.0	.001b	.86*,a
7	Yazoo River below Steele Bayou near Long Lake, MS	34,589	101.6	26.3	11.1	39.7	0.1	16.1	4.9	1.9	.36*,a	.93*,a
8	North Canadian River near Harrah, OK	35,677	44.5	9.9	49.0	24.6	0.1	1.2	4.8	10.3	.05b	.86*,a
9	Des Moines River at Keosauqua, IA	36,358	59.7	8.9	13.8	66.5	0.1	3.4	7.1	0.1	.15*,b	.78*,a
10	Osage River near St. Thomas, MO	37,772	76.2	30.9	45.7	13.2	0.1	4.5	5.3	0.3	.001a	.80*,a
11	Illinois R. at Valley City, IL	69,264	76.2	11.2	5.5	65.4	0.2	4.0	13.7	0.1	.45*,b	.82*,a
12	Wabash River at New Harmony, IN	75,716	76.2	20.0	6.8	61.6	0.1	2.7	8.7	0.1	.18*,a	.90*,a
13	Mississippi R. at Hastings, MN	96,089	50.8	15.5	9.5	46.6	0.2	21.0	6.6	0.5	.73*,a	.92*,a
14	Tennessee River at Highway 60 near Paducah, KY	104,454	93.9	58.0	22.5	4.0	0.2	4.3	9.2	1.9	.045b	.24*,a
15	Kansas River at DeSoto, KS	154,767	50.8	1.5	40.0	53.6	0.1	1.1	3.5	0.2	.40*,a	.94*,a
16	Red River at Alexandria, LA	174,824	63.5	20.9	37.0	15.1	0.4	6.2	4.2	16.1	.08a	.97*,a
17	Yellowstone River near Sidney, MT	178,924	25.4	12.0	33.5	4.3	0.9	2.3	0.8	46.2	.74*,a	.84*,a
18	Platte River at Louisville, NE	221,107	34.3	8.4	51.5	15.7	0.2	3.6	3.0	17.8	.24*,a	.79*,a
19	Mississippi River at Clinton, IA	221,703	63.5	25.8	11.2	37.1	0.1	19.4	5.8	0.6	.35*,a	.88*,a
20	Ohio River at Cannelton Dam at Cannelton, IN	251,229	78.7	59.1	17.4	11.2	0.4	1.8	9.4	0.7	.81*,a	.87*,a
21	Arkansas River at David D Terry Lock and Dam below Little Rock, AR	410,329	50.8	14.7	44.6	21.5	0.2	1.9	4.1	13.0	.80*,a	.97*,a
22	Mississippi River Below Grafton, IL	443,665	66.0	18.0	11.1	51.0	0.1	11.9	7.6	0.3	.44*,a	.93*,a
23	Ohio R. at Olmsted, IL	525,768	85.1	53.2	17.6	18.4	0.3	2.7	7.0	0.8	.86*,a	.97*,a
24	Missouri River at Omaha, NE	836,048	30.5	8.0	42.5	22.9	0.5	3.7	1.8	20.6	.38*,a	.65*,a
25	Missouri River at Hermann, MO	1,353,269	38.1	8.9	43.6	26.4	0.4	3.4	2.7	14.7	.71*,a	.84*,a
26	Mississippi River at Thebes, IL	1,847,180	50.8	11.0	34.9	33.3	0.3	5.7	4.0	10.8	.54*,a	.91*,a

[a]Positive correlation. [b]Negative correlation.
*Significant at the .05 probability level.

TABLE 3 Correlations (r values) between catchment area, median monthly precipitation, and land cover categories

	Area[a]	Median monthly precipitation[b]	Land cover category: Barren	Agriculture	Forest	Water/wetland	Pasture/grassland	Shrub/scrub	Urban
Area	1.00								
Median monthly precipitation	−.27	1.00							
Land cover category									
Barren	.28	−.43*	1.00						
Agriculture	−.18	.17	−.61*	1.00					
Forest	−.10	.61*	.19	−.54*	1.00				
Water/wetland	−.04	.19	−.16	.13	.05	1.00			
Pasture/grassland	.26	−.57*	.17	−.55*	−.27	−.42*	1.00		
Shrub/scrub	.25	−.69*	.83*	−.57*	−.18	−.21	.48*	1.00	
Urban	−.33	.60*	−.27	.29	.47*	−.02	−.69*	−.57*	1.00

[a]Correlation between area and all land cover categories (r^2 = .21; p > .05). [b]Correlation between precipitation and all land cover categories (r^2 = .79; p < .05).
*Significant at the .05 probability level.

TABLE 4 Catchment area, area-weighted discharge (Q_{area}), total P (TP) concentration, and TP yield of the study sites

Catchment	Area	Median Q_{area}	Median TP concentration	Median TP yield
	km^2	mm min^{-1}	mg L^{-1}	mg m^{-2} min^{-1}
1	3,209	3.96×10^{-5}	0.983	3.07×10^{-5}
2	17,819	2.77×10^{-4}	0.588	2.20×10^{-4}
3	17,871	1.63×10^{-4}	0.700	1.03×10^{-4}
4	25,022	6.28×10^{-5}	0.699	4.88×10^{-5}
5	29,280	8.36×10^{-4}	0.246	2.02×10^{-4}
6	32,375	6.00×10^{-4}	0.435	2.55×10^{-4}
7	34,589	7.75×10^{-4}	0.381	2.89×10^{-4}
8	35,677	1.04×10^{-5}	1.301	1.32×10^{-5}
9	36,358	4.25×10^{-4}	0.389	1.73×10^{-4}
10	37,772	3.11×10^{-4}	0.084	2.46×10^{-5}
11	69,264	6.04×10^{-4}	0.860	2.64×10^{-4}
12	75,716	7.48×10^{-4}	0.916	2.45×10^{-4}
13	96,089	3.18×10^{-4}	0.126	4.00×10^{-5}
14	104,454	7.50×10^{-4}	0.068	4.98×10^{-5}
15	154,767	3.12×10^{-5}	0.449	1.36×10^{-5}
16	174,824	1.81×10^{-4}	0.137	2.75×10^{-5}
17	178,924	7.39×10^{-5}	0.121	8.36×10^{-6}
18	221,107	5.78×10^{-5}	0.594	3.52×10^{-5}
19	221,703	4.38×10^{-4}	0.143	6.27×10^{-5}
20	251,229	8.50×10^{-4}	0.173	1.51×10^{-4}
21	410,330	1.13×10^{-4}	0.131	1.26×10^{-5}
22	443,665	4.94×10^{-4}	0.256	1.30×10^{-4}
23	525,768	8.76×10^{-4}	0.169	1.41×10^{-4}
24	836,049	6.77×10^{-5}	0.292	1.88×10^{-5}
25	1,353,270	9.01×10^{-5}	0.488	4.62×10^{-5}
26	1,847,181	2.26×10^{-4}	0.402	8.17×10^{-5}

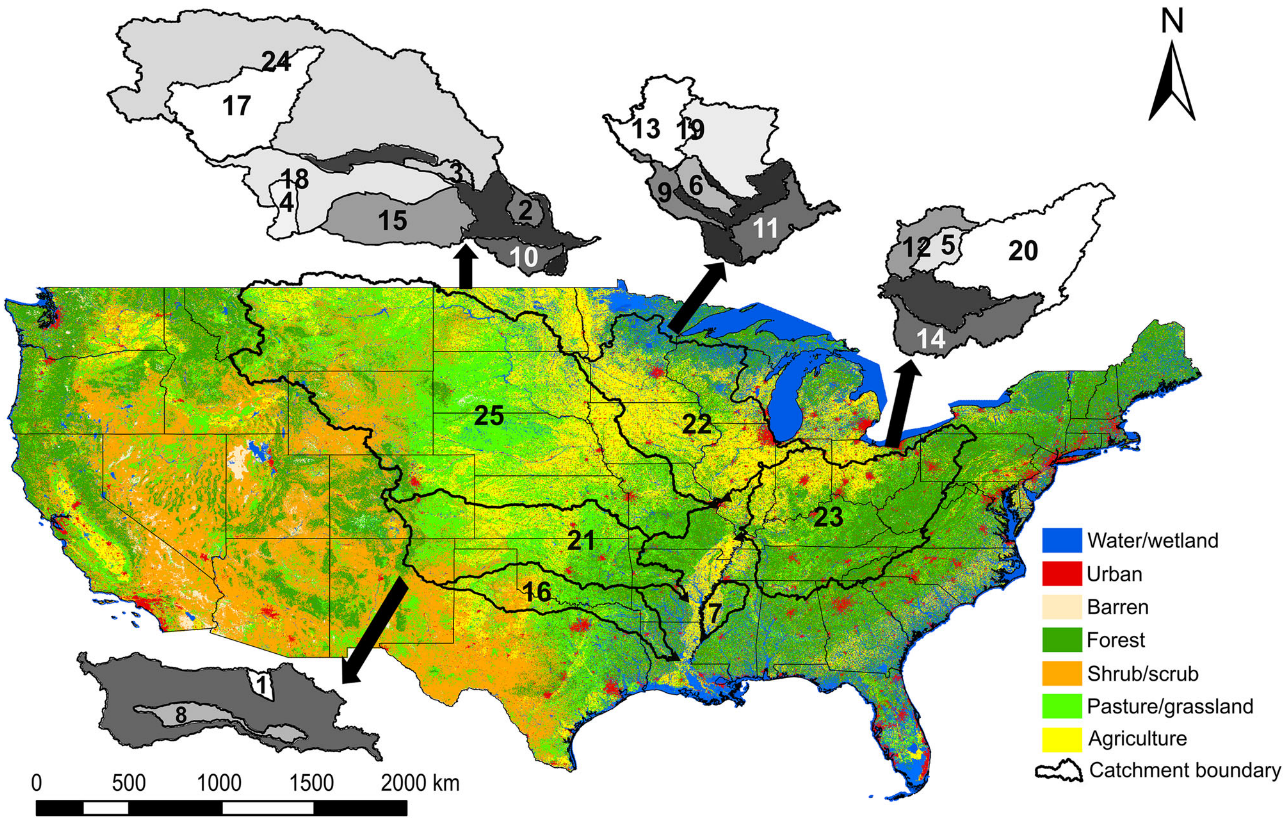

FIGURE 1 Study sites

TABLE 5 Correlation (r values) of area-weighted discharge (Q_{area}), median total P (TP) concentration, median TP yield with catchment area, median monthly precipitation, and land cover categories

Characteristics	Median Q_{area}	Median TP concen-tration	TP yield
Area	−.18	−.16	−.22
Median monthly precipitation	.86*	−.21	.62*
Land cover category			
Barren	−.15	−.34	−.29
Agriculture	.17	.39*	.53*
Forest	.67*	−.47*	.12
Water/wetland	.16	−.37*	.08
Pasture/grassland	−.75*	−.11	−.64*
Shrub/scrub	−.54*	−.10	−.50*
Urban	.67*	.14	−.50*

*Significant at the .05 probability level.

discharge. The relation between element concentrations and discharge is widely used to examine if catchments exhibit chemostatic behavior (i.e., concentrations are nearly constant across different discharges), flushing, or dilution behavior (i.e., concentrations are increasing or decreasing with discharge, respectively) (Godsey, Kirchner, & Clow, 2009). Unless TP concentrations sharply decrease with discharge (dilution), constant or increasing concentration with discharge produces increasing P yields with discharge because yield has a positive correlation with both concentration and discharge, as stated in Equation 1. Next, we calculated the slope of the TP yield–discharge relationship (TP yield rate, henceforth) for each river and projected it versus the corresponding catchment area on a log-log scale. The statistical analyses (Tables 2, 3, and 5) were conducted using JMP 14.2 (SAS Institute). The significance level in our analysis is .05; $p \leq .05$ was considered statistically significant.

3 | RESULTS

There was up to 79% colinearity (r^2) between precipitation and land cover. Correlation analyses showed that the ratios of forest and urban land covers increase significantly ($p < .05$) with precipitation, whereas the ratios of barren land, pasture/grassland, and shrub/scrub land covers decrease significantly with precipitation (Table 3). No significant correlation was found between catchment area and precipitation across the studies catchments (Table 3), implying that our data were not biased by climate or catchment area. We detected a significant negative relationship between barren and agricultural land covers; a significant positive relationship between barren and shrub/scrub land covers; significant negative relationships between agricultural land cover and forest, pasture/grassland, and shrub/scrub land covers; a significant positive relationship between forest and urban land covers; a significant negative relationship between water/wetland and pasture/grassland covers; a significant positive relationship between pasture/grassland and shrub/scrub land covers; and significant negative relationships between pasture/grassland and urban land covers and between shrub/scrub and urban land covers (Table 3).

3.1 | Total P, land cover, precipitation, and area

Median TP concentration has a significant ($p < .05$) positive correlation with the ratio of agricultural land cover and significant negative correlations with the ratios of both forest and water/wetland covers (Table 5). Median Q_{area} changed significantly and positively with precipitation, forest, and urban land cover (Table 5). Median Q_{area}, however, changed significantly and negatively with the fractions of both pasture/grassland and shrub/scrub land covers (Table 5). Median TP yield has significant positive correlations with precipitation, agricultural, and urban land covers and significant negative correlations with the ratios of pasture/grassland and shrub/scrub land covers (Table 5). Concentration–discharge relationships showed significant positive correlations in 17 catchments, significant negative correlations in four catchments, and nonsignificant correlations in five catchments (Table 2). Total P yield-discharge plots showed strong positive relationships between TP yields and discharge across all study sites (Table 2; Figure 2).

3.2 | TP yield rate

Our plots displayed an overall increase in TP yields with discharge, albeit the rates of this increase (i.e., TP yield rates) became smaller with catchment area. Total P yield rates against area plot (Figure 3) demonstrated a strong negative ($r^2 = -.74$) significant ($p < .0001$) correlation as determined by the following equation:

$$\text{Log TP yield rate} = -6.24 - 1.026 \times \text{Log catchment area} \tag{2}$$

4 | DISCUSSION

Precipitation is widely reported to be a limiting climatic factor for vegetation growth and distribution (e.g., Mi, Zhang, Zhang, & Shangguan, 1996; Wu, 1982; Zhang, 2002; Zhang, Ru, & Li, 2006). Goward and Prince (1995) detected a strong positive correlation between precipitation and vegetation density. Fan, Ma, Yang, Han, and Mahmood (2015) investigated the impact of precipitation on land cover and found that precipitation gradually increases from barren to grassland to cropland to forest. Land cover, in turn, has a significant impact on precipitation distribution, as reported by many studies. For example, Kishtawal, Niyogi, Tewari, PielkeSr, and Shepherd (2010) found that regions of dense urbanization are associated with increasing trends of heavy precipitation events. Costa, Yanagi, Oliveira, Ribeiro, and Rocha (2007) and Sampaio et al. (2007) concluded that deforestation tends to decrease precipitation in Amazonia and that the precipitation reduction depends on the land cover type that replaces the forest land cover. They found that agricultural land cover that replaces forests causes a higher reduction in precipitation compared with pasture land cover of the same area. In contrast, studies found that afforestation leads to an increase in precipitation in the United States (Notaro & Liu, 2006). Likewise, other studies demonstrated that precipitation tends to increase as vegetation density increases (e.g., Clark & Arritt, 1995; Sud, Mocko, & Walker, 2001). The positive correlation reported between vegetation density and precipitation can be attributed to the fact that the increased evapotranspiration associated with increased vegetation density results in a reduction in the vapor pressure deficit, which, in turn, enhances clouds and rainfall (Freedman, Fitzjarrald, Moore, & Sakai, 2001; McPherson, 2007; Schickedanz, 1976). These findings can explain the positive correlations between forest and urban land covers with precipitation and the negative correlations between barren, pasture/grassland, and shrub/scrub land covers with precipitation in the current study (Table 3). In agreement with the literature, Q_{area} across catchments increases with precipitation ($r = .86$; Table 5), likely owing to increased water availability for runoff (Chai et al., 2020; Rossi, Whipple, & Vivoni, 2016; Zhou, Yang, Zhang, Jin, & Zhang, 2015). As precipitation represents a driver for Q_{area}, it is not surprising that the correlations of Q_{area} with land cover follow the same correlations of precipitation with land cover (i.e., positive correlations with forest and urban land covers and negative correlations with both pasture/grassland and shrub/scrub land covers) (Tables 3 and 4).

4.1 | Total P, land cover, precipitation, and area

Total P concentrations across catchments increase with agricultural land cover (Table 5). Whereas the application of fertilizers in agricultural lands contributes to higher P sourcing in soil and runoff (e.g., Lou et al., 2015; Sharpley & Smith, 1989; Wu et al., 2013), agricultural activities such as tillage promote erosion and consequently result in higher P

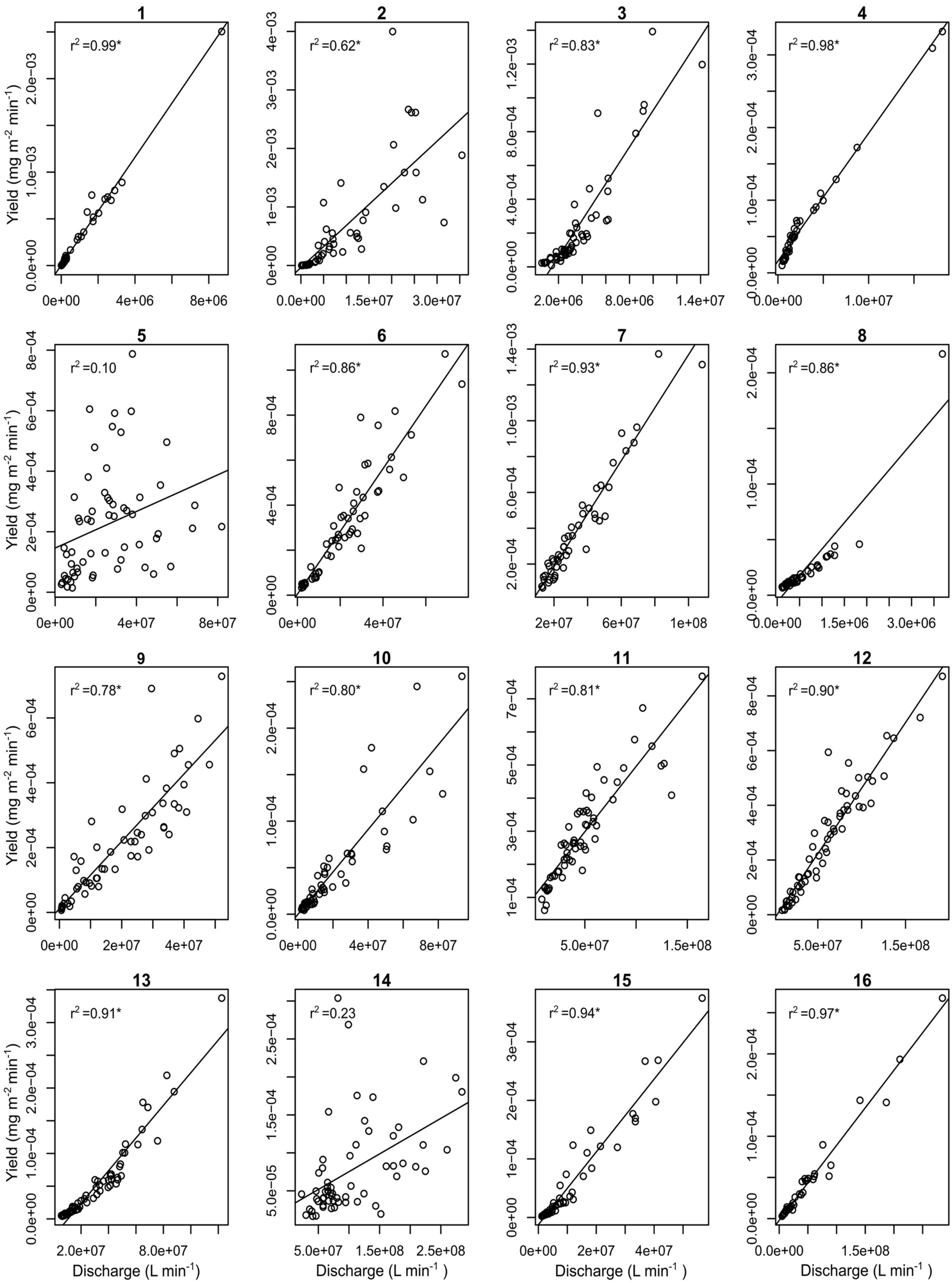

FIGURE 2 Instantaneous total P (TP) yields as a function of instantaneous discharge for studied catchments. Q denotes discharge measured at the catchment outlet (L min^{-1}). *Significant at $p < .05$

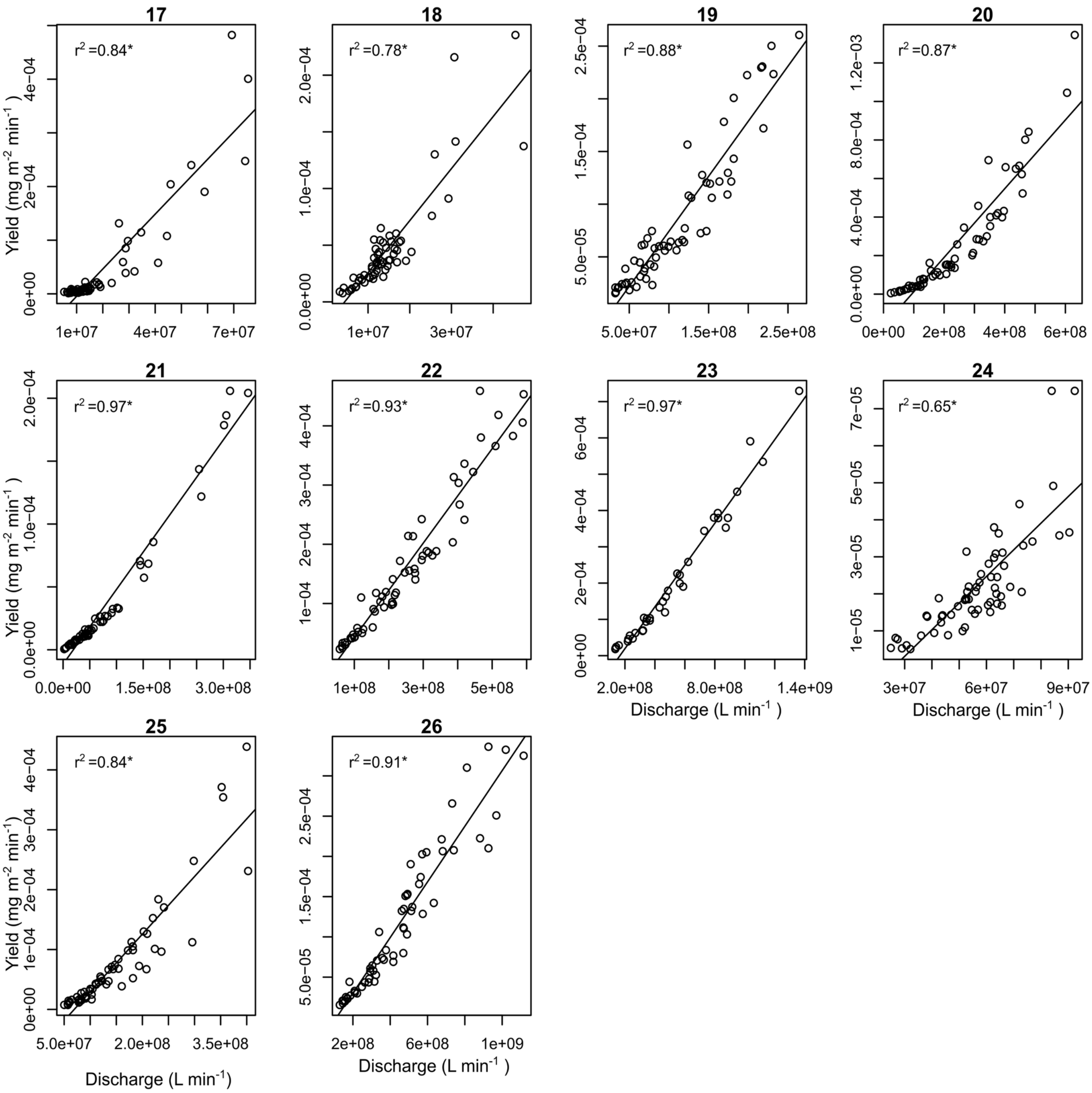

FIGURE 2 Continued

loss. Many studies have found that traditional tillage practices produce higher erosion and consequently higher P losses compared with no-till practice (Andraski, Mueller, & Daniel, 1985; Chichester & Richardson, 1992; Franklin et al., 2012; Sharpley & Smith, 1994). In contrast, relatively low TP concentrations at forested sites (Table 5) compared with agricultural lands are attributed to the forest's permeable underlying surface characteristics, limited P inputs, and dense vegetative cover (Thompson, 2019; Zhuang, Hong, Zhan, & Zhang, 2015). Phosphorus often ties to soil grains and either stays close to the source area or flows to rivers by soil erosion (USGS, 1999). The good vegetation cover of forested areas can efficiently minimize runoff and soil erosion and consequently limits P loss, owing to the vegetation cover's capacity to stabilize soils and intercept precipitation (Kim et al., 2018; Ochoa-Cueva, Fries, Montesinos, Rodriguez-Diaz, & Boll, 2015; Zhuang et al., 2015). The decreasing TP concentrations with increasing of the fraction of water/wetland land cover in this study (Table 5) can be attributed to a combination of biogeochemical and physical processes in water bodies. Such processes remove and/or transform P, allowing opportunities for biotic and abiotic assimilation (Withersa & Jarvieb, 2008). Vegetation in wetlands plays a vital role in P assimilation and storage. For example, emergent macrophytes possess broad networks of rhizomes and roots with a substantial capacity to store P. These macrophytes have more underground biomass (rhizomes and roots) compared with aboveground biomass (leaves and stems), offering suitable

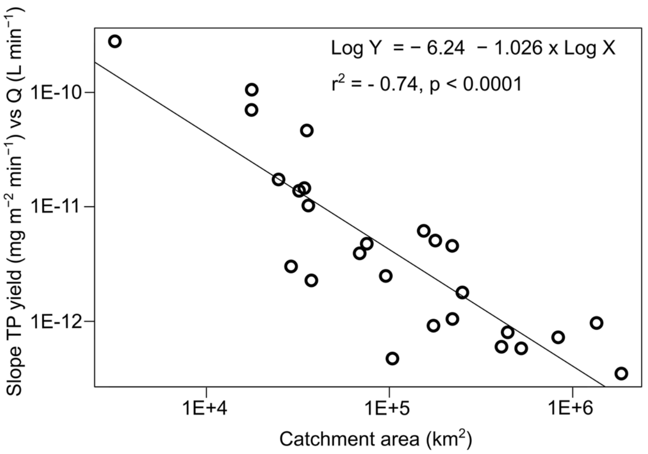

FIGURE 3 Total P (TP) yield rate (i.e., the slope of TP yield − Q regression) against catchment area

medians for P storage (Reddy, Kadlec, Flaig, & Gale, 1999). Contrary to our expectations, we found no correlation between TP concentration and urban land cover ratios (Table 5). A previous study on large catchments of mixed land cover (e.g., Connecticut River, Altamaha River, Menominee River, Upper Snake River) reported low TP concentrations. In these large catchments, nutrient-rich runoff from urban and agricultural areas can be diluted by forest and other relatively undeveloped land covers (USGS, 1999). Our results appear consistent with such prior research (i.e., P originating from urban areas would be most likely diluted by undeveloped land cover).

The analysis demonstrated strong positive correlations between TP yield and discharge that can be interpreted based on the correlations between TP concentration and discharge. The positive correlations that we found between concentrations and discharge across most sites (Table 2) can rationalize the positive correlations between TP yield and discharge (Table 2; Figure 2). We found that the four catchments with a negative concentration–discharge slope have relatively high urban land cover percentage compared with other catchments. Moreover, urban land cover includes high, medium, and low intensities, and these four catchments have a larger percentage of high-intensity urban land cover than other catchments. Furthermore, data from the SPARROW (SPAtially Referenced Regression On Watershed attributes) model (https://sparrow.wim.usgs.gov/sparrow-midwest-2012/) showed that these four catchments have relatively higher municipal wastewater treatment discharge percentages compared with other catchments. The negative concentration–discharge slope of these catchments indicates high P concentrations at low discharge, which could be attributed to a constant source of P that is diluted at high discharge (i.e., municipal effluent in the present study). Mathematically, although these four sites had a negative concentration–discharge slope, they had a positive slope between TP yields and discharge, and this can be ascribed to the variations in magnitude of concentrations and discharges. Even though it had the biggest negative slope of the concentration–discharge relationship, the Illinois River at Valley City still had an increasing TP yield with discharge. This positive yield–discharge correlation occurs because, as TP concentration decreases by a factor of 3.9, discharge rises by a factor of 20.4. Our findings are thus consistent with Schlesinger, Ward, and Anderson (2000) in that streamflows, rather than concentrations, are mainly controlling nutrient yield variations. Likewise, TP yield (concentration × Q_{area}) depends on Q_{area} more than on concentration because the former changes by higher orders of magnitude in this study. Although it had the largest negative slope of the concentration–Q_{area} relationship, the North Canadian River near Harrah still had an increasing TP yield with Q_{area}. This positive yield–Q_{area} correlation occurs because, as TP concentration decreases by a factor of 2.8, Q_{area} rises by a factor of 33.8. Therefore, the analysis showed that the TP yield following Q_{area} has a significant positive correlation with precipitation and urban land cover and has significant negative correlations with both pasture/grassland and shrub/scrub land covers (Table 5). Whereas forest land cover has relatively low TP concentrations, TP yields exhibit no correlation with forest land cover (Table 5). The low TP concentrations in forests is offset by the elevated Q_{area} in such land cover, resulting in unaffected TP yield (Table 5).

4.2 | TP yield rate

Total P yields increased with discharge. However, the rates of such increase significantly decreased with catchment area. Soil erosion by water is considered a significant source of P in ecosystems (Carpenter & Bennett, 2011). The main part of soil P is adsorbed to surface of soil particles, attached to organic matter, or precipitated as salts. Phosphorus is primarily exported from soil to water through erosion. Only a small percentage of soil P is available to plants or can be leached as dissolved soluble P (Helfenstein et al., 2018; Riskin et al., 2013), with the exception of highly fertilized lands with excessive P availability (Frossard, Condron, Oberson, Sinaj, & Fardeau, 2000; Sattari, Bouwman, Giller, & van Ittersum, 2012). Erosion and, consequently, sediment yield, have been reported to decline with catchment area in catchments larger than 10 km^2 (de Vente & Poesen, 2005; de Vente, Poesen, Arabkhedri, & Verstraeten, 2007; Osterkamp & Toy, 1997). In catchments larger than 10 km^2, the effect of sediment sinking generally exceeds sediment sourcing as catchment area increases, causing a gradual decrease in sediment yields (Osterkamp & Toy, 1997). This can be attributed to the fact that that large catchments have more floodplain development and foot slope terrains where sediments can be stored (de Vente & Poesen, 2005). Additionally, the longer travel distance for sediments through larger catchments provides

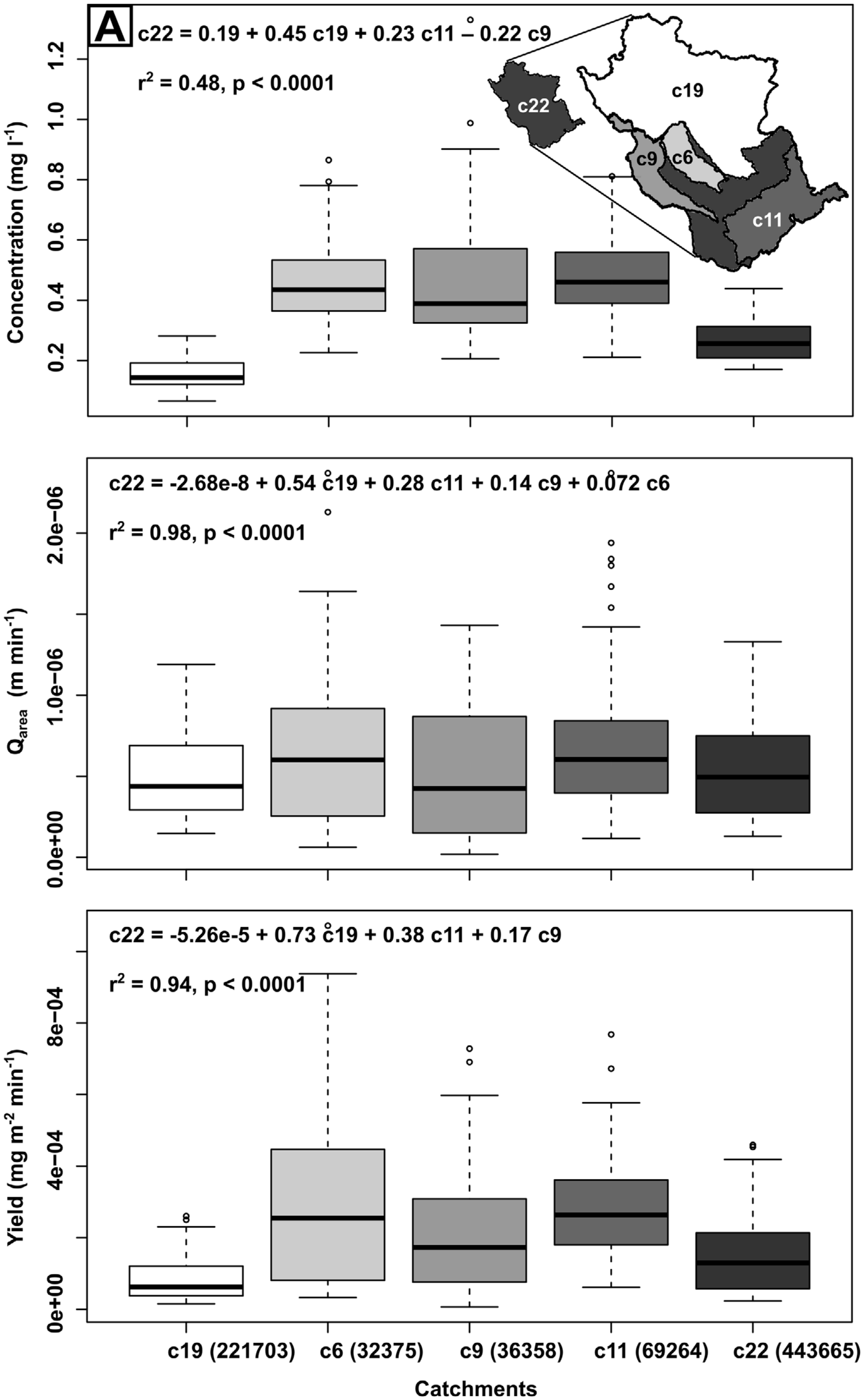

FIGURE 4 The x axis denotes catchments (e.g., c19 stands for catchment 19), and the adjacent numbers between parentheses refer to catchment area (km^2). The y axes are P concentration, area-weighted discharge (Q_{area}), and P yield. The horizontal black lines (inside the boxes) denote the medians. The bottom and top of the box show the first and third quartiles (Q1 and Q3). The whiskers are the lines inside the region defined by Q1 − 1.5 (Q3 − Q1) and Q3 + 1.5 (Q3 − Q1). The individual points with values outside these limits represent outliers. Only catchments that contribute significantly ($p < .05$) to the multiple linear regressions were included. (A) Catchments 19, 6, 9, 11, and 22 (c19, c6, c9, c11, and c22). (B) Catchments 20, 12, 14, and 23 (c20, c12, c14, and c23). (C) Catchments 18, 3, 24, 15, 2, 10, and 25 (c18, c3, c24, c15, c2, c10, and c25)

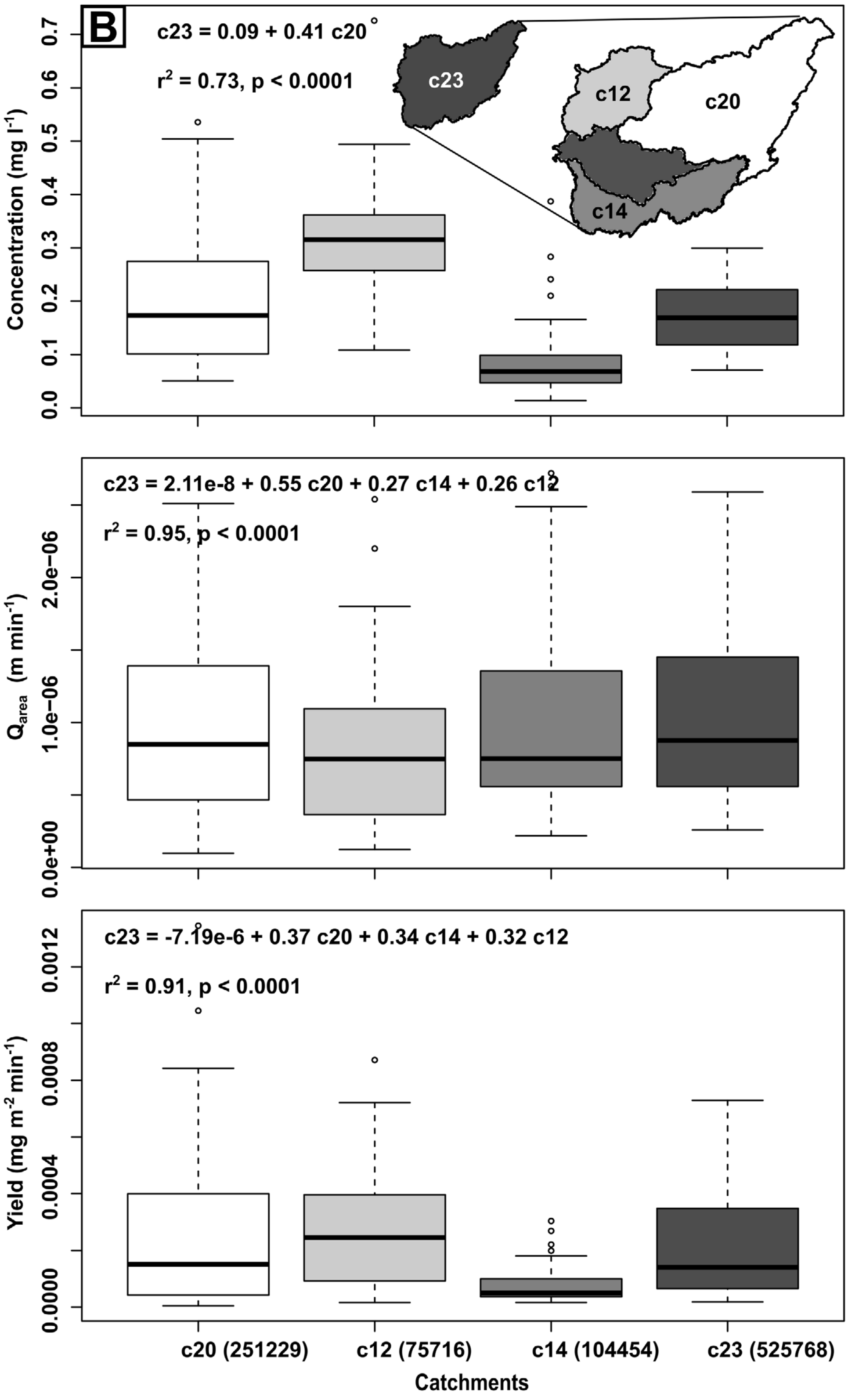

FIGURE 4 Continued

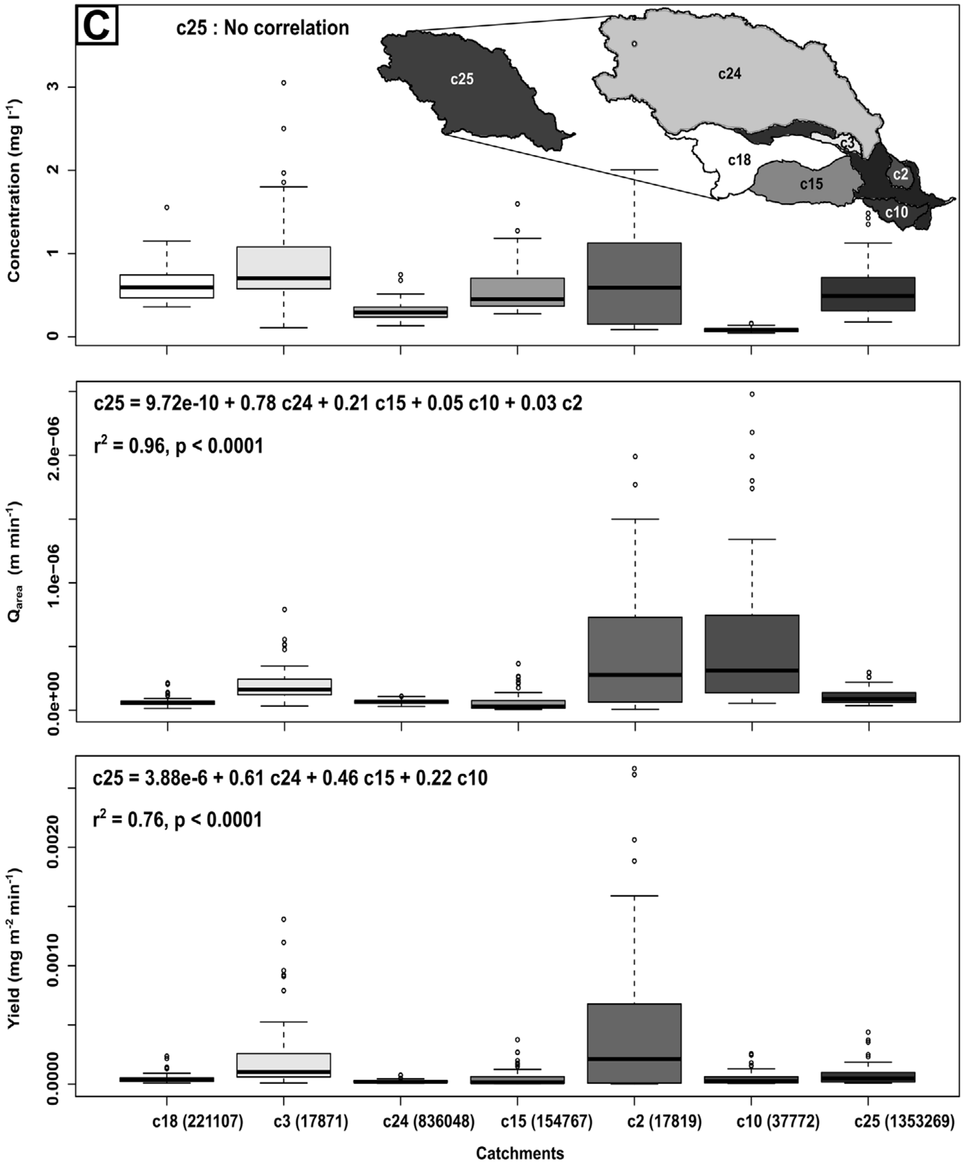

FIGURE 4 Continued

more chances for sediment deposition, which produce lower sediment yields at the catchment outlet (Walling, 1983; Syvitski, 2003). Many studies confirm the negative correlation between sediment yield and catchment area (e.g., Lane, Hernandez, & Nichols, 1997; Milliman & Meade, 1983; Milliman & Syvitski, 1992), and this negative correlation can explain the inverse correlation between TP yield rate and catchment area in the current study (Figure 3). In other words, smaller catchments tend to have higher erosion rates, and because erosion is a major driver for P export, smaller catchments exhibited higher P yield rates compared with large catchments (Mutema, Chaplot, Jewitt, Chivenge, & Bloschl, 2015).

Although understanding the controls of P movement through catchments is crucial for enhanced landscape management, P transport in watersheds is complex. For example, the P adsorption capacity of soils plays an important role in P transport to streams. In other words, soils with low P adsorption capacity are expected to export relatively large volumes of P to rivers (USGS, 1999). Ige, Akinremi, Flaten, Ajiboye, and Kashem (2005) detected a negative relation between P sorption capacity and sand contents in soil. Similarly, Mutema et al. (2015) found that sand has higher P loss compared with loam and clay. In contrast, Alovisi et al. (2020) concluded that soils with higher clay contents fix more P in their matrix. Furthermore, in some regions, high P content in soils can occur naturally. High soil P levels can get transferred to the water through runoff, and the transfer can be facilitated by steep slope terrains, resulting in high P concentrations in rivers. For example, the P concentration of P in the Pembina River, Canada, was high because the agricultural lands in its catchment contain P-rich soil in considerably steep and easily eroded topography (USGS, 1999). Likewise, increases in rainfall intensity are likely to promote higher P transfers through increased surface runoff and associated soil erosion (Ockenden et al., 2017). However, further investigation of the impacts of such features (i.e., soil properties and content, slope, and precipitation pattern) can be a stand-alone topic in a further study.

There are many factors that determine the water quality and quantity in a basin. The main factors are precipitation; land cover; infiltration, which depends on soil characteristics, soil saturation, land cover, and slope; evapotranspiration; and water consumption by humans (USGS, 2020). In our analysis, the subcatchments nested in a main catchment have different characteristics, such as precipitation, land cover, and area. However, we were able to predict, with high confidence, TP concentration, Q_{area}, and TP yield in the main catchment based on the concentration, Q_{area}, and yield of the subcatchments using multiple linear regression analysis (Figure 4). Results show that, irrespective of precipitation and land cover, bigger subcatchments have greater control on TP concentration, Q_{area}, and TP yield of the main catchment (e.g., in the upper plot of Figure 4, Subcatchments 19, 11, and 9 with declining areas of 221,703, 69,264, and 36,358 km^2, respectively, have declining coefficients of 0.45, 0.23, and 0.22, respectively).

The current study covered sites that are geographically widespread with a broad range of catchment areas, land covers, and precipitation, and the investigated data were not biased by climate or scale. As such, the relationship in Figure 3 can be applied for the catchments in the Mississippi basin to estimate the TP yield rate. By knowing the TP yield rate for a specific catchment, its TP yield and, consequently, TP concentration can be determined for each specific discharge.

5 | CONCLUSIONS

Total P yield (product of Q_{area} and concentration) is mainly governed by Q_{area} because the latter changes by higher order of magnitude compared with concentration in the present analysis. Precipitation and land cover significantly affect TP concentration and Q_{area}. Moreover, TP concentration increases with discharge across most catchments in the Mississippi basin except in four catchments. In these four catchments, the municipal wastewater treatment discharge represents a significant source of P, which is, in fact, a constant source of P that is diluted at high discharge. Likewise, TP yield increases with discharge, albeit the rates of this increase (i.e., TP yield rates) decline with catchment area. Finally, our analysis covered a wide range of spatial scale, precipitation, and land cover of catchments in the Mississippi basin. As such, findings reported in this paper provide empirical support for predicting TP concentration and yield of these catchments based on measurements of discharge at the outlet of a certain size catchment.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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