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Hydrological controls on nutrient dynamics and load estimation in an agricultural watershed: a case study in Rock Creek, Ohio

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Abstract: This study investigates the spatiotemporal variability of nutrient concentrations (soluble reactive phosphorus, SRP; total phosphorus, TP; and nitrate, NO_3^-) and their relationships with hydrological conditions in the Rock Creek watershed, a representative agricultural basin in northwestern Ohio. High-temporal-resolution water quality and discharge data were analyzed over a two-year period (2010–2011) to elucidate seasonal trends, flow-nutrient correlations, and to compare nutrient load estimation methods. The results demonstrate that nutrient transport in the watershed is strongly event-driven, with SRP and TP concentrations peaking during high-flow periods (spring snowmelt and summer/fall storms), exhibiting significant positive correlations with discharge (log-transformed R^2 = 0.27–0.47). In contrast, nitrate concentrations displayed a distinct seasonal pattern, with a spring flush followed by declining concentrations, suggesting depletion of legacy storage. Notably, flow-weighted mean concentrations (FWMC) exceeded arithmetic means by 2–3 times, revealing that conventional averaging methods underestimate nutrient loads during high-flow events. These findings emphasize the dominance of non-point source pollution during episodic runoff events and underscore the need for targeted management strategies to mitigate nutrient pollution in similar agricultural watersheds.

Keywords: Agricultural watershed; nutrient dynamics; hydrological controls; event-driven runoff; water quality management

1. Introduction

Nutrient pollution in agricultural watersheds remains a pervasive global issue, threatening aquatic ecosystems and degrading water quality[1]. Elevated concentrations of nitrogen and phosphorus, primarily from agricultural activities, can lead to eutrophication and harmful algal blooms. Understanding the spatiotemporal variability of nutrient concentrations and their relationships with hydrological conditions is vital for developing effective management strategies[2].

Agricultural watersheds, characterized by complex land use patterns and intensive farming practices, exhibit dynamic nutrient cycling processes that are intricately linked to hydrological factors such as precipitation, runoff, and streamflow[3]. These interactions significantly influence nutrient loading and water quality, necessitating a detailed examination of nutrient dynamics in these systems[4].

The Rock Creek watershed in northwestern Ohio, USA, was selected for this study due to its representativeness as a typical agricultural basin[5]. This watershed experiences significant nutrient runoff from farming activities, making it an ideal location to investigate the relationships between nutrient concentrations and hydrological conditions[6]. Furthermore, the availability of high-temporal-resolution water quality and discharge data enables a thorough analysis of seasonal trends, flow-nutrient correlations, and nutrient load estimation methods, contributing to a broader understanding of nutrient pollution in agricultural watersheds[7].

2. Materials and Methods

2.1 Study Area

The Rock Creek watershed is located in northwestern Ohio, USA, near the city of Tiffin (coordinates: 41.113611, -83.168333). The watershed covers an area of 89 km^2 and exhibits a mixed land use pattern consisting of agricultural fields, residential areas, and forested lands[8]. The primary soil types in the watershed are well-drained loams and silts, which are conducive to agricultural production but also prone to nutrient runoff during rainfall events[9].

2.2 Data Collection

2.2.1 Water Quality Data

Daily water samples were collected from the Rock Creek watershed outlet from January 1, 2010, to December 31, 2011. Samples were collected mid-stream at mid-depth using pre-rinsed 500 mL polyethylene bottles. To minimize contamination, bottles were triple rinsed with deionized water, stored immediately in coolers with ice packs, and transported to the laboratory within 24 hours for analysis.

Water samples were analyzed for soluble reactive phosphorus (SRP), total phosphorus (TP), and nitrate (NO_3^-) concentrations using standardized laboratory procedures. SRP concentrations were determined colorimetrically using the PhosVer3 Powder Pillow reagent at 880 nm. Total phosphorus concentrations were measured by digesting unfiltered samples with potassium persulfate to convert all phosphorus forms into orthophosphate, followed by colorimetric analysis. Nitrate concentrations were determined using the cadmium reduction method with absorbance measured at 540 nm.

2.2.2 Streamflow Data

Streamflow measurements were conducted using the Float-Area Method due to high-flow conditions during the study period. Stream cross-sectional area was determined from a bridge using measuring tapes and meter sticks to measure width and depth at multiple points along the stream. Velocity was measured by timing a buoyant object (e.g., orange peel) traveling between marked upstream and downstream points, and the mean velocity was estimated by correcting the measured velocity by a factor of 0.8. Streamflow (Q, m^3/s) was calculated by multiplying the mean velocity by the cross-sectional area.

2.3 Data Processing and Analysis

2.3.1 Data Import and Cleaning

The dataset was imported into Python using the Pandas and NumPy libraries. Erroneous entries (e.g., "=-@Inf") were removed, and columns were converted to numeric data types. Missing values were addressed by filling with subsequent valid measurements where possible.

2.3.2 Date Conversion and Classification

Dates were converted to datetime format, and seasons were defined as follows: Winter (January-March), Spring (April-June), Summer (July-September), and Autumn (October-December).

2.3.3 Statistical Calculations

Descriptive statistics (mean, standard deviation, median, minimum, maximum) were calculated by year and season using the groupby function in Pandas. Results were formatted using the tabulate library in Python.

2.3.4 Nutrient Loss Estimation

Nutrient loss estimates were calculated using two distinct methods: the arithmetic mean and the flow-weighted mean concentration (FWMC). Data were organized by year and season in Excel, with flow volumes calculated by converting daily streamflow from m^3/s to L/day. Missing nutrient concentration values were filled with subsequent valid measurements.

Arithmetic Mean: Calculated by averaging all nutrient concentrations (mg/L) within each specified period.

Flow-Weighted Mean Concentration (FWMC): Calculated by multiplying daily nutrient concentrations (mg/L) by corresponding daily flows (L/day), summing these products, and dividing by total flow volume.

Total loads (kg) were calculated by multiplying mean concentrations by total seasonal or annual flow volumes and converting from milligrams to kilograms. Yields (kg/ha) were computed by dividing these total loads by the watershed area (8900 ha). Excel's built-in functions (e.g., AVERAGEIFS, SUMIFS, SUMPRODUCT) were used to efficiently perform calculations and summarize results into tables for comparison.

2.3.5 Correlation and Regression Analysis

Pearson correlations between stream discharge and nutrient concentrations were calculated using the corr function in Pandas. Ordinary Least Squares (OLS) regressions were performed to explore relationships using both original and log-transformed stream discharge values. The statsmodels library in Python was used to perform the OLS regressions and generate regression tables.

2.3.6 Visualization

Scatter plots with regression lines were created using the seaborn and matplotlib libraries in Python to visually interpret relationships between stream discharge and nutrient concentrations.

2.3.7 Quality Control

Procedural quality controls included meticulous rinsing of bottles, minimal environmental exposure during sample collection, careful laboratory timing, and strict adherence to drying and weighing protocols during sample analysis.

3. Results

3.1 Full-Period Graphs

Total discharge varied significantly throughout the study period. The highest discharge occurred in the spring months, particularly during snowmelt and rain events, while the lowest discharge was observed during late summer and early fall. Soluble Reactive Phosphorus (SRP) concentrations fluctuated over time, with generally elevated concentrations occurring from mid-summer to fall. SRP peaks were often associated with storm events or periods of increased discharge, suggesting a relationship between runoff and phosphorus transport.

Total phosphorus (TP) concentrations exhibited similar variability throughout the study period. Elevated TP concentrations were most frequently observed during periods of high discharge, particularly during storm events or high-flow periods in late spring and summer. This suggests that TP transport is strongly influenced by runoff events, likely due to mobilization of phosphorus from surrounding land surfaces and upstream inputs during periods of increased flow.

Nitrate (NO_3^-) concentrations displayed a distinct seasonal pattern compared to phosphorus concentrations. Elevated NO_3^- concentrations were observed during the spring and early summer of 2010, coinciding with periods of higher discharge. However, in subsequent years, NO_3^- concentrations were generally lower, with modest peaks occurring sporadically and often not directly associated with discharge events. This pattern may reflect legacy nitrate stored in the watershed that was flushed out early in the study period, followed by depletion or reduced mobilization in later years.

3.2 Seasonal Graphs

Seasonal graphs were created to examine the variability of nutrient concentrations and streamflow within each season.

Spring

During the spring season, total discharge was highly variable, with frequent peak flow events associated with snowmelt and spring rainfall. SRP concentrations fluctuated accordingly, with elevated concentrations observed following high discharge events. This pattern suggests strong event-driven mobilization of phosphorus during the spring season.

Total phosphorus (TP) concentrations also showed elevated levels during spring storm events, with the highest concentrations observed during late spring. This indicates that TP transport is strongly influenced by runoff during the spring season.

Nitrate (NO_3^-) concentrations exhibited pronounced peaks during the spring season, particularly in 2010. This may reflect the mobilization of legacy nitrate stores in the watershed due to increased runoff and mixing of soil layers.

Summer

During the summer season, baseflow gradually declined, and total discharge remained low except for a few isolated storm events. SRP concentrations were moderate but showed several sharp increases corresponding to small discharge peaks. This indicates that even relatively minor flow events can transport notable amounts of phosphorus during dry summer conditions when background concentrations are lower.

TP concentrations also showed moderate variability during the summer season, with elevated levels observed during storm events. However, overall concentrations were lower compared to spring and autumn seasons.

Nitrate (NO_3^-) concentrations were generally lower during the summer season compared to spring, with modest peaks occurring sporadically. This suggests that nitrate sources may have been depleted or reduced in mobility following the spring flush.

Autumn

Autumn discharge remained low for most of the season, except for a single intense storm event at the end of October that caused a significant spike in flow (>4 m^3/s). SRP concentrations were higher leading up to the storm but peaked concurrently with the flow spike, suggesting that autumn storms play a critical role in flushing accumulated phosphorus from the landscape.

TP concentrations also showed a significant increase during the autumn storm event, with the highest concentrations observed during late autumn. This indicates that runoff from autumn storms can mobilize substantial amounts of phosphorus from the watershed.

Nitrate (NO_3^-) concentrations exhibited moderate variability during the autumn season, with no clear association with discharge events. This suggests that nitrate dynamics may be influenced by other factors beyond hydrologically-driven flushing.

Winter

Winter flow conditions were mostly stable with low discharge, apart from a few major flow events in early March associated with snowmelt or rain-on-snow events. SRP concentrations were moderate during the winter season, with noticeable spikes only during high-flow conditions.

TP concentrations also showed moderate variability during the winter season, with no clear seasonal trend observed. However, elevated concentrations were occasionally observed during snowmelt events.

Nitrate (NO_3^-) concentrations were generally stable during the winter season, with no clear association with discharge events. This further supports the hypothesis that nitrate dynamics may be influenced by factors other than hydrologically-driven flushing.

3.3 Hydrological Events

Storm events were defined as continuous or semi-continuous rainfall periods during which precipitation intensity remained above 0.5 mm/hour, with no breaks exceeding 2 hours below this threshold (Figure 1).

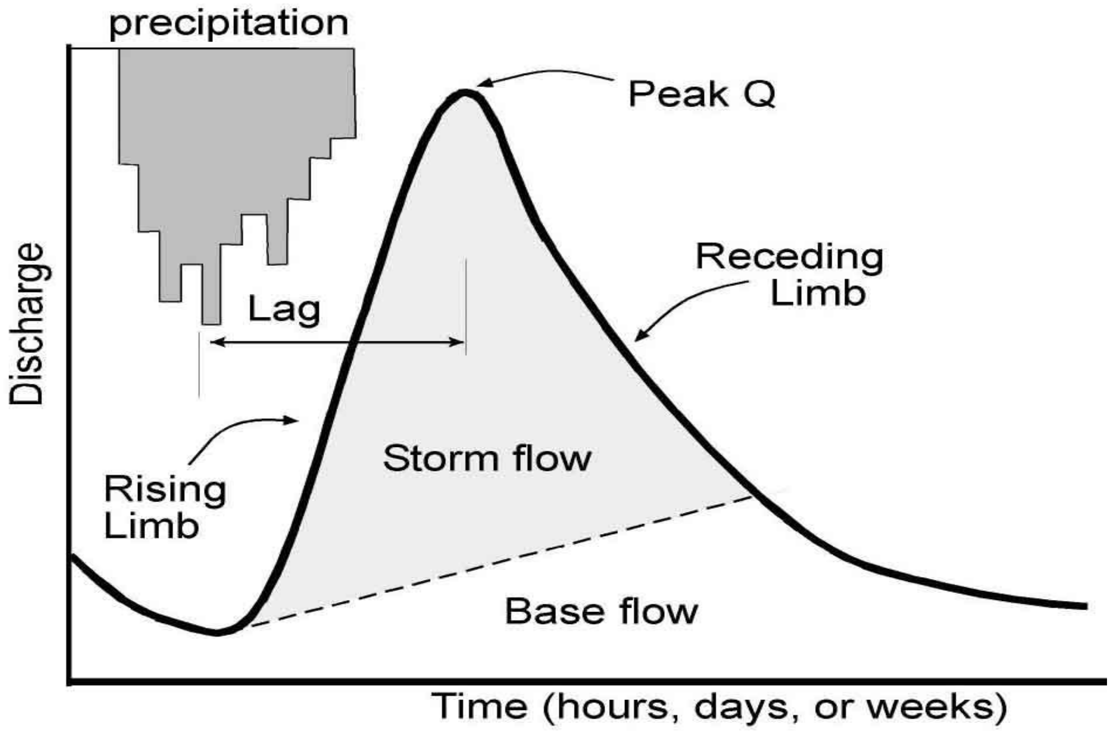

Figure 1. Conceptual diagram illustrating how storm events were defined.

A total of 11 hydrological events were identified during the 2010 study period (Table 1). Seasonal Distribution: Winter and spring seasons contributed the majority of storm events, with 7 out of 11 events occurring during these periods. Spring events, in particular, were characterized by longer durations and higher total flow contributions, possibly due to snowmelt and intensifying spring rains. Event Duration: The duration of storm events ranged from 2 to 15 days, with the longest event (Event 6) spanning 15 days and contributing significantly to the total flow (58.94 mm). Flow Contribution: Total flow contributions varied widely among events, with the highest contribution (58.94 mm) from Event 6 and the lowest (3.35 mm) from Event 4. These variations highlight the importance of considering event duration and intensity when assessing their cumulative impact on streamflow and nutrient transport. Critical Periods:The identification of these storm events provides crucial information for water resource managers, enabling them to target critical periods for flood control, water quality monitoring, and nutrient management strategies.

Table 1. Start and end dates for hydrological events in 2010.

Event	Begin Date	End Date	Length (days)	Season	Total Flow (mm)
1	2010/01/25	2010/01/26	2	Winter	11.27
2	2010/03/09	2010/03/15	7	Winter	43.27
3	2010/03/23	2010/03/30	8	Spring	39.37
4	2010/04/08	2010/04/09	2	Spring	3.35
5	2010/04/26	2010/04/27	2	Spring	12.59
6	2010/05/08	2010/05/22	15	Spring	58.94
7	2010/06/01	2010/06/10	10	Summer	24.15
8	2010/06/23	2010/06/24	2	Summe	6.84
9	2010/06/28	2010/06/29	2	Summer	13.16
10	2010/11/30	2010/12/01	2	Autumn	3.79
11	2010/12/31	2011/01/02	3	Winter	20.46

3.4 Descriptive Statistics of Nutrient Concentrations

Descriptive statistics were calculated to summarize the variations in nutrient concentrations (Soluble Reactive Phosphorus - SRP, Total Phosphorus - TP, and Nitrate - NO_3^-) over the study period (2010-2011). The statistics include mean, standard deviation, median, maximum, and minimum concentrations for both annual and seasonal data(Table 2-5). Annual Variations: The annual mean concentrations of SRP and TP showed an increasing trend from 2010 to 2011, indicating potential accumulation or enhanced mobilization of phosphorus sources. In contrast, mean NO_3^- concentrations decreased slightly, possibly due to changes in fertilizer application practices or depletion of legacy nitrate stores.Seasonal Patterns: SRP and TP concentrations peaked during spring and summer, coinciding with high-flow periods driven by snowmelt and storm events. These results underscore the importance of event-driven nutrient transport in agricultural watersheds. NO_3^- concentrations exhibited a more pronounced spring flush, likely related to fertilizer application and mobilization of stored nitrate.Variability: High standard deviations, particularly for TP and NO_3^- , indicate substantial variability in nutrient concentrations within and across seasons. This variability emphasizes the need for continuous monitoring and targeted management strategies to address nutrient pollution.Extremes: Maximum nutrient concentrations, particularly for TP and NO_3^-, highlight the potential for severe water quality impairment during storm events. Identifying and mitigating these extreme events are crucial for protecting aquatic ecosystems.

Table 2. Annual Descriptive Statistics for SRP, TP, and NO_3^- concentrations.

Nutrient	Year	Mean (mg/L)	Std.Dev. (mg/L)	Median (mg/L)	Max (mg/L)	Min (mg/L)
SRP	2010	0.049	0.046	0.041	0.484	0.004
	2011	0.057	0.056	0.040	0.459	0.004
TP	2010	0.165	0.217	0.086	1.751	0.019
	2011	0.211	0.268	0.105	1.924	0.015
NO_3^-	2010	2.263	2.609	1.100	11.730	0.040
	2011	1.775	1.110	1.515	6.140	0.300

Table 3. Seasonal Descriptive Statistics for Soluble Reactive Phosphorus (SRP) Concentrations.

Year	Season	Mean (mg/L)	Std.Dev. (mg/L)	Median (mg/L)	Max (mg/L)	Min (mg/L)
2010	Fall	0.049	0.052	0.033	0.235	0.007
	Spring	0.054	0.039	0.053	0.175	0.004
	Summer	0.063	0.052	0.055	0.484	0.004
	Winter	0.027	0.030	0.013	0.118	0.004
2011	Fall	0.077	0.071	0.056	0.459	0.005

	Spring	0.046	0.035	0.040	0.204	0.004
	Summer	0.066	0.061	0.038	0.299	0.005
	Winter	0.035	0.040	0.011	0.147	0.004

Table 4. Seasonal Descriptive Statistics for Total Phosphorus (TP) Concentrations.

Year	Season	Mean (mg/L)	Std.Dev. (mg/L)	Median (mg/L)	Max (mg/L)	Min (mg/L)
2010	Fall	0.133	0.171	0.073	0.850	0.032
	Spring	0.287	0.331	0.162	1.751	0.028
	Summer	0.117	0.061	0.102	0.521	0.058
	Winter	0.116	0.142	0.059	0.772	0.019
2011	Fall	0.209	0.177	0.146	0.891	0.033
	Spring	0.306	0.388	0.136	1.924	0.016
	Summer	0.176	0.187	0.098	1.155	0.035
	Winter	0.145	0.249	0.040	1.528	0.015

Table 5. Seasonal Descriptive Statistics for Nitrate (NO_3^-) Concentrations.

Year	Season	Mean (mg/L)	Std.Dev. (mg/L)	Median (mg/L)	Max (mg/L)	Min (mg/L)
2010	Fall	1.184	2.116	0.040	7.810	0.040
	Spring	4.567	2.961	4.010	11.730	0.230

	Summer	0.412	0.662	0.155	3.550	0.040
	Winter	2.701	1.824	2.575	7.390	0.470
2011	Fall	1.317	0.399	1.420	1.910	0.340
	Spring	2.441	0.956	2.315	6.140	1.040
	Summer	1.136	0.770	0.940	4.410	0.300
	Winter	2.304	1.456	2.030	6.000	0.470

3.5 Relationships Between Stream Discharge and Nutrient Concentration

To explore the relationships between stream discharge and nutrient concentrations (SRP, TP, and NO_3^-), we conducted detailed correlation and regression analyses. The results reveal insights into how hydrological conditions influence nutrient dynamics in the Rock Creek watershed.

3.5.1 Correlation Analysis

To understand the relationships between stream discharge and nutrient concentrations (soluble reactive phosphorus, SRP; total phosphorus, TP; and nitrate, NO_3^-), we conducted correlation analyses. The results revealed significant positive correlations between nutrient concentrations and stream discharge, indicating that nutrient mobilization is strongly influenced by hydrological conditions.

Specifically, the Pearson correlation coefficient between SRP concentrations and stream discharge was 0.407 on the linear scale and increased to 0.517 when the discharge data was log-transformed. Similarly, TP concentrations showed a stronger correlation with stream discharge, with correlation coefficients of 0.626 on the linear scale and 0.687 on the log-transformed scale. Nitrate concentrations, on the other hand, exhibited a weaker correlation with stream discharge, with coefficients of 0.136 on the linear scale and 0.478 on the log-transformed scale.

These findings suggest that TP concentrations are most strongly influenced by hydrological conditions, followed by SRP, and then NO_3^-. The improvement in correlation coefficients when using log-transformed discharge data indicates that nutrient concentrations rise more steeply at higher flow rates, highlighting the importance of considering flow variability when assessing nutrient dynamics in agricultural watersheds.

3.5.2 Regression Analysis

OLS regression revealed that TP concentrations had the strongest relationship with stream discharge (R^2=0.472

on log-scale), followed by SRP (R^2=0.268) and nitrate (R^2=0.229). TP concentrations increased by 0.0325 mg/L per unit log-transformed discharge, while SRP and nitrate increased by 0.0044 mg/L and 0.0582 mg/L, respectively. Log-transformed models provided better fits, suggesting nutrient concentrations rise more steeply at higher flow rates. This underscores the importance of considering flow variability in nutrient dynamics assessments.

3.5.3 Visual Representation

The relationships between stream discharge and nutrient concentrations (SRP, TP, and NO_3^-) were further illustrated through visual representation. Scatter plots depicting the distribution of nutrient concentrations versus stream discharge were created for both linear and log-transformed scales. The plots revealed distinct patterns, with nutrient concentrations tending to increase more markedly at higher flow rates when the discharge data was log-transformed. This trend was most pronounced for TP, followed by SRP, and then NO_3^-, consistent with the regression analysis results. The visual inspection of these plots reinforced the notion that nutrient mobilization in the Rock Creek watershed is strongly influenced by hydrological conditions, particularly during high-flow events. The steep increase in nutrient concentrations at higher discharge rates underscores the importance of considering flow variability when assessing nutrient dynamics and developing water quality management strategies in agricultural watersheds.

4. Discussion

4.1 Seasonal Variations and Hydrological Controls on Nutrient Dynamics

The temporal patterns in streamflow and nutrient concentrations reveal that peak discharges occur during spring and summer due to snowmelt and increased precipitation. Nutrient mobilization is influenced by hydrological conditions, as evidenced by strong positive correlations between SRP, TP, and streamflow, with TP exhibiting the strongest correlation. Correlation coefficients under log-transformed discharge models indicate that nutrient concentrations rise more rapidly at higher flow rates.

4.2 Flow Components and Nutrient Transport Mechanisms

When comparing event-driven flows with baseflow, it is evident that event-driven flows significantly contribute to nutrient transport during spring and summer. The seasonal variability in nutrient dynamics underscores the importance of considering flow conditions when assessing nutrient dynamics. Regarding nutrient load estimation methods, arithmetic mean concentrations have limitations, whereas flow-weighted mean concentrations (FWMC) offer advantages.

4.3 Management Implications and Future Research Directions

Water quality impairment during high-flow events highlights the necessity for targeted management strategies to reduce nutrient losses. Precision interventions, such as the use of cover crops, controlled drainage systems, and adaptive fertilizer timing, are essential. The patterns observed in the Rock Creek watershed are representative of other agricultural regions, indicating broader significance. Future research should integrate longer-term data with land-use and climate projections to explore the efficacy of various best management practices.

5. Conclusions

This study provides a comprehensive assessment of the spatiotemporal variability of nutrient concentrations (soluble reactive phosphorus, SRP; total phosphorus, TP; and nitrate, NO_3^-) and their relationships with hydrological conditions in the Rock Creek watershed, a typical agricultural basin in northwestern Ohio. Our analysis, based on high-temporal-resolution water quality and discharge data over a two-year period (2010–2011), reveals that nutrient transport in this watershed is strongly influenced by episodic runoff events. Specifically, SRP and TP concentrations peak during high-flow periods such as spring snowmelt and summer/fall storms, showing significant positive correlations with discharge. In contrast, nitrate concentrations exhibit a distinct seasonal pattern with a spring flush followed by declining concentrations, indicative of legacy storage depletion. Additionally, we find that flow-weighted mean concentrations (FWMC) substantially exceed arithmetic means, indicating that conventional averaging methods underestimate nutrient loads during critical runoff periods.

The findings of this study have important implications for water quality management in agricultural watersheds. They underscore the need for targeted management strategies aimed at reducing nutrient losses during high-risk periods, such as spring thaw and heavy rainfall. These strategies may include the use of cover crops, controlled drainage systems, or wetlands to buffer event flows, as well as adaptive fertilizer timing to minimize runoff risks. However, it is important to acknowledge that the study was conducted over a limited time period and in a specific geographic location. Therefore, the generalizability of our findings to other agricultural watersheds may be limited.

Future research should aim to integrate longer-term data with land-use and climate projections to assess trends in nutrient dynamics under changing precipitation regimes. Additionally, studies should explore the efficacy of various best management practices (BMPs) in mitigating nutrient pollution, taking into account the dominant flow pathways identified in this and other similar studies. By doing so, we can develop more effective and tailored strategies to address nutrient pollution in agricultural watersheds globally.

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