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Nitrogen dynamics and nitrogen-to-phosphorus stoichiometry in cold region agricultural streams

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Abstract

Cold agricultural regions are getting warmer and experiencing shifts in precipitation patterns, which affect hydrological transport of nutrients through reduced snowpack and higher annual proportions of summer rainfall. Previous work has demonstrated that the timing of phosphorus (P) concentrations is regionally coherent in streams of the northern Great Plains, suggesting a common climatic driver. There has been less investigation into patterns of stream nitrogen (N), despite its importance for water quality. Using high-frequency water quality data collected over 6 yr from three southern Manitoba agricultural streams, the goal of this research was to investigate seasonal patterns in N and P concentrations and the resultant impacts of these patterns on N/P stoichiometry. In the spring, high concentrations of inorganic N were associated with snowmelt runoff, while summer N was dominated by organic forms; inorganic N concentrations remained consistently low in the summer, suggesting increased biological N transformation and N removal. Relationships between N concentration and discharge showed generally weak model fits (r^2 values for significant relationships ranging from .33 to .48), and the strength and direction of model fits differed among streams, seasons, and forms of N. Dissolved organic N concentrations were strongly associated with dissolved organic carbon. Nitrogen-to-phosphorus ratios varied among streams but were significantly lower during summer storm events ($p < .0001$). These results suggest that climate-driven shifts in temperature and precipitation may negatively affect downstream water quality in this region.

1 | INTRODUCTION

The northern Great Plains is a cold region with widespread agriculture, low relief topography, short growing seasons, and a semi-arid to sub-humid climate (Baulch et al., 2019; Liu et al., 2019a). In this region, agricultural productivity and nutrient export tend to be limited by moisture and hydrological connectivity (Baulch et al., 2019). The hydrology of this region is dominated by cold region processes, and the spring snowmelt accounts for a large proportion of water and nutrient transport as snowmelt waters flow over frozen and impermeable soil (Corriveau et al., 2011; Costa et al., 2017; Pomeroy et al., 2007). Nutrient loads in cold regions are also influenced by local hydrology and weather conditions (Shrestha et al., 2012; Costa et al., 2017), as well as soil properties and agricultural practices (Baulch et al., 2019; Liu et al., 2019a).

Abbreviations: c-Q, concentration-discharge; DIN, dissolved inorganic nitrogen; DOC, dissolved organic carbon; DON, dissolved organic nitrogen; OR, Oak River; TDN, total dissolved nitrogen; TDP, total dissolved phosphorus; TN, total nitrogen; TP, total phosphorus; WCE, Willow Creek East; WCW, Willow Creek West.

Annual maximum temperatures in a proximal Canadian Prairie basin have increased by 1.2 ˚C from 1942 to 2014 (Dumanski et al., 2015), and annual mean temperatures in this region are expected to increase 2 ˚C by 2050 (Töyrä et al., 2005). The rainfall fraction of precipitation has increased from 68 to 78% from 1942 to 2014 in this region and is predicted to gradually increase as temperatures rise (Dumanski et al., 2015). Increasing temperatures associated with climate change are also leading to an earlier snowmelt by 2 wk (Dumanski et al., 2015). Summer and autumn precipitation events have also become larger and more common in this region (Spence et al., 2011; Shook & Pomeroy, 2012).

These climate-driven shifts in hydrology are overlain on a landscape that has undergone substantial human modification, including draining of natural wetlands to enable the development of agriculture areas (Dahl & Allord, 1996). Much of this region is naturally poorly drained, and large portions of the landscape are designated as noncontributing, as they do not contribute flow to the stream network in a typical year; the proportion of noncontributing area varies among catchments (Ali & English, 2019). Growing networks of anthropogenic surface drainage have resulted in reduced water retention and increased hydrological connectivity, which leads to more frequent floods and amplified flood volume and peak discharge (Spence, 2007; Dumanski et al., 2015; Szeto et al., 2015; Blais et al., 2016). Taken together, these anthropogenic pressures have profound consequences for nutrient dynamics and water quality of downstream aquatic systems (Baulch et al., 2019; Wilson et al., 2019), and indeed, nutrient concentrations and nuisance algal blooms have been increasing in the region (Schindler, 2012).

Because of the concerns about algal blooms, much of the research in this region has focused on phosphorus (P) concentrations and loads (Ulrich et al., 2016). Although P removal has been successful in improving water quality of numerous lakes (Schindler et al, 2016), many anthropogenically affected systems have not responded as well to P removal (Paerl et al., 2016). Colimitation of productivity by both nitrogen (N) and P is frequently observed in fluvial systems (Dodds & Smith, 2016; Paerl et al., 2016), and the ratio of N/P can affect algal community composition and toxin production (Orihel et al., 2012; Donald et al., 2013). Colimitation of N and P occurs in fluvial systems when the N/P ratios lie between 20 and 50 (Guildford & Hecky, 2000). Furthermore, investigating N/P ratios can reveal whether the response of these two nutrients to a regional or local driver is similar or whether environmental changes may differentially affect the processes controlling the export of each nutrient (Collins et al., 2017).

Investigations into hydrological controls on P behavior in the northern Great Plains have demonstrated that concentration-discharge (c-Q) relationships are complex with low explanatory power (Ali et al., 2017; Casson et al., 2019). Work from other intensively managed agricultural catchments has suggested that large legacy sources of nutrients result in chemostatic conditions (Basu et al., 2010; Thompson et al., 2011). However, in the Canadian Prairies, soil sources of P are heterogeneous (Wilson et al., 2016) and runoff generation mechanisms are complex due to the flat topography and the large amount of depressional storage across this landscape (Ali et al., 2017). As a result, stream nutrient concentrations in this region can be highly variable through time.

Core Ideas

- Stream nitrogen and phosphorus concentrations peak with snowmelt.
- Potential for high concentrations of stream N is lower in summer.
- Organic and inorganic forms of stream N have different patterns and drivers.
- Seasonal patterns of stream N and P differ, which affects N/P ratios.
- High flow events drive N/P ratios down, sometimes to the point of N limitation.

Recent work on P dynamics demonstrated that concentrations are regionally coherent across southern Manitoba agricultural streams, with a major peak of P concentration around the time of snowmelt and a smaller concentration peak in the summer (Casson et al., 2019). The timing of the observed summer peaks of P concentrations were independent of storms, suggesting riparian or in-stream processes may drive summer dynamics. An analysis of an extreme rainfall-runoff event revealed that large summer storms may result in opposite trajectories of N and P export; total phosphorus (TP) concentrations were as high during the event as were observed during snowmelt, but the N/P ratio was substantially lower (Wilson et al., 2019). These seasonal patterns were mediated by land use in the catchment.

Land management and hydrological factors affect N/P ratios in streams in the northern Great Plains. Factors such as tillage practices (Tiessen et al., 2010; Baulch et al., 2019), sewage discharge, fertilizer management (Rattan et al., 2017; Liu et al., 2019b; Cormier et al., 2020), and extent of wetland drainage (Wilson et al., 2019) drive differences in N and P concentrations among watersheds. As well, antecedent conditions have a major influence on interannual variability of nutrient transport to streams (Macrae et al., 2010; McMillan et al., 2018). The extent to which stream N and P respond similarly or differently to hydrological, land use, or climatic drivers is critical to understand in order to project how water quality may shift in the future.

The objective of this study was to examine the influence of seasonal patterns in N and P concentrations on N/P stoichiometry in agricultural streams of the northern Great

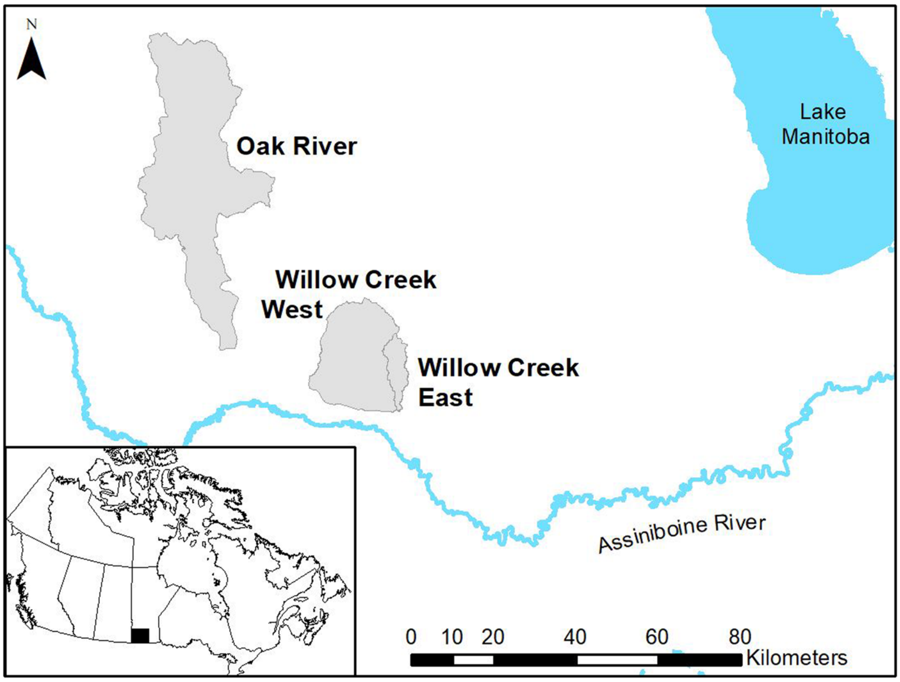

FIGURE 1 Three study catchments in southwestern Manitoba. Data obtained from Agriculture and Agri-Food Canada

Plains. We used stream chemistry samples and discharge data from three streams monitored over 6 yr to address three objectives: (a) to compare seasonal patterns of stream N concentrations among organic and inorganic forms; (b) to assess differences in stream N and P concentrations across streams and seasons; and (c) to investigate the implications of contrasting seasonal drivers of stream N and P concentrations on N/P stoichiometry.

2 | MATERIALS AND METHODS

2.1 | Study area and catchment characteristics

This study examined three catchments located in the Assiniboine River watershed in southwestern Manitoba, Canada, north of Brandon (Figure 1). These catchments were selected on the basis of data availability and catchment characteristics. The climate in this region is continental and associated with a wide annual temperature range (from monthly mean temperatures in January of −16.6 to 18.5 ˚C in July); precipitation during open-water season, which spanned April–October at these sites, averages 379 mm annually, while the nongrowing season (November–March) averages 96 mm (climate data are based on records for "BRANDON A" from 1981 to 2010, which were retrieved from https://climate.weather.gc.ca). These catchments are located within the Aspen Parkland ecoregion, which has experienced a gradual shift from a landscape dominated by grasslands, forests, and wetlands to primarily agricultural land (Smith et al., 2001; Casson et al., 2019) (Table 1). During the reference period used in this paper (2013–2018), canola (*Brassica napus* L. var. *napus*), wheat (*Triticum aestivum* L.), and soybean [*Glycine max* (L.) Merr.] were the most commonly grown crops in Manitoba (Statistics Canada 2021a). In 2016, in Agricultural Region 2, Manitoba (where our study catchments our located), the most common tillage practice was conservation tillage (41.7%), followed by zero tillage (32.8%) and conventional tillage (25.5%) (Statistics Canada 2021b). The predominant soils in these catchments are Black Chernozems, formed on kettled or gently undulating calcareous glacial till (Kodama et al., 1993; Casson et al., 2019). This soil type is associated with high proportions of organic material and is widespread across the Canadian Prairies. The catchments are located within the Pothole Till class of the Prairie Pothole watershed classification, a category that is associated with glacial till, hummocky landforms, high wetland density, and a reduced areal water extent contained within the largest wetland when compared to other categories (Wolfe et al., 2019).

The catchments vary significantly in size, with Oak River (OR) being the largest (2,883 km^2), followed by Willow Creek West (WCW) (1,031 km^2) and Willow Creek East (WCE) (157 km^2). Oak River has the highest wetland proportion (10.4%), while WCE and WCW have lower proportions of wetland coverage (WCE = 1.7%, WCW = 3.5%) (Table 1). Wetlands also make up a significantly higher proportion of riparian area in OR (14.0%) than they do in WCE (1.3%) and WCW (2.5%). The proportion of streamline open water is also significantly higher in OR (9.8%) than in WCE (2.6%) and WCW (2.2%). Streamline open water is the proportion

TABLE 1 Catchment characteristics. Data obtained from Agriculture and Agri-Food Canada

Characteristic	Oak River	Willow Creek East	Willow Creek West
Catchment size, km^2	2,883.3	156.8	1,030.7
Effective drainage area, %	23.7	98.4	65.4
Annual cropland, %	57.7	75.0	72.8
Forest, %	5.3	1.9	4.0
Wetland, %	10.4	1.7	3.5
Riparian cropland, %	45.7	48.8	41.7
Riparian forest, %	28.7	32.4	39.2
Riparian wetland, %	14.0	1.3	2.5
Riparian grassland, %	7.6	9.6	9.0
Streamline open water, %	9.8	2.6	2.2

of a line that follows the center of the stream that intersects with open water. Effective drainage area was lower in OR (23.7%) than in WCW (65.4%) and WCE (98.4%). Effective drainage area is defined as the area of the catchment that is expected to contribute flow to the stream during an event with a return period of 2 yr (Godwin & Martin, 1975). The differences among catchments in wetland proportion, cropland proportion, size, and effective drainage area reflect the typical range in this region (Casson et al., 2019; Wilson et al., 2019). The catchments were similar in other characteristics such as riparian cropland proportion and riparian grassland proportion and somewhat similar in riparian forest proportion (Table 1). Riparian proportions refer to the proportion of riparian area within a catchment that is composed of that ecosystem type. These proportions were determined by creating a 60-m buffer around the provincial drain map streamline, all surface waters that connect to the main streamline, and the outside of all lakes and ponds that intersect the streamlines.

2.2 | Water chemistry

Streams were sampled on a daily to weekly basis throughout the 2013–2018 growing seasons (roughly March–November) for total nitrogen (TN), total dissolved nitrogen (TDN), NO_3^-, NH_4^+, dissolved organic carbon (DOC), total phosphorus (TP), total dissolved phosphorus (TDP), and specific ultraviolet absorbance. Using twice-rinsed polycarbonate bottles, water samples were taken from well-mixed areas of the streams and stored frozen in a cooler before analysis (Casson et al., 2019). A flow analyzer with a NO_3^- reducing coil was used to colorimetrically determine NH_4^+ and NO_3^- (as NO_3^- + NO_2^-) concentrations. Total dissolved N and DOC concentrations were determined through the combustion method using a Shimadzu TOC-VCSn analyzer. Particulate N was determined by analyzing a mass of filtered material using a Thermo Scientific Flash 2000 CHNS/O elemental analyzer. Total N is the sum of TDN and particulate N. Total P and TDP concentration were determined through sulfuric acid/persulfate digestions and colorimetry using the ascorbic acid method (Wilson et al., 2019). The N/P ratios were calculated using TDN and TDP. Dissolved inorganic nitrogen (DIN) describes the combined concentration of NO_3^- and NH_4^+. Dissolved organic nitrogen (DON) was calculated as TDN – DIN. Total dissolved N and P are strongly correlated with TN and TP, respectively, and the dissolved fraction makes up a high proportion of the total nutrient concentration in these regions (McCullough et al., 2012; Liu et al., 2013). The relationship between the total and dissolved fractions for both N and P is shown in Supplemental Figures S1 and S2.

Discharge data were acquired from the Water Survey of Canada hydrometric database (https://wateroffice.ec.gc.ca/) for OR (Wilson et al., 2019). For WCE and WCW, flow was measured by Agriculture and Agri-Food Canada and a stage-rating curve was generated using manual streamflow measurements in combination with depth measurements from pressure transducers (Onset HOBO U20-001-04) that logged continuously (Wilson et al., 2019). Streams were not monitored in the winter due to lack of access. Seasonal separations (spring, summer) and storm events were determined by visual inspection of hydrographs, nutrient concentrations, and manual hydrograph separation (Linsley Jr et al., 1975). One extreme rainfall-runoff event in the 2014 growing season (called "2014 Storm") was highlighted as a separate condition as it was unique in its magnitude and its effect on nutrient dynamics in all three streams (Wilson et al., 2019).

2.3 | Statistical analyses

To understand the characteristics of nutrient flowpaths in these catchments, threshold models were fit to c-Q data for each stream, following the method used by Ali et al. (2017).

The threshold models used the following equation:

$$\text{When } Q < \text{ThresQ}, \ c = C_g$$
$$\text{Otherwise}: c = C_g + C_r$$

where c = nutrient concentration, Q = discharge, ThresQ = breakpoint, $C_g = c$ at baseflow, and $C_g + C_r$ = solute concentration when both baseflow and runoff contribute to stream flow (Ali et al., 2017; Casson et al., 2019). ThresQ was identified from fitting the segmented package for the threshold model (Muggeo, 2003; Muggeo, 2008; Muggeo, 2016; Muggeo, 2017). The Davies test was used to test if the breakpoint of the threshold model was significant (i.e., if there was nonzero difference in slope between the two segments) (Davies, 2002).

All models were calculated with all years of data available (2013–2018). The c-Q relationships were calculated over the entire growing season as well as individually for spring and summer. In accordance with the study by Ali et al. (2017), r^2 values above .2, .4, .6, and .8 were described as fair, reasonable, good, and very good model fits, respectively. We used a pairwise Wilcoxon rank sum test to calculate pairwise statistical comparisons between seasons and stormflow conditions of N/P ratios. All statistical analyses were done using R (R Core Team, 2020).

3 | RESULTS

3.1 | Seasonal patterns of discharge

At all three streams, seasonal patterns of discharge were similar. The spring snowmelt was usually the time when discharge was highest, with lower, secondary peaks of discharge occurring in the summer (Figure 2). There were exceptions, such as in 2013 when the secondary discharge peak was close in magnitude to the spring snowmelt peak in all three streams. In 2014, there was an extreme rainfall-runoff event at all three streams, attributed to a heavy rainstorm (124.4 mm in 3 d [data retrieved from the "BRANDON A" historical weather station data from https://climate.weather.gc.ca]) in combination with very wet antecedent conditions (Ahmari et al., 2016; Wilson et al., 2019). Based on intensity–duration–frequency curves for the Brandon A weather station, a 100-yr event has a magnitude of 109 mm over 24 h, while a 25-yr event has a magnitude of 84 mm over 24 h (Schardong et al., 2020). Pre-snowmelt precipitation (1 November to 30 April) ranged from 145 to 200 mm, and the total rainfall in May and June that contributed to the extreme rainfall-runoff event ranged from 249 to 268 mm at these sites (Wilson et al., 2019). Water yield from this event was similar in magnitude to the snowmelt of that year (snowmelt water yield ranging from 40 to 64 mm; extreme rainfall-runoff water yield ranging from 36 to 49 mm; Wilson et al., 2019).

3.2 | Seasonal patterns of stream nutrients

There were strong seasonal patterns of N concentration across all streams. For all forms of N, concentrations were highest at the onset of spring snowmelt and declined as the snowmelt progressed (Figure 3). Patterns of N concentration varied significantly between organic and inorganic forms. In all three streams, there were no correlations between DIN and DON when we looked at the full growing season, spring, or the summer. The DIN concentrations were consistently low throughout the summer, while DON concentrations typically rose to a secondary peak after dropping to the lowest point following snowmelt. Total dissolved N and TDP were fairly well correlated in all three streams across the entire growing season (r^2 range = .38–.52, $p < .0001$). Dissolved organic N and DOC concentrations were fairly well correlated in all three streams across the entire growing season (r^2 range = .34–.71, $p < .0001$) and very well correlated during the summer (r^2 range = .80–.86, $p < .0001$).

3.3 | Concentration-discharge relationships

Throughout the full growing season, both TDN and TDP were fairly to reasonably well fit by threshold models where concentrations increased after the breakpoint, but only in WCE ($r^2 = .41$, $p < .001$ for both TDN and TDP) and WCW ($r^2 = .33$, $p < .001$ for TDN; $r^2 = .44$; $p < .001$ for TDP) (Figure 4; Table 2). Dissolved inorganic N was fairly to reasonably well fit by threshold models where concentrations increased after the breakpoint, but only in WCE and WCW ($r^2 = .40$ and .36, respectively, $p < .001$ at both streams) (Figure 4; Table 2). DON and DOC were reasonably well fit by threshold models, but only in OR ($r^2 = .44$ and .48, respectively, $p < .001$ for both DON and DOC) (Figure 4; Table 2). The slopes of these model fits were negative after the breakpoint, indicating hydrological dilution at high flow (Figure 4; Table 2) (Moatar et al., 2017).

3.4 | Seasonal patterns of stream N/P stoichiometry

There were significant differences in N/P ratios among seasons (Figure 5). In OR, N/P was not significantly different between spring and summer baseflow, N/P in summer stormflow was significantly lower than both spring and summer baseflow ($p < .001$), and the N/P of the extreme 2014 storm event was significantly lower than summer stormflow

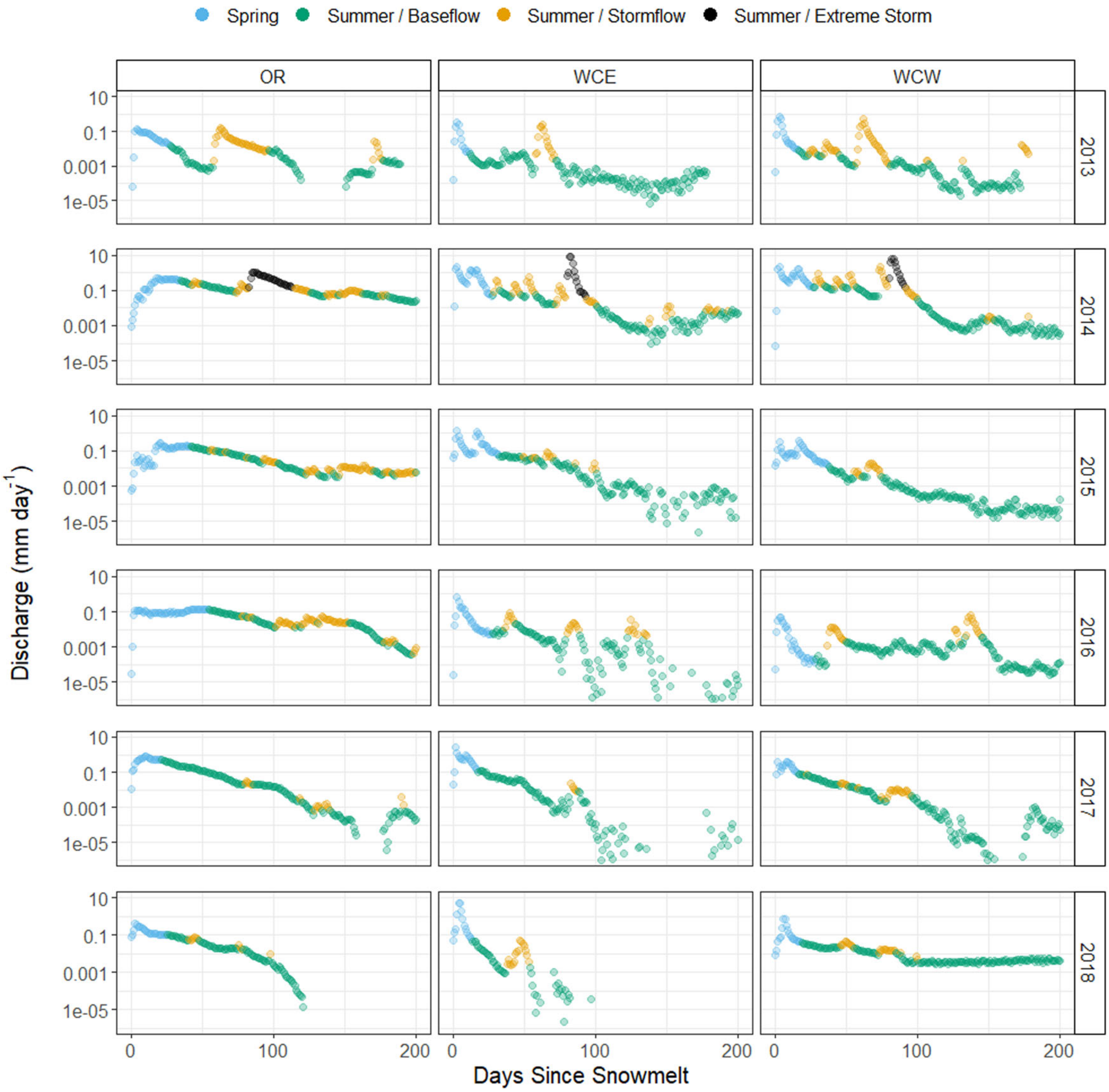

FIGURE 2 Time series of discharge (log10 transformed) starting at the first day of the spring snowmelt. Each column of plots corresponds to a different stream, and each row corresponds to a different year. OR = Oak River; WCE = Willow Creek East, WCW = Willow Creek West. Colored by condition (season or stormflow). A few data points from the midsummer of 2017 in WCW are not displayed as the discharge values were extremely low. The stream was almost certainly not flowing during this period

($p < .005$) (Figure 5; Supplemental Table S2). In WCE, N/P was highest during summer baseflow, there was no significant difference between N/P of spring and summer stormflow ($p > .05$), and the extreme 2014 storm was significantly lower than summer stormflow ($p < .001$) (Figure 5; Supplemental Table S2). In WCW, N/P was also highest during the summer baseflow; however N/P in spring was significantly lower than in summer stormflow ($p < .001$) (Figure 5; Supplemental Table S2). The N/P in the extreme storm event was also lower than the summer stormflow ($p < .001$) (Figure 5; Supplemental Table S2). The impact of storm events on N/P ratios was strongly dependent on when storm events occurred; storm events that directly followed snowmelt typically did not depress N/P ratios, whereas midsummer events almost always resulted in the lowest N/P ratios of the year.

4 | DISCUSSION

Nitrogen concentrations in these three streams showed strong, consistent seasonal patterns. There were high concentrations of all forms of N associated with spring snowmelt, and these concentrations declined sharply as spring progressed. The summer months were characterized by either low N concentrations relative to the spring snowmelt concentration peak—which was seen in both forms of DIN (NO_3^- and NH_4^+)—or a gradual rise to a smaller midsummer concentration peak, which was seen in DON. The c-Q threshold model fits for all analytes during the full growing season were significant exclusively in OR or exclusively in WCE and WCW. This is likely a reflection of catchment characteristics. Willow Creek East and WCW have more similar characteristics to each other

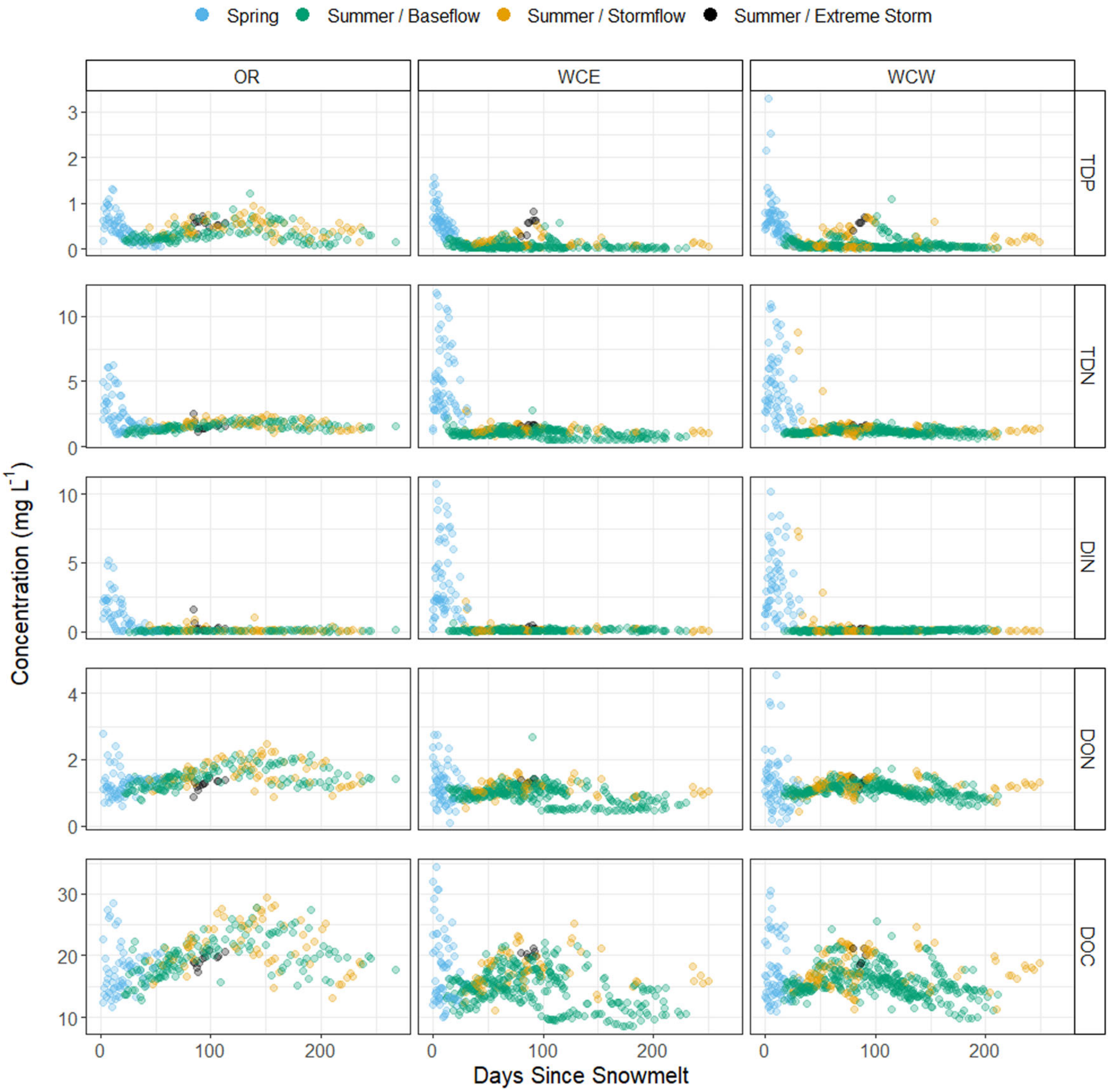

FIGURE 3 Time series of the concentration of total dissolved P (TDP), total dissolved N (TDN), dissolved inorganic N (DIN), dissolved organic N (DON), and dissolved organic C (DOC) starting at the first day of the spring snowmelt. Each column of plots corresponds to a different stream, and each row corresponds to a different analyte. OR = Oak River, WCE = Willow Creek East, WCW = Willow Creek West. Colored by condition (season or stormflow). Data for all years (2013–2018) are superimposed to illustrate seasonal patterns

than to OR. Both WCE and WCW have similar areal proportions of annual cropland, wetland, and streamline open water, and they are closer in proximity. While they also differ in many categories such as effective drainage area, catchment size, and areal proportions of forest and riparian forest, they had similar c-Q threhold model fits for all analytes.

As observed in Casson et al. (2019), there were high concentrations of TDP associated with spring snowmelt, and c-Q threshold model fits were either fair (WCW and WCE) or poor (OR) (Table 2). However, there were high midsummer TDP concentrations associated with the 2014 extreme rainfall-runoff event (Figure 2, Figure 3) (Wilson et al., 2019). The response of TDP across catchments to this extreme rainfall event is contrary to timing and magnitude of secondary concentration peaks observed in most forms of N, especially inorganic forms, which did not respond to this event to the same degree (Figure 3). The contrast between N and P dynamics led to significant differences among seasons and hydrological conditions. The N/P ratio in streams was significantly higher during summer baseflow compared with summer stormflow at all catchments, and this difference is even greater when comparing N/P ratios during the 2014 extreme event.

4.1 | Controls on N concentrations in spring

Spring patterns of N concentrations in these streams were strongly driven by snowmelt runoff processes. These patterns are consistent with other agricultural streams in this region,

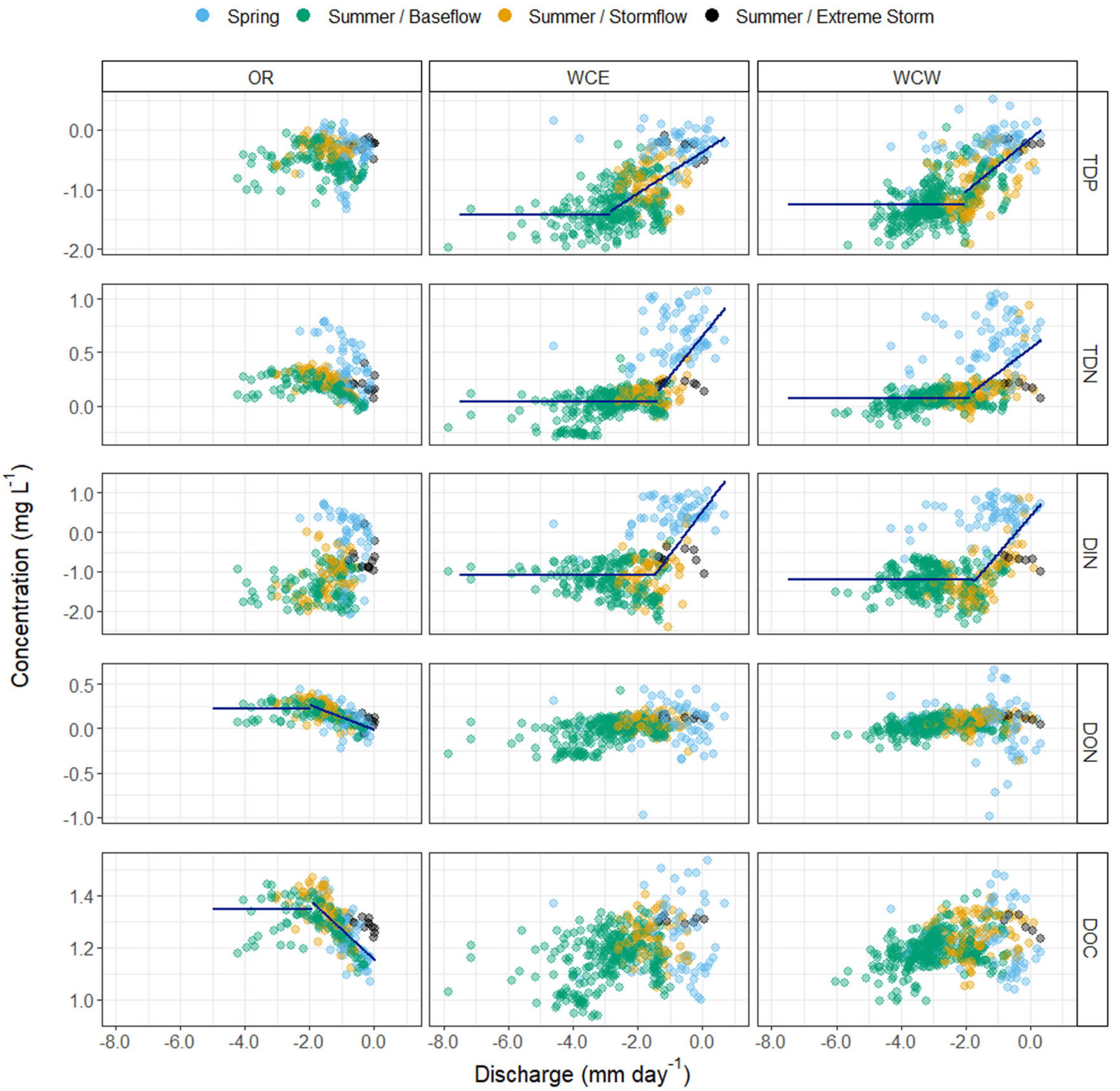

FIGURE 4 Concentration-discharge plots (both axes are log10 transformed) of total dissolved P (TDP), total dissolved N (TDN), dissolved inorganic N (DIN), dissolved organic N (DON), and dissolved organic C (DOC). Segmented lines illustrate significant threshold relationships. Each column of plots corresponds to a different stream, and each row corresponds to a different analyte. OR = Oak River, WCE = Willow Creek East, WCW = Willow Creek West. Colored by condition (season or stormflow). Data for all years (2013–2018) are superimposed to illustrate seasonal patterns

as both TN and TP typically respond strongly to snowmelt discharge runoff (Corriveau et al., 2013; Rattan et al., 2017; Casson et al., 2019). Hydrological connection to upland and cropland areas is highest in the early spring. Snowmelt runoff over frozen soils drives much of the nutrient transport in this region, and the snowmelt rate (Rattan et al., 2017), snowmelt volume (Schneider et al., 2019), and accumulation of chemicals in the snowpack over the winter months (Costa et al., 2018) contribute significantly to this annual nutrient load. However, discharge by itself was not a strong predictor of N concentrations in the spring (Supplemental Table S1). This result is consistent with research demonstrating that the sources of DIN shift as the melt progresses, and the peak in DIN concentration is not necessarily coincident with the peak in discharge (Brunet & Westbrook, 2012; Costa et al., 2017).

Catchment characteristics may have had an effect on peak spring concentrations of both TDN and TDP, which were often significantly higher than OR in WCE and WCW. Peak spring TDN concentrations were 89.4 and 75.3% higher than OR in WCE and WCW, respectively. Peak TDP concentrations were 17.42 and 149.2% higher than OR in WCE and WCW, respectively. This is consistent with findings of Wilson et al. (2019), where flow-weighted mean concentrations of TN and TP were positively associated with cropland and negatively associated with wetlands. Both WCE and WCW have higher areal proportions of cropland and lower areal proportions of wetland and

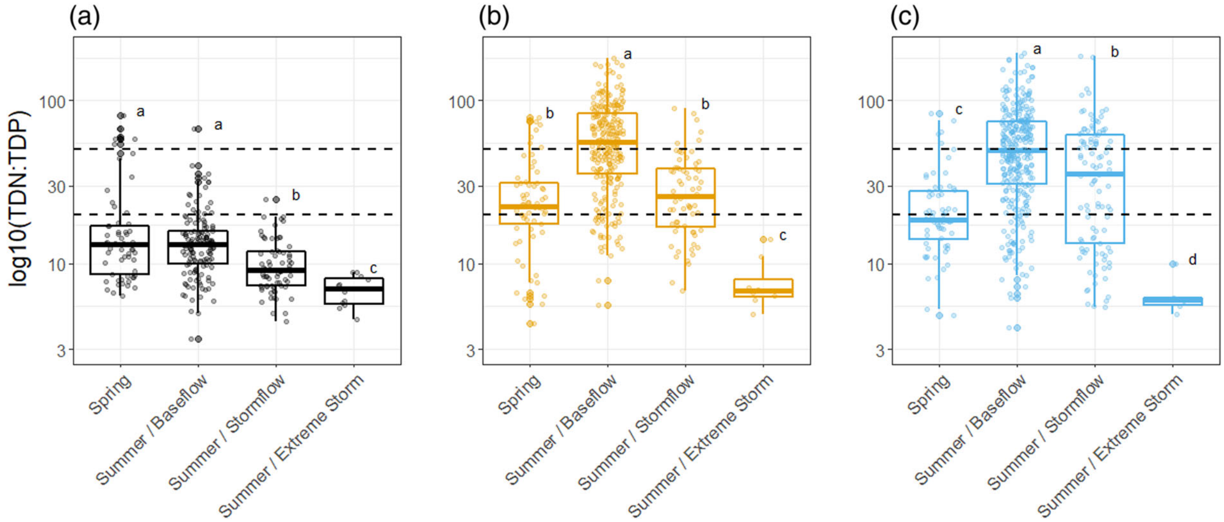

FIGURE 5 Boxplots of the molar ratios between total dissolved N and total dissolved P (TDN:TDP) among season and stormflow condition (log10 transformed). The horizontal dotted lines at 20 and 50 indicate the boundaries of N and P colimitation of productivity (Guildford & Hecky, 2000). Letters represent statistically significant differences among conditions ($p < .05$), which were determined from pairwise Wilcoxon rank sum tests (shown in Supplemental Table S2). Each plot corresponds to one of three study streams (a = Oak River, b = Willow Creek East, c = Willow Creek West)

riparian forest. Higher areal proportion of cropland may be associated with higher peak TDN and TDP concentrations due to greater inputs of fertilizer (Carpenter et al., 1998). Higher peak TDN and TDP concentrations may occur with lower areal proportions of wetland and riparian forest because nutrient retention is reduced (Satchithanantham et al., 2019).

During the spring snowmelt, DIN concentrations were high and comprised a large proportion of TDN (the mean of the proportion of TDN that is DIN during spring was 38.5% in OR, 67.6% in WCE, and 66.3% in WCW). Nitrate is highly soluble in water and resides primarily in soil pore water which makes it easily transported with runoff (Costa et al., 2017; Snider et al., 2017). Despite its high retention on negatively charged soil particles, snowpack NH_4^+ is easily transported from the landscape with spring snowmelt runoff (Stottlemyer & Toczydlowski, 1996; Costa et al., 2020). Biological processes such as mineralization, nitrification, and denitrification have also been shown to occur at potentially significant rates in frozen agricultural soils, and these processes could have increased snowmelt export of inorganic N from the soils (Clark et al., 2009). Even so, the extent to which these biological N transformations occur during the winter in this region is perhaps quite low, given the degree of freezing in soils (Costa et al., 2017). The spring snowmelt was also associated with high DON concentrations. While the predominant form of N in snowpacks is usually inorganic, organic N can be present due to leaching from vegetation and surficial soil layers (Elliot, 2013; Costa et al., 2017). However, unlike NO_3^- and NH_4^+, there were also significant levels of organic N present during the summer (Figure 3).

4.2 | Controls on N concentrations in summer

Summer patterns of N differed between organic and inorganic forms. Throughout the summer, DIN remained at consistently low levels (mean = 0.12 mg L^{-1}, SD = 0.38 mg L^{-1}), and DON fluctuated (mean = 1.16 mg L^{-1}, SD = 0.32 mg L^{-1}). This fluctuation was most pronounced in OR, where both summer DON and DOC levels approached or exceeded spring snowmelt levels (maximum summer DON and DOC values were 88.8 and 103.5% of the maximum spring DON and DOC values, respectively) (Figure 3). The c-Q threshold model fits for both DON and DOC in OR were independent of discharge at low flows and negative at high flows, following the "flat-down" pattern characterized by Moatar et al. (2017), with the breakpoints close to the median flow values (Table 2); this suggests a dilution of pools of DON and DOC with larger fluxes of water (Godsey et al., 2009).

The large catchment size, high proportion of wetlands, large amounts of open water, and low proportion of effective drainage area in OR may explain why DON and DOC were source-limited, as well as why concentrations of all other nutrients were weakly predicted by discharge in this stream (Table 1; Supplemental Table S1; Basu et al., 2011). These factors tend to hinder nutrient transport and can indicate that stream concentrations of these nutrients depend more on in-stream processes (Basu et al., 2011). The negative c-Q threshold model fits may suggest that the depressional storage in the OR catchment was such that the rainfall-runoff events did not connect the streams to wetland sources of DOC and DON enough to affect stream nutrient concentrations in a meaningful way.

TABLE 2 Concentration-discharge relationship data for the entire growing season. Only significant relationships are shown. The reported *p* values were calculated using the Davies test, which tests for a non-zero difference-in-slope parameter of a threshold relationship

Analyte	r^2	*p*	ThresQ[a]	Slope[a]	Median discharge
TDP					
OR					−1.60
WCE	.41	<.001	−2.87	0.35	−2.62
WCW	.44	<.001	−2.03	0.45	−2.60
TDN					
OR					
WCE	.41	<.001	−1.37	0.37	
WCW	.33	<.001	−1.83	0.23	
DIN					
OR					
WCE	.40	<.001	−1.48	1.09	
WCW	.36	<.001	−1.76	0.94	
DON					
OR	.44	<.001	−2.00	−0.14	
WCE					
WCW					
DOC					
OR	.48	<.001	−1.91	−0.12	
WCE					
WCW					

Notes. DIN, dissolved inorganic N; DOC, dissolved organic C; DON, dissolved organic N; OR, Oak River; TDN, total dissolved N; TDP, total dissolved P; WCE, Willow Creek East; WCW, Willow Creek West.

[a]ThresQ = breakpoint. Slope = the slope of the threshold model following the breakpoint.

Given the lack of relationship between DON and discharge in WCE and WCW, it seems likely that in-stream or near-stream processes are driving these patterns. During these periods of low flow and high temperatures, organic matter may accumulate in streams because of primary production (Webster & Meyer, 1997). This hypothesis is further supported by the pattern of low absorbance values during the summer (Wilson, unpublished data), suggesting that the organic matter in the stream is less terrestrially derived and therefore more likely to have been produced in-stream (Vidon et al., 2008). The strong relationship between DOC and DON suggests that the N dynamics during this period are tightly coupled to organic matter dynamics.

Concentrations of DIN were consistently low throughout the summer and showed very little if any response to storm events (Figure 3). In some aquatic systems where C is the limiting nutrient for microbial activity, addition of DOC can prompt increases in microbial activity, which leads to a quicker uptake time and reductions to stream NO_3^- and possibly NH_4^+ concentrations (Bernhardt & Likens, 2002). Summer periods of low flow also favor NO_3^- uptake due to the increased water residence time and ratio between streambed surface area and water volume, both of which accelerate stream microbial uptake and NO_3^- removal in hyporheic and riparian zones by denitrifying microorganisms (Peterson et al., 2001; Mulholland et al., 2008; Zarnetske et al., 2012; Moatar et al., 2017).

4.3 | N/P ratios

The N/P ratio in surface waters is a critical determinant of water quality, as it can drive algal community composition (Schindler et al., 2016) and toxin production (Orihel et al., 2012). The streams in this region drain into Lake Winnipeg, which is affected by freshwater eutrophication (Schindler, 2012). These results provide clear evidence that summer high-flow events drive N/P ratios down, in many cases below the critical threshold of 20, when N becomes limiting to algal growth (Guildford & Hecky, 2000). Other work assessing drivers of N/P ratios in agricultural streams has also observed greater transport of P during rain events compared with N (Green et al., 2007; Green & Wang, 2008; Green & Finlay, 2010; Rattan & Chambers, 2017), consistent with our finding that N/P ratios were significantly lower during storm events compared with summer baseflow. In this region, P transport from low-lying soils and riparian buffers during storms is mediated by abiotic adsorption–desorption and is strongly related to soil test P concentrations (Wilson et al., 2016; Satchithanantham et al., 2019). Conversely, warm, wet conditions may promote NO_3^- removal via denitrification (Satchithanantham et al., 2019; Baulch et al., 2019).

The N/P ratios responded more strongly to high-flow conditions in streams from well-drained catchments (WCE and WCW) than a poorly drained catchment (OR), which may be due to differences in hydrological connectivity (Rose et al., 2018; Kincaid et al., 2020) that arise from the differences among catchment characteristics such as effective drainage area, proportion of wetland, and catchment size. Stronger hydrological connectivity coupled with the high proportion of conservation tillage practiced in this region (41.7%) (Statistics Canada, 2021b) may explain the lowered N/P ratios observed in WCE and WCW during the spring (Tiessen et al., 2010).

Larger summer rainfall events tend to drive N/P ratios down (Correll et al., 1999; Green et al., 2007; Green & Finlay, 2010; Kincaid et al., 2020), which is consistent with our finding that the extreme rainfall-runoff event of 2014 had the lowest N/P ratios in each stream. In a detailed study of the 2014 extreme rainfall event, Wilson et al. (2019) attribute low N/P ratios (mean = 7.1, SD = 2.1) to the efficient transport of P but not N from the watershed to the stream network via surface drainage ditches. Prior to this extreme event, the landscape was saturated, so disproportionate transport of P via drainage ditches was perhaps enhanced even relative to the large size of this event. By contextualizing this event with additional years of data, we can see that although other summer storms exhibit depressions in N/P ratios (mean = 29.6, SD = 27.7), the N/P ratios associated with this extreme event were significantly lower in all streams (mean = 7.1, SD = 2.1). The data resolution in the present study did not allow us to assess the role of antecedent moisture in driving N/P ratios, and so it is difficult to disentangle whether the differences are due to the size of the extreme event or due to the conditions leading up to the event. Given the trends toward more frequent and intense summer storms (Shook & Pomeroy, 2012; Dumanski et al., 2015), there is an urgent need to understand how summer events affect stream N and P dynamics.

4.4 | Implications under a changing climate

Climate-induced changes to hydrology on the Canadian Prairies will have important implications for nutrient transport. Higher proportions of precipitation falling as rain, smaller snowpacks, and early snowmelts will affect the timing, frequency, and magnitude of runoff (Shook & Pomeroy, 2012; Dumanski et al., 2015). This will have implications for seasonal patterns of hydrological connectivity, which is heavily affected by fill-and-spill mechanisms in catchments with large fractions of noncontributing area due to low topography, potholes, and wetlands (Coles & McDonnell, 2018; Wolfe et al., 2019). Increased rainfall and changes to hydrology may significantly alter the spatial, temporal, and compositional variability of N and P concentrations in northern Great Plains agricultural streams (Shook & Pomeroy, 2012; Dumanski et al., 2015; Rattan et al., 2019). Reductions to snowpack volume and more frequent midsummer extreme rainfall events should also shift the timing of nutrient loads away from the spring and perhaps toward the summer (Spence et al., 2011; Dumanski et al., 2015). Since midsummer N and P transport appears to respond to different drivers in this region, climate change may also affect N/P ratios (Wilson et al., 2019) and thus adversely affect downstream water quality (Paerl et al., 2016). Understanding how climate change is affecting N transport in cold agricultural catchments and developing and refining regional-scale models based on more detailed local conditions will support informed landscape management decisions in this region, where water quality is vulnerable to human activities across the landscape.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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