AGU100 ADVANCING EARTH AND SPACE SCIENCE

Water Resources Research

RESEARCH ARTICLE
10.1029/2018WR024009

Special Section:
Dynamics in Intensively Managed Landscapes: Water, Sediment, Nutrient, Carbon, and Ecohydrology

Phosphorus Transport in Intensively Managed Watersheds

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Key Points:
- Specific places, processes, and land use practices mediate P concentration-discharge relationships within agricultural watersheds
- Dissolved and particulate P often contribute equally to total P loads, underscoring the importance of strategies to reduce both forms
- The majority of P export occurs during large storms, indicating strong intersecting roles of climate and agriculture in driving P losses

Supporting Information:
- Supporting Information S1
- Table S1
- Table S2
- Table S3
- Table S4
- Table S5
- Table S6
- Table S7
- Table S8
- Table S9
- Table S10

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Citation:
Dolph, C. L., Boardman, E., Danesh-Yazdi, M., Finlay, J. C., Hansen, A. T., Baker, A. C., & Dalzell, B. (2019). Phosphorus Transport in Intensively Managed Watersheds. *Water Resources Research*, *55*, 9148–9172. https://doi.org/10.1029/2018WR024009

Received 30 AUG 2018
Accepted 15 OCT 2019
Accepted article online 24 OCT 2019
Published online 16 NOV 2019

Abstract Understanding controls of P movement through watersheds are essential for improved landscape management in intensively managed regions. Here, we analyze observational data from 104 gaged river sites and 176 nongaged river sites within agriculturally dominated watersheds of Minnesota, USA, to understand the role of landscape features, land use practices, climate variability, and biogeochemical processes in total, dissolved and particulate P dynamics at daily to annual scales. Our analyses demonstrate that factors mediating P concentration-discharge relationships varied greatly across watersheds and included near-channel sediment sources, lake and wetland interception, assimilation by algal P, and artificial land drainage. The majority of gaged sites exhibited mobilizing behavior for all forms of P at event (i.e., daily) timescales and chemostatic behavior at annual timescales. The large majority of watershed P export (>70%, on average) occurred during high flow conditions, suggesting that more frequent large storm events arising from climate change will drive increased P losses from agricultural watersheds without substantial management changes. We found that P export could be dominated by dissolved P, particulate P, or an even mix of the two forms, depending on watershed attributes. Implementation of management practices to control P losses must be guided by understanding of how local landscapes interact with current and future climate conditions. Managing for both dissolved and particulate P is required to reduce overall P load in many agricultural watersheds.

Plain Language Summary When phosphorus from farm fertilizer, eroded soil, and septic waste enters our water, it leads to problems like toxic algae blooms, fish kills, and contaminated drinking supplies. In this study, we examine how phosphorus travels through streams and rivers of farmed areas. In the past, soil lost from farm fields was considered the biggest contributor to phosphorus pollution in agricultural areas, but our study shows that phosphorus originating from fertilizer stores in the soil and from crop residue, as well as from soil eroded from sensitive ravines and bluffs, contributes strongly to the total amount of phosphorus pollution in agricultural rivers. We also found that most phosphorus leaves farmed watersheds during the very highest river flows. Increased frequency of large storms due to climate chaos will therefore likely worsen water quality in areas that are heavily loaded with phosphorus from farm fertilizers. Protecting water in agricultural watersheds will require knowledge of the local landscape along with strategies to address (1) drivers of climate chaos, (2) reduction in the highest river flows, and (3) ongoing inputs and legacy stores of phosphorus that are readily transported across land and water.

1. Introduction

1.1. Background

Excessive nutrient loading from agricultural watersheds is a dominant contributor to eutrophication of freshwater and marine systems throughout the globe (Anderson et al., 2002; Michalak et al., 2013; Paerl, 2018; Russell et al., 2008). In the United States, investments for mitigating nonpoint source pollution to lakes and rivers have remained flat since the 1970s (Keiser et al., 2019). Perhaps not surprisingly, eutrophication problems persist and, in some cases, appear to be worsening (Dubrovsky et al., 2010; Oliver et al., 2017; Stoddard et al., 2016). While decades of research have established the role of phosphorus (P) in contributing to degraded water quality and eutrophication (Paerl et al., 2016; Schindler et al., 2016), management of

nonpoint source P in particular has proven challenging because of ongoing inputs from intensive farming as well as legacy P stores in soil, together with difficulties tracing and curbing hydrologic losses of both dissolved and particulate forms (Jarvie et al., 2013; Rissman & Carpenter, 2015; Sharpley et al., 2013).

1.2. Concentration-Discharge Power Law Relationships

The relationship between the concentration (C) of particulates and solutes across varying levels of discharge (Q), when examined in relation to other watershed attributes, can reveal ways in which natural and anthropogenic factors affect water quality (Warrick, 2015). These relationships have been used to infer the source of weathering products, nutrients, and sediment, as well as the conditions which mobilize them (e.g., Asselman, 2000; Basu et al., 2010, 2011; Godsey et al., 2009; Lawrence & Driscoll, 1990; Moatar et al., 2017; Syvitski et al., 2000; Thompson et al., 2011; Vaughan et al., 2017). These relationships are often described by the power function equation $C = aQ^b$ where a describes the vertical offset of the curve and b describes the per unit increase in concentration as discharge increases (Godsey et al., 2009). Concentrating relationships ($b > 0$) imply higher flows are mobilizing more of a waterborne constituent, particularly through erosion or greater landscape connectivity. Diluting relationships ($b < 0$) suggest that constituents are source-limited or that relatively consistent inputs are diluted by greater discharge (Godsey et al., 2009). Chemostatic relationships ($b = 0$) suggest no significant change in concentration across a range of discharges, a pattern often observed for mineral weathering products (Godsey et al., 2009; Musolff et al., 2015).

1.3. Biogeochemical Stationarity and Potential Alternative Controls on P Transport

Previous studies have established the concept of "biogeochemical stationarity," which holds that for agricultural landscapes with large legacy stores of nutrients due to decades of fertilization, average annual nutrient concentrations will be relatively stable regardless of flow condition (Basu et al., 2010, 2011; Thompson et al., 2011; Van Meter et al., 2018). Under stationarity, annual discharge is hypothesized to serve as a proxy for annual loads exported from agricultural watersheds at multiple spatial scales (Basu et al., 2010). This hypothesis has been successfully applied to both geogenic solutes in modified and unmodified landscapes and nitrogen in heavily managed landscapes over annual timescales (Basu et al., 2010, 2011; Thompson et al., 2011). However, despite known legacy stores of P in agricultural soils (Jarvie et al., 2013; Powers et al., 2016), P transport does not appear to be fully explained by the biogeochemical stationarity concept (Ali et al., 2017; Basu et al., 2011; Musolff et al., 2015), suggesting additional controls on P concentrations beyond flow dynamics and activation of legacy stores. Such additional controls have not been fully articulated at watershed scales (Fox et al., 2016; Haygarth et al., 2012).

It is important to note that the biogeochemical stationarity hypothesis was based on annual, rather than event-based (i.e., daily) measures of nutrient transport. By contrast, a number of studies have shown both nitrogen and P to exhibit nonchemostatic behavior on event timescales (Ali et al., 2017; Basu et al., 2011; Musolff et al., 2015). Analysis at different temporal scales can thus confound the ways nutrient transport is characterized and interpreted. To resolve these issues, it is important to explicitly parse the issue of temporal scale (i.e., daily vs annual) when characterizing nutrient transport regimes. In addition, information about relationships between discharge and nutrient loads, in addition to concentrations, can provide important insights about the consequences of nutrient C-Q relationships to downstream water bodies on daily, annual, and multiyear timescales.

1.4. Objectives

Here, we use a data set derived from extensive sampling of 281 watersheds draining intensively managed agricultural areas in Minnesota, USA, to characterize P export from agricultural watersheds and investigate the potential watershed-scale controls on P transport dynamics at multiple temporal scales. We used C-Q relationships, water yield, and annual load information to understand and characterize the contribution of both particulate and dissolved P to total P transport for 104 gaged river sites under various seasonal and flow conditions. We complemented this analysis with a field data set collected from an additional set of 176 agricultural stream and river sites within three study watersheds (Dolph et al., 2017), sampled repeatedly for a suite of water chemistry over a range of flow conditions, between 2013 and 2016. Using these two large data sets, we examined the importance of climate, land use practices, landscape features, and biogeochemical processes in mediating transport behavior of particulate and dissolved P from agricultural watersheds.

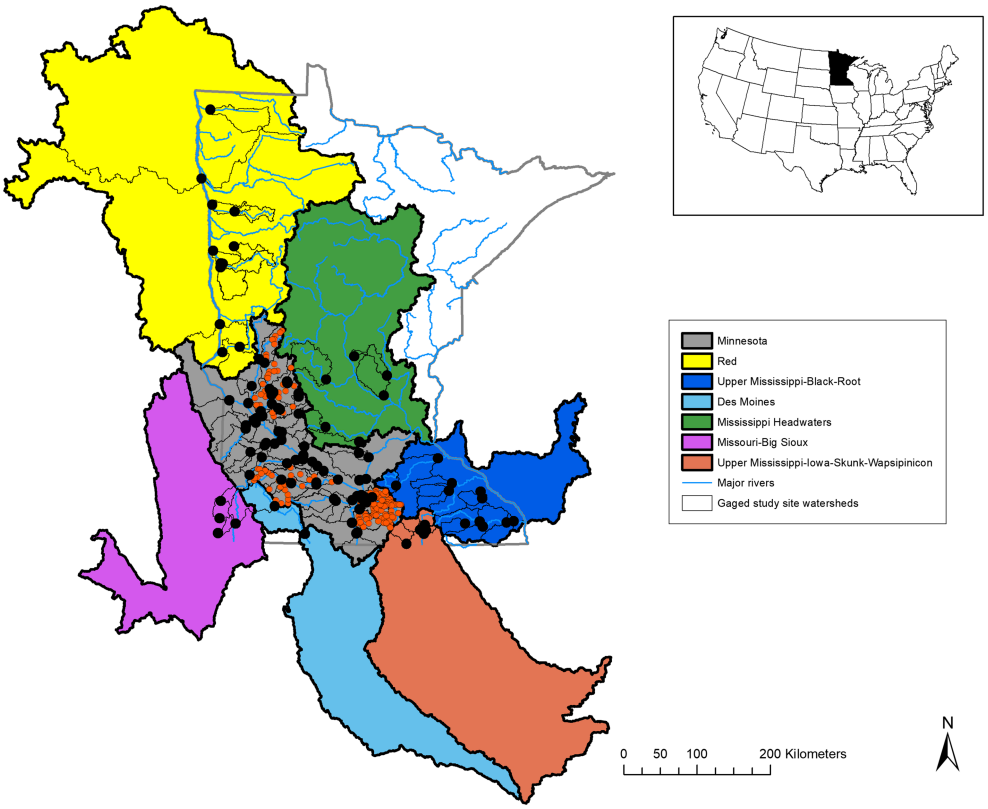

Figure 1. Locations (black circles) of 104 agriculturally dominated gage sites included in this study. Orange circles indicate additional field sites (n = 176) sampled repeatedly for water chemistry under various flow conditions, 2013–2016. Colors indicate major river basins (HUC4) in which sites are located.

2. Materials and Methods

2.1. Study Area

This study was conducted using water chemistry and flow information for stream and river sites draining agriculturally dominated watersheds located predominantly in southern and northwest Minnesota (Figure 1). The study area intersects seven major (HUC4 scale; USGS, 2017) river basins: the Red River Basin, the Minnesota River Basin, the Upper Mississippi-Black-Root River (UMBR) Basin, the Des Moines River Basin, the Mississippi Headwaters Basin, the Missouri-Big Sioux River Basin, and the Upper Mississippi-Iowa-Skunk-Wapsipinicon River Basin.

Many of the physiographic characteristics of these different basins are a function of their unique geologic histories (see Appendix S1 for more detailed information about geologic context). Soil types across the study region range from (1) silty soils formed from loess deposits in forests, with a thin layer of topsoil in the southeast to (2) loamy glacial till with thick topsoil formed from tall grass prairie in south-center Minnesota to (3) lacustrine sediments rich in organic matter and covered in thick, dark topsoil from tall grass prairie in the northwest Minnesota (Anderson et al., 2001). The region is characterized by a climate gradient, with generally drier conditions in the northwest (mean annual precipitation = 510 mm/yr) and wetter conditions in the southeast (mean annual precipitation = 890 mm/yr; MNDNR, 2016a; Vandegrift & Stefan, 2010).

Beginning ~150 years ago, European settlers rapidly converted the region from forest (in the southeast) and prairie (in the south central and northwest) landscapes to farmed land. Today, agricultural land use dominates the region, with the most pervasive type being corn/soy row crops grown in rotation, as well as pasture and concentrated animal feeding operations. Most of the region's wetlands have been drained via surface ditches and subsurface drain pipes or “tiles.” These changes in land drainage, together with recent human-induced changes in climate, have resulted in changes to watershed hydrology, including higher

peak flows and steeper rising limbs of river hydrographs (Foufoula Georgiou et al., 2015; Schottler et al., 2013). Water quality impairments throughout the region are widespread, with the most ubiquitous attributed to turbidity, total phosphorus (TP), fecal coliform, impaired biota, and low dissolved oxygen (MPCA, 2018a).

2.2. Water Chemistry and Flow Data: Gaged Watersheds

We used concentration and mean daily discharge data from 104 gaged sites monitored by Minnesota's Watershed Pollutant Load Monitoring Network (MPCA, 2018b). Periodic water samples and continuous flow data were collected by the Minnesota Pollution Control Agency (MPCA) throughout the year at major watershed sites (watershed areas greater than ~4000 km^2) and during the period of ice-out through 31 October at smaller subwatershed sites (MPCA, 2015). Water quality sampling efforts are conducted ~biweekly with more intensive sampling focused on snowmelt and storm events, resulting in observations distributed across the range of flows observed at each site (average # of samples per year = 25 for subwatersheds and 35 for major watersheds; MPCA, 2015). The 104 gage sites we selected for this study had >25 water chemistry samples collected across the sampling period (2000–2016) and were located in watersheds where agricultural land use is >50%. Agricultural land use included both row crop agriculture (primarily corn and soy beans) and pasture for hay.

Water chemistry samples collected at gages were analyzed for TP and soluble reactive phosphorus (SRP). Detailed methods for water chemistry data collection are described in Appendix S2. We estimated particulate phosphorus (PP) as the difference between TP and SRP. Using this approach to estimate PP is not strictly accurate, as PP estimates will also include dissolved organic phosphorus. The lack of DOP concentration data for gaged study sites causes small overestimates of the true PP concentrations and slightly underestimates the concentration of total dissolved (SRP + DOP) P concentrations.

2.3. Land Cover Attributes for Gage Sites

While all our study watersheds were dominated by agricultural land use, they spanned gradients in climate, drainage practices, lake cover, topography, and availability of near-channel sediment sources (Table S1). We delineated study watersheds using the locations of gaged monitoring sites provided by the MPCA, the USGS National Hydrography Dataset flowlines (USGS, 2015), and the USGS National Elevation Dataset 30 m digital elevation model (USGS, 2013). We used the 2011 National Land Cover Database (Homer et al., 2015) to calculate the proportional land cover of each watershed (e.g., percent agriculture, percent crops, percent pasture, percent wetlands).

We estimated river bluff area for each gaged watershed using a 3-m digital elevation model derived from LiDAR elevation data; this data set is available from the Minnesota Geospatial Information Office (http://www.mngeo.state.mn.us/chouse/elevation/lidar.html). Within a moving 12-m by 12-m window, features with elevation differences greater than 4 m were selected and converted to polygons. These polygons were clipped to a buffer that extended 3 m beyond the calculated channel size for each watershed, to select only bluff features that were adjacent to river channels. We normalized the total bluff area determined with this method by the watershed area at each gage.

The percentage of each gaged study watershed that drained through lakes (i.e., percent lake interception) was estimated by selecting lakes larger than 4 hectares, placing a pour point at the area of greatest flow accumulation in each lake and delineating the upstream watershed. We summed these "lakeshed" areas within each study watershed and divided by the study watershed area to estimate the portion of each study watershed draining through lakes.

We estimated the percent of each study watershed drained by tile (percent tile) using available estimates of the extent of tiled land area at the county level for the Upper Mississippi Basin (Schwartz, 2015) to calculate the weighted average of percent tile in each study watershed, where weights were equivalent to the portion of each watershed in each county. For study watersheds with land area not covered by Schwartz (2015), we supplemented with county-level percent tile estimates from the U.S. Department of Agriculture National Agricultural Statistics Service 2012 Census of Agriculture (USDA, 2014).

To account for large point source inputs of P, we obtained data from the MPCA for all permitted facility discharges of P between 2007 and 2011 in gaged watersheds. Permitted discharges are any discharges requiring

a permit from the National Pollutant Discharge Elimination System or State Disposal System; that is, those discharges arising from industrial facilities or wastewater treatment plants. We calculated the 5-year average annual sum of total P loads from these point sources normalized by watershed area and evaluated the average differences in point source inputs for gages exhibiting different types of P transport behavior (mobilizing, diluting, chemostatic, etc.) to assess the effect of point sources on *C*-*Q* relationships.

2.4. Characterizing P Concentration-Discharge Relationships at Multiple Temporal Scales

2.4.1. Event-Based P Transport

To characterize event-based (i.e., daily) transport behavior at gaged sites, we evaluated the parameters of the *C*-*Q* power law relationship. The power law or rating curve equation relating concentration (C) and discharge (Q) is expressed as:

$$C = aQ^b \tag{1}$$

where the curve's coefficient (a) and exponent (b) are representative of the degree, direction, and rate at which nutrients are transported as a function of stream flow. This equation can alternatively be expressed in log-log scale as:

$$\log(C) = b\log(Q) + \log(a) \tag{2}$$

where b is the slope of the linear log-log relation, and $\log(a)$ is the y-intercept. As Warrick (2015) noted, normalizing Q by the geometric mean of discharge (Q_{GM}) shifts the center of mass of the log-transformed Q data to the y-intercept, which facilitates comparison of rating curves among different watersheds and converts a into a measure of solute/particulate concentration ($\hat{a}$) at the geometric mean of Q values. Thus, we used linear regression of log-transformed P concentration on log-transformed normalized discharge using the following equation:

$$\log(C) = b\log(Q/Q_{GM}) + log\ \hat{a} \tag{3}$$

All regressions were performed in R. We evaluated the fit of the power law relationship to the *C*-*Q* data for TP, SRP, and PP using the p and R^2 values of this linear regression. We visually inspected plots of *C*-*Q* data for (1) linearity and (2) seasonal trends. Where threshold relationships between C and Q were evident, we conducted breakpoint regression using the *segmented*() package in R (Muggeo, 2017), to quantify breakpoint values and slope values before and after the breakpoint.

We used the slope b of the log-log *C*-*Q* power law together with the coefficient of variation of C relative to the coefficient of variation of Q (CV_C/CV_Q), to summarize key elements of transport on event-based timescales. This approach, demonstrated by Musolff et al. (2015), provides useful information about multiple possible transport behavior mechanisms. A $CV_C/CV_Q << 1$ suggests that concentrations are relatively constant compared to variability in flow, indicating chemostatic behavior; by contrast, a larger CV_C/CV_Q indicates chemodynamic behavior (i.e., comparatively large variations in concentration relative to variation in flow). Thompson et al. (2011) suggested that CV_C/CV_Q values ≈ 0.3 or less were indicative of chemostatic behavior. Plotting CV_C/CV_Q in relation to the slope b of the power law yields information about whether chemodynamic behavior follows a diluting ($b < 0$), mobilizing ($b > 0$), or reactive ($b \approx 0$) pattern.

We sought to evaluate whether phosphorus transport behavior was related to land cover and land use by conducting linear regression of b on the following attributes: bluff area, percent lake interception area, percent wetland cover, percent agriculture, percent row crops, percent pasture, and percent tile. All explanatory variables were inspected and transformed for normality prior to regression (see Appendix S3). We conducted analysis of b in relation to land cover and land use attributes only across sites with significant *C*-*Q* relationships ($p < 0.05$).

2.4.2. Interannual P Transport

To evaluate how P concentrations varied with flow on an interannual basis, we calculated the slope (b_{ann}) of the relationship between mean annual flow-weighted P concentrations and annual water yield for each gaged watershed on a log-log scale (*sensu* Godsey et al., 2009). Mean annual flow-weighted concentrations were calculated as $\Sigma\ (Q_iC_i)/\Sigma\ (Q_i)$, where i refers to each sample collected during the calendar year. We

calculated water yield (mm/yr) by converting average daily flows (m^3/s) at each site, available from Minnesota Department of Natural Resources (2018), to total daily flows, dividing by watershed area, and then summing normalized daily flow values over the course of a calendar year. Slope (b_{ann}) values near zero on the log-log plot suggest a chemostatic or chemoreactive regime, whereas slope values near −1 and 1 would reflect simple dilution and mobilization of P, respectively, as a function of discharge on an interannual basis. We restricted this analysis to sites with at least 10 water chemistry measurements per year and at least 5 years of data, leaving 55 gaged watersheds (of the original 104) for analysis of interannual P transport.

2.5. Phosphorus Loads as a Function of Discharge and Season

While *C-Q* relationships are often used to characterize transport behavior of water chemistry constituents, effective nutrient management is also contingent on understanding the comparative importance of various flow conditions to nutrient export in terms of mass (e.g., Hubbard et al., 2011; Turner et al., 2007). Thus, we used daily load estimates for phosphorus, available for a subset of gages from the MPCA's Watershed Pollutant Monitoring Network data portal (see Appendix S4), to evaluate export of P load as a function of discharge and to identify which flow conditions were the most important in contributing to export of TP, SRP, and PP. We restricted our analysis of phosphorus loads and flow conditions to gages with at least 5 years of daily load and flow data available during 2009–2015, leaving 22 gages. To characterize daily flow condition, we estimated exceedance probability (EP) of daily flow values at each gage over the period of record (2009–2015) and matched daily EP values to the daily load data. We then estimated the percentage of total P load that was accounted for by SRP and PP exported under various flow conditions (as indicated by EP) in different seasons, over the whole period of record for each gage.

For the same subset of gage sites (i.e., sites with > = 5 years of annual load and flow data available between 2009 and 2015, n = 22), we further examined the sensitivity of nutrient export to variation in runoff on an interannual basis, by evaluating the relationship between annual load and annual water yield. Annual loads were obtained by summing daily loads over the course of a year.

2.6. Field Data Set: Dissolved and Particulate P Under Multiple Flow Conditions

To better understand how phosphorus transport was influenced by biogeochemical processes and landscape effects, we supplemented our analysis of *C-Q* relationships at gage sites with an extensive field data set collected at ditch, stream, and river sites in the same study region between 2013 and 2016 (Figure 1). This data set is publicly available and described in detail by Dolph, Hansen, Kemmitt, et al. (2017) as well as in Appendix S2. Briefly, SRP, PP, and suspended chlorophyll *a* (Chla) concentrations were determined for water samples collected from 176 sites located in three major watersheds (HUC8 scale; USGS, 2017), during 14 independent sampling events that targeted differing flow conditions and times during the growing season (Table S2). Only a subset of sites was sampled during each sampling event (Table S2). Two of the sampling events occurred in the Chippewa River Basin, 2 in the Cottonwood River Basin, and 10 in the Le Sueur River Basin. Flow conditions at the time of sampling were characterized by the 25-year EP of flow at the gaged outlet of each major watershed (i.e., Chippewa, Cottonwood, and Le Sueur), based on daily discharge data available from MNDR (2018). Although flow at the outlet is not precisely representative of flow conditions further upstream in the basin, we have shown previously that discharge conditions across study sites scaled reasonably well with drainage area for multiple flow events (Dolph et al., 2017).

We evaluated SRP and PP concentration data in relation to Chla, across all sampling events, to determine how Chla (as a proxy for suspended algal biomass) might be related to phosphorus concentrations under a range of flow conditions. Using previously published estimates for stoichiometric relationships between algal carbon and chlorophyll (Dolph, Hansen, & Finlay, 2017) and stoichiometric ratio between algal carbon and phosphorus using the Redfield ratio, we estimated the contribution of algal P to PP and TP concentrations during each of our sampling events. We also evaluated SRP and PP concentrations in relation to percent lake interception area and percent wetland cover across all sites.

3. Results

3.1. Event-Based Transport Behavior

Measured TP concentrations across the 104 gage sites included in this study ranged from 0.01 to 8.40 mg/L (mean = 0.26 mg/L; Table S3). Although we observed varied types of P transport behavior across the entire

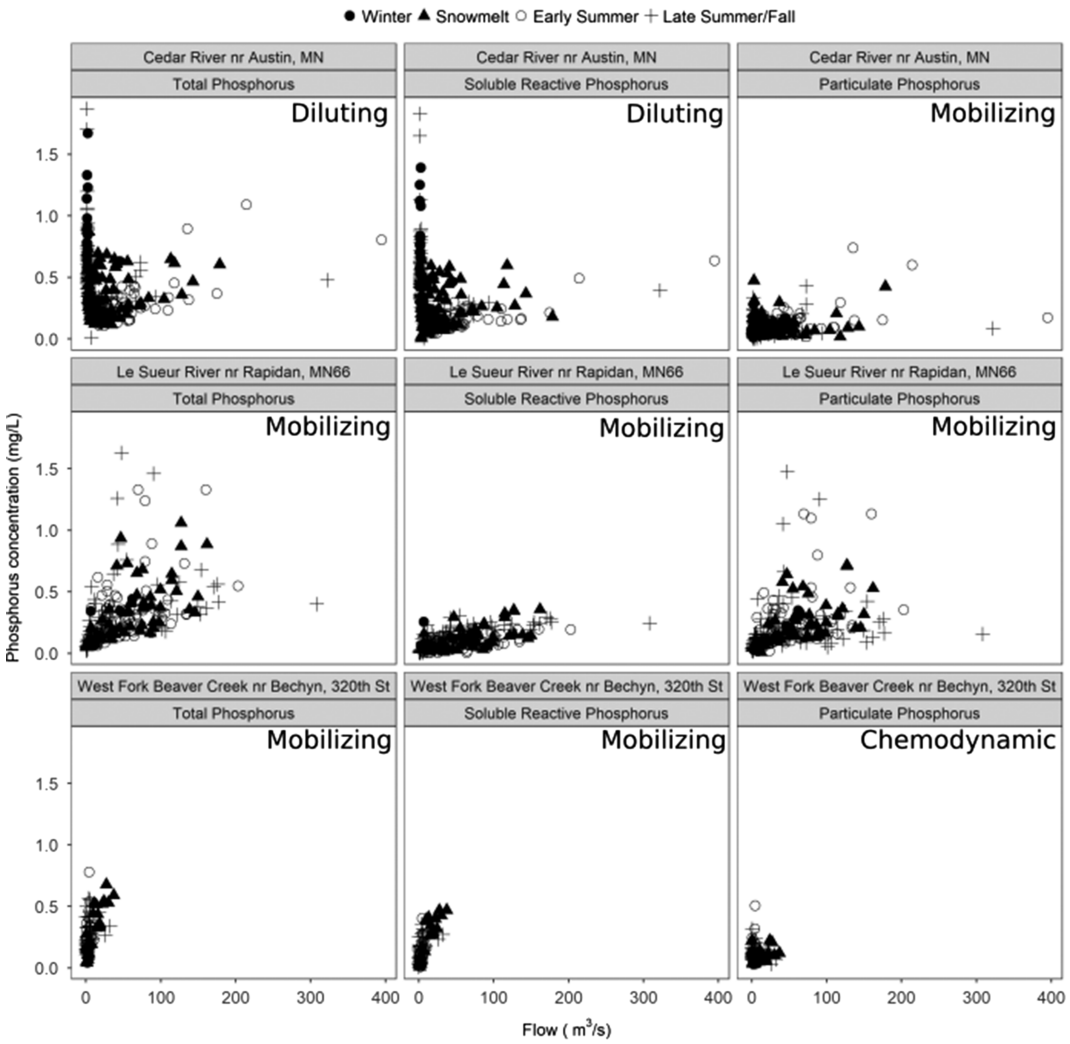

Figure 2. Examples of raw concentration-discharge relationships for a subset of three study sites illustrating the variety of transport regimes (mobilizing, diluting, and chemodynamic) observed across the study dataset for total phosphorus (left panels), soluble reactive phosphorus (middle panels), and particulate phosphorus (right panels).

data set (e.g., mobilizing, diluting, chemodynamic; e.g., Figure 2), mobilizing behavior was by far the most common, observed for ~80% of study watersheds on a daily timescale (Figure 3). However, approximately half of all sites with mobilizing behavior exhibited *C*-*Q* relationships with low R^2 values (<0.2) and *b* values considerably <1, indicating that mobilizing behavior at these sites was weak (Table S4).

A comparatively small number of sites exhibited diluting behavior ($b < 0$) for TP (12%), SRP (10%), and PP (9%). These sites were characterized by much higher P inputs from permitted discharges (i.e., wastewater treatment plants), on average, than sites characterized by other types of transport behavior (Table S5). On average across all gages, permitted facility point source discharges constituted a small proportion of annual river P export (average = 9.5%). However, the small number of sites exhibiting diluting behavior for P (e.g., the Shell Rock and Cedar Rivers) stood out as outliers with permitted discharges accounting for 55% and 59% of annual P export, respectively.

A relatively small number of sites exhibited chemodynamic behavior for TP, SRP, or PP (6%, 8%, and 9%, respectively). Only one site exhibited *C*-*Q* behavior that could be readily classified as "chemostatic" (for SRP) on an event timescale.

Although power law relationships between *C* and *Q* were statistically significant for the majority of sites included in this study (Figure 3), many of these would be better described with threshold relationships,

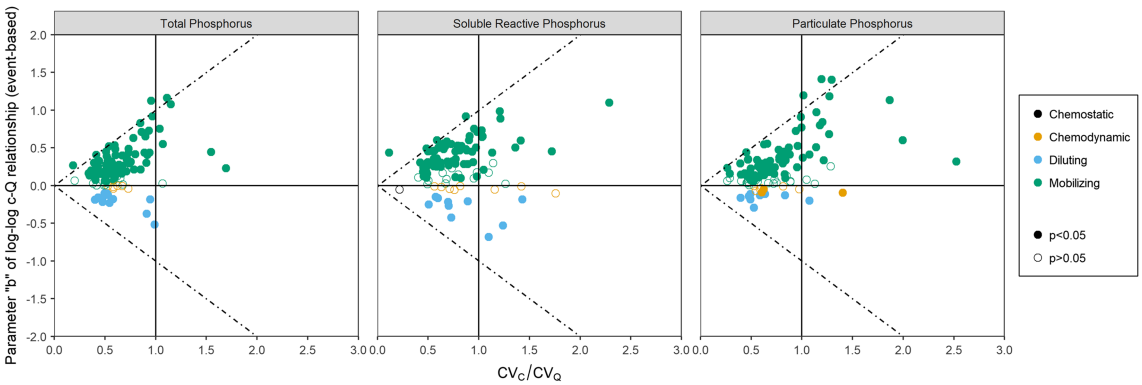

Figure 3. Parameter *b* (slope) of the event-scale log-log *C-Q* relationship for total phosphorus (left), soluble reactive phosphorus (middle), and particulate phosphorus (right), in relation to CV_C/CV_Q for 104 agriculturally dominated gaged watersheds. Symbols indicate whether the power law relationship for *C-Q* was significant ($p < 0.05$, solid circles) or not ($p > 0.05$, open circles) for each P constituent. Color indicates export behavior based on criteria defined for *b* and CV_C/CV_Q. Chemostatic: $-0.1 < b < 0$ and $CV_C/CV_Q < 0.3$ (sensu Thompson et al., 2011); chemodynamic: $-0.1 < b < 0$ and $CV_C/CV_Q > 0.3$; diluting: $b < -0.1$; mobilizing: $b > 0$.

especially for PP. Nearly a fifth of gaged sites (19%; n = 20/104) exhibited threshold behavior for PP in relation to *Q* on a log-log scale, with a lower and higher slope below and above a breakpoint value, respectively (Figure 4; Figures S3–S6). All but one of these sites was located in the Minnesota River Basin, and most of these were characterized by high bluff extent (i.e., normalized bluff area above the median value across all sites; Figures S5–S6). Breakpoint regression at these sites indicated that the inflection point for sites exhibiting this threshold relationship occurred at log $Q/Q_{GM} = 0.16$, on average (range = −2.21–1.75; Table S6). These values corresponded to an average flow EP of 30% (range = 5–74%). In contrast to sites exhibiting threshold relationships, a number of sites were characterized by steep and linear mobilizing relationships between *Q* and PP; this group included all of the sites with high bluff extent in the UMBR Basin (Figure 4; Figure S6). Finally, a small number of sites with positive slopes for the PP-*Q* relationship exhibited peaked threshold relationships (i.e., positive slope before the breakpoint, negative slope after the breakpoint; Figure S3).

Mobilizing relationships for SRP appeared largely linear (Figures S7–S10). When samples were viewed on a seasonal basis, it became evident that samples collected in late summer and fall (July–October) contributed to considerable scatter in the *C-Q* relationships for SRP at many sites, particularly at lower flows (e.g., Figure 4, top panel). At 27% of sites (n = 28), SRP concentrations were considerably elevated during late summer low flows compared to other times of year, modifying the overall nature of *C-Q* relationships across all samples (Figure 4; also see Appendix Figures S7–S10).

3.2. Landscape Modifiers of Event-Scale Hydrological Responses

Across the entire set of gaged agricultural watersheds, simple linear regression indicated a significant positive relationship between normalized bluff area and the slope *b* of the *C-Q* relationship for TP and PP but not SRP (Table S7). When we split the data set by major river basin, however, we observed distinct behaviors between *b* and bluff extent. We restricted this analysis to those major river basins that contained at least 10 gages (i.e., the Minnesota River Basin, the Red River Basin, and the UMBR Basin). For all three major basins, the slope of *b* for TP-*Q* was significantly related to bluff area across sites (Figure 5; Table S7). However, the rate of increase in *b* of TP per unit bluff area appeared higher across sites in the UMBR basins relative to sites in the Minnesota and Red River Basins. The slope of PP-*Q* was also significantly related to bluff area in the Minnesota and UMBR Basins but not in the Red River Basin (Figure 5; Table S7), with the rate of increase in *b* per unit bluff area higher in the UMBR than in the Minnesota. Finally, slope *b* of the SRP-*Q* relationship was related to bluff extent in the UMBR and Red River Basins but not in the Minnesota River Basin.

Across all gages, simple linear regression indicated a significant negative relationship between percent lake interception area and the slope *b* of the *C-Q* relationship for TP, PP, and SRP. However, bluff extent and percent lake interception area were also significantly and negatively correlated across sites ($F = 10.7$, df = 1,109, $R^2 = 0.09$, $p = 0.001$), confounding lake and bluff effects. Once bluff effects were accounted for, there was a

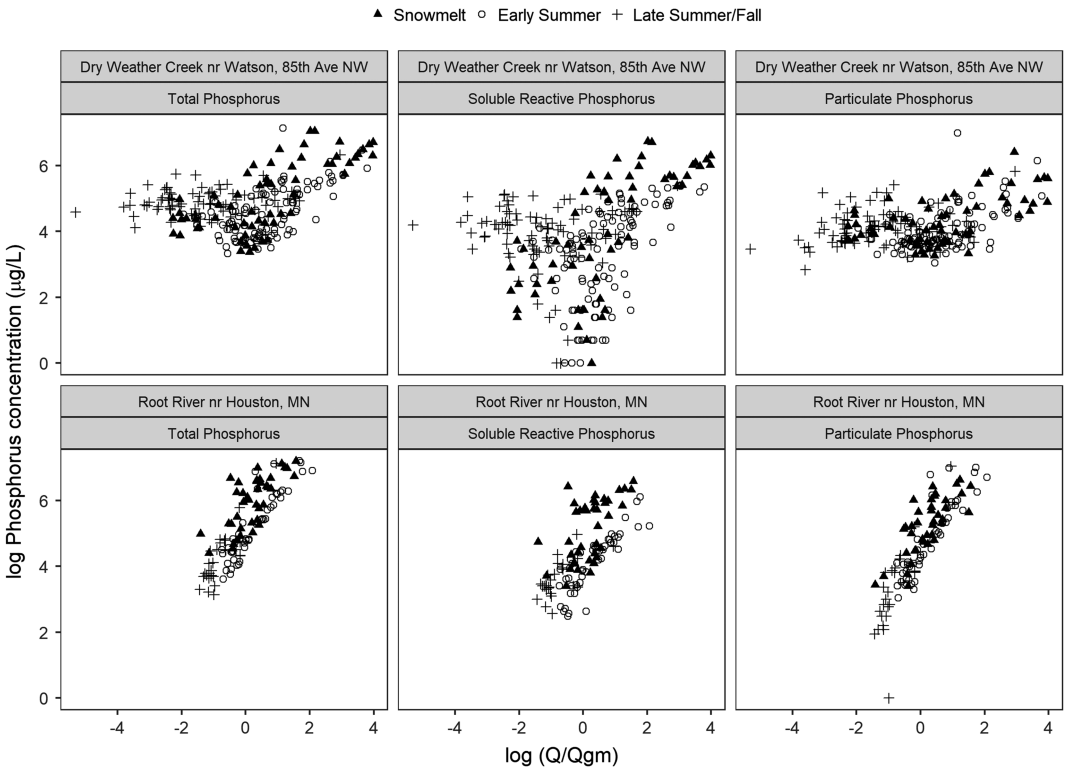

Figure 4. Concentration-discharge relationships for total phosphorus (TP; left panels), soluble reactive phosphorus (SRP; middle panels), and particulate phosphorus (PP; right panels) from two representative sites characterized by high bluff extent in the Minnesota River Basin (top; Dry Weather Creek nr Watson, 85th Ave NW) and the Upper Mississippi-Black-Root River Basin (bottom; Root River nr Houston, MN). Symbols indicate the season in which P samples were collected. No winter samples are available for these gages. In the Minnesota River Basin site, PP and TP show a threshold relationship to discharge, whereas SRP shows an approximately linear response to discharge during snowmelt and early summer, but elevated concentrations at low discharge in late summer/fall modify the overall *C-Q* relationship. By contrast, TP, PP, and SRP show approximately linear relationships to flow at the Root River gage site in the Upper Mississippi-Black-Root Basin.

remaining weak and marginally significant ($p < 0.1$) negative relationship between the resulting residuals and percent lake interception area across all gaged sites for TP and PP but not SRP (Table S7). Because bluff effects on b were distinct across major river basins (i.e., stronger effects in the UMBR vs the Minnesota River Basin and Red River Basin), we also tested the effects of percent lake interception area separately for the three major basins. In the Red River and UMBR Basins, there was no effect of percent lake interception area on b after the effects of bluffs were accounted for, for any P constituent (Table S7). In the Minnesota River Basin, there was a significant negative effect of percent lake interception area on b of PP (but not of TP or SRP), after accounting for bluff effects. We likewise examined relationships between percent wetland cover and b. Across all sites, we did observe apparent significant negative effects between percent wetland cover and b of TP, PP, and OP, after bluff effects were accounted for. However, this effect was eliminated when we evaluated sites separately by major river basin, suggesting that the apparent relationship with wetlands across all sites was likely a spurious effect stemming from the stronger positive influence of bluffs on P transport in the UMBR compared to other basins. After accounting for bluff effects and major river basin, there were no significant relationships between b and percent wetland cover, for sites in any of the three major river basins we studied (Table S7).

To further examine the potential for lake interception and wetland cover to impact PP or SRP concentrations in agricultural river networks under various flow conditions, we evaluated SRP and PP concentrations in relation to percent lake interception and percent wetland cover for 176 ditch, stream, and river sites located within our study region (Figure 1). These sites were located predominantly upstream of areas with high bluff extent. For 7 of 14 sampling events during which we sampled these sites, PP exhibited significant positive

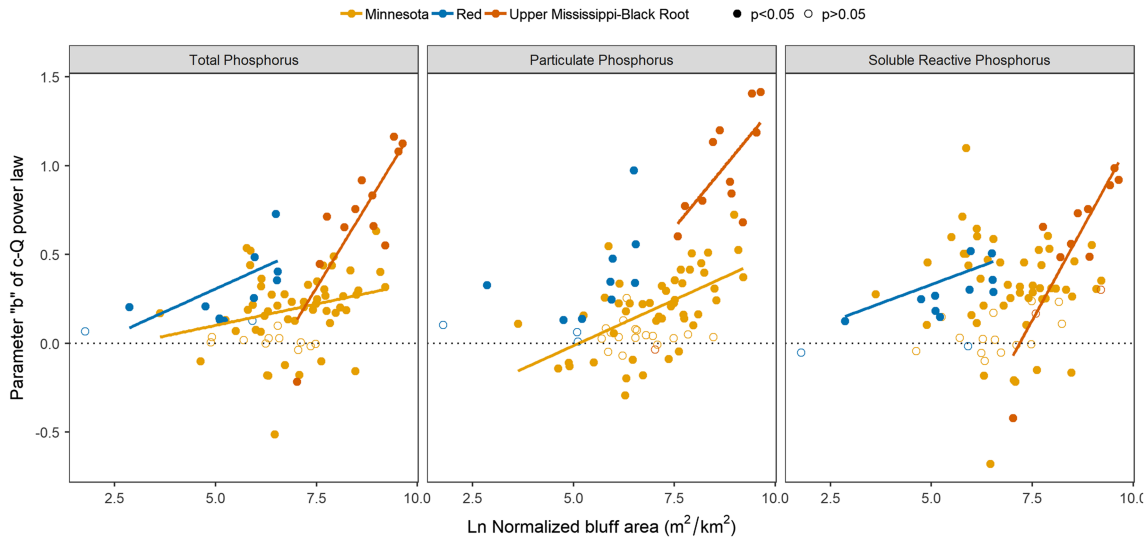

Figure 5. Parameter *b* of the *C-Q* power law relationship for total phosphorus, particulate phosphorus, and soluble reactive phosphorus, in relation to normalized bluff area (log transformed), across sites in the Red River (blue; n = 12), Minnesota River (light orange; n = 64), and Upper Mississippi-Black Root River (dark orange; n = 12) basins. Symbols indicate whether the power law relationship for *C-Q* was significant ($p < 0.05$, solid circles) or not ($p > 0.05$, open circles) for each P constituent. Solid lines show significant statistical relationships between *b* and bluff extent for each P constituent (across sites with statistically significant power law relationships). All regression parameters are shown in Appendix Table S7.

relationships to percent lake interception (Figure S11; Table S8). SRP concentrations showed slight negative relationships to percent lake interception in 2 of the 14 sampling events, both of which took place in the Chippewa River Basin (Figure S12; Table S8). The net effect of percent lake interception on TP concentrations was positive relationships in 7 of 14 sampling events and a negative relationship between TP and percent lake interception in one sampling event (Figure S13; Table S8).

In addition to lake effects, we also evaluated the impact of wetland cover on SRP, PP, and TP concentrations across field sites. Because percent lake interception and percent wetland cover were correlated across sites ($F = 40.77$, df = 1, 170, $R^2 = 0.19$, $p < 0.0001$,), we evaluated wetland effects after accounting for lake interception effects, by evaluating the residuals of the regression between P concentration versus lake interception in relation to percent wetland cover. After accounting for lake interception effects, we found significant positive relationships between TP and percent wetland cover during the highest flow event we sampled (in September 2016) and during two low flow events (one in August 2013 and one in August 2015; Table S9). We also found positive relationships between percent wetland cover and PP during a moderate-high flow event in July 2015 and a low flow event in November 2015 (Table S9). We found positive relationships between wetland cover and SRP during the high flow event in September 2016 and during the moderate high flow event in July 2015 (Table S9).

Slope (*b*) values were not correlated with watershed size for TP, SRP, or PP (Figure S2).

3.3. Effect of Land Use Practices on P Transport

We evaluated relationships between *b* of SRP, PP, and TP with percent agriculture, percent crops, percent pasture, and percent tile to understand potential impacts of different agricultural land use practices on P transport. Most of our sites were dominated by row crops (average % crops across sites = 72.4%) rather than pasture (average % pasture across sites = 6.5%; Table S1). However, a small subset of sites was characterized by comparatively less crop cover (minimum value = 29.4%) and comparatively more pasture cover (maximum value = 29.3%). As for lake cover, the amount of land in crops versus pasture was related to bluff extent. Sites in the UMBR in particular were characterized by relatively high prevalence of bluffs and pasture and relatively low prevalence of crops (Figure S14). Thus, to account for confounding effects of basin, bluff extent, and different types of agricultural land cover, we evaluated the relationship between *b* and percent pasture and percent crops and percent agriculture (pasture + crops) separately for each major river basin, after accounting for bluff effects. There were no relationships between percent agriculture, percent crops,

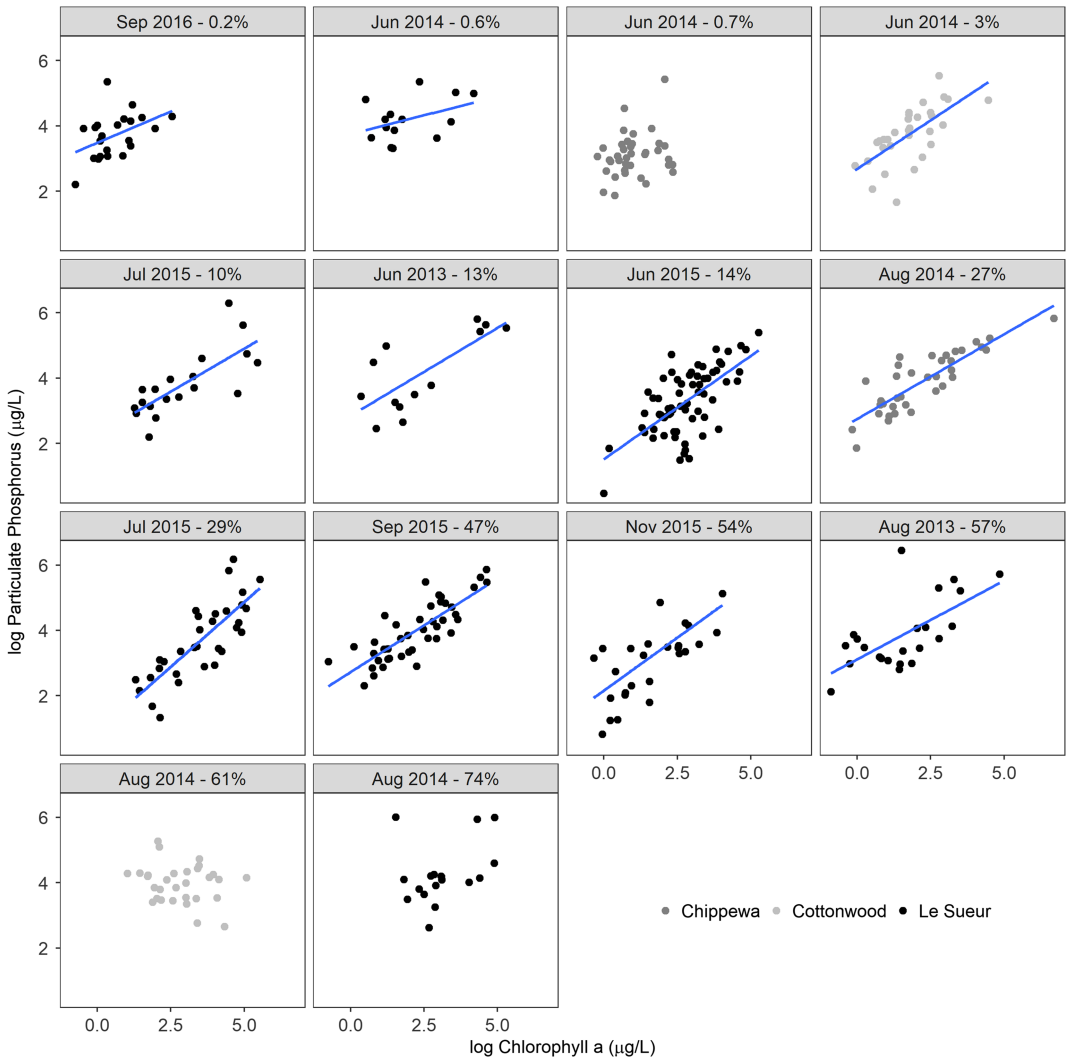

Figure 6. Particulate phosphorus concentrations in relation to chlorophyll a concentrations measured at a total of 176 ditch, stream, and river sites sampled over 14 different sampling events and 3 major (HUC8 scale) watersheds. Point color indicates major watershed where sites were located. Lines indicate statistically significant linear regression relationships. The percent values in the facet titles indicate the exceedance probability of flow at the outlet of each major watershed during sampling.

or percent pasture and *b* of TP, PP, or SRP for sites in the Minnesota or Red River Basins, after accounting for bluff effects (Table S10). However, in the UMBR, there was a significant negative relationship between *b* of SRP and percent pasture, once bluff effects were accounted for (Table S10). Conversely, there was a significant positive relationship between *b* of SRP and percent crops in the UMBR, after accounting for bluff effects. There were no relationships between percent pasture or percent crops and *b* of PP or TP in the UMBR, after accounting for bluff effects.

Across all sites, percent tile drainage showed significant negative relationships with *b* for TP and PP but not SRP (Table S11; Figure S15). After the effects of bluff extent were accounted for, significant and stronger negative relationships between percent tile and *b* were evident for TP, PP, and SRP (Table S11). When sites were analyzed separately by major river basins, however, there were no significant relationships between *b* and percent tile for any P constituent in any major basin, after bluffs effects were accounted for (Table S11).

3.4. Effects of Algal Assimilation on P Transport

We used water chemistry data, which included Chla concentrations, collected from the 176 additional field sites to examine the potential for biological processes to impact PP or SRP concentrations. PP concentrations

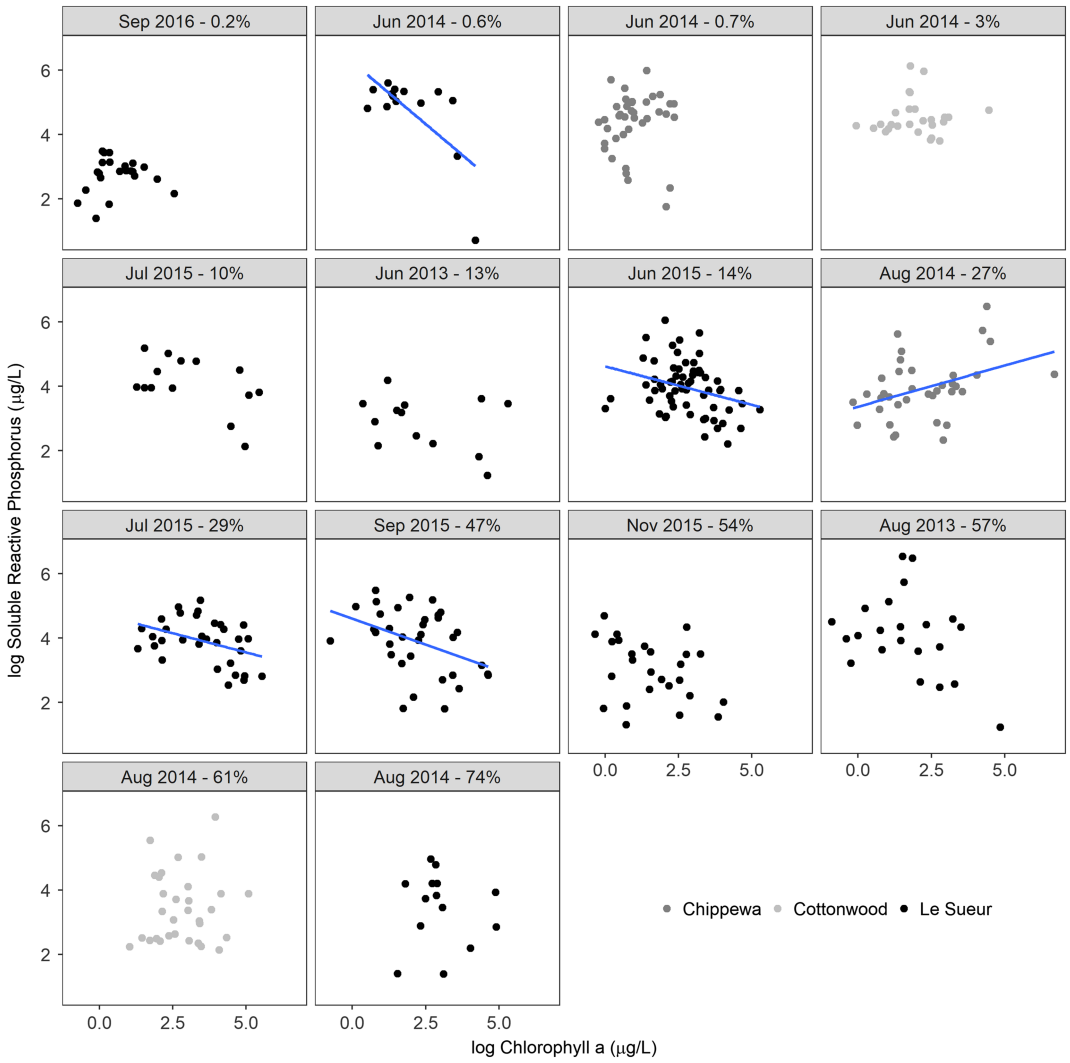

Figure 7. Soluble reactive phosphorus concentrations in relation to chlorophyll a concentrations measured at a total of 176 ditch, stream, and river sites sampled over 14 different sampling events and 3 major (HUC8 scale) watersheds. Point color indicates major watershed where sites were located. Solid lines indicate statistically significant linear regression relationships ($p < 0.05$). The percent values in the plot headings indicate the exceedance probability of flow at the outlet of each major watershed during sampling.

were significantly and positively correlated with Chla concentrations for 11 of the 14 sampling events we conducted (Figure 6; Table S12). SRP concentrations were significantly and negatively correlated with Chla during 4 of 14 sampling events and positively correlated during 1 sampling event (Figure 7; Table S12). For an additional three sampling events, there were marginally significant negative relationships between Chla and SRP ($p < 0.1$; Figure 7).

Previously, we estimated the ratio of C:Chla for suspended algae in one subbasin of our study region as 23.60gC/gChla (Dolph, Hansen, & Finlay, 2017). Based on the Redfield ratio, the approximate molar ratio of C:P in algal tissue is expected to be 106:1 or 41.10 gC/gP by mass. Using these conversion factors, we estimated that the mass ratio of P:Chla for our field site streams would be 23.60 gC/gChla/41.10 gC/gP = 0.57 gP/gChla. We estimated the proportional contribution of suspended algal biomass to concentrations of PP and TP in the water column by multiplying suspended Chla by the P:Chla ratio of 0.57 and by dividing the concentration of PP and TP. Across all study sites and sample dates, algal biomass accounted for approximately 22% of PP concentrations and 9% of TP concentrations, on average. However, the proportional contribution of suspended algae to PP and TP concentrations in the water column was highly dependent on site

and sampling date (Figure S16). Mean contribution of estimated algal P to PP concentrations across all sites ranged from 3% (during an extreme flooding event in September 2016) to 54% (during moderately high flows in July 2015).

3.5. Interannual Transport Behavior

For the 55 agriculturally dominated gaged watersheds in our study for which water yield and annual concentration data were available, we found no statistically significant relationship (at $p < 0.05$) between mean annual P concentrations and water yield for >80% of sites (Table S12; Figures S17–S19). This finding suggests largely chemostatic or chemoreactive behavior for all forms of P over interannual timescales. However, these relationships were based on a relatively small number of data points (i.e., 5–10) for each site, making evaluation of statistical significance difficult. A number of sites appeared to exhibit at least weakly mobilizing or diluting behavior for one or more P constituents, despite lack of statistical significance in these relationships (Figures S17–S19). For example, 29% (n = 16/55) of sites exhibited marginally significant mobilizing behavior ($b_{\mathrm{ann}} > 0$, $R^2 > 0.2$ and $p < 0.1$) for SRP at interannual scales. A smaller number of sites exhibited marginally significant mobilizing behavior for PP and TP (7% and 15%, respectively). A small percentage of sites also indicated marginally significant diluting behavior ($b_{\mathrm{ann}} < 0$ and $p < 0.1$) for SRP (2%, n = 1/55), PP (9%, n = 5/55), and TP (4%, n = 2/55). b_{ann} was not related to watershed size for TP, SRP, or PP (Figure S2).

3.6. Contribution of Soluble Reactive P and Particulate P to Total P Export

On average across all gaged sites for which load information was available (n = 22), SRP and PP accounted for 53% and 47% of the total P load, respectively, over the period of record between 2009 and 2015. At some gages, the total P load was dominated by contributions from SRP, ranging as high as 74% of TP load for the gage at Cedar River nr Austin, MN (Table S1). Conversely, other gages were dominated by PP export, with the contribution of PP to TP load ranging as high as 71%, for the gage at the Le Sueur River nr Rapidan, CR8 gage. (Table S1).

3.7. P Export and Flow Condition

We observed strong linear fits between mean annual loads of SRP and PP and annual water yield, for ~80% of gage sites included in this study for which load information was available (n = 22; Figure 8). For most sites, the slope of the relationship between annual load and water yield was higher for SRP than for PP (i.e., indicating a greater increase in SRP load per unit discharge). However, at sites with high bluff extent (Cottonwood River nr New Ulm; Le Sueur River nr Rapidan, CR8; Le Sueur River nr Rapidan, MN66; Maple River nr Rapidan, CR35; Redwood River nr Redwood Falls, MN), SRP and PP load-water yield relationships tended to exhibit similar slope values. There was a smaller subset of sites (n = 4; 18%) that exhibited no significant linear relationship between load and discharge for one or more P constituents (Table S13). One gage site with high bluff extent (Whitewater River nr Beaver, CSAH30) exported disproportionately high loads of TP, PP, and SRP relative to water yield in 1 year (2010) that prevented linear relationships between water yield and annual load for TP and PP. It is worth noting that the region near the Whitewater River gage experienced an extremely large storm event in September 2010 (Ellison et al., 2011).

On average across gaged sites, 73% of TP exported load occurred during flows associated with = <10% EP (range = 50–92%; Table 1), over the period of record from 2009 to 2015. Flows with EPs between 10% and 25% accounted for 15% of TP export, on average (range = 5–26%), and flows with EPs between 25% and 100% accounted for 12% of TP export, on average (range = 2–35%). High flows during snowmelt and spring/early summer seasons contributed the greatest cumulative loads to TP export across most sites, although high flows during late summer and fall also made important contributions to cumulative TP export (Figure 9). The site with the highest bluff extent in Figure 9 (Whitewater River nr Beaver, CSAH30) exported the largest portion of cumulative TP load during a high flow event in late summer/fall; this export corresponds to the same high flow event in September 2010 mentioned above.

SRP and PP accounted for similar proportions of total TP export under high flow conditions. On average across gages, 38% and 34% of cumulative TP export was contributed by SRP and PP during high flows, respectively (Table 1). The contribution of SRP was higher than that of PP during snowmelt high flows, on average, and the relative contribution of PP was higher than that of SRP during spring/early summer high flows (Figure 9). When viewed across individual sites, it was evident that TP export at high flow condition is dominated by PP export at sites with higher bluff extent and dominated by SRP export at sites with lower

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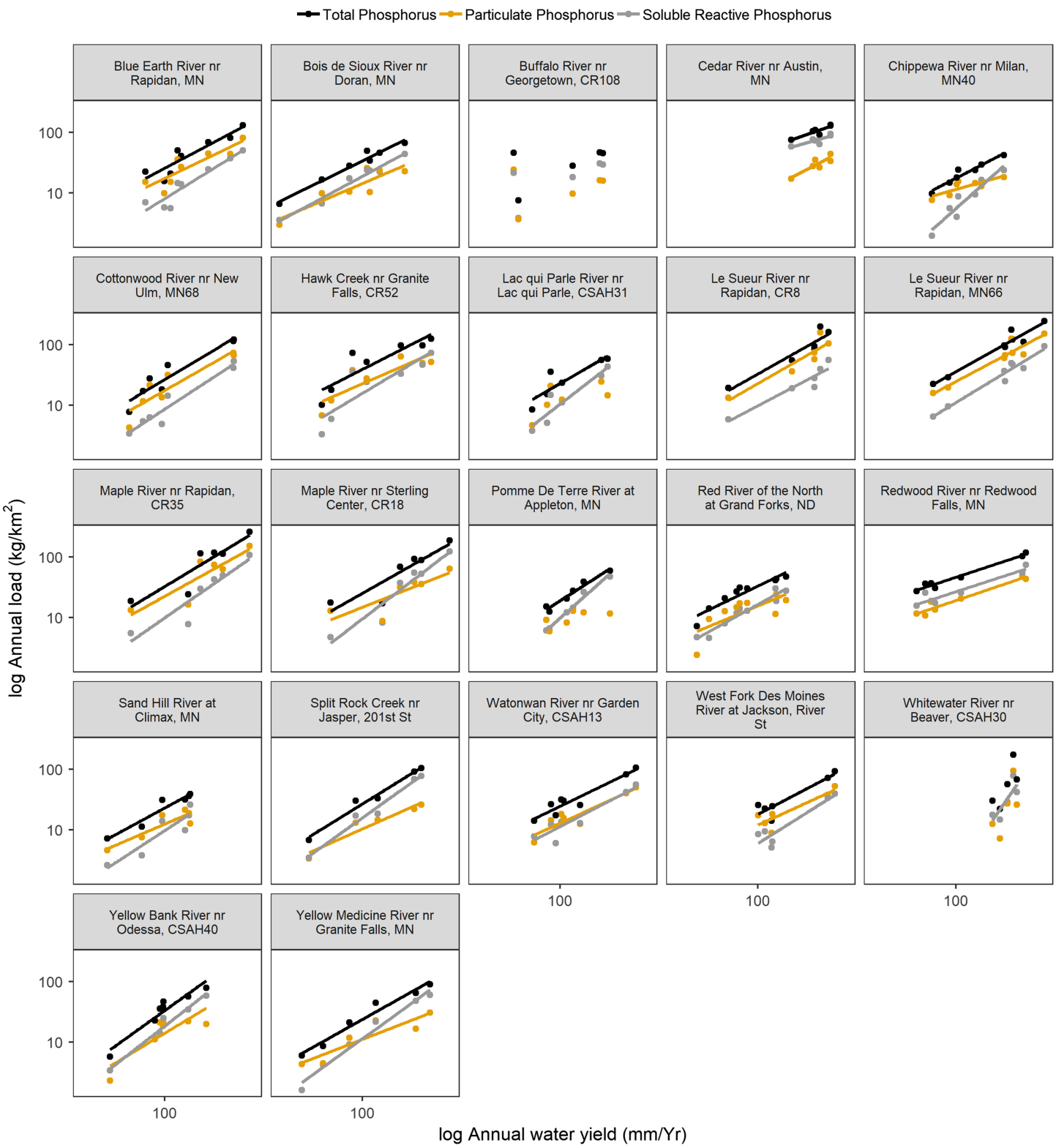

Figure 8. Annual load of total phosphorus, soluble reactive phosphorus, and particulate phosphorus in relation to annual water yield (log-log scale) for 22 gage sites for which at least 5 years of annual load data were available. Solid lines show linear regression relationships.

Table 1
Proportional Contribution of SRP and PP to Cumulative TP Export Over the Period of Record (2009–2015), During High Flow Conditions (Flow Exceedance Probability < = 10%), Moderate Flows (Flow Exceedance Probability 10–25%), and Low Flows (Flow Exceedance Probability 25–100%) for 22 Gages With Load Information Available.

Name	P Constituent	EP 0–10%	EP 10–25%	EP 25–100%	% Contribution to total TP export
Blue Earth River nr Rapidan, MN	Total phosphorus	68.59	17.34	14.07	100.00
Blue Earth River nr Rapidan, MN	Soluble reactive phosphorus	25.82	6.04	5.25	37.12
Blue Earth River nr Rapidan, MN	Particulate phosphorus	42.77	11.30	8.82	62.88
Bois de Sioux River nr Doran, MN	Total phosphorus	64.04	26.26	9.70	100.00
Bois de Sioux River nr Doran, MN	Soluble reactive phosphorus	38.06	15.61	6.06	59.74
Bois de Sioux River nr Doran, MN	Particulate phosphorus	25.98	10.64	3.64	40.26
Buffalo River nr Georgetown, CR108	Total phosphorus	68.93	19.75	11.32	100.00
Buffalo River nr Georgetown, CR108	Soluble reactive phosphorus	45.57	11.36	7.08	64.01
Buffalo River nr Georgetown, CR108	Particulate phosphorus	23.36	8.39	4.25	35.99
Cedar River nr Austin, MN	Total phosphorus	49.87	15.10	35.03	100.00
Cedar River nr Austin, MN	Soluble reactive phosphorus	33.17	11.33	29.00	73.49
Cedar River nr Austin, MN	Particulate phosphorus	16.71	3.77	6.03	26.51
Chippewa River nr Milan, MN40	Total phosphorus	64.83	18.61	16.56	100.00
Chippewa River nr Milan, MN40	Soluble reactive phosphorus	32.57	5.31	5.32	43.21
Chippewa River nr Milan, MN40	Particulate phosphorus	32.26	13.29	11.25	56.79
Cottonwood River nr New Ulm, MN68	Total phosphorus	78.26	13.15	8.60	100.00
Cottonwood River nr New Ulm, MN68	Soluble reactive phosphorus	29.40	5.03	3.00	37.43
Cottonwood River nr New Ulm, MN68	Particulate phosphorus	48.86	8.12	5.59	62.57
Hawk Creek nr Granite Falls, CR52	Total phosphorus	79.14	11.25	9.60	100.00
Hawk Creek nr Granite Falls, CR52	Soluble reactive phosphorus	34.42	6.31	6.32	47.05
Hawk Creek nr Granite Falls, CR52	Particulate phosphorus	44.72	4.94	3.28	52.95
Lac qui Parle River nr Lac qui Parle, CSAH31	Total phosphorus	83.05	11.82	5.13	100.00
Lac qui Parle River nr Lac qui Parle, CSAH31	Soluble reactive phosphorus	47.46	5.56	2.58	55.60
Lac qui Parle River nr Lac qui Parle, CSAH31	Particulate phosphorus	35.59	6.26	2.55	44.40
Le Sueur River nr Rapidan, CR8	Total phosphorus	73.59	16.11	10.30	100.00
Le Sueur River nr Rapidan, CR8	Soluble reactive phosphorus	20.29	4.95	3.40	28.64
Le Sueur River nr Rapidan, CR8	Particulate phosphorus	53.30	11.17	6.90	71.36
Le Sueur River nr Rapidan, MN66	Total phosphorus	73.69	18.28	8.03	100.00
Le Sueur River nr Rapidan, MN66	Soluble reactive phosphorus	23.91	7.18	3.00	34.09
Le Sueur River nr Rapidan, MN66	Particulate phosphorus	49.79	11.10	5.02	65.91
Maple River nr Rapidan, CR35	Total phosphorus	78.50	12.21	9.28	100.00
Maple River nr Rapidan, CR35	Soluble reactive phosphorus	29.79	5.28	3.45	38.52
Maple River nr Rapidan, CR35	Particulate phosphorus	48.71	6.93	5.84	61.48
Maple River nr Sterling Center, CR18	Total phosphorus	72.24	15.12	12.64	100.00
Maple River nr Sterling Center, CR18	Soluble reactive phosphorus	45.31	8.59	6.24	60.14
Maple River nr Sterling Center, CR18	Particulate phosphorus	26.93	6.53	6.40	39.86
Mustinka River nr Wheaton, CSAH9	Total phosphorus	80.63	14.83	4.54	100.00
Mustinka River nr Wheaton, CSAH9	Soluble reactive phosphorus	57.86	9.21	2.88	69.96
Mustinka River nr Wheaton, CSAH9	Particulate phosphorus	22.76	5.62	1.66	30.04
Pomme De Terre River at Appleton, MN	Total phosphorus	66.08	19.78	14.13	100.00
Pomme De Terre River at Appleton, MN	Soluble reactive phosphorus	52.31	9.24	6.77	68.32
Pomme De Terre River at Appleton, MN	Particulate phosphorus	13.78	10.54	7.37	31.68
Redwood River nr Redwood Falls, MN	Total phosphorus	59.79	14.62	25.59	100.00
Redwood River nr Redwood Falls, MN	Soluble reactive phosphorus	32.26	8.20	17.73	58.19
Redwood River nr Redwood Falls, MN	Particulate phosphorus	27.54	6.42	7.85	41.81
Sand Hill River at Climax, MN	Total phosphorus	83.39	10.65	5.95	100.00
Sand Hill River at Climax, MN	Soluble reactive phosphorus	40.39	4.34	3.01	47.74
Sand Hill River at Climax, MN	Particulate phosphorus	43.00	6.31	2.95	52.26
Split Rock Creek nr Jasper, 201st St	Total phosphorus	79.83	12.12	8.06	100.00
Split Rock Creek nr Jasper, 201st St	Soluble reactive phosphorus	58.96	6.88	4.33	70.18
Split Rock Creek nr Jasper, 201st St	Particulate phosphorus	20.86	5.23	3.72	29.82
Watonwan River nr Garden City, CSAH13	Total phosphorus	69.83	17.88	12.30	100.00
Watonwan River nr Garden City, CSAH13	Soluble reactive phosphorus	35.36	8.29	6.03	49.68
Watonwan River nr Garden City, CSAH13	Particulate phosphorus	34.46	9.59	6.27	50.32
West Fork Des Moines River at Jackson, River St	Total phosphorus	57.25	23.40	19.35	100.00
West Fork Des Moines River at Jackson, River St	Soluble reactive phosphorus	27.56	6.77	6.93	41.27
West Fork Des Moines River at Jackson, River St	Particulate phosphorus	29.69	16.63	12.41	58.73
Whitewater River nr Beaver, CSAH30	Total phosphorus	74.66	9.48	15.86	100.00

Table 1 *(continued)*

Name	P Constituent	EP 0–10%	EP 10–25%	EP 25–100%	% Contribution to total TP export
Whitewater River nr Beaver, CSAH30	Soluble reactive phosphorus	35.37	6.44	10.95	52.76
Whitewater River nr Beaver, CSAH30	Particulate phosphorus	39.29	3.05	4.91	47.24
Yellow Bank River nr Odessa, CSAH40	Total phosphorus	92.20	5.41	2.39	100.00
Yellow Bank River nr Odessa, CSAH40	Soluble reactive phosphorus	55.10	3.31	1.67	60.08
Yellow Bank River nr Odessa, CSAH40	Particulate phosphorus	37.10	2.10	0.72	39.92
Yellow Medicine River nr Granite Falls, MN	Total phosphorus	85.30	10.40	4.30	100.00
Yellow Medicine River nr Granite Falls, MN	Soluble reactive phosphorus	53.62	5.64	2.23	61.50
Yellow Medicine River nr Granite Falls, MN	Particulate phosphorus	31.68	4.76	2.06	38.50
Mean across all gages	**Total phosphorus**	**72.90**	**15.16**	**11.94**	**100.00**
Mean across all gages	**Soluble reactive phosphorus**	**38.84**	**7.31**	**6.51**	**52.67**
Mean across all gages	**Particulate phosphorus**	**34.05**	**7.85**	**5.43**	**47.33**

Note. The right-most column shows total contribution of SRP and PP to TP export across all flow conditions. EP = exceedance probability; TP = total phosphorus.

bluff extent (Figure 9). Under moderate to low flow conditions (i.e., EPs >10%) in early summer, PP contributed twice as much to TP export relative to SRP, on average across all sites. By contrast, in late summer/fall, TP export appears dominated more strongly by SRP or an equal mix of SRP and PP, depending on the site.

4. Discussion

Several recent papers have concluded that hydrologic forcing of legacy stores is the key mechanism explaining nitrogen export in agriculturally dominated watersheds, leading to biogeochemical stationarity (Basu et al., 2011; Thompson et al., 2011; Van Meter et al., 2016, 2018). However, the articulation of simple theoretical frameworks for P transport has proven more challenging. Here, our findings illustrate the complexity of P dynamics and show the need to account for landscape heterogeneity and biogeochemical processes in developing frameworks for P transport and in devising management scenarios to reduce downstream P pollution. Specifically, our results indicate that specific places (e.g., bluffs, lakes, wetlands, wastewater treatment plants), times (e.g., snowmelt, late summer), and processes (e.g., assimilation) can mediate P transport in agriculturally dominated landscapes and complicate P-discharge relationships. As a result of these mediating factors, P transport can exhibit diverse patterns across watersheds, seasons, and flow conditions. These patterns, while evident in visual inspection of the *C-Q* data as presented here, can be obscured by reporting summary statistics such as the slope of the *C-Q* relationship.

While *C-Q* relationships for P on daily timescales can be confounded by landscape complexity and biogeochemical processes, our study has confirmed hydrology as the primary factor determining both dissolved and particulate P export from agricultural landscapes over interannual timescales, similar to previously reported results for nitrogen. For gages with interannual load information available, the large majority of total P export (>70%, on average) occurred during large storm events. This finding is particularly pertinent for future water quality in our study region, where climate models predict increased magnitude and frequency of large storms (Pryor et al., 2013) and where, due to past and current agricultural modifications, the land is primed for P loss and transport. The findings shown here across a large number of agricultural watersheds in the midwestern United States parallel those recently shown for nitrogen across the continental United States (Sinha et al., 2017) and for phosphorus in a small number of watersheds in Wisconsin (Carpenter et al., 2018)—namely, that the intersection of more large storms with a landscape primed for nutrient loss by decades of intensive land use will result in more eutrophication of downstream waters.

Our findings also indicate the importance of managing for both dissolved and particulate P in many agricultural landscapes. While management efforts in agricultural regions have historically been focused on control of particulate P via practices intended to reduce field-scale erosion (e.g., Dodd & Sharpley, 2016; Sharpley et al., 2001), analysis of P loads for the agriculturally dominated gages presented here indicated that dissolved P can account for half or more of the P load exported from many agricultural basins. Although some have previously speculated that dissolved P dynamics in agricultural river systems might be associated

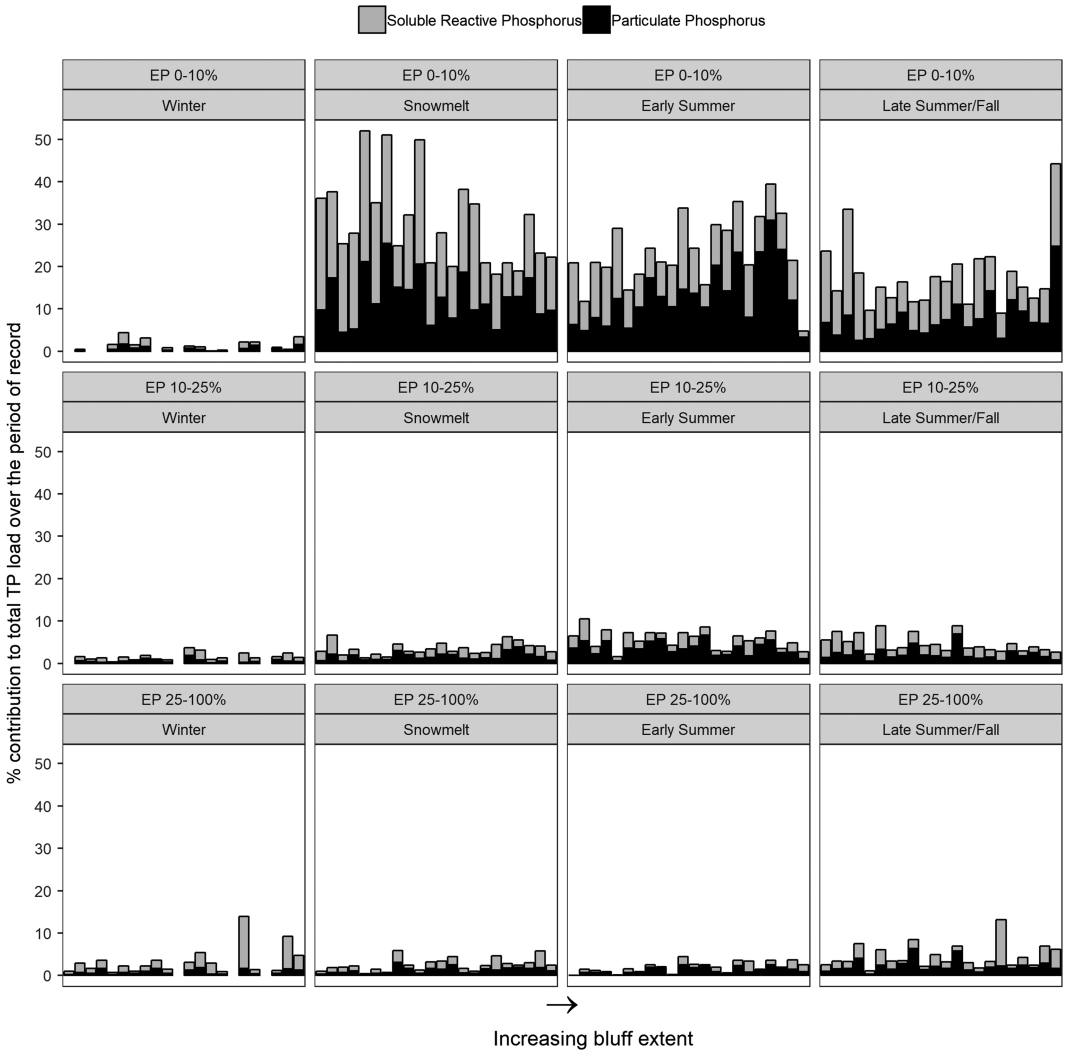

Figure 9. Percent of total phosphorus export accounted for by soluble reactive phosphorus (gray bars) and particulate phosphorus (black bars) during the period of record (2009–2015) for all gages with load and exceedance probability (EP) information available (n = 22). Contribution to total the total phosphorus load over the 6-year period is shown for high flows (with flow EP = 0–10%; top row), moderately high flows (EP = 10–25%; middle row), and moderate to low flows (EP = 25–100%; bottom row) across seasons. EPs were determined for all gages based on daily flows between 2009 and 2015. Gages are arranged from left to right according to increasing normalized bluff area.

largely with inputs from sewage or industrial wastewater (e.g., Grundtner et al., 2014), our findings suggest that agricultural watersheds with large influences from wastewater can be distinguished by diluting *C-Q* relationships for dissolved P that do not apply to most watersheds we studied. Thus, for most agriculturally dominated watersheds, influences from wastewater treatment plants or industrial discharges do not appear to be the primary factor governing mobilization of dissolved P. Rather, given decades of high-P inputs from fertilizer and manure, much of the dissolved P in agricultural landscapes likely originates from diffuse sources associated with current and legacy agricultural inputs. Meanwhile, basins with a high prevalence of near-channel sediment sources (i.e., bluffs) are characterized by large losses of particulate P that will not be adequately controlled by field-based management practices.

4.1. Biogeochemical Processes and P Transport

Dodd and Sharpley (2016) noted that biotic processes, though rarely considered, represent an important source of complexity in governing P transport and availability. Indeed, we observed that PP and SRP concentrations were often related to Chla concentrations during a range of flow conditions, suggesting that high

rates of assimilation and algal production in agricultural river networks may modify *C-Q* relationships toward reactive behavior via draw down of SRP and conversion to PP in the water column. Our findings also indicate that the role of algal biomass in modifying P concentrations is much stronger at moderate to low flow conditions. At high flows, dilution of algal biomass and mobilization of sediment sources renders the contribution of algal P relatively small compared to inorganic PP sources. Similar flow-related changes between organic-dominated versus sediment-dominated TSS concentrations have been previously observed for agricultural rivers in our study region by Lenhart et al. (2010).

4.2. Agricultural Land Use and Artificial Drainage Effects

Much of our study region is highly homogenous for row crops with relatively small land cover in pasture, providing limited potential to assess the effect of crops versus pasture on P transport. When we broke sites out by major river basin, however, we did observe negative effects of percent pasture and positive effects of percent crops on mobilization of SRP in the UMBR Basin. The UMBR is the only basin included in our study with a substantial range in percent pasture cover across sites. As this basin has more topography and poorer soils, it is somewhat less amenable to row crop farming (Lueth, 1984). The finding of crop versus pasture effects in this basin conforms to a long history of earlier studies, suggesting that intensively managed row crops are associated with higher mobilization of P from the landscape compared to pasture (e.g., Beaulac & Reckhow, 1982).

We observed negative effects of percent tile drainage on *b* for TP, PP, and SRP, consistent with a homogenizing influence of artificial drainage that may be driving agricultural watersheds toward more chemostatic behavior (Basu et al., 2011). Tile drains represent an increased connection between river networks and terrestrial soils saturated for P and have been shown to contribute substantially to downstream P loads in agricultural watersheds (Jarvie et al., 2017; King et al., 2015), particularly during baseflow conditions (Gentry et al., 2007; Schilling et al., 2017). Contributions of tile drainage to increased P concentrations at low flows could help explain the elevated SRP concentrations we observed at many gage sites during low flow conditions in late summer. This tendency of tile drainage to move watersheds toward chemostatic behavior may also explain why P transport appears only weakly mobilizing in most study watersheds at event scales. However, one caveat is that percent tile did not appear related to P transport when study watersheds were analyzed separately by major river basin. This diminished effect may have resulted from narrower rangers of percent tile across individual basins. Study watersheds in the Red and UMBR Basins were characterized by an average of 6% (range 0–16%) and 18% (range = 3–36%) tile, respectively, whereas study watersheds in the Minnesota River Basin were characterized by a higher extent of tiled area (38%, on average; range = 10–60%). Thus, it is possible that the effects of % tile on P transport are only evident across a larger range of tile extent from 0% to 60%. Alternatively, percent tile could be correlated with some additional unmeasured factor (such as varied P content of soils) that varies strongly by major river basin and that also affects P mobilization.

4.3. Landscape Features and P Transport

Our study indicates that particulate P transport is governed by the availability of vulnerable near-channel sediment sources (bluffs and ravines) within river networks. Recent studies have identified near-channel sediments as an increasingly important, and sometimes dominant, contributor to suspended sediment loads in incised rivers of our study region (Belmont et al., 2011; Gellis et al., 2016; Gran et al., 2011). These near-channel sediments have also been shown to be mobilized primarily under high flow conditions (Kelly & Belmont, 2018). Previous studies have estimated that bank and bluff sediments might contribute anywhere from 7% to 49% of the annual TP loads in the Le Sueur and Blue Earth Rivers, both located in our study region (Kessler et al., 2012; Sekely et al., 2002). Suspended sediment from bluffs may act either as a direct source of PP to river networks or as a carrier (via sorption of dissolved P).

Many of the high bluff sites that appeared mobilizing for PP as a function of discharge exhibited threshold rather than linear relationships to flow. A similar pattern was observed by Vaughan et al. (2017) for TSS-*Q* relationships at some of the same gage sites we studied. This finding may be consistent with recent work indicating that near-channel sediments are mobilized via a threshold relationship to river discharge, particularly from watersheds with highly incised river corridors and high bluff extent (Day et al., 2013; Higson & Singer, 2015; Kelly & Belmont, 2018). Higson and Singer (2015) showed that bluff stability is

strongly controlled by the elevation of the water table within the lateral boundary, with catastrophic bluff collapse occurring at discharge conditions above a particular threshold. Likewise, Day et al. (2013) and Kelly and Belmont (2018) identified flow thresholds for bluff failure in the Le Sueur River watershed at flow EPs ≈15–20%. These threshold values correspond reasonably well to the inflection point observed at many (though not all) sites characterized by high bluff extent in this study, above which PP concentrations increased rapidly as a function of discharge. The parallel threshold relationships suggest that, at discharge conditions above a certain threshold, PP mobilization could be governed by catastrophic mass movement of bank and bluff sediments, particularly for watersheds with high bluff extent.

Interestingly, however, we did not observe a threshold relationship for PP mobilization relative to discharge among gaged watersheds in the UMBR Basin. Like many sites in the lower part of the Minnesota River Basin, these sites are characterized by high bluff extent, but PP-*Q* relationships were relatively steep and linear on a log-log scale. Stout et al. (2014) traced suspended sediment in a subbasin of the UMBR basin (the Root River) to near-channel sources; however, sediment fingerprinting indicated that the ultimate origin of these sources was field sediment that had eroded and accumulated near stream banks during the initial conversion of the landscape to agriculture by European settlers. Moreover, the soil types in this region tend to be fine, powdery, and highly mobile (Anderson et al., 2001). By contrast, near-channel sediment from sites in the Minnesota River Basin is derived from bluffs that were carved by the catastrophic drainage of Glacial Lake Agassiz beginning ~14,000 years ago. Thus, the two major basins have very different geologic histories and soils, which could affect (1) the erodibility of near-channel sources and whether or not these sources are mobilized via thresholds in bluff collapse, (2) the background P content of these sediments and their cation exchange capacity, that is, their potential to sorb or desorb dissolved P, and, finally, (3) whether these bluff sediments contribute to mobilization of PP, SRP, or both.

Further highlighting the importance of context in understanding P transport across agricultural watersheds, our combined gage and field data sets yielded a complex relationship between lakes, wetlands, and P concentrations in river networks. In the Minnesota River Basin, lake interception was associated with decreased mobilization of PP among gage sites, which contributed to a weak negative relationship between PP and lake interception across all gage sites. These findings are consistent with storage of sediment-bound PP (Engstrom et al., 2009). By contrast with the gage data set, our field data set indicated that lake interception area was more commonly associated with increased concentrations of downstream PP. It is important to note that this data set was mostly comprised of sites located upstream of large near-channel sediment sources like bluffs. Thus, our findings may point to the effects of context on lake P relationships in river networks. At upstream sites where field erosion is largely controlled via tillage management and near-channel sources are comparatively small, sediment-bound P may be relatively limited compared to other P sources. In this setting, the impact of lakes on PP via sediment storage may be overshadowed by the production of PP associated with algae and macrophytes in lakes, which is evident predominantly during moderate and baseflow conditions, as opposed to very high and very low flows. By contrast, in watersheds characterized by larger inputs and concentrations of sediment-bound P (i.e., watersheds with sizeable sources of near-channel sediment), lake interception may have a net negative effect on PP concentrations, via sediment storage, if lakes are located downstream of near-channel sediment sources. Additional analysis of TSS-*Q* relationships and quantification of near-channel sediment sources and delivery rates up, and downstream of lakes could further elucidate these phenomena.

In terms of SRP, lake interception was only associated with decreased concentrations of SRP during two sampling events in the Chippewa River Basin, one at high flow and one at moderate flow. However, relationships with lake interception and SRP were quite weak. The Chippewa is notable for a relatively high amount of lake interception across the basin as well as more forest in the upper reaches. Our findings indicate that lakes in this watershed may serve as sinks for SRP. However, in the other basins we sampled, there were many flow conditions we sampled under which lakes did not appear to impact SRP concentrations across field sites, again suggesting that lakes storage or conversion of SRP may be context specific.

Wetland cover also appeared to have subtle effects on downstream P concentrations in the river networks we studied. Among upland field sites, increased wetland cover was associated with higher TP, SRP, and PP concentrations for a small number of sampling events, including an extreme high flow event in September 2016, as well as a few other moderate and low flow events. Among gaged sites, however, wetland cover did not

appear related to transport of any P constituent, once basin and bluff effects were accounted for. Taken together, these findings indicate that wetlands may intermittently release P to river networks, depending on a combination of flow, season, and other conditions. This finding is in line with a recent review of P conservation practices, suggesting that wetlands may sometimes switch from sinks to sources of P, as they accumulate P inputs over time (Dodd & Sharpley, 2016). However, these effects, observed for smaller upland watersheds, may be washed out in larger watersheds by other determinants of P concentration.

One other potential effect of lakes and wetlands that we did not address here is their role in increasing water residence time in river networks and thus mitigating peak flows and prolonging the downstream river hydrograph (Honti et al., 2010). Potentially, these hydrological effects could have cascading effects on the mobilization of P, by altering the size and shape of the river hydrograph and thereby mitigating the erosion of sediment-bound P from near-channel sources under high discharge conditions. Increases in residence time could also affect biogeochemical processing of P. In a lake and wetland modeling study, Zhang et al. (2012) found that wetlands reduced P loads to downstream waters but also reduced downstream flows, thus resulting in increased P concentrations in downstream waters. Further research is needed to examine such indirect impacts of water storage on P transport and cycling in agricultural watersheds. Water storage in the form of upland and in-channel wetlands and reservoirs has been proposed as a conservation management option with the potential to mitigate both nitrogen and suspended sediment loads in intensively managed agricultural landscapes (Hansen et al., 2018; Passeport et al., 2013; Passy et al., 2012). Demonstrating the role that lakes and wetlands play in mediating P concentrations is important to predicting the cumulative impact such conservation measures might have on river networks.

One other landscape feature we did not address explicitly here is floodplain access. Floodplain storage has the potential to mitigate or alter transport of dissolved and particulate P (Hoffman et al., 2009). While many of the rivers in our study region are heavily incised and thus don't readily access their floodplains, the small number of gaged rivers that showed "peaked" relationships for P in this study (e.g., Chippewa River, Pomme de Terre River, Red River of the North) do have relatively more floodplain access (Simonovic & Carson, 2003). Thus, floodplain interactions likely affect P transport for a small number of rivers in our study area.

4.4. P Transport Over Interannual Timescales

The majority of agricultural watersheds we studied appeared chemostatic or reactive for P over multiyear periods. However, approximately one third of sites appeared to show weak to strong mobilizing behavior for SRP at annual scales. This finding suggests spatial heterogeneity for SRP stores in at least some agricultural landscapes, with areas of higher P accumulation increasingly mobilized with increasing flow. Some previous work supports the notion that P stores may be heterogeneous across even intensively management agricultural landscapes; low-lying wet areas in particular may accumulate SRP (Bennett et al., 2004; Wilson et al., 2016). In our landscape, remnant depressional areas are widespread (MNDNR, 2016b) and represent potential locations from where SRP concentrations could accumulate and then mobilize, as increasing flows increase landscape connectivity. Likewise, Hansen et al. (2018) found that the potential for ephemeral wetlands to affect watershed-scale nitrate concentrations depends strongly on flow conditions and resulting hydrologic connectivity of these wetlands to river networks. Riparian buffers with soils saturated for P could also become sources of SRP at high flows (Dodd & Sharpley, 2016).

Positive and significant relationships between annual load and discharge indicated a strong role of hydrologic forcing in determining P transport from agricultural watersheds on an annual basis. High flow conditions accounted for a large majority of total P export (>70%, on average) to downstream water bodies and were important in determining export of both PP and SRP loads. Whereas PP transport has generally been understood to occur predominantly via episodic transport of field and near-channel sediment during storm events, previous frameworks have emphasized the importance of baseflow for dissolved P delivery (Schilling et al., 2017). The large proportional contribution of SRP and PP loads transported during high flow events to total cumulative TP loads over time at most gages in this study indicates that episodic transport is an important mechanism for export of both particulate and dissolved P.

Because of the disproportionate contribution of large storms and high flows to total P export, more frequent large storm events—an observed and predicted impact of human-induced climate change in the Upper Midwest region (Pryor et al., 2013)—may counteract improvements to P retention due to conservation

measures and may increase total P export from agricultural watersheds. Carpenter et al. (2018) likewise showed that more frequent and intense precipitation events were associated with extreme increases in P delivery from two agricultural watersheds to Lake Mendota in Wisconsin. These findings are consistent with a substantial body of work illustrating the disproportionate impact of large storm events on P export (e.g., Hubbard et al., 2011; Royer et al., 2006; Tomer et al., 2003; Vanni et al., 2001) and speak to the need for big picture management solutions that can address (1) drivers of climate change, (2) reduction in peak river flows, and (3) ongoing inputs and legacy stores of highly mobilizable P.

We also found that total P loads could be dominated by SRP, PP, or an approximately even mix of the two depending on the watershed in question. While conventional understanding historically defined PP as the dominant component of P in agricultural river networks (Dodd & Sharpley, 2016; Withers & Jarvie, 2008), a greater importance of dissolved P is consistent with recent published studies indicating a wide range in the contribution of dissolved versus particulate P to total P in midwestern agricultural watersheds, with dissolved P the dominant contributor in many cases (Gentry et al., 2007; King et al., 2015; Schilling et al., 2017). For a small number of sites with identified point source inputs, wastewater likely contributes heavily to SRP losses. For most other agricultural watersheds, SRP losses are likely due to the flushing of reactive P from manure and fertilizer newly applied to fields and from legacy P associated with past fertilization (Gentry et al., 2007; King et al., 2015; Smith et al., 2015), as well as from senescing crop residue and in-channel vegetation in late winter and early spring (Elliott, 2013; Robertson et al., 2007). Boardman (2016) showed that fertilizer use in the watersheds we studied here has remained consistently high over the past several decades. Given legacy and current fertilizer inputs, most agricultural watersheds are likely well beyond the buffering capacity at which they can retain P (Goyette et al., 2018). Moreover, in a review of the impacts of conversation practices on P loss, Dodd and Sharpley (2016) also found that practices implemented to control particulate P (i.e., tillage practices, cover crops, wetlands, riparian buffers) often resulted in increased export of dissolved P to downstream waters. At the same time, for watersheds with high availability of near-channel sediment, PP represents the larger component of TP load and thus represents an important target for management action. Overall, our findings point to the need for management strategies that can reduce both forms of P.

4.5. Sources of Uncertainty and Areas for Future Study

There are several aspects of a complete framework for P transport that we did not address explicitly here and that represent important areas for further study. A more detailed analysis of the underlying soil properties for the larger set of watersheds included in this study could provide information about whether soils and sediments are likely to be sources or vectors of P. Differences in soil P content or exchange capacity across watersheds could also possibly explain why bluff extent was associated with mobilization of SRP in the UMBR and Red River Basins but not in the Minnesota River Basin. Alternatively, it is also possible that nanoparticles passing through the filter pore size used to collect SRP samples used in this study contribute substantial P (Haygarth et al., 1997) and thus contributed to the relationship between bluff extent and SRP. Further analysis of P contribution by particle size is needed to ascertain influence of nanoparticles on P mobilization for the watersheds we studied.

Additional analysis of available gage and stormflow data to evaluate concordant changes in SRP, PP, and TSS concentrations for individual storm events could further reveal the extent to which sediment may "convert" SRP to PP via adsorption in different watersheds, as well as provide information about the role of hysteresis in determining *C*-*Q* relationships. Vaughan et al. (2017) showed that hysteresis is common for TSS in many of the rivers in our study region, with rising limbs showing higher sediment concentrations than falling limbs. In that study, hysteresis was positively related to the extent of near-channel sources and mean annual precipitation and negatively related to the percent of wetland cover. Kelly and Belmont (2018) showed even more complex relationships between *Q* and TSS for the Le Sueur River during a large storm event, reflecting a sequence of events that includes flushing of accumulated bed sediment followed by additional sediment inputs from bluff collapse. In general, we would like to further analyze the detailed sequence of events linking large storms to P export for the watersheds we studied, especially in light of antecedent hydrologic conditions. Such findings could enable us to better predict climate-related P export for watersheds in our region. Our finding of disproportionate P export relative to annual water yield for one high bluff watershed

following an extreme storm in 2010 provides a hint that large individual storm events may supersede the impact of annual water yield on exported nutrient load in some cases.

Finally, we did not evaluate the effects of field-scale variability on P transport in this paper. Differences in cropping systems, such as the use of cover crops and tillage practices, as well as differences in the timing and type of fertilizer application could affect the loss of SRP and PP from fields (e.g. Bundy et al., 2001; Sharpley et al., 2000; van Es et al., 2004). However, these smaller scale effects may also be overshadowed by other more dominant processes (e.g., hydrology, gross inputs) at the watershed scale (Haygarth et al., 2012).

5. Conclusion

This paper demonstrates that, while P transport is potentially complicated by variation in landscape features, land use practices, and biogeochemical processes, these factors can be teased out if we measure them. Our paper also demonstrates the importance of both dissolved and particulate forms of P to total P export in agricultural watersheds and quantifies the importance of flow conditions to P export in different seasons. These findings are relevant to selecting effective P management actions, which must take into consideration when and how P concentrations and loads can be most effectively reduced. While traditional P management strategies have focused on field-scale reduction of sediment-associated P sources, our findings underline the need to identify land use and management strategies that will mitigate losses of dissolved P lost from P-saturated field and riparian soils. Management strategies must apply not just to new inputs of P but to mitigating the loss of legacy stores, which will take centuries to eliminate via runoff (Goyette et al., 2018). These strategies will also need to target reduced mobilization of near-channel sediment that can serve as a direct source and/or a carrier of P. While we have highlighted the importance of high flows in determining mass of P export, managing P concentrations at lower and moderate flows is also important for restoring and protecting habitat conditions necessary for the conservation of stream biota and ecosystem function (Wagenhoff et al., 2017).

Finally, our analysis highlights the converging impacts of climate chaos and intensive agricultural land use on water quality for rivers in the Midwest. Increased frequency of large storm events due to climate change will likely result in increased export of both dissolved and particulate P from agricultural watersheds on an annual basis. Effectively managing P export to downstream water bodies will therefore be contingent on the speed with which climate mitigation strategies can be implemented, as well as on transformative strategies to eliminate new agricultural P inputs and retain legacy stores in the soil. It will be critical to consider whether management actions can reduce P export by targeting reductions in peak flows, as well as the extent to which P loads and concentrations can be reduced with conservation techniques that are applicable to more frequent and moderate flow conditions.

Acknowledgments
Data supporting the conclusions in this paper can be found in the tables, references and supplemental text. Raw water chemistry from field study sites is available at Springe Link (http://doi.org/10.1007/s10750-016-2911-7). Water chemistry and flow data from gaged sites is available at Department of Natural Resources website (https://www.dnr.state.mn.us/waters/csg/index.html) and Minnesota Pollution Control Agency website (https://www.pca.state.mn.us/wplmn/data-viewer). This research was supported by the National Science Foundation under grant 1209402 Water, Sustainability and Climate (WSC)—Category 2, Collaborative: Climate and human dynamics as amplifiers of natural change: a framework for vulnerability assessment and mitigation planning. C. L. Dolph received additional support from the US Environmental Protection Agency under grant. R836166 Valuing Water Quality Improvements in Midwestern Ecosystems: Spatial Variability, Validity and Extent of the Market for Total Value. C.L. Dolph, E. Boardman, A.C. Baker and B. Dalzell also received support from the Minnesota Department of Agriculture under a Clean Water Fund Grant: Measuring and Modeling Watershed Phosphorus Loss and Transport For Improved Management of Agricultural Landscapes. We thank two anonymous reviewers and the journal editors for highly constructive comments that improved this manuscript.

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