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River phosphorus cycling during high flow may constrain Lake Erie cyanobacteria blooms

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ABSTRACT

Cyanobacterial harmful blooms have been increasing worldwide, due in part to excessive phosphorus (P) losses from agriculture-dominated watersheds. Unfortunately, cyanobacteria bloom management is often complicated by uncertainty associated with river P cycling. River P cycling mediates P exports during low flow but has been assumed to be unimportant during high flows. Thus, we examined interactions between dissolved reactive phosphorus (DRP) and suspended sediment P during high flows in the Maumee River network, focusing on March–June Maumee River DRP exports, which fuel recurring cyanobacteria blooms in Lake Erie. We estimate that during 2003–2019 March to June high flow events, P sorption reduced DRP exports by an average of 13–27%, depending upon the colloidal-P:DRP ratio, decreasing the bioavailability of P exports, and potentially constraining cyanobacteria blooms by 13–40%. Phosphorus sorption was likely lower during 2003–2019 than 1975–2002 due to reductions in suspended sediment loads, associated with soil-erosion-minimizing agricultural practices. This unintended outcome of erosion management has likely decreased P sorption, increased DRP exports to Lake Erie, and subsequent cyanobacteria blooms. In other watersheds, DRP–sediment P interactions during high flow could have a positive or negative effect on DRP exports; therefore, P management should consider riverine P cycles, particularly during high flow events, to avoid undermining expensive P mitigation efforts.

1. Introduction

Cyanobacteria harmful blooms (cyanoHABs), which have been increasing worldwide, negatively affect freshwater ecosystems, human livelihoods, and human health (Kouakou and Poder, 2019; Paerl et al., 2016). One primary cause of cyanoHABs are phosphorus (P) losses from agricultural production, particularly the loss of dissolved reactive P (DRP) which is more bioavailable to cyanobacteria than sediment-bound P (Baker et al., 2014a). Thus, it is a global environmental priority to understand and reduce watershed P exports (Glibert and Burford, 2017). However, P management is complicated by uncertainty associated with P retention and transformation during downstream transport through river networks (Jarvie et al., 2013; Sharpley et al., 2009). In streams and rivers, biogeochemical processes alter the magnitude and bioavailability (e.g., DRP versus sediment–P) of P transported downstream exerting controls on P exports to recipient water bodies during low flow (Withers and Jarvie, 2008). Yet, most P and sediment export occurs during high flows (Correll et al., 1999; Gentry et al., 2007; Sharpley et al., 2008) and we know little about P cycling during high flows (Edwards and Withers, 2008; Withers and Jarvie, 2008). This knowledge gap limits our ability to successfully manage P pollution and cyanoHABs.

One potentially important aspect of river P cycling during high flows is P sorption-desorption by suspended sediment, which can increase or decrease DRP concentrations and, therefore, the bioavailability of P exports to cyanoHABs. Phosphorus sorption-desorption during high

Abbreviations: P, phosphorus; EPC_0, zero-equilibrium phosphorus concentration; LM, linear model; SMAR, standardized major axis regression; GLM, generalized linear models; GAM, generalized additive models; AICc, akaike information criterion–corrected; LFR, Little Flat Rock; PC, platter creek; PR, potato run; STF, South Turkey Foot; UTLC, unnamed tributary to lost creek; WC, west creek; cyanoHABs, cyanobacteria harmful blooms; DRP, dissolved reactive phosphorus; DM, dry mass.

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flows, which is rarely quantified, is perceived to be unimportant at the watershed scale because rapid downstream transport limits the time for sorption-desorption to influence DRP exports (Bukaveckas, 2007; Withers and Jarvie, 2008). Yet, in many river systems rainfall-driven runoff travels hours to days from catchment headwater streams to recipient water bodies (Jobson, 1997; Verhoff et al., 1979), allowing sufficient time for P sorption-desorption to influence DRP exports (Zhang et al., 2012). Unfortunately, it is unknown how much P sorption-desorption affects DRP exports during high flows and, thus, subsequently mediates cyanoHABs in recipient ecosystems.

Our poor understanding of P cycling during high flows may mask an important riverine process that could mediate the influence of agricultural practices on bioavailable P exports and subsequent cyanoHABs (Jarvie et al., 2013; Sharpley et al., 2009). During high flows, the magnitude of P sorption-desorption is likely determined by DRP concentrations, suspended sediment concentrations, and river discharge (Zhang and Huang, 2007; Zhou et al., 2005). While DRP is commonly considered 100% bioavailable (Baker et al., 2014a; Bertani et al., 2016) and capable of being sorbed by suspended sediment, a portion of DRP is colloidal-P (~1–450 nm; Gu et al., 2020; Nagul et al., 2015; River and Richardson, 2019). Colloidal-P may be less bioavailable (Baken et al., 2014) and does not sorb to suspended sediment. These factors control the magnitude of P sorption-desorption in a volume of river water and ultimately, in conjunction with hydrologic travel time, the total net P sorption-desorption within a river network. Thus, controls on these factors (e.g., climate or agricultural management practices; Daryanto et al., 2017; Osmond et al., 2019) effect the magnitude and direction of P sorption-desorption and the bioavailability of exports to recipient ecosystems.

The effect of river P exports on cyanoHABs in recipient lakes and reservoirs will depend upon environmental conditions, how P is partitioned among fractions differing in bioavailability, and how those fractions are shaped by riverine processes. When environmental conditions (e.g., temperature, light, nitrogen) are suitable for bloom-forming cyanobacteria, bioavailable P loads may directly fuel the growth of cyanoHABs and other phytoplankton (Hamilton et al., 2016; Paerl et al., 2016). The contribution of non-bioavailable P to cyanoHABs will depend upon the nature of P cycling in these systems. The majority of non-bioavailable P in agriculture-dominated watersheds is bound to sediment or colloids (Baker et al., 2014a; Matisoff et al., 2017). Sediment-P often settles to the bottom of a lake or reservoir where it can be a P sink or an important source of internal P loading (Orihel et al., 2017), depending upon dissolved oxygen concentrations, temperature, and P concentrations (Sondergaard et al., 2003).

Here, we examined the influence of P sorption-desorption during high flows on DRP exports and cyanoHABs. We hypothesized that during high flow, suspended sediment concentration shapes the magnitude of P sorption-desorption within a river network altering the bioavailability of P exports and potentially cyanoHABs severity in recipient ecosystems. We evaluated this hypothesis by measuring the magnitude of P sorption-desorption by suspended sediment during high flow events in six Maumee River tributaries and by estimating P partitioning coefficients (Lin et al., 2016; Santschi, 1995), Then, we scaled up P sorption-desorption to the tributary and river network level to estimate the downstream effect on DRP loads and cyanoHABs in Lake Erie. Given the limited information about the concentration, dynamics, and bioavailability of colloidal–P within DRP (River and Richardson, 2019), we modeled two scenarios assuming that colloidal-P did not sorb to suspended sediment and constituted 0% or 50% of DRP (River and Richardson, 2019).

2. Materials and methods

2.1. Study system

We tested our hypothesis in the agricultural-dominated Maumee River watershed (17,000 km^2) which drains into Lake Erie (Fig. 1; Ohio EPA, 2018). The Maumee River watershed is an excellent model system for agricultural watersheds because it is representative in terms of topography (generally flat), land use (87% agriculture), crop rotations (primarily soybean and corn), and agricultural practices (high prevalence of tile drains and mixture of tillage practices). The Maumee River watershed has also been intensively studied and monitored for decades which provides data to support and inform models.

The western basin of Lake Erie experienced cyanobacteria blooms between the 1960′s and early 1980′s and has seen recurring cyanobacteria blooms since ~2003 (Baker et al., 2014a); a threshold year for

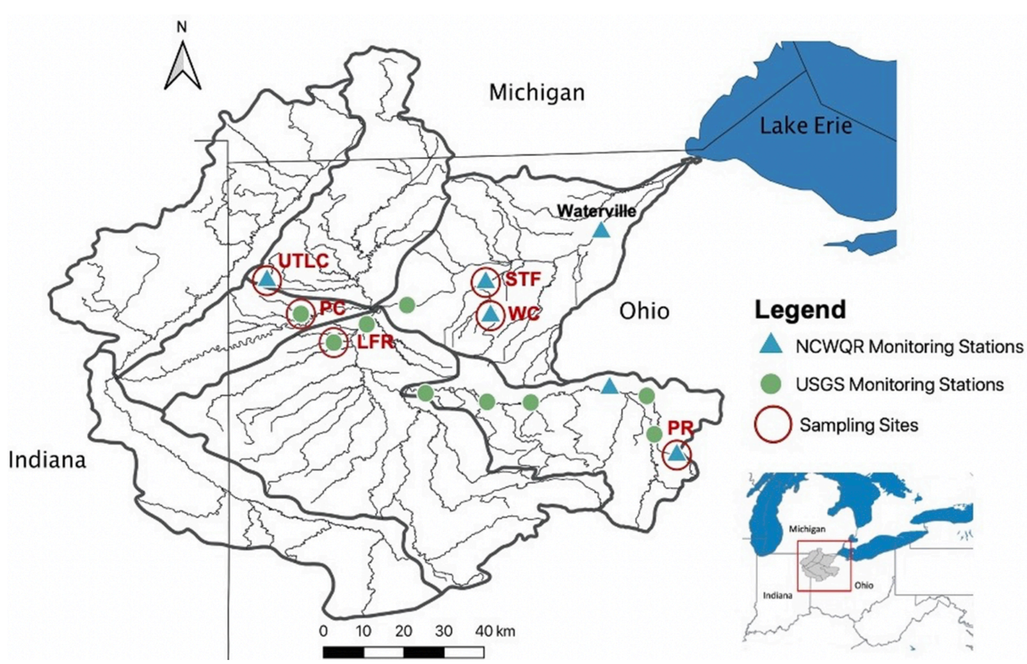

Fig. 1. Map of the Maumee River watershed illustrating the location of study sites and relevant discharge (U.S. Geological Survey [USGS]) and water quality (National Center for Water Quality Research [NCWQR]) monitoring stations. Stream codes are: Little Flat Rock = LFR; Platter Creek = PC; Potato Run = PR; South Turkey Foot = STF; Unnamed Tributary to Lost Creek = UTLC; West Creek = WC; Maumee River at Waterville, OH = Waterville.

increased discharge, DRP loading, and cyanoHABs in Lake Erie (Jarvie et al., 2017; Stumpf et al., 2016). The severity of recent cyanoHABs is associated with March to July bioavailable P exports, particularly those from the Maumee watershed (Baker et al., 2014a; Maccoux et al., 2016; Michalak et al., 2013; Stumpf et al., 2016). Bioavailable P exports are typically assumed to be approximately 8% of sediment-P and 100% of DRP loads to Lake Erie (Baker et al., 2014a; Bertani et al., 2016; Stumpf et al., 2016). However, half of DRP may be colloidal-P, which is associated with iron, and may not be 100% bioavailable (Baken et al., 2014; River and Richardson, 2019). On average, 85% and 93% of Maumee River March–July DRP and sediment-bound P exports, respectively, occur during high flows (Fig. S1; also see: Baker et al., 2014a). The majority of suspended sediment (~70%; Stumpf et al., 2016), and presumably sediment-bound P, exported from the Maumee watershed is deposited in and near the Maumee river mouth (Baker et al., 2014b) which has low rates of internal P recycling (<7% of cyanobacteria P demand) due to the high oxygen concentrations in overlying waters (Matisoff et al., 2016).

2.2. Stormwater sampling

Between January and June 2019, we sampled six focal stream sites located within the Maumee River watershed (Fig. 1 and Table S1) during 13 storm events for suspended sediment, DRP, and aspects of P sorption-desorption (i.e., sorption isotherms and P sorption-desorption rates). Each site was located near a USGS stream gaging station and four cooccurred with a Heidelberg University National Center for Water Quality Research (NCWQR) water quality monitoring stations (Fig. 1). Each focal stream was sampled once per storm event from a bridge by deploying 19 L containers to collect 75 L of stream water from the main channel's center.

Immediately following stream water collection, we homogenized the sample and collected triplicate DRP and suspended sediment samples. Dissolved reactive phosphorus samples were immediately 0.7 μm filtered (glass fiber filters; Whatman GF/F, Cytiva, Marlborough, MA, USA) into 20 mL HDPE scintillation vials (Fisher Scientific, Pittsburgh, PA, USA) using acid-washed syringes and kept cold (~ 4 °C) until frozen in the laboratory. Dissolved reactive phosphorus was analyzed within two days on a spectrophotometer using the colorimetric molybdenum blue reaction method (Strickland and Parsons, 1972). Suspended sediment samples were stored in 250 mL acid-washed HDPE plastic bottles, kept cold (~ 4 °C) until filtered onto pre-weighed and ashed glass fiber filters (Whatman™ GF/F), and subsequently dried at 60 °C and then reweighed.

The remainder of stream water was used to measure aspects of sediment P sorption-desorption. This water was transported to the laboratory in 19 L containers and stored in a dark environmental chamber set to the mean water temperature of the six streams. To consolidate the suspended sediment for analyses, we used a WVO Raw Power Continuous Flow Centrifuge (6000 RPM; WVO designs, Charleston, SC, USA) which was set to a low flow-through rate (~2 L h^{-1}) to minimize sediment loss through the centrifuge outflow. Upon return to the laboratory, centrifugation began immediately and was completed within four days.

2.3. Phosphorus sorption-desorption

To characterize suspended sediment – DRP interactions, we used an approach which began with measurement of P sorption isotherms and ended with the calculation of mass-specific (mg P mg dry mass $[DM]^{-1}h^{-1}$) and volumetric (mg P m^{-3} h^{-1}) P sorption-desorption rates. We measured P sorption-desorption isotherms and rates, using three separate measurement procedures, following Jarvie et al. (2005); detailed methods are described in the Supporting Information (SI Section 1.1). Briefly, sorption rate and isotherm measurements were conducted within one week of collection at the mean ambient stream temperature. Isotherm data were fit with a Langmuir adsorption isotherm model following Lai and Lam (2009). The isotherm fits were used to calculate aspects of P sorption-desorption including: the zero-equilibrium phosphorus concentration (EPC_0; mg P L^{-1}) and the P sorption capacity of suspended sediment particles during downstream transport (mg P mg DM^{-1}). EPC_0 is the DRP concentration separating P sorption (DRP > EPC_0) and desorption (DRP < EPC_0). Phosphorus sorption capacity is the difference between the maximum sorption capacity and the native P content; it reflects the total P mass suspended sediment particles can sorb during downstream travel from the sampling site. We measured both P sorption and desorption rates by suspended sediment; however, since suspended sediment desorbed P under ambient conditions in only one of 78 samples (based on the difference between EPC_0 and stream water DRP concentrations) we only present P sorption rates.

2.4. Estimating total P sorption in tributary waters

To estimate P sorption by tributary suspended sediment downstream of our sampling sites, we combined P sorption parameters with discharge (SI Section 1.2), DRP, and suspended sediment data from three of the focal tributaries with sufficient DRP and suspended sediment monitoring data: South Turkey Foot (STF), Unnamed Tributary to Lost Creek (UTLC), and West Creek (WC). Focusing on high flow events during March–June 2019, we estimated the magnitude of P sorption by suspended sediment exported from these tributaries in four steps which are described in detail in SI Section 1.3. (1) We calculated potential mass-specific P sorption (g P sorbed g DM^{-1} h^{-1}) during transport between the tributaries and the furthest downstream Maumee River monitoring station (Waterville, OH; 26 km from Lake Erie; Fig. 1) by combining estimates of P sorption rate and hydrologic travel time (SI Section 1.4). (2) We constrained P sorption to not exceed the sediment sorption capacity (SI Section 2.2). (3) We calculated total P sorption (kg P day^{-1}) as the product of mass-specific sorption rates and suspended sediment loads. We constrained total P sorption so that it could not decrease DRP concentrations below the threshold at which sediment switch from P sorption to desorption (i.e., EPC_0). (4) To estimate the impact of P sorption on DRP export from our focal tributaries before the water arrived at Waterville, OH, we integrated total P sorption across high flow events during March–June 2019 estimating P sorption by all sediment transported through our sampling sites during this focal period (metric tons P). We calculated the uncertainty in this estimate using a bootstrapping approach (Manly, 1997) which resampled (n = 500) paired measurements of mass-specific sorption rate, sorption capacity, and EPC_0 to make the calculations outlined in steps 1–4.

2.5. Total P sorption in Maumee River network

To investigate the effect of P sorption within the Maumee River network on Lake Erie DRP loads and cyanoHABs, we combined our tributary sorption measurements with discharge and water quality monitoring data from the Maumee River at Waterville, OH (1975–1977 and 1982–2019; Fig. 1 and Table S1). We estimated P sorption within the Maumee River network by combining data on Maumee River suspended sediment loads and total mass-specific sorption rates from the tributaries, which were calculated as the quotient of total P sorption and suspended sediment concentration (SI section 1.5). This approach assumes that abiotic P cycling by suspended sediment did not change substantially during 1975–2019; an assumption supported by comparison of recent (Fig. 3; also see: Williamson et al., 2020) and older (i.e., 1978; Green et al., 1978; McCallister and Logan, 1978) research demonstrating that suspended sediment is enriched in P relative to agricultural soils, sorbs P during high flows, and had similar P bioavailability (Baker et al., 2014a; Bertani et al., 2016). We integrated estimates for each year across March–June high flow events and calculated the uncertainty in our measurements using a bootstrapping approach (Manly, 1997) which sampled (n = 500) from all estimates of total mass-specific sorption rates. To determine the effect of P sorption on cyanoHABs in Lake Erie, we used an ensemble of two models (Bertani et al., 2016; Stumpf et al., 2016) to estimate the magnitude of cyanobacteria blooms from bioavailable P loads calculated with and without P sorption (SI section 1.6). Finally, to characterize P partitioning between dissolved and particulate phases as well as sediment-P reactivity we calculated partitioning coefficients (K_d; see SI section 1.7) for both tributary and Maumee River waters during high flow.

2.6. Evaluating effect of colloidal-P on P sorption estimates

Within the Maumee River network, some fraction of DRP is likely associated with colloidal-P. Unfortunately, variation in colloid-P:DRP ratios within the Maumee River network have only been characterized for Maumee River at Waterville, OH during median February flows (River and Richardson, 2019). Colloid-P:DRP ratios upstream of Waterville are unknow, but could be lower due to sorption of phosphate onto iron-rich colloids (Baken et al., 2016). Given this uncertainty, we estimated P sorption in tributaries and the Maumee River network assuming that all DRP (colloid-P:DRP = 0) and only 50% (colloid-P:DRP = 0.5) of DRP can sorb to suspended sediment; this likely bounds conditions in the Maumee River network.

2.7. Statistical analyses

To examine patterns and controls of K_d, EPC_0, P sorption in tributaries, and P sorption in the Maumee River network, we used a combination of linear models (LM), standardized major axis regression (SMAR), generalized linear models (GLM), and generalized additive models (GAM). We used an information theoretic approach (Burnham and Anderson, 2002) to select the most likely model from a group of candidate models. Models were ranked by AIC_C and models with a ΔAIC_C less than two were considered to have the most support (Burnham and Anderson, 2002). Details on these models are supplied in SI section 1.8.

Next, we asked how declines in suspended sediment loads during 1975–2019 shaped P sorption and ultimately DRP exports to Lake Erie. Due to the large intra-annual changes in discharge, we approached this by examining changes in the DRP load-discharge relationship, following a four-step process. (1) We built a GLM, using a gamma distribution, relating Maumee River high flow March–June suspended sediment loads to discharge and year. (2) We used that GLM to predict March-June suspended sediment loads during 1975–2019 (excluding 1978–1981) with the observed discharge and the year coefficient predicting loads for 1975. (3) We used these predicted historic (i.e., discharge set to observed, year set to 1975) suspended sediment loads to estimate P sorption and, finally, DRP loads with historic discharge-adjusted suspended sediment loads and P sorption. (4) We used GLMs, with a gamma distribution, to ask whether DRP load-discharge relationships differed between 1975–2022 observed DRP loads and 2003–2019 DRP loads predicted with historic suspended sediment loads and P sorption rates. To evaluate the models, we used qqplots to assess model residuals.

3. Results

3.1. DRP–sediment P interactions: focal tributaries

3.1.1. Zero equilibrium P concentration (EPC_0)

Eighty-six percent of our samples were collected during high flows (Fig. S3; ≤ 25% exceedance). Tributary DRP concentrations averaged ~800% higher than EPC_0, indicating that under ambient nutrient conditions suspended sediment sorbed P in 98% of our measurements (77 of 78 samples; Fig. S4). If colloidal-P:DRP was 0.5, suspended sediment would still be predicted to sorb P. At colloidal-P:DRP ratios of 0.75 and 0.9, sorption would be predicted in 91% and 19% of the samples, respectively. EPC_0 increased with DRP concentrations with a positive intercept and slope (SMAR; $R^2 = 0.52$, $P < 0.001$) suggesting that declines in DRP concentrations might lower EPC_0 but not alter DRP–sediment P dynamics. The relationship between EPC_0 and DRP did not vary among streams in elevation (SMAR; $P < 0.001$; H_0 = intercept is equal) or slope (SMAR; $P < 0.001$; H0 = slope is equal).

3.1.2. Phosphorus sorption – desorption

Phosphorus sorption varied widely from 0.001 to 72.5 mg P m^{-3} h^{-1}, differed among streams, and increased with suspended sediment concentrations ($R^2 = 0.90$; Fig. S5 and Table S2) and discharge ($R^2 = 0.71$), which were strongly correlated ($r_{pearson} = 0.70$). At the median sediment concentration across all streams (234 g DM m^{-3}), P sorption was 313% higher in the stream with the highest P sorption (PR; 11.6 mg P m^{-3} h^{-1}) compared to the stream with the lowest P sorption (LFR; 2.8 mg P m^{-3} h^{-1}).

3.1.3. Influence of P sorption on DRP exports

In the three tributaries with suspended sediment and discharge records sufficient for upscaling (UTLC, WC, and STF), P sorption by suspended sediment substantially reduced DRP exports. Assuming a colloidal-P:DRP ratio of 0 or 0.5, suspended sediment sorbed, respectively, 38 – 50% (0.1–1.4 tons P) or 25 – 48% (0.05–0.5 tons P) of observed DRP exports (Fig. 2a). Daily tributary P sorption increased with discharge and DRP loads (Fig. 2b) as well as suspended sediment loads (not shown); three tightly linked exports from agricultural watersheds. As a result, the daily percent of DRP exports sorbed increased from ~0% to 50% with discharge. If colloidal-P:DRP was 0.5, we predict that P sorption (kg P day^{-1}) would be greater than zero during March–June high flow events on 72%, 69%, and 57% of days in UTLC, WC, and STF respectively.

Assuming a colloidal-P:DRP of 0, P sorption saturated before suspended sediment had traveled an average of 11.7 km, 11 to 55% of the distance to the downstream Maumee River monitoring station (Fig. 2c). If colloidal-P:DRP was 0.5, this distance was considerably shorter, particularly in WC and STF. Thus, DRP – sediment P interactions likely reached a quasi-equilibrium well before sediment was exported from the Maumee watershed, indicating that suspended sediment originating from most of the Maumee watershed had ample time during transport to shape DRP exports.

3.2. DRP – sediment P interactions: Maumee River network

3.2.1. Influence on DRP loads and cyanoHABs

During March-June high flow events between 1975 and 2019 (excluding 1979–1981), suspended sediment sorbed, depending upon the colloid-P:DRP ratio, an average of 34–83 tons P per year (33–83% of observed DRP loads) likely decreasing the bioavailability of total P loads to Lake Erie (Fig. 3). If colloidal-P:DRP was 0, suspended sediment sorbed 7 – 167 tons P per year (20–575% of observed DRP loads; Figs. 3 and S6). However, if colloidal-P:DRP was 0.5, suspended sediment sorbed 3 – 69 tons P per year (~40% less P) or 8 – 230% of observed DRP loads (Figs. 3 and S7). These conservative estimates for all suspended sediment passing through the Maumee River at Waterville, OH does not include P sorption by colloids or sediment retained in the river system or its floodplain.

Averaging two Lake Erie cyanoHABs forecasting models, we predicted that the maximum annual cyanobacteria density would be on average 40% (colloidal-P:DRP = 0; range = 4% – 139%) or 13% (colloidal-P:DRP = 0.5; range = 2% – 40%) higher in the absence of P sorption (Fig. 3c).

3.2.2. Historical patterns in DRP – sediment P interactions

At a colloidal-P:DRP ratio of 0 and 0.5, the percent of DRP sorbed was, respectively, 192% or 197% higher during 1975–2002 than 2002–2019 (Fig. 3b). This difference was primarily due to changes in suspended sediment loads which drives interannual variation in P sorption in our model (SI section 1.5). Suspended sediment loads are

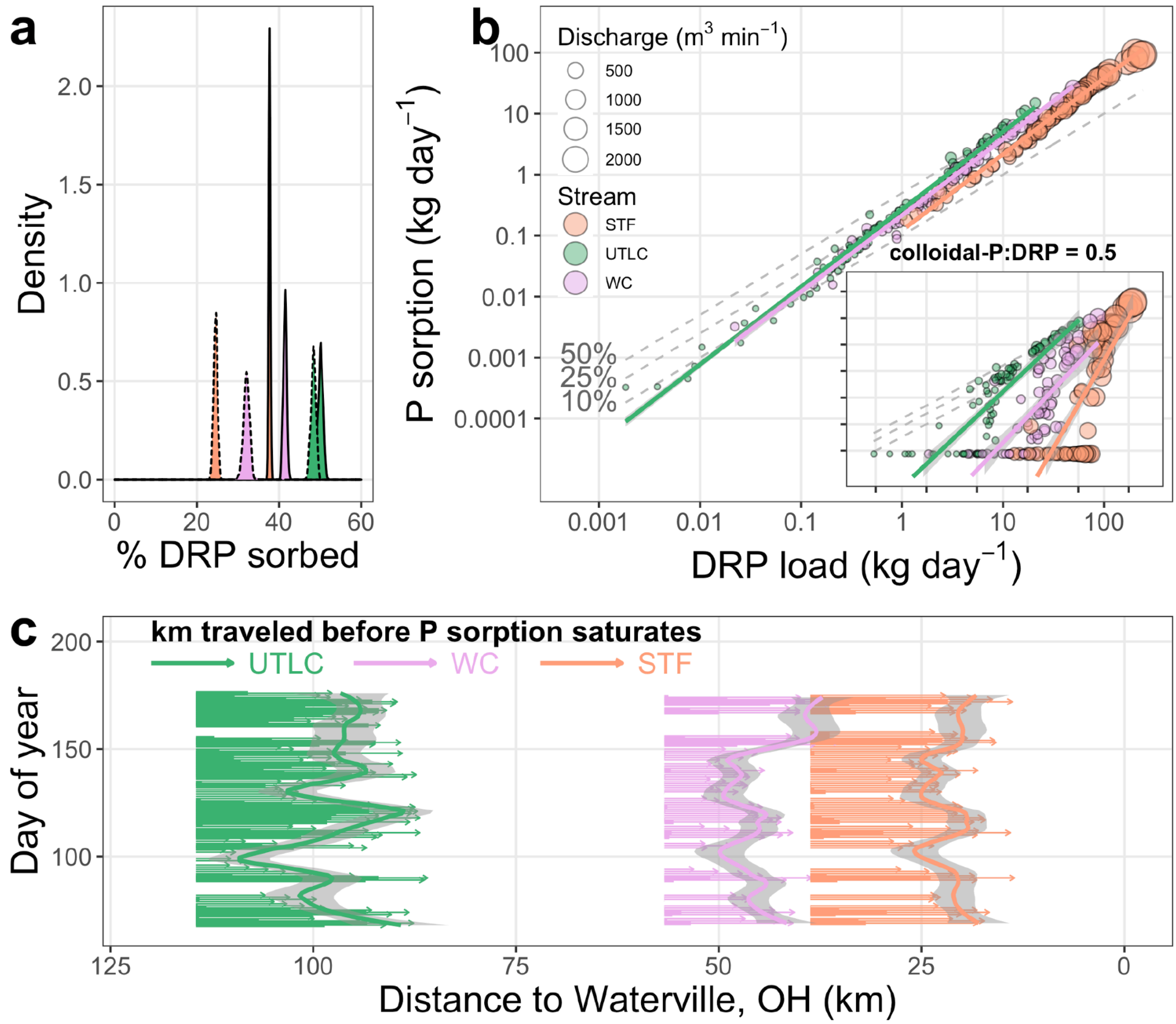

Fig. 2. Characteristics of P sorption in three Maumee River tributaries with sufficient discharge and suspended sediment monitoring data to support these calculations. (a), The percent of DRP sorbed during March–June 2019 at high flows (≥ 75% flows) assuming colloidal-P:DRP ratios of 0 (solid lines) and 0.5 (dashed lines). (b), Phosphorus sorption increases more rapidly than DRP loading, indicating that the percent of DRP sorbed (dashed gray lines) increases from <10% to >50% with DRP loads, discharge (point size), and suspended sediment loads (not shown). The main plot shows results for a colloidal-P:DRP ratio of 0 while the inset shows results for a ratio of 0.5. (c), The daily mean distance suspended sediment travel during high flow before P sorption saturates (each arrow) is shorter than the distance to Lake Erie (Waterville, OH is 26 km from Lake Erie). The thicker line shows predictions for colloidal-P:DRP ratio of 0.5 while a ratio of 0 is shown with a thin line. Splines are a LOESS fit for a colloidal-P:DRP ratio of 00 0 to aid visualization. Stream codes are: Unnamed tributary to Lost Creek = UTLC; West Creek = WC; South Turkey Food = STF.

shaped by discharge and sediment delivery to this river system. Discharge, integrated across March-June high flow events for each year, exhibited no directional trend during 1975–2019, but increased during 1985–2019 (Fig. S8a; R^2 = 0.30; P < 0.001). Similarly, during 1975–2019, suspended sediment loads exhibited no directional trend (Fig. S8b) but were positively correlated with discharge (Fig. S8c). After accounting for changes in discharge, suspended sediment loads generally decreased during 1975–2019 (Fig. S8d; see Stow et al., 2015 for a comprehensive analysis). For example, at a discharge of 4000 m^3 x 10^6, suspended sediment loads decreased 58% between 1975 and 2019 (1.89 × 10^3 tons dry mass decade^{-1}; Fig. S8d).

Declines in P sorption related to lower suspended sediment loads helped explain increased DRP loading to Lake Erie during 2003–2019. For colloidal-P:DRP ratio of 0 and 0.5, the most likely multiple regression model of observed DRP loads contained an interaction between discharge and year group (i.e., 1975–2002 versus 2003–2019) indicating that DRP loads increased more rapidly with discharge after 2003 then before (Fig. 4, Tables 1 and S3). At a discharge of 4000 m^3 x 10^6, observed DRP loads were 57% higher after 2003 than before (1975–2002: 223 tons P; 2003–2019: 351 tons P; also see Stow et al., 2015). Yet, when we estimated 2003–2019 DRP loads with historic suspended sediment concentrations and P sorption rates, we found that the DRP load – discharge relationship became more similar before and after 2003. At a discharge of 4000 m^3 × 10^6 and a colloidal-P:DRP ratio of 0 or 0.5, DRP load predicted with historic sediment loads was, respectively, only 11% (1975–2002: 225 tons P; 2003–2019: 250 tons P; Figs. 4, S9 and Table 1) or 29% (1975–2002: 223 tons P; 2003–2019: 289 tons P; Figs. 4, S10 and Table S3) higher after 2003 than before. Thus, increased DRP loading to Lake Erie during 2003–2019, was likely driven, in part, by an increase in discharge (Fig. S8a) and a decrease in P sorption associated with declines in suspended sediment (Figs. 4 and S8d).

3.3. Phosphorus partitioning (K_d)

The P partitioning coefficient (K_d) calculated for tributary waters and

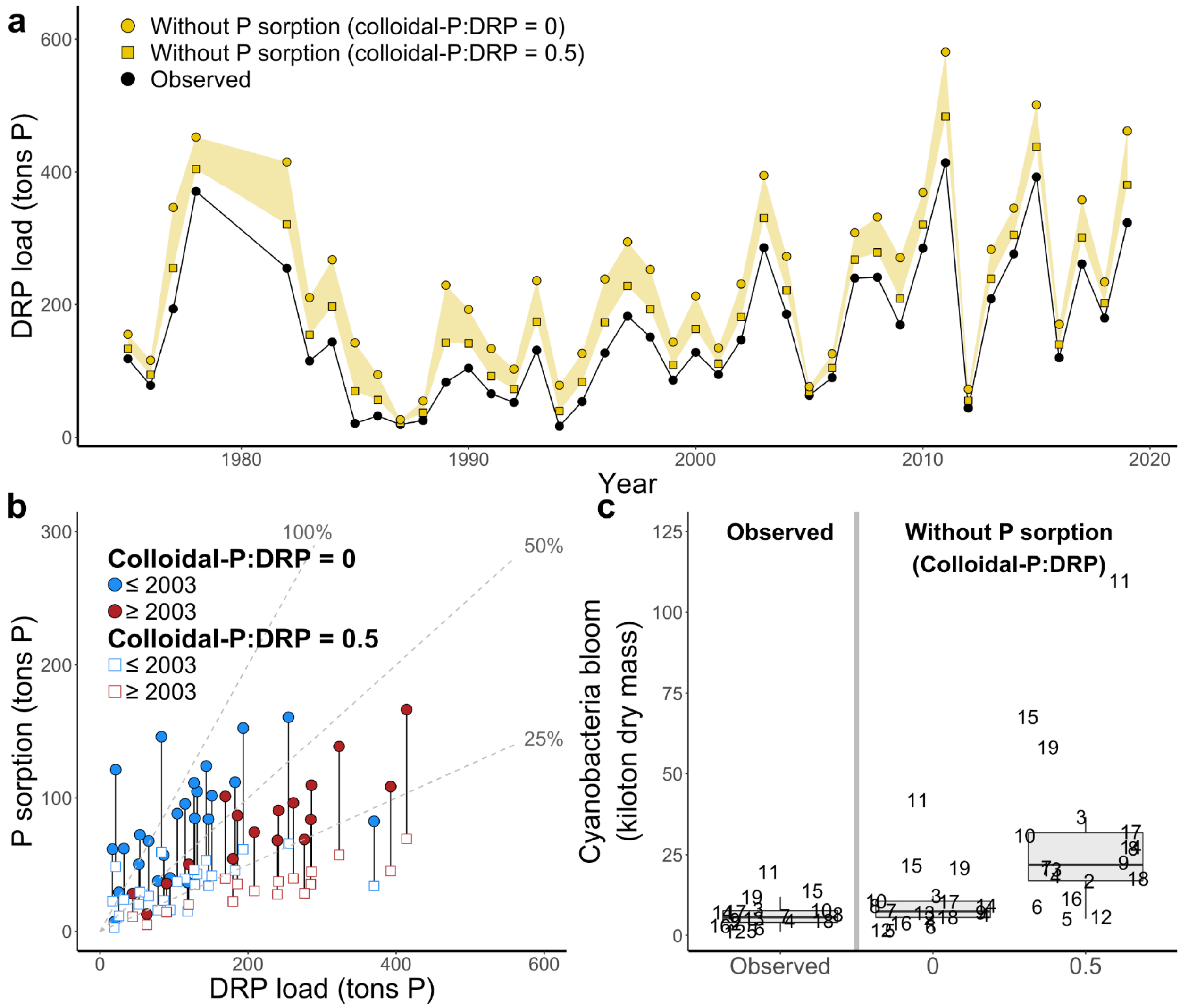

Fig. 3. Dynamics and effects of P sorption in the Maumee River network. (a), Patterns in Maumee River DRP loads as observed and estimated in the absence of P sorption (i.e., observed DRP load + P sorption). The gold ribbon shows estimated DRP in the absence of P sorption assuming a colloidal-P:DRP ratio of 0 and 0.5. (b), Relationship between P sorption (assuming a colloidal-P:DRP ratio of 0 and 0.5) and DRP load illustrating differences in the percent of DRP sorbed (gray lines) for periods before and after 2003. Estimates of P sorption with 95% confidence intervals are shown in Figs. S6 and S7. (c), Estimated effect of P sorption on the maximum cyanobacterial density during 2002–2019 assuming a colloidal-P:DRP ratio of 0 and 0.5. Values in a–c were calculated for high flows (≤ 25% exceedance) between March and June.

the Maumee River (March-June of 1975–2019, excluding 1979–1981) during high flow events indicated that sediment-P was highly reactive but varied through time and among streams (Fig. S11 and SI Section 2.1). In the tributaries, K_d varied among streams and declined with suspended sediment concentrations (Pseudo $R^2 = 0.79$, Fig. S11a). In the Maumee River, K_d indicated that the reactivity of sediment-P declined between March and June and was highest during 1985–1995 (Fig. S11b–d). After accounting for suspended sediment concentration, K_d increased with $\log_{10}$ watershed area (Fig. S12; $R^2 = 0.92$, $P < 0.001$) suggesting that during high flow events suspended sediment sorbed P during downstream transport.

4. Discussion

4.1. Overview

The expectation that rivers function like pipes during high flow events, transporting P downstream with minimal impact on the magnitude or forms of P, has greatly simplified watershed scale P modeling and management, however, our results challenge that prediction. We show that within the Maumee River system, suspended sediment transported during high flow can sorb a substantial quantity of DRP, likely constraining cyanoHABs and the resulting consequences. Furthermore, we show that declines in sediment exports, likely linked to on-field sediment erosion control measures, decreased P sorption and increased DRP exports partially explaining the recent proliferation of cyanoHABs within Lake Erie. While we make several assumptions that require further examination (see Section 4.4), our measurements and modeling indicate that in 10's of river kilometers, river P cycling during high flow can influence bioavailable P exports and potentially cyanoHABs in recipient ecosystems. These processes are strongly influenced by climate and land use practices, particularly those affecting P and sediment exports, and discharge. Thus, there is a need to better understand how DRP–sediment P interactions during high flows influences DRP exports in other agricultural watersheds to inform management and policy.

4.2. River P cycling mediates downstream water quality

Our results indicate that during 2003–2019 March to June high flow

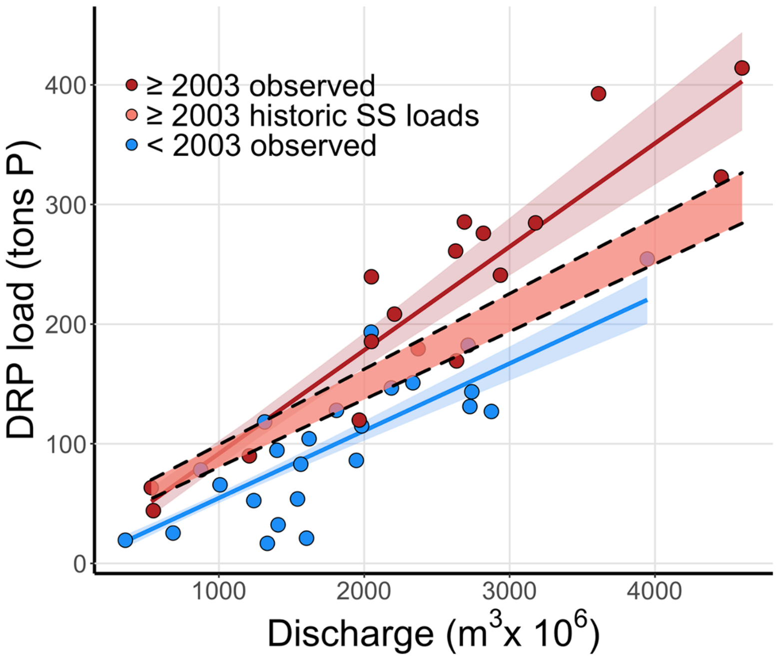

Fig. 4. Relationship between dissolved reactive phosphorus (DRP) load and discharge during 1975–2002, 2003–2019, and 2003–2019 with DRP loads estimated using historic suspended sediment – discharge relationships. The salmon-colored ribbon bounds estimates assuming a colloidal-P:DRP ratio of 0 and 0.5; point estimates are provided in Figs. S9 and S10. These models predict that if the suspended sediment – discharge relationship had not changed, 2002–2019 DRP loads would be more similar to observed loads during 1975–2002. Values were calculated for high flows (≤ 25% exceedance) between March and June.

Table 1
Summary statistics for generalized linear models predicting Maumee River dissolved reactive phosphorus (DRP) load – discharge relationships for two time periods, assuming the colloidal-P:DRP ratio is 0.[1] .

Group	1975–2002 observed v. 2003–2019 observed		1975–2002 observed v. 2003 – 2019 predicted with historic sediment loads	
Model	Multiplicative	Additive	Multiplicative	Additive
Intercept	−1.61 (± 7.03; 0.821)	−7.18 (± 5.94; 0.234)	−1.61 (± 7.45; 8.31)	−1.94 (± 6.47; 0.766)
Discharge	0.06 (± 0.01; < 0.001)	0.06 (0.01; < 0.001)	0.06 (± 0.01; < 0.001)	0.057 (± 0.005; < 0.001)
G	6.96 (± 17.35; 0.691)	45.40 (± 13.47; 0.002)	24.36 (± 18.01; 0.184)	25.75 (± 11.04; 0.025)
Discharge × G	0.03 (± 0.01; 0.026)	–	0.00 (± 0.01; 0.921)	–
Pseudo R^2	0.77	0.74	0.67	0.67
df	37	38	37	38
AICc	436.7	438.6	431.9	429.3

[1] The first comparison examines differences in DRP load – discharge relationships using a categorical term separating two groups (G): observed 1975–2002 and 2003–2019 loads. The second comparison examines differences in DRP load – discharge relationships using a categorical term comparing 1975–2002 observed DRP loads with 2003–2019 DRP loads estimated using historic (1975), discharge-adjusted suspended sediment loads and sorption based on the model in Table S2. Values provided for model coefficients (e.g., intercept and discharge) are the estimate, standard error, and p-value. Discharge and DRP load values are for high flows (≤ 25% exceedance) during March–June. These relationships are shown in Fig. 4.

events, P sorption by suspended sediment decreased DRP exports to western Lake Erie by 27% (or 13% assuming colloidal-P:DRP ratio of 0.5) and increased sediment-P exports by a similar percent. Since DRP is more bioavailable to cyanoHABs than sediment-P (Baker et al., 2014a; Bertani et al., 2016); this process likely decreased bioavailable P loading to the lake. In this system, immobilization of DRP onto suspended sediment currently represents a long-term P sink because ~70% of sediment exports are buried near the Maumee River mouth (Baker et al., 2014b) where bottom sediment contributes little to internal P loading (Matisoff et al., 2016). Thus, we estimate that P cycling in the Maumee River system may have constrained cyanoHABs by up to 40% (13% with a colloidal-P:DRP ratio of 0.5). While nitrogen or light limitation might keep cyanobacteria from reaching these levels (Chaffin et al., 2018), sediment–dissolved P interactions likely reduce the bioavailability of P exports to Lake Erie and serve as a substantial and previously unknown constraint on cyanoHABs.

One important gap in our understanding of river P cycling during high flow events is associated with composition and bioavailability of DRP. Approximately, 50% of DRP in the Maumee River may be associated with colloids, at least during median February flows (River and Richardson, 2019). We estimate that if colloidal-P:DRP is 0.5 and colloids do not sorb P, that P sorption during high flow events would decline by 4 – 34% in tributary waters and 40% in Maumee River waters, relative to estimates assuming that all DRP can sorb to suspended sediment. Unfortunately, evaluation of these predictions will require more information on longitudinal and seasonal variation in colloidal-P: DRP ratios. While colloidal-P could be no more bioavailable than suspended sediment, colloids do sorb P (Baken et al., 2016, 2014). It is possible that during downstream transport from headwaters to the Maumee River at Waterville, phosphate is sorbed to both colloids and suspended sediment, increasing the colloid-P:DRP ratio as well as decreasing both DRP and bioavailable P concentrations.

Changes in P sorption rates during high flow, due to declining sediment loads can help explain increases in DRP loading to western Lake Erie during 2003–2019. Our results indicate that increases in DRP loads to Lake Erie can partially be explained by increases in March to June discharge and, after changes in discharge are accounted for, declines in P sorption associated with declining suspended sediment loads. Suspended sediment exports from the Maumee watershed have been reduced by agricultural conservation practices (e.g., cover crops and reductions in tillage) which have decreased soil erosion on agricultural fields (Richards et al., 2009). Unfortunately, the relative effect of other proposed mechanisms for increased DRP loading to Lake Erie (e.g., soil stratification, macropores, legacy P, or tile drains) have not been estimated at spatiotemporal scales that facilitate a comparison with P sorption (e.g., the Maumee River watershed; Jarvie et al., 2017; Smith et al., 2018); however, these processes also shape patterns in discharge and DRP loads at edge-of-field sites and thus have also contributed to increases in DRP loads and cyanoHABs since 2003.

Climate change may have unanticipated effects on the role river P cycles play in watershed nutrient budgets. In the Maumee watershed, climate change, which is predicted to increase spring precipitation by up to 20% by 2100 (Hayhoe et al., 2010), could increase river discharge (Bosch et al., 2014; Culbertson et al., 2016; but see Kalcic et al., 2019), likely leading to more erosion, higher suspended sediment loads, and more P sorption; potentially decreasing the bioavailability of P loads to Lake Erie. However, the cumulative impact of river P cycling on cyanoHABs will depend upon these processes as well as other climate impacts on internal P loading in western Lake Erie. While rates of P release from benthic sediment in western Lake Erie are currently low relative to cyanoHAB demand (Matisoff et al., 2016), changes in water temperature or the prevalence of anoxia could greatly increase internal recycling rates leading to the release of sorbed P from lake sediment (Gibbons and Bridgeman, 2020).

4.3. Relevance to other watersheds

We hypothesize that our central message is transferable to other agriculture-dominated systems: during high flow, sediment–dissolved P interactions influences bioavailable P exports –increasing or decreasing these exports depending upon the balance of EPC_0 and phosphate– but that the influence of these riverine processes on downstream water quality has been decreasing due to declining suspended sediment loads. Our results indicate that within 10's of river kilometers there is sufficient time during high flow events for P cycling to influence bioavailable P exports. Yet, depending upon whether suspended sediment sorb or release P, riverine P cycles could enhance or mitigate cyanoHAB severity. The magnitude of this effect is dependent upon suspended sediment loads which have declined over the last 50 years in many large and small river systems (e.g., Mississippi, Ohio, Yangtze, and Yellow rivers), due to changes in climate, reservoir impoundment, and agricultural practices (Lu et al., 2013; Meade and Moody, 2009; Mize et al., 2018). While these changes in suspended sediment exports have a positive effect on many aspects of aquatic health and water quality, our results indicate that they may be altering instream P cycling through unappreciated mechanisms.

In other large watersheds, there is insufficient information to predict DRP-sediment P interactions during high flow events. Measures of P sorption and desorption by suspended sediment during high flow are rare and it is unlikely that P sorption measures for benthic sediment, which are common (Simpson et al., 2021), can help predict P cycling during high flows. Compared to benthic sediment, suspended sediment transported during high flow may be newly eroded or resuspended benthic material, which may have different P cycling characteristics due to its biogeochemical history and changes in environmental conditions.

Finally, our prediction that a decrease in bioavailable P and increase in sediment-P constrains cyanoHABs over the long-term may be limited to lakes similar to our study system. Western Lake Erie is a model system for shallow large lakes that are productive, found in relatively flat agriculture-dominated systems, and have low P regeneration rates from lake sediments (Orihel et al., 2017; Sondergaard et al., 2003). In lakes with low internal P regeneration rates, external bioavailable P loads are a dominant driver of cyanoHABS. In contrast, in lakes with high sediment-P regeneration rates, changes in DRP loading due to DRP–sediment P interactions will alter the bioavailability of P loads and the response of the lake to P management.

4.4. Potential limitations

Our study makes several assumptions related to the generalizability of P sorption in tributary waters to the whole Maumee river network. During 1975–2019, changes in sediment composition may have altered P sorption characteristics. However, comparison of our results with earlier work (Green et al., 1978) indicates that between 1976 and 2019 suspended sediment sorbed P during high flow and had similar EPC_0 values (Green: 30–180 μg P/L; this study: 1–55 μg P/L) and sorption maxima (Green: 510–2063 μg P/g; this study: 103–3167 μg P/g). It is also possible that we did not adequately characterize the full range of sediment sorption-desorption across this large watershed. However, we sampled P sorption in six tributaries during 13 storm events, capturing wide variation in discharge and seasonality in ground cover and agricultural practices. Our sites are also representative of the major land use and represent the dominant geologic parent material in the watershed. The sites we used to scale up P sorption estimates reflect the range of sorption rates and suspended sediment concentrations we observed in our six study sites (Fig. S5).

4.5. Implications for P and cyanoHAB management

We describe an apparent tradeoff in water quality management: suspended sediment, which is transported to streams following erosion, has a negative effect on many aquatic biota but potentially a positive benefit for cyanoHABs control. Nevertheless, the best way to manage cyanoHABs is to reduce P losses at the source through limiting P application on fields. Our results do not indicate that management of sediment erosion should be halted to control cyanoHABs. Erosion control practices provide benefits to agricultural systems (Osmond et al., 2019) and reduces the negative effects of sediment pollution in freshwater ecosystems (Blann et al., 2009). Furthermore, with changing environmental conditions, P bound in lake sediment could fuel internal P loading and cyanoHABs (Gibbons and Bridgeman, 2020). Instead, our results provide insight into the processes which shape DRP and sediment-P exports to recipient ecosystems and illustrate how management of one pollutant (sediment) can exacerbate the effects of another pollutant (phosphorus).

A lack of understanding of riverine P cycling can lead to a misattribution of P loads to the wrong location, contributing uncertainty to P management. For instance, our results suggest that relative to a model assuming conservative downstream transport of DRP and sediment-P, land in the Maumee watershed exported 4–10% less sediment-bound P (based on colloidal-P:DRP = 0–0.5) than river monitoring indicates, but 14–36% more DRP (81 metric tons P). Thus, to achieve a 40% reduction in DRP exports, the current target for the Maumee watershed, P losses from agricultural fields need to be reduced by 14–36% more than previously thought (7.1–8.4 kg km^{-2} versus 6.2 kg km^{-2}). In addition, agricultural best management practices which reduce soil erosion more than DRP losses, require special consideration because they may inadvertently increase DRP losses from the watershed (Osmond et al., 2019).

Identifying small watersheds with especially high P exports is important for efficiently targeting management actions (Osmond et al., 2019); yet riverine processes may complicate this targeting. For example, DRP losses from agricultural lands in the STF and UTLC watersheds might be ~24–37% and 48–50% higher, respectively, than monitoring at the terminal end of the watershed suggests due to P sorption. These differences in STF and UTLC can largely be attributed to differences in mass-specific P sorption rates (e.g., g P g DM^{-1} h^{-1}) of suspended sediment. At the median suspended sediment concentrations across all tributaries, UTLC suspended sediment exhibited a 2.5-fold higher sorption rate than STF suspended sediment (Fig. S5).

Thus, to improve identification of watersheds with high P exports and evaluate interactions between management of sediment erosion and P losses; it is important to understand colloidal-P dynamics and incorporate river P cycling into watershed models and management. Indeed, our results, contribute to numerous low-flow studies demonstrating that river P cycles can alter the magnitude and bioavailability of P exports (Jarvie et al., 2011; Withers and Jarvie, 2008). Yet, the role of riverine processes in shaping P exports, particularly during high flow events when most P export occurs, is rarely incorporated into watershed models or P management (Jarvie et al., 2012, 2013; White et al., 2014). Our research emphasizes the need to simultaneously manage sediment and nutrients with a watershed-scale approach that considers P sources, sinks, and transformations (Kreiling et al., 2018). Such an approach would help address potential unanticipated consequences that could undermine management, waste conservation funds, and erode public trust.

5. Conclusions

During high flow events, P sorption-desorption by suspended sediment can alter bioavailable P exports to recipient ecosystems.

During 2002–2019 March–June high flow events, P sorption by suspended sediment in the Maumee River network likely reduced DRP exports by 13–27%, depending upon the colloidal-P:DRP ratio, potentially constraining cyanobacteria blooms by 13–40%.

The magnitude of P sorption was controlled by suspended sediment concentrations, which have, after accounting for changes in discharge, decreased in the Maumee River between 1975 and 2019.

The decline in suspended sediment concentrations was associated with a decline in P sorption which could partially explain increases in DRP loading to Lake Erie during 2002–2019.

Our results provide evidence of interactions between sediment and nutrient management, emphasizing the need to simultaneously manage both substances with a watershed-scale approach.

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Data availability statement

Code and data necessary to reproduce all results are available on GitHub (https://github.com/hood211/HighFlowSorption).

CRediT authorship contribution statement

Whitney M. King: Conceptualization, Methodology, Formal analysis, Visualization, Investigation, Funding acquisition, Writing – review & editing. **Susan E. Curless:** Methodology, Investigation, Writing – review & editing. **James M. Hood:** Conceptualization, Methodology, Formal analysis, Visualization, Investigation, Funding acquisition, Project administration, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

Authors declare that they have no competing interests.

Data availability

All data and analysis scripts can be found in our GitHub repository: https://github.com/hood211/HighFlowSorption.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.118845.

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