Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2019, 53, 5613−5621

pubs.acs.org/est

Stream Nitrogen and Phosphorus Loads Are Differentially Affected by Storm Events and the Difference May Be Exacerbated by Conservation Tillage

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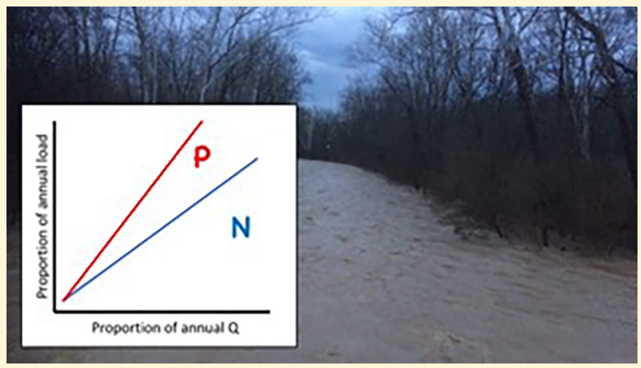
Supporting Information

ABSTRACT: Storm events disproportionately mobilize dissolved phosphorus (P) compared to nitrogen (N), contributing to reduction in load N:P. In agricultural watersheds, conservation tillage may lead to even further declines in load N:P due to dissolved P accumulation in the top soil layers. Due to an increase in this management activity, we were interested in the impacts of conservation tillage on N and P loads during storm events. Using a 20 year data set of nutrient loads to a hypereutrophic reservoir, we observed disproportionately increasing P loads relative to base flow during storm events, whereas N loads were proportional to discharge. We also observed a change in that relationship, i.e., even greater P load relative to base flow with more conservation tillage in the watershed. This suggests conservation tillage may contribute to significantly reduced N:P loads during storms with potential implications for the water quality of receiving water bodies.



■ INTRODUCTION

Anthropogenic inputs of nitrogen (N) and phosphorus (P) to aquatic ecosystems can result in algal blooms, hypoxia, and other symptoms of eutrophication.[1] Furthermore, nutrient loading to aquatic systems may be exacerbated by climate change, especially by increases in total precipitation as well as in the relative contribution of storm events with very heavy precipitation. Nutrient inputs during just a few storm events may represent the bulk of annual nutrient load to many lakes.[2−4] This may be especially true in agricultural watersheds, as spring storms coincide with fertilizer application onto farm fields.[5] Because high nutrient runoff may lead to eutrophication and the dominance of cyanobacteria and associated cyanotoxins,[1] high nutrient loads during storm events may be of concern for lake managers interested in preserving water quality and ecosystem services of the receiving water bodies. Further understanding of how N and P loads respond to large precipitation events is important in developing more effective management plans, especially in light of documented and predicted further increases in large events with future climate change.[6]

While the absolute loads of N and P into lakes are of concern for eutrophication, the ratio of N to P (N:P) may also be important, especially in structuring phytoplankton community composition. Low N:P in lakes has been associated with greater cyanobacterial dominance of the phytoplankton community, as some cyanobacteria taxa can overcome N-limitation through N-fixation.[7−11] Because low N:P supply potentially plays a role in creating harmful algal blooms and the associated reduction in ecosystem services, a better understanding of what regulates load N:P ratios is important. Previous work pointed to the potential role of storms in mediating N:P ratios.[12,13] At present, we know little about how N:P loads from large storm events are changing as a result of long-term climate shifts or land management practices.

Management techniques have been implemented at large scale in agricultural watersheds in order to mitigate soil erosion, and therefore the loads of sediment-associated nutrients to water bodies. One such management technique is conservation tillage, which includes reduced- and no-till methods, and is defined as leaving at least 30% of the soil surface covered by crop residue after tillage activities. The use of this technique has increased in the Lake Erie watershed,[14,15] as well as other agriculturally dominated landscapes.[16] While demonstrated to be effective in reducing soil erosion and particulate nutrient loads to water bodies, after several years conservation tillage may actually increase dissolved nutrient

Received: September 12, 2018
Revised: January 4, 2019
Accepted: March 12, 2019
Published: March 12, 2019

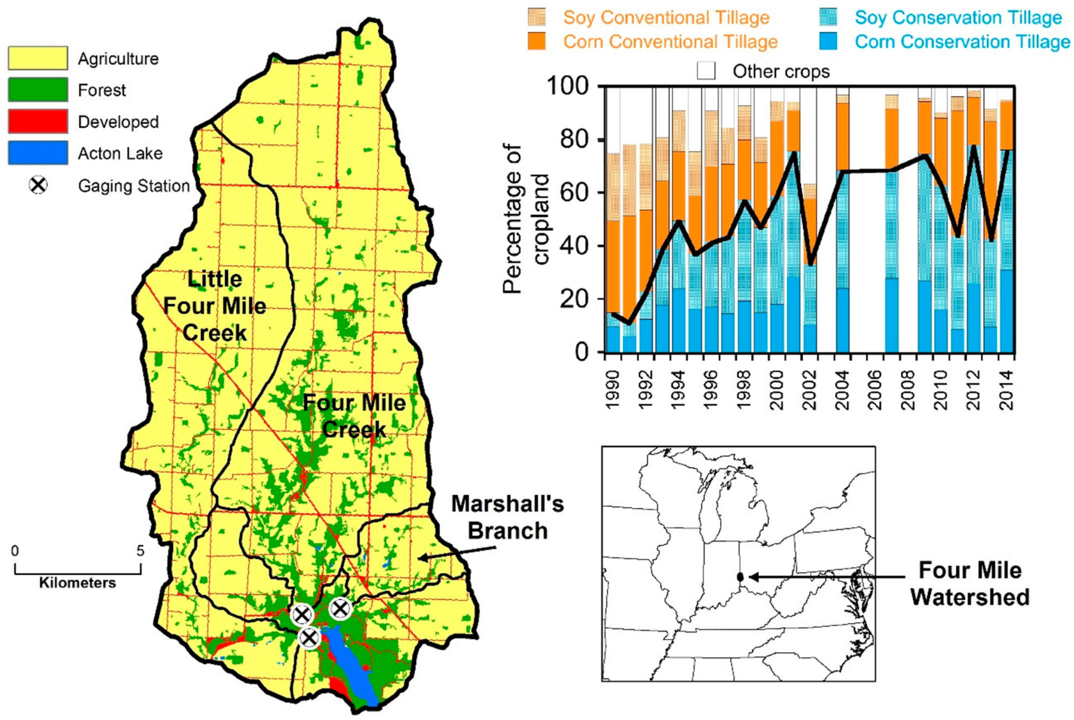


Figure 1. Map of the Acton Lake watershed showing three inlet streams, land use patterns, and location of gauging stations. Also shown is a stacked barplot of trends in both tillage and crop type as a percentage of cropland in the watershed through time. Solid line represents the total percentage of cropland in conservation tillage.

loads compared to conventionally tilled fields due to an accumulation of soluble P in the top soil layers.[17,18] This "stratification" of P in soil may also mean that in addition to increases in overall loads of dissolved P, there may be greater mobilization of P during storm events and ultimately an even more disproportionate effect of high precipitation events on delivery P to the lake. In contrast, dissolved N loads are more driven by shallow subsurface flow.[3] In addition, conservation tillage may affect N and P loads differently. In particular, stream nitrate concentrations seem to respond more slowly than P concentrations to conservation tillage, but after 10−20 years, declines in stream nitrate concentrations can be substantial.[19,20] These differences in nutrient mobilization dynamics, especially in landscapes with widespread conservation tillage, may therefore significantly reduce N:P load during storm events.

Given the relative importance of storm events in contributing to the annual nutrient budget of many lakes, a greater understanding of how extreme events mobilize nutrients, and how storm-mediated mobilization differs for N versus P, will be useful in developing management approaches for highly impacted lakes under new precipitation regimes. In particular, we need to understand the implications for reduced eutrophication and cyanobacteria populations, especially under scenarios of predicted increases in storms with climate change. Additionally, there has been a great deal of interest in the efficacy of conservation tillage as a management solution to reduce N and P loads. However, given that dissolved and particulate nutrient fractions often respond differently to conservation tillage and that N and P also respond differentially, we still know relatively little about how N and P, and the N:P ratio, may react to large storm events under increased conservation tillage. To achieve this understanding, we used a 20 year data set of daily N and P load estimates to Acton Lake, a hypereutrophic reservoir in southwest Ohio, United States, whose watershed has undergone a large increase in conservation tillage over approximately the last 2.5 decades. The goals of this study are to (1) compare how dissolved and total N and P loads are affected by storm events and (2) determine whether the relationships between storms and nutrient loads have changed over a time period (20 years) associated with increased conservation tillage.

■ MATERIALS AND METHODS

Site Description. Acton Lake is situated within the Upper Four Mile Creek (UFMC) watershed in southwestern Ohio and southeastern Indiana.[21] The UFMC watershed is comprised mostly of agricultural land[22,23] (∼80%, Figure 1) with poorly drained soils of high-lime glacial until capped with silt loess. As such, tile draining is a common practice within the watershed, and it is estimated that at least 50% of cropland is artificially drained, with that extent likely increasing, but not rapidly.[24] The lake is a ∼ 250 ha eutrophic reservoir that typically exhibits poor water quality, including high nutrient concentration, turbidity, and phytoplankton biomass.[25] Dynamics of changes in constituent concentration with stream discharge and season are variable and described in detail in ref 21. The loads calculated in this study were from three inlet streams which collectively drain approximately 86% of the watershed (Four Mile Creek, Little Four Mile Creek, and Marshall's Branch). Detailed descriptions of the hydrology and nutrient concentrations in these streams have been described elsewhere.[16,20,26] The Acton Lake watershed was targeted for erosion control in the early 1990s and as such has undergone increases in the proportion of land in conservation tillage, mainly between 1991 and 2001[16,23] (Figure 1). These management techniques led to substantial declines in bank erosion and concentrations of suspended solids and soluble

DOI: 10.1021/acs.est.8b05152
Environ. Sci. Technol. 2019, 53, 5613−5621

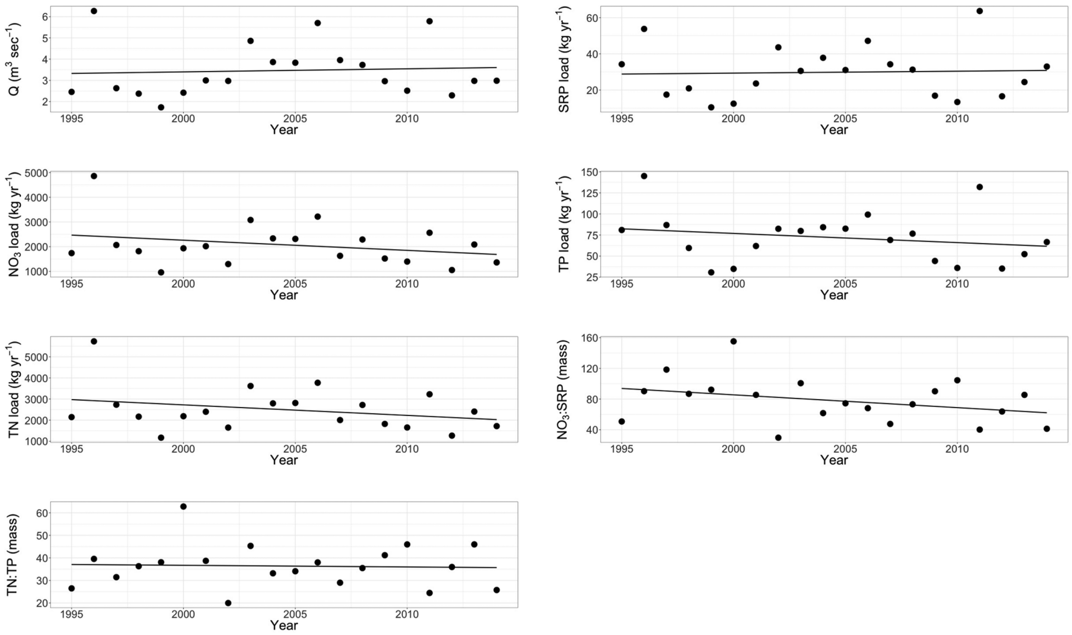


Figure 2. Trend in average discharge and loads for NO_3–N, total nitrogen (TN), SRP, total phosphorus (TP), NO_3/SRP, and TN/TP. Each point represents a yearly average, and the line represents linear regression.

reactive phosphorus (SRP) in the inlet streams, standardized for discharge and season, from 1994 to 2006.[16,20,27] However, streamwater quality trends have varied over time. In particular, although stream SRP concentrations declined over roughly the first decade of our study (1994–2004), they actually increased over approximately the second decade (2004–2014), although they are still lower than at the beginning of the 20 year period. In contrast, stream NO_3–N did not change much in the first decade but declined rapidly in the second decade.[20] Constituent concentrations in these streams vary by 2–5 orders of magnitude but averaged 63 μg L^{-1} for SRP and 5966 μg L^{-1} for NO_3–N over our study period. While there is some evidence that precipitation amount and intensity have changed over the last two decades in this region and will likely continue to change,[28,29] there is has been no discernible trend in mean annual discharge that would suggest systematic increasing trends in mean annual precipitation (Figure 2).

Stream Sampling and Constituent Analysis. Stream sampling stations have been installed in all the inlet streams since 1994; however, sampling was initiated midseason in 1994; therefore, data included in our analyses begin in 1995. Detailed sampling and analytical methods are presented in refs 16 and 21. Stage is recorded in each of the three inlet streams at 10 min intervals using pressure transducers installed in stilling wells to monitor discharge and is converted to discharge (m sec^{-1}) using rating curves. Water samples for nutrient analyses were collected using ISCO pumping samplers (Teledyne ISCO, Lincoln, NE) at 6–8 h intervals. All samples were processed at high flow events, while three or four samples per week were processed during low flow periods (because concentrations do not change rapidly during low flow). Samples were analyzed for nitrate plus nitrite-N (hereafter, NO_3), soluble reactive phosphorus (SRP), and suspended sediments (SS) over all years of the study period (1995–2014). From 1994 to 1998, nutrients were analyzed manually, and from 1999 on, they were measured on a Lachat autoanalyzer. Throughout the study, SRP was assayed with the molybdenum blue method. NO_3–N was measured with second-derivative spectroscopy from 1994 to 1998 and with cadmium reduction method from 1999 and onward. To standardize concentrations for methodological changes (including the shift from manual methods to the autoanalyzer), we analyzed numerous samples using both pre- and post-1999 methods. The methods gave similar results, but nevertheless, all concentrations were standardized to those based on the autoanalyzer methods as described in ref 16. Suspended sediment concentrations were estimated by passing a known volume of streamwater through a preweighed glass fiber filter (Pall A/E), drying to constant mass, and reweighing.[21] Total N and total P were determined as the sum of total dissolved N (or P) plus particulate N (or P), none of which were directly measured routinely. Instead, total dissolved N and P (TDN and TDP) were determined using stream-specific regression with NO_3–N versus TDN and SRP versus TDP ($r^2 > 0.78$ and 0.81, respectively) on a subset of samples on which both dissolved inorganic and total dissolved fractions were measured. Similarly, particulate N and P (PN and PP) were determined via stream-specific regression with suspended sediment (SS) concentration on a subset of samples on which SS, PN, and PP were all measured ($r^2 > 0.82$ and 0.67 for PN and PP, respectively). For detailed description of regression equations see Table 3 in ref 21. We used this approach because high concentrations of inorganic soil particles in these streams (mainly in storm samples) interferes with common methods for measurement of total P; therefore, we opted to measure dissolved and particulate fractions separately and add them to obtain total N and P (TN and TP).[30]

Load Calculation. We used the *loadflex* package in the R statistical environment[31] to estimate daily constituent loads to Acton Lake. We used the composite method to estimate loads using the *loadComp()* function to give average daily estimates of load. Total loads were then divided by 0.86 to account for fraction of the watershed that is ungauged. More detailed description of the *loadflex* package can be found in ref 32, and that of Acton Lake load calculations is found in ref 26.

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Data Analysis. To determine how N and P loads are influenced by storms relative to base flow conditions, we used two techniques. First, we defined the 10 days from 1995 to 2014 with highest daily discharge as the top 10 "events". For each event, we found a corresponding amount of consecutive days during lower flow conditions (what we define as "base flow", usually July−October) of the same year that cumulatively approximated the discharge from the associated event. Discharge during the "event" day and the corresponding base-flow period differed by <1%. We then compared loads of NO_3−N, SRP, TN, and TP during the event versus the associated base flow period to get a perspective of the difference between extreme events and base flow for each constituent (Figure 3). Our second technique was more comprehensive and objective; for each of the 20 years we calculated the proportion of annual discharge (Q_{prop}) and the proportion of annual load ($load_{prop}$) occurring on each day. Then, we quantified the relationship between the Q_{prop} versus the $load_{prop}$ for each year (n = 365 per year; 366 in leap years). Using proportions of annual discharge and load allows for a comparison among years that may have differed in discharge and among constituents that vary by orders of magnitude in load. The slope of the Q_{prop} versus $load_{prop}$ relationship was determined using a beta generalized additive model (gam) using a logit link function and including a smoothed predictor for day of year to account for temporal autocorrelation. Slope = 1 would indicate that load is simply proportional to discharge, at the daily scale, whereas slope > 1 indicates a disproportionate increase in load during high-discharge events. We compared constituents by comparing the means of the slopes for all constituents across all years of the time series. The years 1995 and 1997 were removed for TN and TP as model fits were poor, defined here as having an $R^2 < 0.85$. We also looked at trends in these slopes over the 20 years, to relate any changes that correspond to changes in the conservation tillage. As the effects of conservation tillage are generally not immediate,[15,18,20] we tested the trends in slopes from the start of the data set as well as the years between 2000−2014, as past work has observed changes in stream nutrient concentrations around that time. Furthermore, the increase in conservation tillage largely occurred in the 1990s; the proportion of cropland in conservation tillage varied from year to year after 2000, but there is no net increasing or decreasing trend.[20] To quantify these trends we used a Mann−Kendall test after checking for significant temporal autocorrelation. All analyses were performed in R,[31] using the "mgcv" package[33] to run gam models and the "trend" package[34] for Mann−Kendall tests.

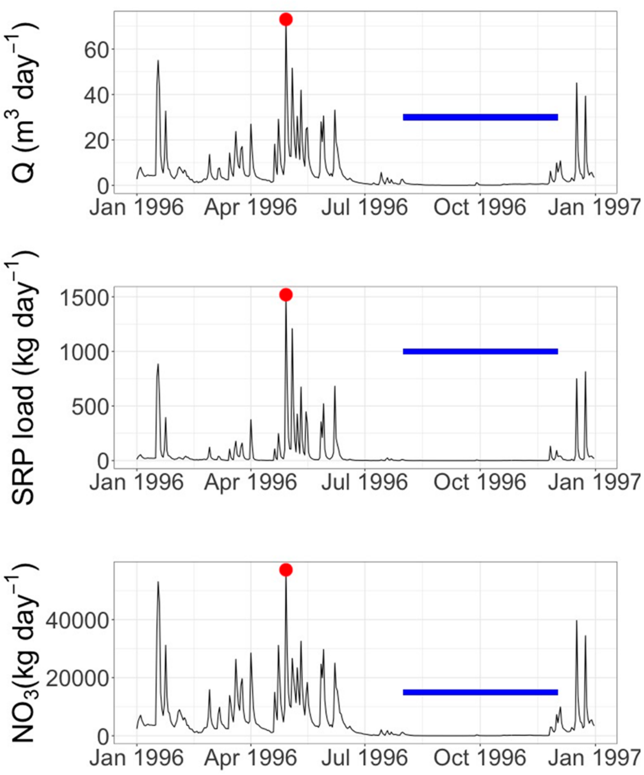

Figure 3. Example of a comparison of SRP and NO_3−N loads for one of the top 10 largest event days during the time series. Red points represent the event, and the blue bars represent the period of the year giving approximately equal cumulative discharge as the event.

RESULTS

Patterns in Discharge and Loads through Time. Annual discharge and constituent loads showed varying patterns throughout the time series, with trends in different directions depending on forms of N and P (Figure 2). Annual mean discharge showed an oscillating pattern of dry and wet and increased slightly, but not significantly, from 1995 to 2014 ($P = 0.58$, $z = 0.55$). Annual mean SRP and TP loads showed different patterns, as SRP load increased throughout the time series while TP declined subtly. Nitrate-N and TN loads both tended to decline throughout the time series. Load ratios for NO_3/SRP and TN/TP were also variable throughout the time series, with a nonsignificant decline in mean NO_3:SRP from 1995−2014 ($P = 0.14$, $z = -1.46$), and no trend in TN/TP. None of the constituent loads displayed a statistically significant trend from 1995−2014 ($P > 0.05$ in all cases); 1996 was an outlier year in both discharge and all constituent loads, as it was a very wet year with very high loads.[21,23]

Relationship between Extreme Events and Loads. P loads increased relatively more during storm events than N loads (Figure 4). When comparing the 10 largest daily events throughout the 20 year time series to comparable cumulative base flow during the same year, the mean ratios of event to baseflow NO3 and TN loads were 1.1 and 1.3, respectively (Figure 4a,c). In contrast, the mean ratios of event SRP and TP to baseflow loads were 8.4 and 5.5 (Figure 4b,d). The differential responses of N versus P led to declines in load NO_3−N/SRP and TN/TP during storm events. Median NO_3−N/SRP by mass was ∼13 for events, compared to 51 for base flow conditions (Figure 4e). Similarly, median TN/TP by mass was 9 during events compared to 25 during base flow (Figure 4f). Mean event daily discharge was slightly greater than cumulative base flow discharge (mean ratio of event discharge (Q) to baseflow Q = 1.003; Figure 4g).

Our second approach also showed that storms affect P loads more than N loads. The slopes of the relationship between $load_{prop}$ versus Q_{prop} were greater for P than for N for both dissolved and total fractions (Figures 5 and 6). The average slope of this relationship, across all years (n = 20), was 1.51 and 1.35 for SRP and TP (SE = 0.03 and 0.03), respectively. In contrast, slopes for NO_3−N and TN were 0.95 and 1.00 (SE = 0.01 and 0.00), respectively (Figures 5 and 6). The slopes near 1 for N fractions show that loads are proportional to discharge, whereas for P loads increase more than proportionally with discharge.

DOI: 10.1021/acs.est.8b05152
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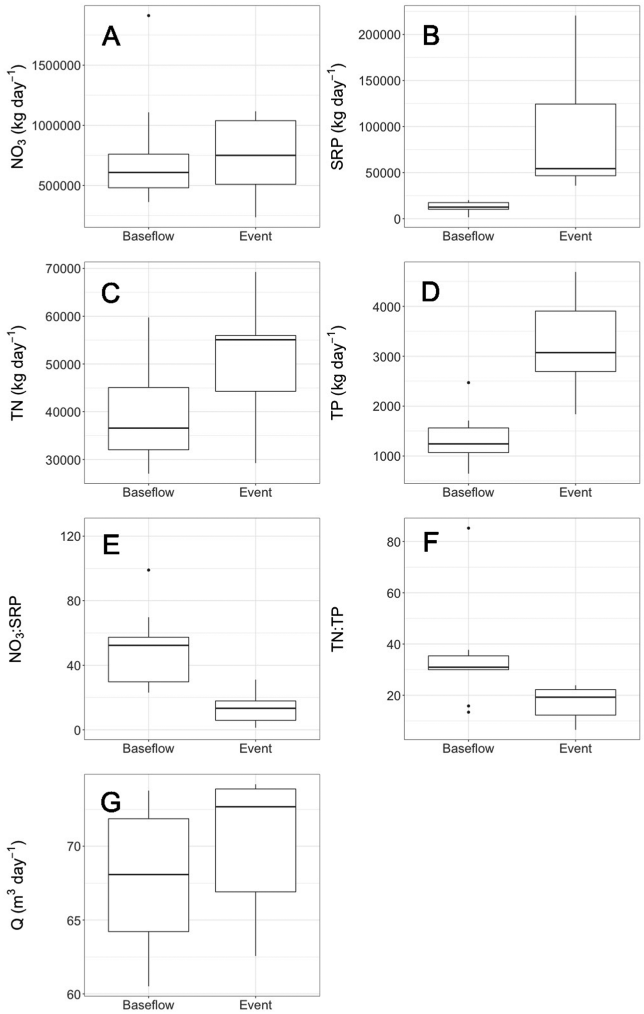

Figure 4. Boxplots for constituent loads (a–d), load ratios (e and f), and discharge (g) for the top 10 events throughout the time series. Boxes represent quantiles 5, 25, 50, 75, and 95 of the 10 data points for the base flow period and the event.

The slope of the relationship of $load_{prop}$ versus Q_{prop} increased over time for both P forms (SRP: z = 2.14, P = 0.03, TP: z = 2.68, P < 0.01; Figure 7). Slopes for N declined, but not significantly (NO_3: z = −0.09, P = 0.92; TN: z = −0.27, P = 0.79). These trends were different when looking at 2000–2014, with stronger trends in SRP compared to those for TP (SRP: z = 2.77, P < 0.01, TP: z = 1.88, P = 0.06). Trends in N were similar (NO_3: z = −0.39, P = 0.69; TN: z = 0, P = 1).

■ DISCUSSION

Loads of N versus P may be an important influence on lake phytoplankton community composition, as a low N:P load may contribute to N-limitation and ultimately an increase in prevalence of N-fixing cyanobacteria. Storm events tend to generate large fractions of both N and P loads for a given year because of their significant contribution to the annual discharge[21] (and for P, because of increased concentrations at high stream discharge). Therefore, storms may be important in regulating N:P of the lake, particularly during and after the events. We observed differences in the way N and P react to storm events versus base flow conditions, with larger storms bringing in proportionally more P than N, leading to sharply declining N:P during events. This pattern held for both dissolved and total fractions of N and P. We found that the relationship between proportional discharge versus proportional load also changed over time during the 20 years, but only for P, while N stayed relatively static. Our data suggest a larger proportion of the annual P load may be currently contributed by large storm events than in the past, presumably as a response to increased conservation tillage in combination with or interacting with extensive tile drainage in the watershed. This indicates management efforts aimed at reducing nutrient load have the potential to lead to changes in the mobilization of P during storm events, thereby increasing SRP loads during storms and reducing load N:P.

Relationship between Storm Events and N and P Loads. Large storm events bring significant pulses of both dissolved and total P to Acton Lake. This is characteristic of many agricultural watersheds, as the primary flow path for dissolved P is overland flow, leading to mobilization and transport downstream in runoff.[35−37] Particulate P is also driven exclusively by overland flow as it is coupled to sediment fluxes.[36] As a consequence, the proportion of annual P input budgets are almost entirely dominated by relatively few days of high discharge events.[4] For example, in Lake Mendota, WI, a majority of the P load for the year (∼74%) was delivered over a span of 29 days, with predicted annual P loads increasing as the number of high discharge days increase.[4,38] While these dynamics may, in part, be a function of timing of events and application of fertilizer on the landscape, we observe significant delivery of dissolved P during events throughout the calendar year (Figure 3).

In contrast to the relationship between discharge and P loads, daily N loads were proportional to daily discharge (i.e., we observed an approximate 1:1 relationship between Q_{prop} and $load_{prop}$ for N). Nitrate is more readily mobilized by subsurface flow, especially in areas with significant tile drainage, leading to a greater $load_{prop}$ (compared to that for P) transported during base flow conditions.[3,13,39] Additionally, large storm events may lead to an initial decline in in-stream concentrations of NO_3 due to dilution with surface runoff, before increasing later in the event.[21,26] Therefore, large pulses of water do not increase N load to the same degree as P. Additionally, our comparison of loads during events versus baseflows for the top 10 events throughout the time series includes a seasonal component for NO_3, but no seasonal effect of SRP. Nitrate concentrations in the in-flowing streams tend to be higher in the spring and decline in the middle of the summer, while SRP concentrations remain more seasonally constant.[20,21] As such, the relative difference between the responses of NO_3 compared to SRP is likely conservative, as NO_3 loading should be higher during events partially because NO_3 concentrations are higher during the time of year when large events typically occur (winter and spring). Ammonium (NH_4–N) responds in a manner similar to that for dissolved P, as it is mobilized by large storm events as opposed to subsurface flow.[37] However, NH_4–N is a minor contributor to the total dissolved N load to Acton Lake (median ∼1%) and in most agricultural watersheds in which fertilizers are heavily applied.[5,21]

Particulate fractions of P and N may respond differently than dissolved fractions, because in streams draining agricultural landscapes particulate nutrient concentrations are driven primarily by concentrations of sediment. However, suspended sediment loads to lakes are also heavily influenced by large

DOI: 10.1021/acs.est.8b05152
Environ. Sci. Technol. 2019, 53, 5613−5621

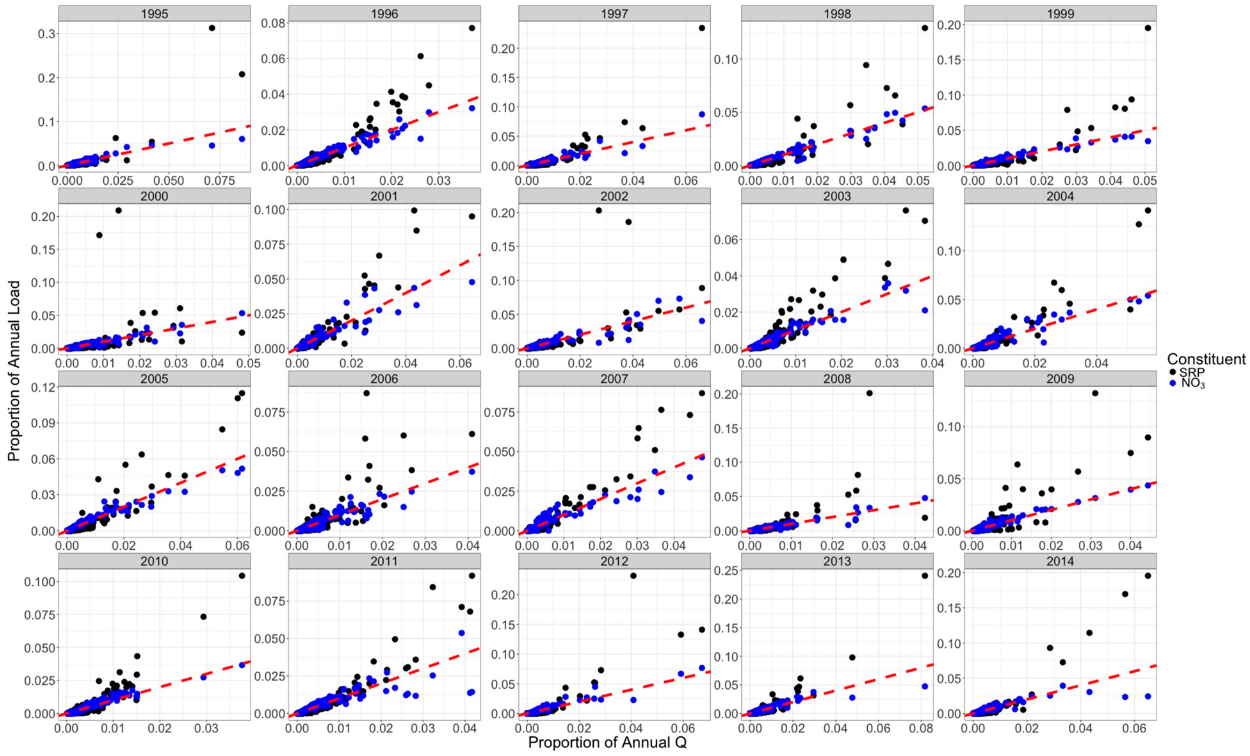

Figure 5. Scatter plots of proportion of annual load vs the proportion of annual discharge for each year of the time series. Black points represent SRP load and blue points represent NO_3−N load (N = 365 or 366). Red dashed line is the 1:1 line. Figure S1 shows only linear relationship of these data.

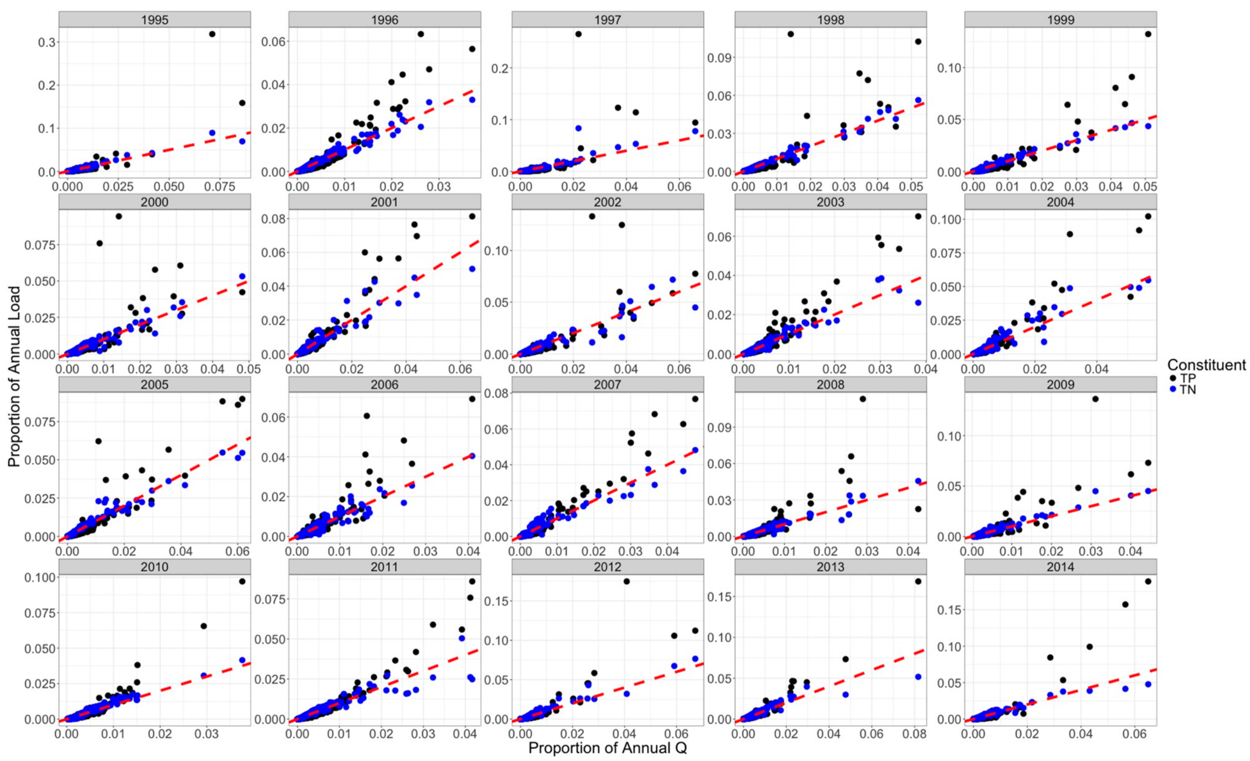

Figure 6. Scatter plots of proportion of annual load vs the proportion of annual discharge for each year of the time series. Black points represent TP load, and blue points represent TN load (N = 365 or 366). Red dashed lines are the 1:1 line. Figure S2 shows only linear relationship of these data.

storm events similar to dissolved P.[40−42] As an example, Sharpley et al. observed a majority of particulate P export (56−93%) in an agricultural watershed occurred during storm flow.[43] The mean slopes of $load_{prop}$ to Q_{prop} for both particulate N and P loads to Acton Lake were 1.16 (SE = 0.06 and 0.04, respectively) over the time series, suggesting a stronger

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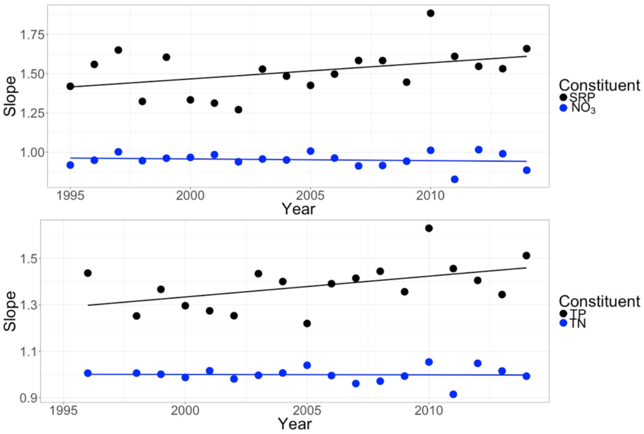

Figure 7. Plots of the GAM slope for the relationship between proportion of annual Q and proportion of annual load for SRP and NO_3 and TP and TN. Each point represents the slope for the year. Black points represent P, and blue points represent N. Years with poor model fits for the relationship between proportion of annual Q and proportion of annual load not shown in the time series.

influence of storm events on particulate nutrient mobilization compared to NO_3, but not SRP. In general, the composition of TN is dominated by NO_3 compared to TP which has more contribution from particulate P.[21] Because of the combination of these factors, the relationship between $load_{prop}$ and Q_{prop} (slope) for TN is similar to but slightly above that for NO_3−N, while the mean slope for TP is somewhat lower than that for SRP. Additionally, slopes between $load_{prop}$ and Q_{prop} for SS were highly variable, as sediment mobilization is related to timing and size of storm event.

The dynamics of both elements during base flow versus storm flow contribute to rapidly declining load N:P during storms. Median load NO_3/SRP (mass) during the top 10 events throughout the time series was approximately 13, compared to 51 for base flow conditions. Median load TN/TP (mass) during those events was 9 compared 25 for base flow conditions. This shift in N:P is important, as these events represent a significant contribution to the annual water and nutrient budgets of the lake. On average, the top 10 event days throughout the time series represent <1% of the days, 6% of the annual water load, and 19% of the total annual SRP load for each of the given years in which the events took place. Cumulative discharge over a storm event (which may occur over multiple days) may contribute up to 20% of the annual water load. As such, these events, while short in duration, represent significant pulses of nutrients that may influence the ultimate nutrient concentrations and ratios of N:P in the lake.[4,44]

Impact of Conservation Tillage. Conservation tillage is a management technique designed to reduce soil erosion, and by extension, soil-bound N and P loading into lakes. However, there is also evidence that over long periods (10−20 years) conservation tillage contributes to accumulation of P in the top soil layers[18,45] especially in landscapes with significant P application from fertilizers.[18,46,47] Tilling reduces this accumulation of P in the top soil layers, distributes P into the soil matrix, and may disrupt preferential flow paths leading to declines in P being leached from the soil compared to conservation tillage.[47] No-till approaches may also increase soil pore size, allowing less water retention compared to conventionally tilled soil.[48,49] Thus, fields under conservation tillage for long periods of time contribute more dissolved P during runoff events compared to conventionally tilled soils.[47,51,52] While we do not have soil P data for the Acton Lake watershed, the trends in P concentrations in the in-flowing streams and conservation tillage are consistent with those of nearby Lake Erie watersheds,[20] where they have observed soil P stratification after years of conservation tillage compared to conventionally tilled fields.[18] The consistency of this pattern across study systems suggests the accumulation and stratification of soil P becomes more readily mobilized and transported during storm events, and highlights this as the likely mechanism in the change in the relationship between Q_{prop} and $load_{prop}$ (increase in slope) for SRP throughout our time series. Potentially as a consequence of this changing relationship between events and P concentration in runoff, time series data suggest initial declines in dissolved P concentrations in in-flowing streams tend to reverse, leading to increases in SRP concentrations and loads after a period of about 5−10 years.[15,18,20] N loads, particularly those of NO_3, seem to show patterns opposite to those of P loads in response to conservation tillage. For example, in the Maumee River (a major Lake Erie inflow), NO_3 loads increased, while TP loads decreased over about a 20 year period (1980−2000) when conservation tillage increased greatly. However, over the following ∼15 years NO_3 load decreased rapidly as loads of both SRP and TP increased.[19] Similarly, in the Acton Lake watershed, NO_3 concentrations declined sharply in the second decade of our study period, as SRP concentrations increased.[20]

In addition to conservation tillage as being a potential driver of P mobilization, tile drains in the watershed may move a significant amount of P off the landscape. Smith et al. observed approximately 50% of P losses in the St. Joseph River in northeastern Indiana, another agriculturally dominated watershed, occurred through tile drains.[50] While we do not have any data on the exact extent of tile drainage in the Acton Lake watershed (estimated to be about 50% of cropland), this artificial drainage represents another potential avenue for similarly significant losses of P from the landscape and may, in part, contribute to the patterns observed in our data set. Subsequently, the increase in conservation tillage in the watershed may play a role in P export via tile drains, as increased soil pore size due to conservation tillage may increase P export via the macropores and ultimately tile drains. In general, subsurface and tile drain transport of NO_3−N is high compared to dissolved P,[41] so while tile drains may be an important source of P transport from the landscape to the in-flowing streams, they alone may not be a likely source of the change in P mobilization observed in the time series.

The increase in SRP concentration and load observed with conversion to no-till techniques has been documented, but in addition we demonstrate here that (1) P loads increase proportionally much more than N loads during storm events and (2) increases in conservation tillage and potential interaction with tile drainage systems may lead to a greater storm-derived mobilization of dissolved P than that of dissolved N (based on the slopes of the relationship between Q_{prop} versus $load_{prop}$). We observe a change in the relationship between Q_{prop} and $load_{prop}$ throughout the time series, suggesting that over time an increasing fraction of the annual SRP load comes from events versus base flow. This is especially true when considering the trends from 2000 to 2014 where previous work has observed significant shifts in stream SRP concentration.[20] The sharp increase in the slope of Q_{prop} versus

DOI: 10.1021/acs.est.8b05152
Environ. Sci. Technol. 2019, 53, 5613−5621

$load_{prop}$ for SRP after 2000, especially when compared to the modest increase in the slope for TP (which includes sediment derived P), suggests this accumulation of dissolved P in the upper sediment layers is potentially contributing to an increase in mobilization during large storm events. We do not see this same pattern in NO_3−N or TN and instead see a subtle decline in the slope between $load_{prop}$ and Q_{prop}. This has implications for load, and ultimately N:P, in the lake, with a possible shift of agricultural lakes to more N-limitation, especially during and after large storm events. Indeed, N-limitation of Acton Lake phytoplankton increased, relative to P limitation, after ∼2010,[53] suggesting that shifts in phytoplankton nutrient status have already started to occur.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05152.

linear model fits of $load_{prop}$ versus Q_{prop} for dissolved and total fractions of N and P (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported mainly by National Science Foundation awards 9318452, 9726877, 0235755, 0743192, and 1255159. Additional support was provided by the Miami Valley Resource Conservation and Development District.

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DOI: 10.1021/acs.est.8b05152
Environ. Sci. Technol. 2019, 53, 5613–5621