Hydrologic and biogeochemical controls on phosphorus export from Western Lake Erie Tributaries

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Abstract

Understanding the processes controlling phosphorus (P) export from agricultural watersheds is essential for predicting and mitigating adverse environmental impacts. In this study, discharge, dissolved reactive P load, total P load, and suspended sediment time-series data (1975-2014) from two Lake Erie tributaries, the Maumee and Sandusky rivers, were evaluated to determine whether hydrologic or biogeochemical processes were responsible for observed patterns in P export. Findings indicate that hydrologic processes in these watersheds controlled P loading patterns, as P export was transport-limited (i.e., P loading was strongly correlated to watershed discharge) and P concentrations exhibited effective chemostatic behavior (i.e., low variability in concentration relative to discharge). The nature and behavior of observed P transport likely stems from a large, ubiquitous source of P present within each watershed as results were similar to those found for geogenic constituents (i.e., silica). Results suggest that changes in both precipitation patterns (e.g., precipitation variability) and watershed hydrologic response (e.g., water residence time) are likely explanations for observed increases in water and P loading in the Maumee and Sandusky watersheds. Future P loading in these watersheds should be expected to continue to be proportional to water flux as long as the magnitude and availability of the P source remains at its current level. Current P management strategies may therefore need to be reevaluated to better balance agricultural P requirements and watershed P loadings.

Keywords

Long-term monitoring, Water quality, Watershed, Legacy phosphorus, Lorenz curve, Spectral analysis

Introduction

Intensive agricultural land management in watersheds around the world has been associated with both hypoxia (Boesch et al., 2001; Conley et al., 2002; Rockwell et al., 2005; Chen et al., 2007; Rabalais et al., 2010; Scavia et al., 2014) and harmful algal blooms (HABs) in receiving surface waters (Michalak et al., 2013; Smith et al., 2015). Hydrology and biogeochemistry, which together determine the fate and transport of water and nutrients, are closely related to these water resource concerns. Indeed, the magnitude and severity of hypoxic zones and HABs have been linked to, among other factors, temporal fluctuations in nutrient loadings from their contributing drainage areas (Rabalais et al., 2010; Stumpf et al., 2012; Smith et al., 2015). Understanding the dominant processes controlling nutrient loading from intensively managed agricultural watersheds is therefore critical for predicting and mitigating associated adverse environmental impacts.

Previous research has indicated that treating a watershed as a ‘filter’ can be a useful approach for identifying the dominant processes controlling watershed hydrology and nutrient loading in managed landscapes (Basu et al., 2010, 2011; Guan et al., 2011; Jawitz and Mitchell, 2011; Gall et al., 2013). As a reactive filter, a watershed’s response (e.g., discharge) relative to an external driver (e.g., precipitation) is typically characterized by phase shifts and changes in amplitude and frequency. The watershed filtering of external drivers also depends upon the initial conditions (e.g., soil moisture) and the magnitude of the input (e.g., precipitation amount). In intensively managed agricultural landscapes, watershed discharge and nutrient export are

largely controlled by a combination of natural (e.g., climatic) and anthropogenic (e.g., management) drivers (e.g., Gall et al., 2013). For instance, both precipitation (e.g., Masaki et al., 2014) and subsurface drainage (e.g., King et al., 2014; 2015a) can influence watershed hydrology and nutrient transport. The role of a watershed as a hydrologic filter in managed landscapes has been widely studied in the literature; however, biogeochemical filtering as driven by watershed hydrology has only recently begun to receive attention (Godsey et al., 2010; Guan et al., 2011; Gall et al., 2013). The transport of nutrients is affected by precipitation events and their hydrologic filtering, but is further complicated because not every precipitation event generates a nutrient flux, similar precipitation amounts do not necessarily result in the same response, and nutrients interact with vegetation and the surrounding soil matrix during transport (e.g., sorption, uptake, nutrient cycling)(Harman et al., 2010).

In this study, the watershed is conceptualized as a nonlinear, hierarchical filter, which transforms input signals from natural and anthropogenic drivers to produce patterns in observed hydrographs, chemographs, and nutrient loads (Basu et al., 2011; Guan et al., 2011; Gall et al., 2013). Using this approach, we evaluate hydrologic and water quality time-series records from two Lake Erie tributaries, the Maumee and Sandusky rivers, which have experienced substantial shifts in P concentration and load over the past 40 years. Elevated dissolved reactive P (DRP) and total P (TP) loads that were observed in the rivers during late-1960s and early-1970s, but were substantially decreased through the early-1990s (Makarewicz and Bertram, 1991; Richards and Baker, 1998, 2002). Increasing trends in DRP loads and flow-weighted mean concentrations since the 1990s, however, have prompted renewed concern, as Lake Erie has been returning to a more eutrophic state (Depew et al., 2011; Stumpf et al., 2012; Zhou et al., 2013; Scavia et al., 2014). The cause of increasing DRP concentrations and loads has been the subject of much

debate (e.g., Smith et al., 2015); therefore, we sought to 1) examine the impact of natural and anthropogenic drivers on observed watershed hydrologic response, and 2) determine whether hydrologic or biogeochemical processes were primarily responsible for past patterns in watershed P load. Given the vast anthropogenic modifications to the hydrology of these watersheds (i.e., subsurface drainage) (Sugg, 2007; NASS, 2016) and accumulation of P on the landscape (Powers et al., 2016), we hypothesized that hydrologic processes would be the dominant control on watershed P export rather than biogeochemical processes. In addition, we hypothesized that changes in climatic factors, such as precipitation amount and timing, over the 40-year record would drive watershed hydrology. Ultimately, understanding these past watershed hydrology and P export patterns will help improve predictions of future watershed response.

Materials and Methods

Maumee and Sandusky watersheds

The Maumee and Sandusky rivers are located in northwestern Ohio, USA and flow into the Western Basin of Lake Erie (Figure 1). Both watersheds are characterized by poorly drained soils, which has resulted in the installation of vast artificial surface and subsurface drainage networks. Agricultural row crop production is the primary land use classification, accounting for approximately 75% of the watershed areas (Table 1). The National Center for Water Quality at Heidelberg University (Tiffin, OH) initiated monitoring of nutrient concentrations in the Maumee and Sandusky rivers in 1974 following severe hypoxia in Lake Erie during the late-1960s. DRP loads in both rivers declined during the initial 20 years of monitoring (1975-1995), but have substantially increased since then (1995-2014) (Figure 2). Increased DRP loading to Lake Erie has resulted in an increase in the magnitude and extent of harmful and nuisance algal

blooms in the western basin of the Lake (e.g., Stumpf et al., 2012) and hypoxic zones in the central basin (e.g., Scavia et al., 2014). The effects of increased P loading on water quality in Lake Erie culminated in August of 2014 when microcystin toxin produced by cyanobacteria was detected and approximately 500,000 residents in Toledo, OH were left without drinking water (Landers, 2014). While numerous hypotheses have been proposed to explain the cause of increasing P loading to Lake Erie (Smith et al., 2015), our objective herein was to differentiate between hydrologic and biogeochemical controls on watershed P loading.

Discharge and water quality data

DRP, TP, suspended sediment (SS), and silica concentrations as well as discharge data from the Maumee and Sandusky rivers were downloaded from the Heidelberg University, National Center for Water Quality Research, Tributary Loading Website (<http://www.heidelberg.edu/academiclife/distinctive/ncwqr/data>). Discharge, DRP, TP, and SS data were available from 1975-1978 and 1982-2014 for the Maumee River and from 1975-1980 and 1982-2014 for the Sandusky River. Silica data were only available from 2000-2014 for both rivers. While datasets were nearly complete at a daily time scale, linear interpolation was used to account for missing data points (Dataset completeness: [Maumee – discharge: 99.9%; DRP: 95.5%; TP: 99.4%; SS: 98.9%; silica: 98.1%]; [Sandusky – discharge: 99.8%; DRP: 94.3%; TP: 99.4%; SS: 99.0%; silica: 99.0%]). Information on sampling procedures and analytical methods are available in the Tributary Loading Program User Guide (<http://www.heidelberg.edu/academiclife/distinctive/ncwqr/data/guide>). Nutrient loads were calculated by multiplying the river discharge by the analyte concentration. Precipitation data from four rain gauges within the Maumee and Sandusky watersheds (Findlay, OH; Wauseon, OH; Defiance, OH; Upper Sandusky, OH) were obtained

from the National Climatic Data Center (<http://www.ncdc.noaa.gov/cdo-web/>) (Table 1). Data from 1915-2014 were used from each gauge, with daily datasets being >90% complete.

Data analysis

To evaluate the impact of external drivers on watershed hydrologic response and determine whether hydrologic or biogeochemical processes were responsible for observed trends in watershed P load, Lorenz inequality and the degree of memory in the time-series data were evaluated. Details of these analyses are described in subsequent sections.

Lorenz inequality

For a given time-series of stochastic events, some events may make an unequal or disproportionate contribution compared to the other events. For instance, a flood event may represent a significant portion of annual discharge from a watershed. Lorenz curves are useful for quantifying this temporal inequality in time-series data (Jawitz and Mitchell, 2011; Gall et al., 2013). Here, the Lorenz curve is a plot of the cumulative percent of watershed responses (i.e., discharge and nutrient load) versus the cumulative percent of time-series observations ranked from lowest to highest. Lorenz curves in the current study were generated based on observed time-series data, but they can also be generated using probability density functions (*pdf*) (e.g., Jawitz and Mitchell, 2011). For a *pdf* $p(x)$ with a cumulative distribution function (*cdf*) $X(x)$ and range $[0, \infty)$, the Lorenz curve $Y[X(x)]$ is:

$$Y[X(x)] = \frac{\int_0^x xp(x)dx}{\int_0^\infty xp(x)dx} \quad (1)$$

The upper and lower limits of the Lorenz curve are “perfect equality” and “perfect inequality”, which stem from its original use in evaluating wealth distribution (Lorenz, 1905).

Perfect equality occurs when a quantity is equally distributed among all observations. For example, every individual in a population has an equal proportion of the total income or, as a hydrology example, daily discharge from a waste water treatment plant is constant for a period of time. In contrast, perfect inequality occurs when all of the quantity is allocated to a single observation. For example, one individual in a population may have all of the income or a flood event may represent all of the annual discharge from a watershed in a given year.

Lorenz inequality is often expressed as the Gini coefficient (G), which is the ratio of the area between the line of perfect equality and the Lorenz curve to the triangular area under the line of perfect equality (Jawitz and Mitchell, 2011). G can be expressed as:

$$G = 1 - \int_0^1 Y[X(x)]dX; 0 \leq G \leq 1 \quad (2)$$

For $G = 0$, all events make an equal contribution (i.e., perfect equality), and as G increases towards 1, the temporal inequality increases (i.e., towards perfect inequality). G is useful for comparing temporal Lorenz inequality among watersheds (e.g., Jawitz and Mitchell, 2011) and among nutrients (e.g., Gall et al., 2013).

Precipitation, discharge, and nutrient loading time-series from the Maumee and Sandusky watersheds were first separated into three year intervals. Lorenz curves and G were subsequently determined for each of the three year periods. Lorenz curves can be used to quantify temporal inequality using time-series of various lengths depending upon study objectives. Indeed, temporal inequality in discharge and water quality time-series has been assessed over time periods ranging from one (e.g., Halliday et al., 2012) to 10 years (e.g., Gall et al., 2013). Hydrologic and biogeochemical response inequalities are often more variable over smaller spatial and temporal scales compared to larger scales (Guan et al., 2011), as averaging of hydrologic responses and nutrient loads at larger scales decreases variability (Halliday et al.,

2012). In the current study, a three year interval was therefore chosen because we were not only interested in determining whether hydrologic or biogeochemical processes controlled watershed P load, but also if the dominant process changed over time.

Comparison of the temporal Lorenz inequality in two signals was also used to quantify the relationship between driver and response and the coupling of hydrologic and biogeochemical processes:

$$\Phi_G = \frac{G_2}{G_1} \quad (3)$$

where G_1 and G_2 are the Gini coefficients for each signal (Gall et al., 2013). For example, if discharge and load have the same Gini coefficient (i.e., $\Phi_G = 1$), the biogeochemical response is chemostatic. However, for chemographs with dilution signals, the inequality of load is smaller than that of discharge (i.e., $\Phi_G < 1$) and for chemographs with accretion signals, the inequality of load is greater than that of discharge (i.e., $\Phi_G > 1$). While Φ_G is a measure of relative inequality between signals, G is a measure of absolute inequality of an individual signal.

Memory assessment

Hydrologic and biogeochemical data from the Maumee and Sandusky Rivers were also evaluated in the Fourier domain to create spectral density plots (*sdp*) and to determine the degree of memory in the time-series signal (Guan et al., 2011). Similar to temporal Lorenz inequality, memory was evaluated in three year intervals over the entire time-series for each watershed. An *sdp* is a log-log plot of the power (i.e., signal strength) and frequency of the time-series data, where the absolute value of the slope, α , is a measure of the memory or temporal autocorrelation of the input signal. Spectral analysis provides insight into the degree of filtering of the driver time-series that was required to produce the response time-series (Gall et al., 2013).

For stochastic processes with long-range persistence of memory, $\alpha = 1$, each event is correlated to all other events (Guan et al., 2011; Gall et al., 2013). For example, numerous natural processes including both breathing and heartbeat time-series exhibit this pattern (e.g., Kello et al., 2010). A memory-less process, such as a Poisson process, is represented by $\alpha = 0$. A process with short-term memory is represented by $\alpha = 2$, as is the case for Brownian motion (Gall et al., 2013). Decreases in α from 1 to 0 indicate that there has been a loss of memory in the signal, while increases in α from 1 to 2 indicate an increasing dominance of short-term memory. Similar to relative temporal Lorenz inequality, α can be used to compare the memory in time-series signals among watersheds, among nutrients (e.g., Gall et al., 2013), and among time periods (e.g., Guan et al., 2011).

Comparison of α values was completed to evaluate the relationship between external drivers and watershed response as well as the coupling of hydrologic and biogeochemical processes (Gall et al., 2013). Relative memory was defined as:

$$\Phi_{\alpha} = \frac{\alpha_2}{\alpha_1} \quad (4)$$

where α_1 and α_2 are the slopes of the *sdp* for a driver and a response, respectively, or two different watershed responses (e.g., discharge and loading). When α_1 and α_2 are both <1 , then $\Phi_{\alpha} > 1$ indicates a gain in memory between driver and response, whereas when α_1 and α_2 are both >1 , then $\Phi_{\alpha} > 1$ indicates a loss of long-term memory. If the reference ($\alpha = 1$) is crossed between the driver and response, then $\Phi_{\alpha} > 1$ indicates the response's increasing dependence on short-term memory, while $\Phi_{\alpha} < 1$ indicates that the driver depends more on short-term memory than the response.

Statistical analysis

Lorenz curves and spectral density plots as well as all subsequent analysis of data were completed in *R* statistical software (*R* Development Core Team, 2011). To assess trends in G , $\Phi_{G,\alpha}$, and Φ_α for precipitation, discharge, DRP, TP, and SS over the 40 year record in the Maumee and Sandusky watersheds, we used the Pearson product-moment correlation coefficient (i.e., Pearson's R) and piecewise linear regression. Prior to correlation analysis, data were tested for normality using the Shapiro-Wilk test. A probability level of 0.05 was used to evaluate statistical significance for all analyses.

Results

Temporal inequality in precipitation, discharge, and load

From 1915 to 2014, G_{Precip} ranged from 0.83 to 0.90 for the four rain gauges in the Maumee and Sandusky watersheds. On average, G_{Precip} at the Findlay, Defiance, and Upper Sandusky gauges was 0.86 ± 0.01 (mean $\pm$ standard deviation), while G_{Precip} at the Wauseon gauge averaged 0.87 ± 0.01 . A Gini coefficient of 0.86 is equivalent to 90% of precipitation occurring during 18% of the time period (e.g., 90% of annual precipitation occurring during 65 d). No trends in G_{Precip} were observed at any of the rain gauges over the 100 year record, indicating that precipitation intensity has not significantly changed in the Maumee and Sandusky watersheds (Figure 3). A decrease or increase in G_{Precip} would suggest that the distribution of precipitation had become either more uniform (less intense; cumulative precipitation distributed over a larger number of days) or less uniform (more intense; cumulative precipitation distributed over fewer days). When only the period from 1975 to 2014 was considered, mean G_{Precip} for the individual rain gauges was equal to their long-term averages. The Upper Sandusky gauge had a significant increase in G_{Precip} over this period (Pearson's $R = 0.62$, $p < 0.05$) from 0.84 to 0.87. This suggests

that precipitation intensity at the Upper Sandusky gauge has increased over the past 40 years, albeit only slightly.

Temporal Lorenz inequality in discharge from the Maumee and Sandusky rivers varied between 1975 and 2014, such that G_Q decreased from the mid-1970s through the late-1990s and subsequently increased to 1970s levels by the end of the monitoring record (Figure 3). Thus, over the first 20 years of the monitoring period discharge had become increasingly uniform in both watersheds, but has since been becoming less uniform. Mean G_Q for the Maumee and Sandusky rivers was 0.57 ± 0.04 and 0.64 ± 0.03 , respectively (Figure 3). Relative temporal Lorenz inequalities (ϕ_G) between discharge and precipitation (i.e., G_Q/G_{Precip}) were calculated to evaluate the relationship between precipitation and watershed hydrologic response (Table 2). Patterns in ϕ_G were similar for both the Maumee and Sandusky watersheds and resembled patterns in G_Q , as G_{Precip} was relatively stable compared to G_Q (Table 2; Figure 3). On average, ϕ_G was 0.66 ± 0.05 and 0.74 ± 0.04 for the Maumee and Sandusky watershed, respectively. Differences in the magnitude of ϕ_G indicate greater hydrologic filtering of precipitation in the Maumee watershed compared to the Sandusky watershed. That is, discharge in the Sandusky River was ‘flashier’ compared to discharge in the Maumee River.

Values of G_{DRP} , G_{TP} , and G_{SS} were consistent across the monitoring period for both the Maumee and Sandusky watersheds, with no significant trends observed through time (Figure 3). Temporal inequality in SS load tended to be greater than temporal inequality in both TP load and DRP load. Mean G_{DRP} , G_{TP} , and G_{SS} for the Maumee watershed were 0.67 ± 0.03 , 0.72 ± 0.03 , and 0.79 ± 0.03 , respectively, while in the Sandusky watershed mean values were 0.75 ± 0.04 , 0.78 ± 0.03 , and 0.83 ± 0.03 . Observed Gini coefficients for TP likely fell between Gini coefficients of DRP and SS because TP includes both dissolved and sediment-bound P fractions.

Temporal inequality in nutrient and sediment loads tended to be greater than temporal inequality in silica load (mean = 0.61; data only available from 2000 through 2014) (Figure 3). Relative temporal inequality between analytes and discharge was determined to quantify the coupling of hydrologic and biogeochemical processes. Values for $\phi_{G-Silica}$ ranged from 0.98 to 1.12 for the Maumee and Sandusky watersheds (Table 3), with $\phi_G = 1.0$ indicating a chemostatic biogeochemical response. Relative inequality for DRP, TP, and SS were greater than 1.0 in both watersheds (Table 3), albeit only slightly, especially for DRP and TP. This suggests that DRP and TP exhibited a nearly chemostatic response.

Degree of memory

Values of α_{Precip} for the rain gauges in the Maumee and Sandusky watersheds were similar between 1915 and 2014. Mean α_{Precip} was 0.11 ± 0.05 , 0.13 ± 0.07 , 0.14 ± 0.06 , and 0.15 ± 0.06 for the Upper Sandusky, Findlay, Wauseon, and Defiance gauges, respectively. Although precipitation is generally modeled as having $\alpha = 0$ (i.e., no memory), results suggest that precipitation in these watersheds have some short-term memory ($\alpha > 0$). No significant trends were observed in α_{Precip} at any of the rain gauges over the 100 year record (Figure 4). From 1975 through 2014, α_{Precip} ranged from 0.01 to 0.31 in individual gauges, with average values at each gauge similar to the long-term mean. Significant piecewise linear relationships ($p < 0.05$) were observed for the Findlay, Defiance, and Wauseon gauges with the change point occurring between 1998 and 2004. Values of α_{Precip} increased from 0.09 to 0.21 and subsequently decreased back to 0.09. This suggests that between 1975 and ~2000, precipitation at these rain gauges was gaining short-term memory (i.e., precipitation autocorrelation was increasing), but since ~2000

have been losing memory (i.e., precipitation autocorrelation was decreasing). Observed α_{Precip} values at the Upper Sandusky gauge tended to increase (0.10 to 0.17) during this period.

Alpha values for discharge significantly increased in both the Maumee (Pearson's $R = 0.74$; $p < 0.01$) and Sandusky rivers (Pearson's $R = 0.52$; $p < 0.05$) between 1975 and 2014 (Figure 4). Increases in α_Q indicate that discharge was becoming increasingly dominated by short-term processes, as α increased from 1.0 (i.e., long-term persistence of memory) toward 2.0 (i.e., short-term memory). Relative memory between discharge and precipitation ($\Phi_\alpha; \alpha_Q/\alpha_{\text{Precip}}$) was greater than 1.0 for both the Maumee (mean = 10.23 ± 4.36) and Sandusky watersheds (mean = 10.30 ± 3.00) (Table 2). Because α_{Precip} was less than 1.0 and α_Q was generally greater than 1.0, $\Phi_\alpha > 1.0$ suggests that discharge was dependent on the short-term memory of precipitation. Thus, as α_{Precip} increased from 1975 through ~2000, discharge became less dependent on precipitation (i.e., Φ_α decreased), but since ~2000 discharge has become increasingly dependent on the short-term memory of precipitation (i.e., Φ_α increased).

Similar to discharge, α_{DRP} , α_{TP} , and α_{SS} increased between 1975 and 2014 in the Maumee and Sandusky watersheds (Figure 4), suggesting that nutrient and sediment transport was becoming increasingly dominated by short-term processes compared to long-term processes. For the Maumee River, α_{DRP} increased from 0.95 to 2.00 (Pearson's $R = 0.49$; $p < 0.05$), while α_{TP} increased from 0.74 to 2.14 (Pearson's $R = 0.70$; $p < 0.01$). Similarly, in the Sandusky River α_{DRP} increased from 0.84 to 1.74 (Pearson's $R = 0.73$; $p < 0.01$) and α_{TP} increased from 0.66 to 1.49 (Pearson's $R = 0.70$; $p < 0.01$). Trends in α_{SS} for the Maumee watershed were also significant (Pearson's $R = 0.66$; $p < 0.01$), but not for the Sandusky watershed. Relative memory between analytes and discharge is presented in Table 3 and no significant trends were observed in either the Maumee or the Sandusky watershed. Mean $\Phi_{\alpha\text{-DRP}}$, $\Phi_{\alpha\text{-TP}}$, and $\Phi_{\alpha\text{-SS}}$ values in the Maumee

watershed were 1.04 ± 0.16 , 1.00 ± 0.18 , and 0.94 ± 0.16 , respectively. In the Sandusky watershed, mean $\Phi_{\alpha\text{-DRP}}$, $\Phi_{\alpha\text{-TP}}$, and $\Phi_{\alpha\text{-SS}}$ values were 0.97 ± 0.12 , 0.97 ± 0.12 , and 0.92 ± 0.14 , respectively. Values of Φ_{α} for nutrient and sediment were similar to silica (Maumee: mean = 1.00 ± 0.02 ; Sandusky: mean = 0.99 ± 0.03). Relative memory results suggest that hydrology was the dominant process controlling nutrient loading in these watersheds, as $\Phi_{\alpha} \approx 1.0$.

Discussion

External drivers and watershed hydrologic response

Relative Lorenz inequality between discharge and precipitation in both the Maumee and Sandusky watersheds was less than 1.0, which indicates that filtering of the precipitation input signal was occurring within the watersheds. Filtering of the precipitation signal was likely due to evapotranspiration, storage of water within each watershed, and water travel times such that G_Q was less than G_{Precip} (Jawitz and Mitchell, 2011; Gall et al., 2013). Relative Lorenz inequality was greater in the Sandusky watershed compared to the Maumee watershed. Indeed, previous research has shown that discharge in the Sandusky watershed responded more rapidly to precipitation inputs compared to the Maumee (i.e., discharge in the Sandusky was ‘flashier’ compared to the Maumee) (Baker et al., 2004). Baker et al. (2004) found in an analysis of 515 Midwestern streams that watershed hydrologic response varied due to watershed area and unit area groundwater inputs. Given the similar land use and topography between these watersheds, we hypothesize that the larger Φ_G values observed for the Sandusky watershed were due to relatively small drainage area compared to the Maumee ($3,240 \text{ km}^2$ vs. $16,395 \text{ km}^2$).

Values of G_{Precip} remained constant over the period from 1915 to 2014 suggesting that precipitation was distributed similarly throughout the monitoring record (i.e., ~90% of

cumulative precipitation occurred in 18% of the time). However, precipitation variability (i.e., memory or autocorrelation) appeared to play an important role in determining watershed hydrologic response, as values of G_Q decreased with increases in α_{Precip} . During periods with increased memory (high autocorrelation, low variability) in precipitation (e.g., 2003-2005), both the Maumee and Sandusky watersheds exhibited more uniform discharge. That is, cumulative discharge tended to be distributed over a larger number of similar magnitude events compared to periods with decreased memory (low autocorrelation, high variability) in precipitation (e.g., 2012-2014), which generally resulted in a few large discharge events accounting for a greater proportion of cumulative discharge. Findings from the current study are similar to that of Masaki et al. (2014), which showed that under future climate scenarios with enhanced variability in precipitation, values of G_Q for large rivers in central North America will likely significantly increase. Basu et al. (2011) also found that hydrological responses in artificially drained agricultural watersheds are controlled primarily by the stochasticity in precipitation.

Significant increasing trends in α_Q in both the Maumee and Sandusky suggest that in addition to precipitation other external factors may also be influencing watershed hydrologic response. Values of α_Q increased from approximately 1.0 in the 1970s to nearly 2.0 by 2014 implying that watershed discharge was becoming increasingly dominated by short-term hydrologic processes ($\alpha = 2$) compared to long-term hydrologic processes ($\alpha = 1$). Increases in α_Q suggest that watershed response has become more event driven over the past 40 years despite increases in α_{Precip} between 1975 and 2005. Results therefore indicate that changes in water flow pathways and water residence time may be linked to increases in the short-term memory present in watershed response. One possible explanation for this pattern is increases in the amount of subsurface tile drainage, which routes water from agricultural fields to nearby streams and

drainage ditches much faster than groundwater flow pathways (King et al., 2015a). While much of the Maumee and Sandusky watersheds were extensively drained prior to 1975 due to very poorly drained soils, subsurface tile drainage increased in Ohio by 23% between 1974 and 2012 (NASS, 2016). There is also anecdotal evidence that the installation of subsurface drainage may be much greater than reported by the Census of Agriculture, as drainage intensity has markedly increased (i.e., decrease in tile spacing) and is not captured in the Census results (King et al., 2015b).

Controls on phosphorus loading

The memory observed in DRP and TP loads was nearly equal to that of discharge in both the Maumee and Sandusky watersheds leading to a value of approximately 1.0 for Φ_a . This finding suggests that P transported from these watersheds stems from a large, ubiquitous source (Basu et al., 2010, 2011; Jawitz and Mitchell, 2011; Guan et al., 2011; Gall et al., 2013; Powers et al., 2016). Given the prevalence of row crop agriculture in both watersheds, it is perhaps not surprising that study results highlight the non-point nature of P transport. However, the relative memory between P and discharge found in the Maumee and Sandusky watersheds was similar to values found for silica. In a recent study, Gall et al. (2013) also found that relative memory between geogenic constituents (e.g., sodium, silica) and discharge ranged from 0.9 to 1.2 in the Mississippi River Basin and was similar to relative memory of both DRP and TP. While geogenic constituents would be expected to be ubiquitous in watersheds stemming from the dissolution of geologic parent material, nutrients such as P, which are primarily applied for crop production, are not often considered an extensive and persistent source analogous to a geologic

material. These results, therefore, underscore the vast anthropogenic modifications to biogeochemical cycles that have occurred in the Maumee and Sandusky watersheds.

Previous studies have interpreted $\Phi_\alpha = 1.0$ as evidence of legacy P and the buildup of P on the landscape resulting from decades of fertilizer addition (Basu et al., 2010; Jawtiz and Mitchell, 2011; Gall et al., 2013). While fertilizer use dramatically increased in the Maumee and Sandusky watersheds from the 1930s through the 1970s (Han et al., 2012), which likely resulted in the buildup of P over time (Powers et al., 2016), it is not possible to separate the contributions of past P additions and ‘newly’ applied P over the 40 year record using the methods employed in the current study. Notwithstanding the source of P (i.e., legacy P vs. newly applied P), memory analysis indicated that P in the Maumee and Sandusky watersheds was transport-limited. That is, hydrologic processes were the primary driver controlling P loading in these watersheds. A lack of a trend in Φ_α between 1975 and 2014 also suggests that the magnitude of the P source across the landscape has either not changed significantly or has remained above an unknown critical threshold. As a result, future P loadings in the Maumee and Sandusky watersheds should be expected to continue to be proportional to water flux as long as the magnitude and availability of the P source across the landscape remains at its current level.

Relative temporal Lorenz inequalities between discharge and P load revealed Φ_G values near 1.2, suggesting that DRP and TP concentration were nearly chemostatic ($\Phi_G = 1.0$). We further examined the relationship between discharge and concentration using metrics proposed by Thompson et al. (2011) to determine if DRP and TP were truly chemostatic. Thompson et al. (2011) showed that the ratio between the coefficient of variation of concentration and discharge (CV_C/CV_Q) can be used as an indicator of true chemostatic behavior. The authors defined a chemostatic CV ratio as being within two standard deviations of the mean geogenic CV_C/CV_Q .

For the Maumee and Sandusky watersheds, mean CV_C/CV_Q for silica was 0.36 ± 0.05 and 0.31 ± 0.04 , respectively; thus, chemostatic behavior for these watersheds could be defined as $CV_C/CV_Q < 0.46$ and 0.39 , respectively. For DRP, CV_C/CV_Q values of 0.52 ± 0.10 and 0.54 ± 0.10 were found for the Maumee and Sandusky watersheds. Similar results were also found for TP, as CV_C/CV_Q values of 0.49 ± 0.04 and 0.57 ± 0.07 were found for the Maumee and Sandusky watersheds, respectively. Similar temporal Lorenz inequality between discharge and P loads combined with CV_C/CV_Q values similar to silica indicate that the P concentrations in these watersheds exhibited ‘effective’ biogeochemical stationarity (i.e., low variability in concentration relative to discharge – effectively chemostatic) (Basu et al., 2010; Jawitz and Mitchell, 2011; Thompson et al., 2011; Gall et al., 2013) and provide additional evidence that hydrologic processes were the dominant control on P export dynamics. Effectively chemostatic does not imply that P concentrations do not vary on a daily or event time scales, but the variations in concentration were constrained such that flow-weighted mean concentration did not vary significantly from period to period. Indeed, annual flow-weighted mean DRP concentration generally only varied by 0.02 mg L^{-1} over the 40 year record in the Maumee and Sandusky rivers (Stumpf et al., 2012; Scavia et al., 2014). Findings from the current study are consistent with the effective chemostatic behavior of P reported in agricultural watersheds within the Mississippi River, Baltic Sea, and Lake Okeechobee basins (Basu et al., 2010; Jawitz and Mitchell, 2011; Gall et al., 2013). This is in contrast to episodic solute transport, which is characterized by intermittent pulses and significant variability in flow-weighted mean concentration (Basu et al., 2010). Chemostatic behavior leads to a strong positive linear correlation between annual exported solute load and discharge similar to findings from the current study, while episodic behavior lowers such correlations.

Forms of solute behavior (i.e., chemostatic vs. episodic) in watersheds have been modeled as a function of chemical reaction rate constants (Basu et al., 2011). When the rate of solute degradation (either due to crop uptake, short half-life, etc.) is very high or low compared to the rate of mass input (i.e., fertilizers), episodic export dynamics result. However, when degradation rates are comparable to rates of mass input, chemostatic export dynamics result. The effective chemostatic P behavior in the Maumee and Sandusky watersheds is consistent with the maintenance fertility management (i.e., maintaining P levels in the soil within an agronomic range through application of P fertilizers) currently practiced in these watersheds. If P is added to the landscape to counter losses, not only would effective chemostatic P export dynamics develop, but also the magnitude of the P source and associated memory would remain consistent through time. Thus, agronomic recommendations may need to be reevaluated in these watersheds to better balance agricultural P requirements and watershed P loadings.

Summary and Conclusions

The main objective of the current study was to determine whether hydrologic or biogeochemical processes were the dominant control on watershed P loading. Our analyses revealed the nature (non-point, large ubiquitous source of P) and behavior (effectively chemostatic, transport-limited) of past P transport in the Maumee and Sandusky watersheds. These findings indicate that hydrology was the dominant factor controlling P loading in these watersheds, with changes in both precipitation patterns (e.g., precipitation variability) and watershed hydrologic response (e.g., water residence time) as likely explanations for observed increases in water and P loading. While results show the importance of watershed hydrology in determining P loading, they do not imply that biogeochemical processes were unimportant. Biogeochemical processes undoubtedly played an important role in determining watershed P

load, but to a lesser extent than hydrology. Memory and temporal Lorenz inequality assessment did not provide direct evidence for the cause of DRP concentration increases since the mid-1990s, but do provide new insights and areas for future research. Results from both analyses suggest that the magnitude of the P source across the landscape has either not significantly changed or remained above an unknown critical threshold over the past 40 years. As a result, increases in DRP concentration were likely due to changes in the lability and/or availability of the P source. Many factors can influence P source lability and/or availability including the source and solubility of applied fertilizers (King et al., 2015b; Smith et al., 2016), the placement (e.g., broadcast vs. incorporated) of fertilizers on agricultural fields (Williams et al., 2016), precipitation and soil chemistry (McDowell et al., 2001), and the distribution of P along the field-stream-river continuum (Johnson et al., 2014). Future research quantifying the magnitude of P stores and its distribution across the landscape as well as determining the effects of both contemporary and legacy P on water quality will be essential for better understanding past P loading patterns, predicting future P loadings in the Maumee and Sandusky watersheds, and mitigating hypoxia and HABs in Lake Erie.

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Table 1. Maumee and Sandusky watershed characteristics and rain gauge information.

					% Land use		
	Station ID	Latitude	Longitude	Area (km ²) [†]	Ag.	Forest	Urban
Watershed							
Maumee	USGS-04193500	41.500	-83.713	16,395	74	6	10
Sandusky	USGS-04198000	41.308	-83.159	3,240	78	9	8
Rain gauge				Location			
Findlay	GHCND:USC00332791	41.046	-83.662	Maumee			
Wauseon	GHCND:USC00338822	41.518	-84.145	Maumee			
Defiance	GHCND:USC00332098	41.278	-84.385	Maumee			
Upper Sandusky	GHCND:USC00338534	40.833	-83.283	Sandusky			

[†]Area upstream of gauge

Table 2. Relative Lorenz inequality (Φ_G) and relative memory (Φ_a) between discharge (Q) and precipitation (Precip) for the Maumee and Sandusky rivers for three year time periods.

Year	$\Phi_G(G_Q/G_{Precip})$		$\Phi_a(a_Q/a_{Precip})$	
	Maumee	Sandusky	Maumee	Sandusky
1975-77	0.75	0.76	14.16	10.80
1978-80		0.79		12.19
1982-84	0.72	0.80	7.06	10.68
1985-87	0.64	0.70	7.77	8.69
1988-90	0.64	0.71	13.38	14.62
1991-93	0.64	0.71	7.02	8.41
1994-96	0.69	0.75	6.62	8.97
1997-99	0.63	0.72	10.04	8.35
2000-02	0.60	0.70	8.49	11.51
2003-05	0.62	0.72	6.62	5.75
2006-08	0.64	0.72	7.49	6.74
2009-11	0.68	0.76	13.26	10.34
2012-14	0.70	0.79	20.80	16.58

Table 3. Relative Lorenz inequality (ϕ_G) and relative memory (ϕ_a) between nutrients (dissolved reactive phosphorus (DRP), total phosphorus (TP), suspended sediment (SS), and silica) and discharge (Q) for the Maumee and Sandusky rivers.

Year	ϕ_G				ϕ_a			
	G_{DRP}/G_Q	G_{TP}/G_Q	G_{SS}/G_Q	G_{Silica}/G_Q	a_{DRP}/a_Q	a_{TP}/a_Q	a_{SS}/a_Q	a_{Silica}/a_Q
Maumee								
1975-77	1.02	1.19	1.29		1.19	1.24	1.22	
1978-80								
1982-84	1.04	1.19	1.32		1.29	1.01	0.95	
1985-87	1.17	1.25	1.39		1.14	0.60	0.68	
1988-90	1.19	1.37	1.53		1.05	0.78	0.78	
1991-93	1.19	1.32	1.47		1.09	1.10	0.80	
1994-96	1.18	1.24	1.36		0.79	0.92	0.84	
1997-99	1.26	1.27	1.37		0.90	0.95	0.84	
2000-02	1.27	1.32	1.48	1.12	1.04	1.15	1.19	1.02
2003-05	1.23	1.28	1.48	1.10	1.02	1.02	0.99	0.96
2006-08	1.18	1.23	1.34	1.08	1.10	1.08	1.04	1.01
2009-11	1.15	1.23	1.35	1.04	0.75	1.02	0.91	1.01
2012-14	1.16	1.22	1.34	1.10	1.11	1.19	1.06	1.00
Sandusky								
1975-77	1.09	1.21	1.29		1.21	0.95	0.94	
1978-80	1.04	1.12	1.21		0.91	0.98	1.04	
1982-84	1.13	1.16	1.24		1.02	1.00	1.13	
1985-87	1.17	1.22	1.30		0.85	0.91	0.87	
1988-90	1.30	1.31	1.37		0.94	0.99	0.91	
1991-93	1.23	1.27	1.33		0.91	0.85	0.81	
1994-96	1.20	1.25	1.31		1.00	1.00	0.99	
1997-99	1.31	1.31	1.38		0.93	0.91	0.86	
2000-02	1.17	1.31	1.40	1.02	1.09	0.28	1.23	1.02
2003-05	1.15	1.21	1.32	0.96	1.06	1.07	0.88	1.01
2006-08	1.17	1.21	1.28	1.01	1.03	1.10	1.09	0.98
2009-11	1.12	1.16	1.23	1.01	1.10	1.15	1.11	1.00
2012-14	1.14	1.15	1.20	1.00	1.21	1.04	0.79	0.96

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Figure 1. Maumee and Sandusky watersheds located in northwestern Ohio, USA.

Figure 2. Observed annual precipitation (Precip), discharge (Q), dissolved reactive phosphorus (DRP) load, and total phosphorus (TP) load from the Maumee and Sandusky watersheds (1975-2014). Precipitation values represent the mean of four rain gauges (see Figure 1 for rain gauge locations).

Figure 3. Gini coefficients (G) for precipitation (Precip), discharge (Q), dissolved reactive phosphorus load (DRP), total phosphorus load (TP), suspended sediment load (SS), and silica load. If $G=0$, then an analyte is equally distributed among all observations (i.e., perfect equality). If $G=1$, then all of an analyte is allocated to a single observation (i.e., perfect inequality).

Increases in G from 0 to 1 indicate that the analyte has become less uniformly distributed among observations, while decreases from 1 to 0 indicate increasing uniformity among observations.

Figure 4. Memory (α) in precipitation (Precip), discharge (Q), dissolved reactive phosphorus load (DRP), total phosphorus load (TP), suspended sediment load (SS), and silica load. A memory-less process is represented by $\alpha=0$. Processes with short-term and long-term memory are represented by $\alpha=2$ and $\alpha=1$, respectively. Decreases in α from 1 to 0 indicate that there has been a loss of memory in the signal, while increases in α from 1 to 2 indicate an increasing dominance of short-term memory.

Figure 1

Figure 2

Figure 3

Figure 4