LIMNOLOGY
and
OCEANOGRAPHY

ASLO

Limnol. Oceanogr. 9999, 2019, 1–15

doi: 10.1002/lno.11353

Biogeochemical asynchrony: Ecosystem drivers of seasonal concentration regimes across the Great Lakes Basin

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Abstract

Changes in seasonal nutrient dynamics are occurring across a range of climates and land use types. Although it is known that seasonal patterns in nutrient availability are key drivers of both stream metabolism and eutrophication, there has been little success in developing a comprehensive understanding of seasonal variations in nutrient export across watersheds or of the relationship between nutrient seasonality and watershed characteristics. In the present study, we have used concentration and discharge data from more than 200 stations across U.S. and Canadian watersheds to identify (1) archetypal seasonal concentration regimes for nitrate, soluble reactive phosphorus (SRP), and total phosphorus, and (2) dominant watershed controls on these regimes across a gradient of climate, land use, and topography. Our analysis shows that less impacted watersheds, with more forested and wetland area, most commonly exhibit concentration regimes that are in phase with discharge, with concentration lows occurring during summer low-flow periods. Agricultural watersheds also commonly exhibit in-phase behavior, though the seasonality is usually muted compared to that seen in less impacted areas. With increasing urban area, however, nutrient concentrations frequently become essentially aseasonal or even exhibit clearly out-of-phase behavior. In addition, our data indicate that seasonal SRP concentration patterns may be strongly influenced by proximal controls such as the presence of dams and reservoirs. In all, these results suggest that human activity is significantly altering nutrient concentration regimes, with large potential consequences for both in-stream metabolism and eutrophication risk in downstream waterbodies.

Changes in climate, land use, and management are fundamentally altering both seasonal and event-scale patterns in nutrient dynamics and ecosystem function. In recent decades, we have seen increases in the length of the growing season, warmer winters, and increasing numbers of freeze-thaw events during the winter season (Clark et al. 2014; Park et al. 2016; Peng et al. 2016; Santos et al. 2014; Solomon 2007; Walther et al. 2002). In agricultural landscapes, which are already associated with higher loadings of nutrients to both streams and groundwater (Van Meter and Basu 2017), tile drainage densities are increasing, changing water pathways, and altering rainfall-runoff relationships (Thompson et al. 2011; Boland-Brien et al. 2014). Wetland drainage and river channelization are reducing hydrologic and biogeochemical connectivity between upland and lowland regions (Van Meter and Basu 2015; Cohen et al. 2016). At the same time, dam building and reservoir development are changing seasonal flow regimes and increasing the residence times of water and nutrients within the landscape (Vörösmarty and Sahagian 2000), thus altering conditions driving biogeochemical cycling within the river network (Maavara et al. 2017). Such alterations are fundamentally disrupting the timing and magnitude of nutrient transport across the landscape, to the river network and, ultimately, to the coasts.

Given the heterogeneity of catchments and accelerated rates of change in climate and land use, researchers across a range of disciplines, from ecology to hydrology, have become increasingly interested in developing metrics for catchment classification that can better our understanding of spatiotemporal patterns of change and allow us to develop better options for water management. In ecology, for example, such metrics include measures of (1) diatom community structure (Potapova and Charles 2007; Smucker et al. 2013), (2) the species richness of fish communities (Karr 1981; Gergel et al. 2002), and (3) annual-scale values for gross and net primary productivity (Bernhardt et al. 2017). In hydrology, a range of metrics have been explored, for example, runoff ratios, slope

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of the flow duration curve, baseflow index (Yadav et al. 2007; Sawicz et al. 2011), and frameworks such as the Budyko curve, with its related climate indicators (aridity index, potential evaporation), have been developed for catchment classification (Carmona et al. 2014). In this context, researchers have used widely available hydrologic data to characterize catchments and to extend this analysis to ungauged basins (Sivapalan 2003; Wagener et al. 2004).

With regard to stream chemistry, a variety of water quality metrics are commonly used in monitoring programs, and suggestions for their use as integrated indices have appeared in the scientific literature since at least the 1950s (Hembree 1952; Cude 2001; Gergel et al. 2002). Some of the simplest metrics for evaluating river water quality are mean annual concentration values for individual solutes as well as measures of water clarity, temperature, and conductivity (Gergel et al. 2002). Many attempts have also been made to link such measures to upland land use (Ahearn et al. 2005; Tu 2011; Zhou et al. 2016), with agricultural land use in particular showing a strong positive correlation with stream nutrient concentrations (Chen et al. 2016; Van Meter and Basu 2017). Recently, there has also been interest in characterizing event-scale concentration dynamics, thus creating integrated metrics of concentration and discharge. In particular, event-scale concentration-discharge metrics have been developed as a means of classifying nutrient export regimes for catchments (Godsey et al. 2009; Basu et al. 2010; Thompson et al. 2011; Musolff et al. 2015). Using metrics related to the strength of the correlation between concentration, C, and discharge, Q, ($C = aQ^b$) as well as comparisons of concentration and discharge variability (CV_C/CV_Q), catchments can be classified as "chemostatic" or "chemodynamic," depending on the extent to which event-scale concentrations vary in response to changes in discharge (Godsey et al. 2009; Basu et al. 2010; Haygarth et al. 2014; Wymore et al. 2017). These relationships have been found to vary as a function of land use (Basu et al. 2010; Musolff et al. 2015), with more pristine landscapes demonstrating more chemodynamic behavior, while agricultural landscapes behave more chemostatically.

Work has also been done to characterize seasonal patterns in nutrient dynamics. Mulholland and Hill (1997) have generalized that while forested areas of Appalachia in the southern U.S. show summer nitrate peaks, concentrations in more northern watersheds, for example, New Hampshire (Vitousek 1977), New York (Murdoch and Stoddard 1992), Ontario (Foster et al. 1989), reach maximum values in the winter or early spring. In this comparison, the higher summer concentrations in the south are attributed to a combination of the concentrating effects of low discharge paired with high net release of nutrients via in-stream processes (Mulholland and Hill 1997). Similarly, Duncan et al. (2015) have presented evidence of the importance of riparian ecohydrologic processes in driving summer concentration peaks. Additionally, combined analysis of spatial and seasonal drivers of nitrate concentrations in the Rocky Mountain West has suggested that while summer concentrations are primarily a function of watershed characteristics related to biological processing, for example, percent forest or the presence of riparian buffers, concentrations from late fall through early spring are more a function of either anthropogenic (wastewater) or geologic (weathering) loading (Gardner et al. 2011). Although attempts have been made to develop metrics to describe these seasonal dynamics (Dupas et al. 2015, 2017; Tian et al. 2016; Abbott et al. 2018), the number of watersheds considered has been small, and there has been limited success in creating a broader framework to link these metrics with watershed characteristics and landscape processes. Furthermore, the majority of studies related to stream nutrient seasonality have focused on natural controls and have not been placed within the context of more direct human impacts on concentration seasonality such as year-round emissions of wastewater effluents in population dense areas (Carey and Migliaccio 2009).

In the present study, to better characterize the ways in which changes in land use and management are disrupting the timing and magnitude of nutrient delivery across gradients of both climate and land use, we have focused our analysis on watersheds across the North American Great Lakes Basin (GLB)—an area subject to myriad anthropogenic pressures, including a rapid expansion of urban areas and intensive agricultural production (Wolter et al. 2006). Lake Erie, in particular, is increasingly threatened by eutrophication and increases in the occurrence of harmful algal blooms, driven by changes in the timing and magnitude of nutrient delivery to the lake (Watson et al. 2016). Our foundational hypothesis in this work is that anthropogenic alterations in both sources and transport pathways for nutrients are changing seasonal concentration dynamics in surface waters. To test this hypothesis, we use discharge and water quality data obtained from more than 200 monitoring stations across the U.S., representing watersheds exhibiting a range of land uses and management, to explore seasonal concentration patterns for nitrate, soluble reactive phosphorus (SRP), and total phosphorus (TP). Observed patterns of seasonal nutrient dynamics are classified, and then paired with land-use and climate data to identify key natural and anthropogenic controls on nutrient seasonality. Through this work, we attempt to answer the following questions: (1) How do seasonal patterns of nutrient delivery vary across the GLB? (2) What are the dominant climatic and land use controls on these patterns? (3) How is human activity influencing patterns of seasonality in stream nutrient concentrations?

Methods

Site description

The GLB covers an area of more than 765,000 km^2. Human population within the GLB is growing steadily, having increased from approximately 43 million in 1990 to 48.5 million in 2010 (Méthot et al. 2015). Urban sprawl is increasing across the basin, and urbanized area in general increased by approximately 10% between 2000 and 2010 (Méthot et al.

2015). Climate within the GLB is seasonally variable and is driven primarily by winter flows of cold air from the Arctic and summer flows of warm air from the Gulf of Mexico (Fuller and Shear 1995). Mean daily temperatures in both winter and summer differ by approximately 10°C from north to south, and mean annual precipitation ranges from 600 to 1300 mm yr^{-1} (EC and USEPA 2009). In the north, granite bedrock underlies acidic soils and a landscape dominated by conifer forests; in the south, the climate is warmer, soils are deeper, and agricultural land use as well as urban sprawl are primary drivers of impaired water quality (Fuller and Shear 1995; Chapra et al. 2016).

Data sources and site selection criteria

The Great Lakes watersheds include parts of the Canadian provinces of Ontario and Quebec and the U.S. states of Illinois, Indiana, Michigan, Minnesota, New York, Ohio, Pennsylvania, and Wisconsin. Water quality data for Ontario were obtained from the Provincial Water Quality Monitoring Network (PWQMN) (Ontario Ministry of Environment). Data for the U.S. states were obtained from the United States Geological Survey (USGS) and from the Water Quality eXchange (WQX) and the Storage and Retrieval Data Warehouse (STORET) databases. Daily discharge data were obtained from the Water Survey of Canada and USGS. Water quality monitoring stations were chosen for the current analysis based on the following decision criteria: (1) location with the GLB; (2) proximity to an MOE (Canada) or USGS (U.S.) flow-monitoring station with temporally corresponding discharge data; and (3) data availability between 2000 and 2016. Based on these criteria, 185 stations were identified with available nitrate (NO_3^-) data, 180 with orthophosphate-P (PO_4-P) data (hereafter referred to as SRP), and 212 with TP data (*see* Fig. 1). Of these stations, 78 had data available for all three solutes.

Land-use data for Canada and the U.S. were obtained from the Annual Crop Inventory (2015) and the National Land Cover Database (Homer et al. 2015), respectively. Tile drainage data for Canada and the U.S. were obtained from the Tile Drainage Area GIS layer (OMAFRA 2015) and the U.S. map of subsurface drains on agricultural land (Nakagaki et al. 2016). Note that while the Canadian tile drainage data set attempts to provide a spatial representation of the actual tile drainage network, it is generally considered to be incomplete and likely an underrepresentation of tiled areas (OMAFRA 2015). In addition, the U.S. tile drainage data set is not based on actual mapping of the tile drainage network, but is instead based on assumptions about drainage densities based on the presence of row crop agriculture and soil type (Nakagaki et al. 2016). Gridded air

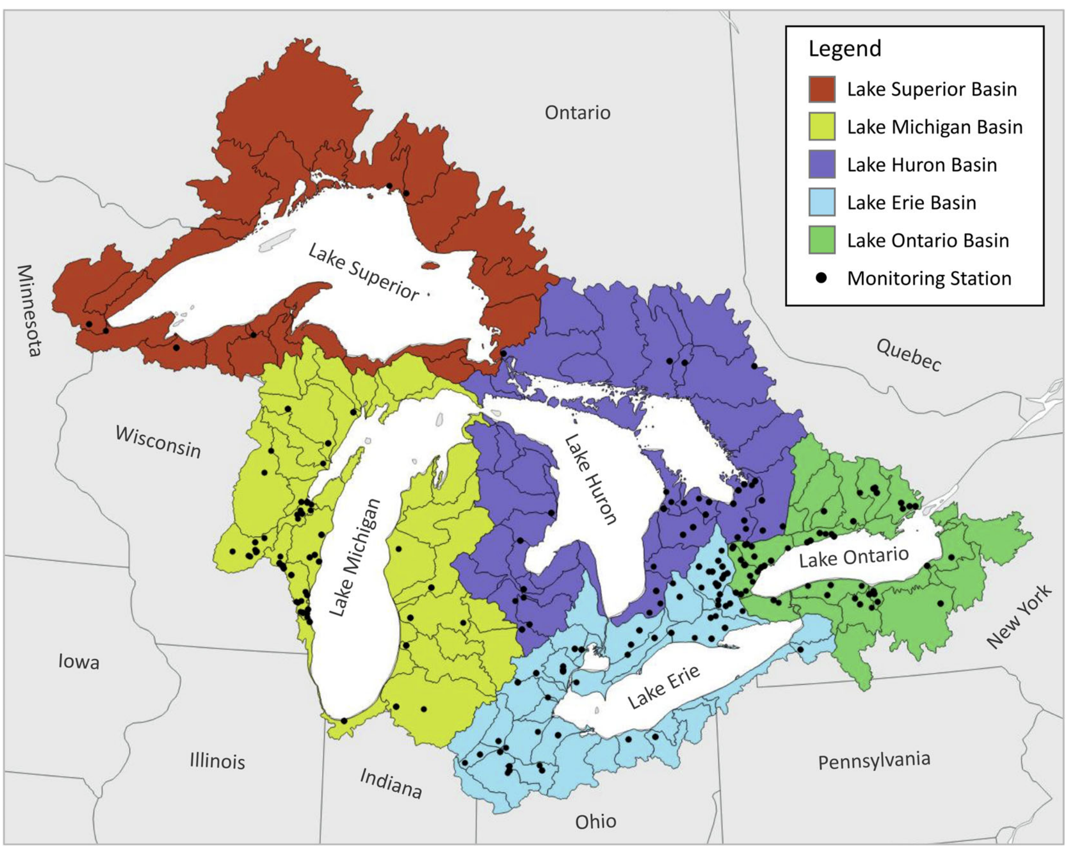

Fig. 1. The Great Lakes Basin, divided by color into its five major sub-basins. Water quality monitoring stations are indicated with black markers.

temperature and precipitation data at 1-km resolution were obtained from the WorldClim database (Fick and Hijmans 2017). Soil data for Canada were extracted from the National Soil Database (NSDB) and the Harmonized World Soil Database (Nachtergaele et al. 2009); for the U.S., data were obtained from the Soil Survey Geographic (SSURGO) Database (USDA). Slope data for U.S. watersheds were obtained using the USGS StreamStats program (USGS 2016). For Canada, slope data were obtained using the Ontario Flow Assessment Tool (OMNRF 2019).

Metrics

Solute concentrations

We used the weighted regression on time, discharge, and season (WRTDS) methodology to obtain daily estimates of concentration for nitrate, SRP, and TP at each of the selected stations using daily discharge data and intermittently measured concentration data (Hirsch et al. 2010). Monthly concentration values were calculated based on simple averaging of WRTDS-estimated daily concentration values.

Seasonality index

The seasonality index (SI) is a simple metric that has been used to assess the seasonality of rainfall (Walsh and Lawler 1981) and, more recently, of discharge and solute loads (Tian et al. 2016). In the present work, we used the SI metric to quantify seasonal variations in monthly discharge, monthly nutrient concentrations, and monthly air temperature. SI values were calculated for discharge (SI_Q) using the following equation:

$$\mathrm{SI}_Q = \frac{1}{Q_\mathrm{A}} \sum_{i=1}^{12} \left| Q_i - \frac{Q_\mathrm{A}}{12} \right|, \tag{1}$$

where Q_A is the total annual discharge (m^3) and Q_i is the total discharge for month *i*. SI values for concentration (SI_C) were calculated using Eq. 2:

$$\mathrm{SI}_C = \frac{1}{C_\mathrm{A}} \sum_{i=1}^{12} \left| C_i - \frac{C_\mathrm{A}}{12} \right|, \tag{2}$$

where C_A is the sum of the monthly concentration values and C_i is the mean concentration for month *i*. SI values for air temperature ($\mathrm{SI}_{\mathrm{temp}}$) were calculated using Eq. 3:

$$\mathrm{SI}_{\mathrm{temp}} = \frac{1}{T_\mathrm{A}} \sum_{i=1}^{12} \left| T_i - \frac{C_\mathrm{A}}{12} \right|, \tag{3}$$

where T_A is the sum of the monthly temperature values and T_i is the mean air temperature for month *i*.

The SI_Q, SI_C, and $\mathrm{SI}_{\mathrm{temp}}$ index values are theoretically bound between 0 and 1.83. In the present work, $\mathrm{SI} < 0.2$ is considered to represent a relatively even seasonal distribution or aseasonal behavior (Walsh and Lawler 1981; Tian et al. 2016).

Event-scale concentration-discharge metrics

We used two well-accepted metrics to characterize event-scale concentration-discharge metrics in the current analysis: (1) *b*-values, as obtained from fitted power law relationships between concentration and discharge

$$C = aQ^b, \tag{4}$$

where *C* is concentration, *Q* is discharge, and *a* and *b* are fitted constants (Basu et al. 2010); and (2) the ratio between the coefficient of variation for concentration and the coefficient of variation for discharge ($\mathrm{CV_R}$) (Thompson et al. 2011):

$$\mathrm{CV_R} = \frac{\mathrm{CV}_C}{\mathrm{CV}_Q}. \tag{5}$$

The *b*-values from Eq. 4 are used to measure the strength and nature of the correlation between *C* and *Q*, with larger values corresponding to higher correlation. $\mathrm{CV_R}$ values are used to measure relative variability between *C* and *Q*, irrespective of the correlation.

Classification of seasonal concentration regimes and identifying dominant controls

As a first step in identifying linkages between seasonal patterns in stream solute concentrations and specific climatic and land use controls, we developed a quantitative approach to classify watersheds according to their seasonal concentration regime—an identifiable pattern of high and low mean monthly nutrient concentrations. Given that riverine discharge within Great Lakes watersheds varies seasonally, driven by both spring snowmelt dynamics, increased summer evapotranspiration, and seasonal precipitation patterns, we define the seasonal concentration regime specifically as a function of the relationship between monthly concentration values and monthly discharge. Accordingly, linear regression analysis was used to determine whether there were significant linear relationships between monthly mean concentrations and monthly mean discharge. Watersheds with positive linear relationships (positive slope, $p < 0.05$) were defined as in-phase, meaning that concentrations are high when discharge is high. Those with negative linear relationships (negative slope, $p < 0.05$) were defined as out-of-phase, meaning that concentrations are high when discharge is low. Finally, those with no significant relationship ($p > 0.05$) and with low seasonality ($\mathrm{SI}_C < 0.2$) were defined as seasonally stationary, or aseasonal.

To identify dominant controls on nutrient seasonality, we obtained climate, land use, and geomorphologic data for all of the study watersheds, as described in the "Methods" section. Focusing specifically on the watersheds with available data for all three solutes of interest (nitrate, SRP, TP), the Wilcoxon Rank Sum test (WRST) was used to test the significance of associations between the nutrient seasonality observed under the identified concentration regimes and various watershed characteristics, for example, percent land use, seasonality metrics, and CQ metrics. We considered p values < 0.10 to indicate significance.

Modeling framework

We developed a simple modeling framework to describe the observed seasonal concentration patterns as a function of varied degrees of contribution from two types of sources: (1) landscape sources (nonpoint sources) and (2) point sources.

For landscape sources, we assume that solute masses delivered to the stream network will vary across seasons depending on variations in discharge. Concentrations associated with these landscape sources are conceptualized as exhibiting a power-law relationship with discharge, according to the following equation:

$$C_{\mathrm{L}}(t) = aQ(t)^{b} \tag{6}$$

where C_{L} is the concentration associated with landscape sources, Q is the daily discharge, and a and b are constants, with higher absolute values of b being associated with greater concentration variability.

For point sources, we assume a constant delivery of solute mass throughout the year, meaning that concentrations will vary with discharge as a function of simple dilution dynamics:

$$C_{\mathrm{c}}(t) = \frac{L_c}{Q(t)}, \tag{7}$$

where C_{c} is the concentration associated with constant sources and L_c is the daily load emanating from the source.

Concentrations at the catchment outlet, C_{out}, then vary as a function of the two different sources:

$$C_{\mathrm{out}}(t) = aQ(t)^{b} + \frac{L_C}{Q(t)}. \tag{8}$$

Parameter values for a and b as well as the magnitudes of loads from constant sources, L_c, were varied to simulate the in-phase, out-of-phase, and aseasonal patterns in nutrient concentrations observed in the current study, as shown in Table 1.

Table 1. Parameter and percent loading values for the conceptual model. The model assumes varying contributions of landscape and point sources across the three different simulations. The parameters a and b are constants in the power law relationship (Eq. 6), and L_c is the daily load emanating from the point source.

Parameters	Sim 1 (in-phase)	Sim 2 (out-of-phase)	Sim 3 (out-of-phase)
a	0.27	0.26	0.20
b	0.47	0.46	0.47
L_c	138	77	16

Results and discussion

Seasonal patterns in stream nutrient concentrations

Understanding controls on seasonal patterns in stream nutrient concentrations is essential to effective watershed management and the protection of downstream waterbodies (Mulholland and Hill 1997). In the present work, we have attempted to characterize seasonal variations in nutrient concentrations using two different approaches: (1) use of a seasonality index (SI), which allows us to quantify the extent of monthly variations in concentration throughout the year; and (2) identification of patterns in seasonal concentration regimes in relation to seasonal flow regimes for the more than 200 study watersheds.

Seasonality index

Concentration seasonality, SI_C, was found to range from a low of 0.02 to a high of 1.20 (theoretical range = 0–1.83). While the distributions of median SI_C values are quite similar across the three solutes (nitrate median SI_C = 0.27; SRP median SI_C = 0.23; TP median SI_C = 0.30) (Fig. 2), there are large differences between concentration seasonality and discharge seasonality, SI_Q. In general, SI_Q was found to be approximately twice that of SI_C (median SI_Q = 0.50). The higher discharge seasonality is a reflection of two major climate signals. First, spring snowmelt drives high spring discharge. Second, there is high monthly temperature seasonality across the Great Lakes region (SI_{temp} = 0.60), leading to large seasonal variations in evapotranspiration. The significant difference observed between concentration seasonality and discharge seasonality (p < 0.001, WRST) conforms with other studies demonstrating that stream concentrations are frequently less variable than discharge (Basu et al. 2010; Thompson et al. 2011).

Monthly regime curves

To better characterize seasonal patterns of nutrient delivery and to determine the extent to which hydrology is driving seasonal variations in concentration, we quantified correlations between concentration and discharge at the monthly scale for individual watersheds. Through this analysis, we first identified three primary patterns of seasonal behavior: (1) in-phase; (2) out-of-phase; and (3) aseasonal (Fig. 3). For all three solutes, approximately 80% of watersheds were found to fall into one of these three clusters (Table 2). Although the in-phase (IP) concentration regime was found to be the most common for all solutes, in-phase behavior was more dominant for nitrate (56% of watersheds) than for either SRP (30%) or TP (42%). For SRP in particular, out-of-phase behavior (OP) was found to be nearly as prevalent as in-phase behavior (29% of watersheds).

Approximately 20% of watersheds do not exhibit any of the three identified concentration patterns (Table 2). For TP and SRP, these “other” watersheds demonstrate no consistent seasonal concentration patterns, but instead show considerable, but unpredictable, seasonal variability across the years

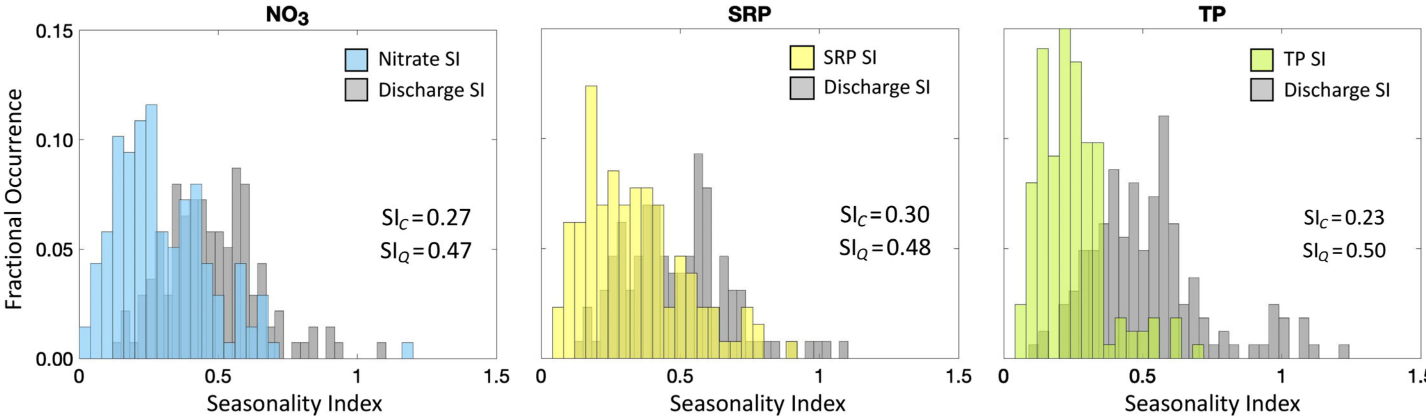

Fig. 2. A comparison of seasonality between solute concentrations (colors) and river discharge (gray). The three histograms show the distributions of seasonality index (SI) values for nitrate (blue), SRP (yellow), and TP (green) in comparison with discharge SI values for watersheds across the GLB. SI values can theoretically range from 0 to 1.83, with values less than 0.2 representing an essentially even seasonal distribution, and values greater than 0.6 representing strong seasonality. Note that not all watersheds have data for all three solutes, meaning that the subset of watersheds included for each solute is different. As a result, SI_Q distributions vary between the different solute groups. The results shown above demonstrate that seasonal solute concentrations are relatively chemostatic in comparison with discharge.

(SRP, $SI_C = 0.26$; TP, $SI_C = 0.48$). For nitrate, however, a consistent pattern is observed. As shown in Fig. 4a, nitrate concentrations in this fourth cluster consistently peak in winter, with concentration lows occurring in early summer. Instead of showing a significant positive or negative relationship between monthly concentrations and discharge, these watersheds actually show a synchronicity with seasonal temperature patterns across the Great Lakes region. More specifically, we see a significant inverse correlation between mean monthly temperatures and mean nitrate concentrations in this group of watersheds, which we will subsequently refer to as the "temperature-driven" cluster ($R^2 = 0.62$, $p < 0.001$) (Fig. 4b). Such a relationship is likely due to a combination of increased plant uptake during the growing season as well as elevated microbial metabolism at higher ambient temperatures (Pfenning and McMahon 1997). This elevated temperature leads to increased microbial activity, higher denitrification rates, and thus lower stream nitrate concentrations in summer and, conversely, the highest concentrations during winter (Pfenning and McMahon 1997; Richardson et al. 2004; Opdyke and David 2007).

Watershed drivers of nutrient seasonality

To better explain the differences in seasonal concentration regimes and to identify likely watershed-scale drivers of these seasonal patterns, we next assessed relationships between seasonal concentrations and climate, geomorphologic, and land-use characteristics for the 78 study watersheds with available concentration data for all three solutes of interest (nitrate, SRP, TP). As described in the "Methods" section, the WRST was used to assessing the significance of associations between specific watershed characteristics and emergent seasonal concentration patterns. The results of this analysis are presented in Fig. 5, with additional results provided in the Supporting Information Table S2.

Watershed drivers of nutrient seasonality: Nitrate

The results of our analysis suggest that seasonal nutrient concentration regimes have clear associations with watershed land use (Fig. 5). The nature and the strength of these associations, however, differ according to the specific solute. For nitrate, the watersheds exhibiting in-phase nitrate concentration behavior (Fig. 5a) are significantly associated with a higher percent agricultural area (median 54.1%) and higher tile-drainage densities (median 7.0%). These results are in line with observations of elevated spring nutrient concentrations in agricultural streams, a seasonal pattern that has been attributed to the timing of fertilizer application as well as the prevalence of tile drainage (Richards and Baker 2002; Royer et al. 2006). With increasing population densities and higher percent urban land use, however, seasonal concentration regimes for nitrate are more likely to exhibit aseasonal or out-of-phase characteristics (Fig. 5b,c). This significant association between the aseasonal and out-of-phase concentration regimes and both urban land use ($p < 0.01$) and human population density ($p < 0.05$) suggests that wastewater effluents as well as other urban point sources may be contributing to higher concentrations during summer low-flow periods and thus further homogenizing or even reversing seasonal concentration patterns across the year.

For nitrate, the more temperature-driven concentration regime (significant negative correlation between temperature and concentration) is significantly associated with indicators suggesting the lowest levels of human impact, that is, lower agricultural land use (median 47.4%), very low tile drainage densities (median 0.2%), low population densities

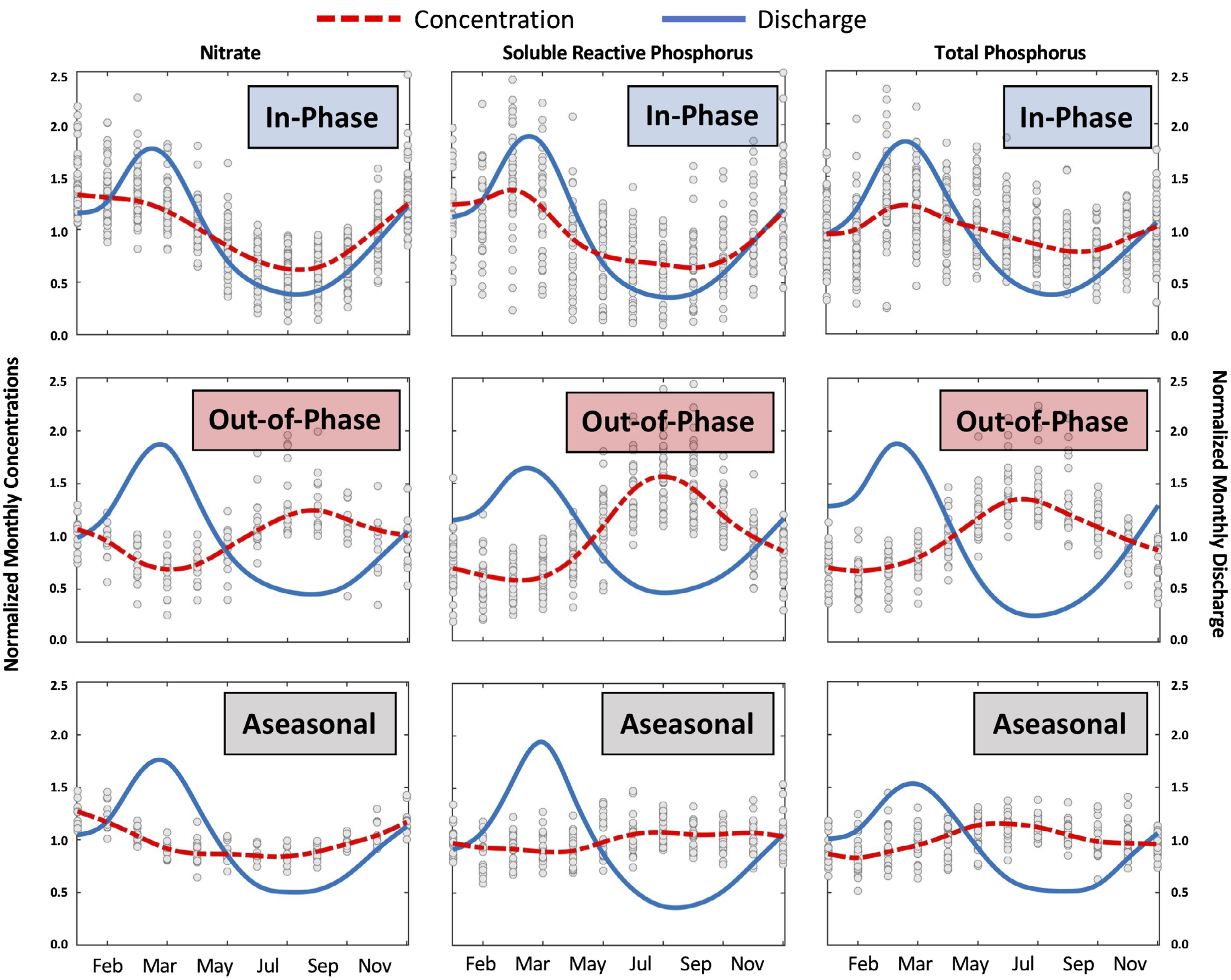

Fig. 3. Concentration and flow regime curves for nitrate, total P, and soluble reactive P across the GLB. Both concentration and discharge are represented here as normalized values to allow for direct comparison between watersheds. Gray circles represent monthly concentration values for individual watersheds, and red lines represent median values across watersheds. Blue lines represent median normalized discharge across watersheds. Our results show three primary patterns of behavior: (1) in-phase, characterized by positive significant relationships ($p < 0.10$) with discharge; (2) out-of-phase, characterized by negative significant relationships ($p < 0.10$) with discharge; and (3) aseasonal, characterized by low seasonality ($SI_C < 0.2$) and no significant relationship with discharge ($p > 0.10$). In all, these three patterns account for 75%, 77%, and 79% of all watersheds for nitrate, TP, and SRP, respectively.

(25.5 persons km^{-2}), and higher relative percentages of forested (median 29.9%) and wetland (median 16.7%) area (Fig. 5d). These watersheds also tend to be at higher latitudes (median 44.146°) with lower mean annual temperatures (median 6.6°C), consistent with the lower levels of agricultural land use and the presence of more forested land in more northern areas of the GLB. As discussed above, these watersheds exhibit the highest concentration and discharge seasonality, and the strong negative correlation between temperature and concentration suggests the importance of seasonally varying denitrification rates in amplifying seasonal concentration dynamics (Pfenning and McMahon 1997). The link between low tile drainage densities and temperature driven seasonal dynamics suggests that the increased residence times for nitrate associated with a slower movement of water and nitrate through the subsurface may allow more time for biogeochemical reactivity and thus weaken the linkage between concentration and discharge in these systems.

Watershed drivers of nutrient seasonality: Phosphorus

Similar to nitrate, hydrologically in-phase seasonality for both SRP and TP is significantly associated with higher levels

Table 2. Summary of seasonality and concentration metrics for nitrate, SRP, and TP. The table provides median values for the four primary concentration regime clusters.

	All sites	Cluster 1 (in-phase)	Cluster 2 (out-of-phase)	Cluster 3 (stationary)	Cluster 4 (other)
Nitrate					
SI_C	0.27	0.26	0.20	0.15	0.44
SI_Q	0.47	0.46	0.47	0.41	0.58
Number	138	77	16	13	30
Percent	—	56	12	9	22
SRP					
SI_C	0.30	0.36	0.35	0.14	0.32
SI_Q	0.48	0.50	0.40	0.57	0.55
Number	129	39	38	21	24
Percent	—	30	29	16	19
Total P					
SI_C	0.23	0.24	0.22	0.13	0.27
SI_Q	0.50	0.52	0.55	0.40	0.48
Number	163	69	24	27	34
Percent	—	42	15	17	21

of agricultural land use and higher tile drainage densities (Fig. 5f,j). These in-phase watersheds also have relatively low levels of urban land use and low population densities.

For SRP, higher population densities and larger percent urban areas are also associated with out-of-phase concentration regimes (Fig. 5h), similar to nitrate. Again, in these more populated areas, point-source dilution behavior downstream from municipal wastewater treatment plants and industrial sources can lead to low concentrations during high winter and spring flows and higher concentrations during summer low-flow periods, thus creating the observed out-of-phase regimes. For TP, however, these out-of-phase dilution effects are not observed, likely because wastewater P discharge is primarily in the form of soluble P, not particulate (Jarvie et al. 2006). For TP, more urban systems have the strongest association with the seasonally aseasonal concentration regime,

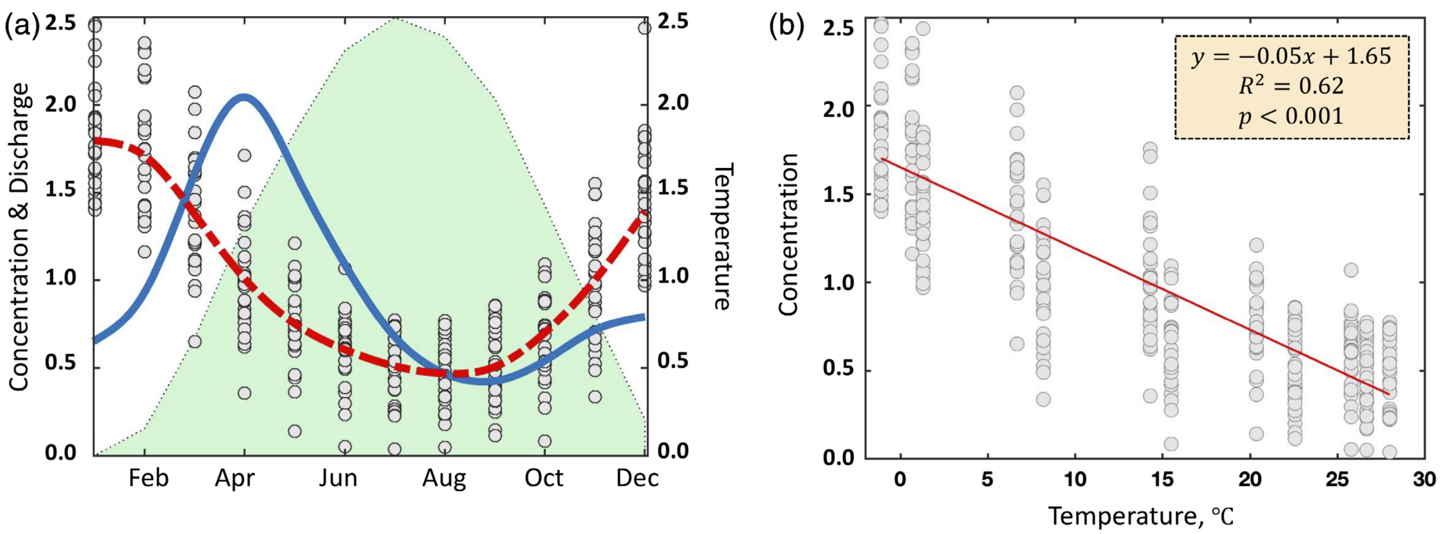

Fig. 4. Concentration, temperature, and flow regime curves for nitrate in the temperature-driven watersheds. In (**a**), temperature, concentration, and discharge are represented as normalized values to allow for direct comparison across watersheds. As in Fig. 3, gray circles represent monthly concentration values for individual watersheds, and red lines represent median concentration values across watersheds. Blue lines represent median normalized discharge across watersheds. The green curve represents temperatures across the Great Lakes region. In these watersheds, there is a strong inverse correlation between concentration and temperature (**b**), with peak concentrations corresponding to low temperature periods in winter and low concentrations corresponding to summer temperature peaks. This more temperature-driven group of watersheds accounts for 22% of all watersheds with nitrate data.

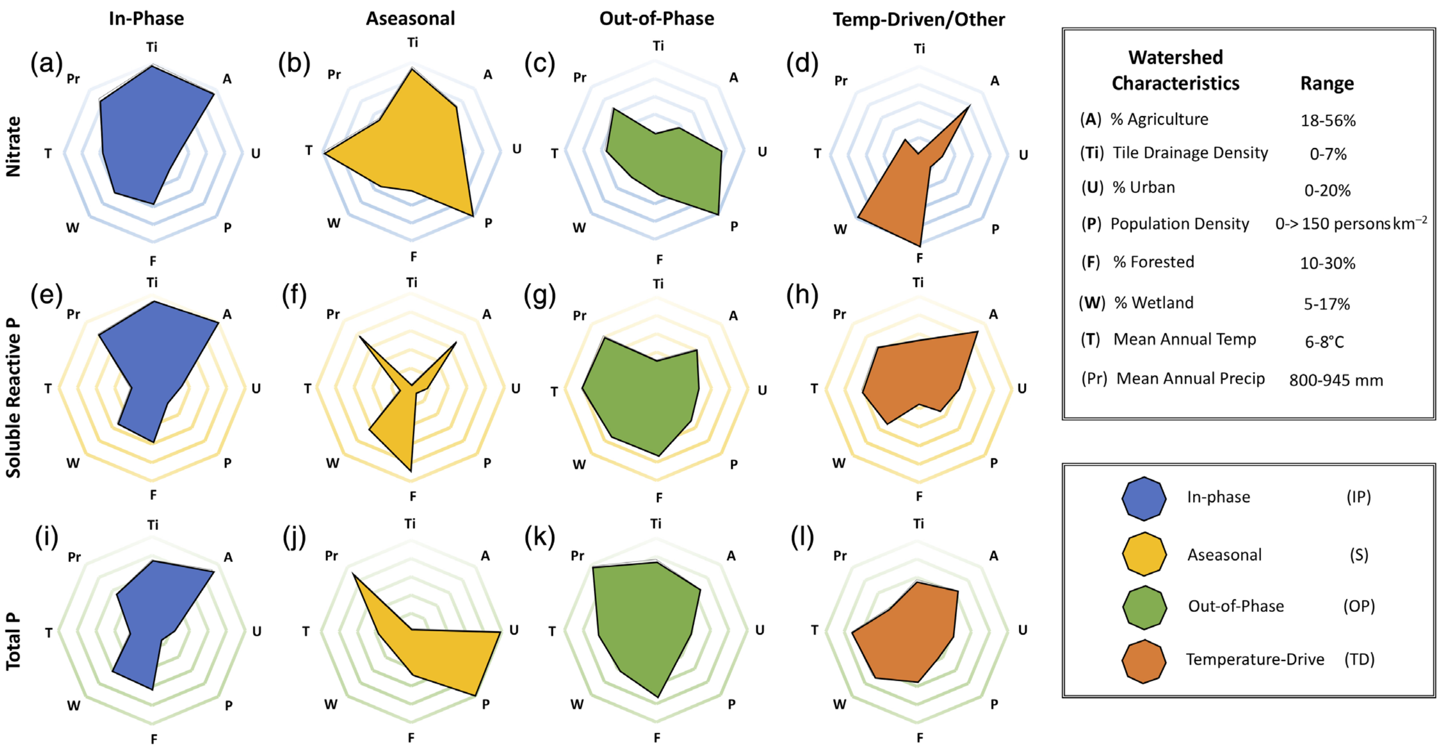

Fig. 5. Radar plots showing associations between land use and seasonal concentration regimes. The plot axes correspond to percent ranges of land-use types, for example, agriculture, urban, and so on. The four columns correspond to the four clustered seasonal concentration regimes, and the rows to the three solutes (nitrate, SRP, total P) (a-l).

suggesting that the high mobilization of sediments and particulate common to agricultural areas may be muted in areas with more lawns and impervious cover.

Contrasting patterns of N and P regimes: Watershed vs. proximal controls

Interestingly, there are many cases in which an individual watershed will exhibit different seasonal regimes for different solutes. As an example, in a direct comparison of the 76 watersheds with data availability for both nitrate and SRP, we found that 29 of these watersheds exhibited in-phase seasonality for nitrate. Of these 29, 11 (38%) showed *out-of-phase* seasonality for SRP. Our analysis of these watersheds suggests that biogeochemically asynchronous behavior between N and P is more likely to occur when proximal sources or controls such as wastewater treatment plants or upstream reservoirs override distal watershed drivers such as widespread use of commercial fertilizers. Six of these 11 asynchronous watersheds are short distances (< 1.5 km) downstream from hydroelectric dams, one is at the outlet of a natural lake and another of a large wetland complex, and two are directly downstream from anthropogenic point sources (one a wastewater plant and the other a large greenhouse operation) (*see* Supporting Information Table S2). In contrast, upstream dams/reservoirs or identifiable proximal control on nutrient dynamics are present at only 2 of the 13 watersheds demonstrating synchronous, in-phase seasonal dynamics for both nitrate and SRP (*see* Supporting Information Table S3).

As an explanation for the 11 watersheds demonstrating asynchronous behavior, it is important to note that in the case of both damming and the presence of natural waterbodies, water residence times are increased within the stream network, thus enhancing opportunities for in-stream nutrient removal (Cheng and Basu 2017). The asynchrony between nitrate and SRP, however, suggests differential effects between the two solutes. For example, while summer nitrate concentrations may be reduced by denitrification, SRP concentrations may actually increase during this period due to increases in internal loading rates (Genkai-Kato and Carpenter 2005; Søndergaard et al. 2013; Song and Burgin 2007), thus leading to the observed asynchronous behavior.

Conceptual framework: Human vs. natural controls on seasonal concentration regimes in the GLB

As suggested by our current results, stream nutrient seasonality can vary as a function of both point-source controls and diffuse inputs across the landscape (Jarvie et al. 2010). In our analysis, we observed what might be considered a continuum of effects on nitrate seasonality, from relatively nonimpacted areas dominated by forests and wetlands, to moderately impacted areas with higher levels of agricultural land use, to highly impacted areas with higher population densities and

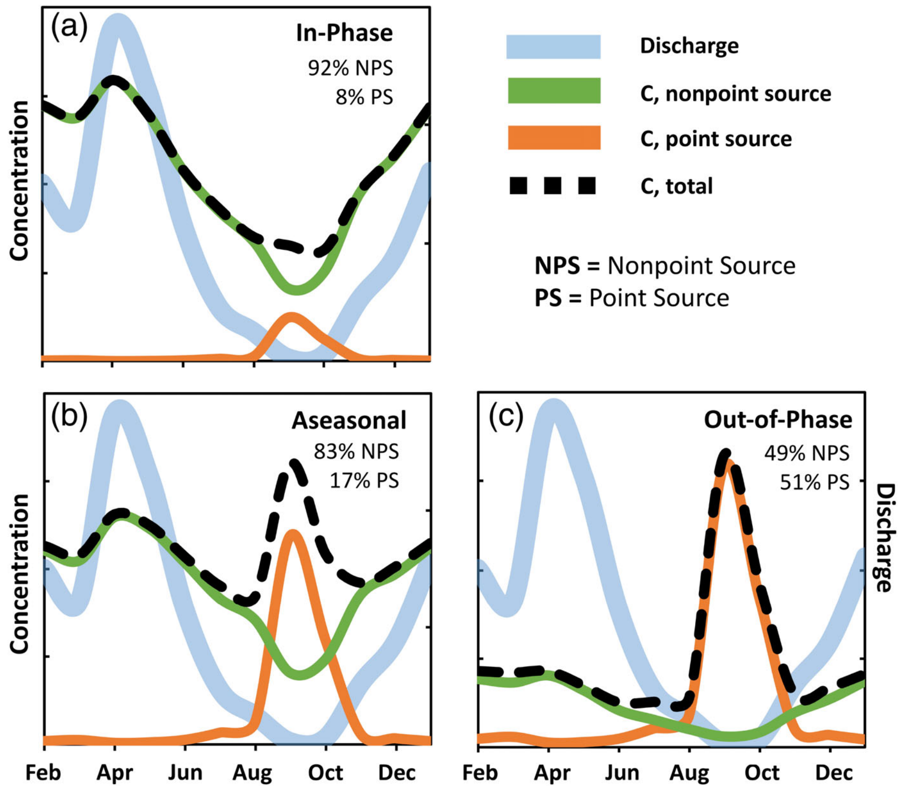

Fig. 6. A conceptual figure demonstrating the varying roles of diffuse and point sources on seasonal concentration dynamics. Note that with in-phase seasonality (**a**), point sources make little contribution to observed stream concentrations, and concentrations peak during months with high flows. For the aseasonal regime (**b**), both point sources and nonpoint sources are contributors. With purely out-of-phase behavior (**c**), concentrations peak at low flows, and point sources become a dominant contributor to overall solute loading. Note that what we label here as "point sources," could also be continuous landscape sources such as internal loading from lakes or groundwater/baseflow with high nitrate concentrations.

more urban land use. These effects were further complicated by the presence of time-varying proximal controls, in particular the presence of reservoirs, wetlands, and lakes. Here, we develop a conceptual framework that can describe the observed seasonal patterns in concentration as a function of varied degrees of contribution from point and nonpoint sources (Fig. 6).

In our simple modeling approach, we first assume that in less populated watersheds, diffuse, landscape nutrient sources will dominate. In the example shown in Fig. 6a, 92% of annual loading originates from nonpoint sources, while only 8% comes from point sources. Assuming even a weakly positive power law relationship between concentration and discharge for landscape sources ($b = 0.23$), we see a clear, positive in-phase relationship between monthly discharge and monthly concentrations, with summer concentration lows and peaks during winter or spring high flows (Fig. 6a). The aseasonal and out-of-phase concentration regimes (Fig. 6b,c) represent different configurations of human impact, as more urban area and higher population densities correlate with a greater relative influence of point source controls on nutrient concentrations compared with the in-phase regime. For the aseasonal regime (Fig. 6b), while there may be moderate variability in concentrations throughout the year, there is no clear seasonality due to the dominance of landscape sources during high-flow periods and the dominance of point sources at low flows. Under this scenario, point source contributions surpass diffuse landscape contributions during the lowest flow periods, even though point sources make up only 17% of total loading for the year. In contrast, in streams more strongly influenced by point sources, there is a clear emergence of the out-of-phase regime (Fig. 6c), with high concentrations at low flows and the lowest concentrations during high-flow periods. Interestingly, even under this point source-driven regime, nonpoint sources may still be a large contributor to total loading (49%), demonstrating that while watershed geomorphology and land use may play a large role in controlling total nutrient loads, proximal sources can be a key driver of seasonal regimes.

It is also important to note that a simple differentiation between nonpoint and point sources of nutrients does not capture the full range of effects seen in human-impacted watersheds. First, the point-source dynamics represented in Fig. 6 do not require that nutrient loading emanate from a single "point," like a wastewater treatment plant; the requirement is only that the loading be relatively *constant* throughout the year (Jarvie et al. 2010). Accordingly, in a watershed where baseflow is dominated by nutrient-laden groundwater, concentrations may be elevated during summer low-flow periods, when there is less dilution from surface water, contributing to more moderate in-phase or aseasonal concentration-regimes. In multiple tributaries across the Mississippi River Basin, for example, it has been shown that while nitrate concentrations overall remained steady or decreased since 2000, low-flow concentrations have actually increased, likely due to contributions of legacy nitrate from groundwater. As groundwater nitrate legacies can be substantial in agricultural catchments (Puckett et al. 2011; Van Meter et al. 2017, 2018), we would suggest that legacy nitrate also likely plays a large role in driving the more moderate to aseasonal seasonality observed in the agricultural catchments in the present study. In other words, continuous nutrient loading from groundwater may function similarly to constant point-source loading, thus modifying more seasonal delivery of nutrients from the landscape.

Our results also demonstrate the importance of landscape-related proximal controls with regard to SRP concentrations. As discussed above, the out-of-phase concentration regime was found to be an important seasonal pattern for SRP, in many cases with no strong association with urban-related point sources. In particular, higher concentrations were commonly found to occur during low-flow periods directly below wetland complexes, reservoirs, and lakes (Supporting Information Table S2). Although low-flow concentration peaks are associated with a dominance of "continuous" point sources, we would suggest that seasonality effects are further enhanced below these waterbodies due to not just continuous, but *increased* loading during the summer months. In particular, it has been found that in shallow, eutrophic waterbodies, concentrations are higher in summer due to net release of phosphorus from sediments (Søndergaard et al. 2003; Song and Burgin 2017). In these cases, nitrogen and phosphorus concentration dynamics commonly become asynchronous, as opportunities for internal P loading are paired with longer water residence times and enhanced opportunities for denitrification. In other words, in rivers below hydroelectric dams or flood-control structures, the asynchronous concentration dynamics such as those observed in the present study, and as discussed above, would make it common to see large differences in soluble N:P ratios across the year, with ratios increasing during winter and then plummeting at low flows. Such asynchronicity would be further enhanced in watersheds with a long history of high watershed P loading and legacy accumulations of P in sediments (Zhang et al. 2016).

Conclusion and implications

In the present study, we have used concentration and discharge data from more than 200 stations across U.S. and Canadian watersheds to identify (1) archetypal seasonal concentration regimes for nitrate, SRP, and TP, and (2) dominant watershed controls on these regimes across a gradient of climate, land use, and topography. Our analysis shows that less impacted watersheds, with more forested and wetland area, most commonly exhibit concentration regimes that are in phase with discharge, with concentration lows occurring during summer low-flow periods. Agricultural watersheds also commonly exhibit in-phase behavior, though the seasonality is usually muted compared to that seen in less impacted areas. With increasing urban area, however, nutrient concentrations frequently become essentially aseasonal or even exhibit clearly out-of-phase behavior. In addition, our data indicate that seasonal SRP concentration patterns may be strongly influenced by proximal controls such as the presence of dams and reservoirs.

Shifts in seasonality have potentially important implications related to both stream metabolism and nutrient dynamics in downstream waterbodies, particularly with regard to increased eutrophication risk. First, there is the issue of the increased seasonal variability of N:P ratios observed in the present results. It is increasingly understood that eutrophication is a complex process associated not just with increased algal growth, but also decreases in biodiversity or changes in microbial community structure (Glibert 2017; McCarthy et al. 2009). Such changes can be strongly dependent on seasonal changes in nutrient ratios, ultimately leading to large changes in nutrient cycling and algal biodiversity. As an example, very low N:P ratios have been found to be associated with the growth of N_2-fixing cyanobacteria, which use atmospheric sources of N to make up for limited availability of N within the water column (Conley et al. 2009), while other non-N_2-fixing cyanobacteria such as *Microcystis* are associated with *high* N:P ratios (Glibert et al. 2014). In any algal assemblage, some species may be limited by N while others are limited by P (Chaffin et al. 2013). Accordingly, increased variability of seasonal N:P ratios may set the stage for seasonal variability in the composition of algal communities and may increase the risk of harmful algal blooms across seasons.

Also of importance is the increased nutrient loads being delivered during the warm, summer months in more human-impacted watersheds. It is well accepted that the abundance of phytoplankton in freshwater systems is strongly correlated with both temperature as well as with nutrient availability (Abrantes et al. 2006; Paerl and Huisman 2008). Indeed, it has been shown that while the average abundance of summer algal blooms can be correlated with nutrient levels at the time of the spring turnover, the timing and intensity of major blooms or eutrophication events is dependent on late summer or early autumn nutrient loading, as these loads coincide with optimal temperatures to drive increased phytoplankton production (French and Petticrew 2007). Accordingly, with many human-impacted watersheds delivering an increasing proportion of their nutrient loads during the summer months, as reflected by aseasonal or out-of-phase seasonal regimes, we may also see an increased risk of large eutrophication events in the late summer months. Of particular concern is the increase in summer SRP:TP ratios, with increased availability of soluble, bioavailable P in the summer months driving increased eutrophication in Lake Erie and numerous other waterbodies across the Great Lakes region.

As we are increasing efforts and agricultural management to address large algal blooms events, it is important to recognize the role of human modifications of the landscape on changing seasonal concentration dynamics, and to identify management choices that can decrease eutrophication risk.

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Acknowledgments

The present work was financially supported by Canada Tri-Agency funding to the Lake Futures, Global Water Futures project (NB), and by University of Illinois at Chicago startup funding to K.J.V.M.

Conflict of Interest

None declared.

Submitted 17 August 2018
Revised 03 April 2019
Accepted 11 September 2019

Associate editor: Emily Bernhardt