Spatiotemporal drivers of tributary nutrient dynamics: Effects of watershed variability and seasonality on concentrations, loads, and yields of Lake Michigan's tributaries

By

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Preamble

When I began my dissertation, I had 4 primary goals: 1. To study seasonal variability of nutrient dynamics in Midwestern, freshwater ecosystems, 2. To complete an extensive field work campaign that would take people by surprise, 3. Become a collaborator that other researchers could count on and would enjoy working with, and 4. To teach as often as my advisor would allow.

The four chapters in my dissertation perfectly represent the four academic and professional development goals that were most important to me when I began pursuing a PhD. Chapter 1 (A day in the Life of a Great Lake: Outsized nutrient contributions from small tributaries) includes what will likely be the coolest, most ambitious field work that I ever complete. Chapter 2 (Seasonality mediates interacting watershed drivers of tributary nutrient inputs to a Great Lake) focuses explicitly on how the changing seasons in the Midwest influence tributary nutrient dynamics. Chapter 3, which is a combination of co-authored papers, influenced the direction of my research and allowed me to share my knowledge on the dynamics of Lake Michigan to make significant contributions across all stages of those two research projects. Finally, chapter 4 (An inquiry-based activity to increase student motivation in college-level taxonomy courses) is the result of my dedication to effective teaching methods and curriculum development in higher education.

I could not have scripted a more ideal dissertation when I started at the University of Wisconsin. I will always be thankful for the support I received to pursue the opportunities that best suited my interests and truly have a "choose your own adventure" experience.

Dissertation abstract

Excessive nitrogen (N) and phosphorus (P) loading is one of the greatest threats to aquatic ecosystems in the Anthropocene, causing eutrophication of rivers, lakes, and marine coastlines worldwide. Despite decades of monitoring and regulatory efforts, tributary stream and river nutrient inputs continue to be problematic throughout developed regions of the world. However, there remains substantial uncertainty of the role that tributary inputs have on coastal nutrient dynamics, especially for large waterbodies that receive water and pollutants from hundreds to thousands of individual inflows. The overarching goal of my dissertation was to address the uncertainty of direct nutrient inputs from tributaries and to further understand how tributaries alter coastal nutrient dynamics in large receiving waterbodies. My research focused on the spatially diverse tributaries of Lake Michigan, one of the planet's largest lakes. I used a combination of synoptic sampling and modeled discharge to determine lake-wide nutrient inputs for Lake Michigan from nearly all perennial tributaries. To expand on that snapshot approach, I used a seasonal synoptic approach for ~100 tributaries, and identified important seasonal controls on watershed drivers of nutrient inputs. Finally, my co-authors and I used several different approaches to identify 1) the spatiotemporal drivers of dissolved organic carbon (DOC) quantity and quality, and 2) how congruent seasonal shifts in lake hydrodynamics and tributary contaminant loads affect coastal water quality. Overall, my dissertation addresses important spatiotemporal drivers of tributary nutrient dynamics and the potential influence that tributaries – both large and small – have in mediating coastal nutrient availability. My results suggest abundant opportunities to advance management goals by addressing nutrient inputs from small watersheds of large lakes, and showcase the important role that seasonality has in mediating how nutrient inputs influence coastal nutrient dynamics and water quality.

Dissertation introduction for chapters one – three

Increases in intensive agricultural practices and urban development have contributed to a myriad of problems for freshwater ecosystems, including pollution, eutrophication, threats to biodiversity, and changes to ecosystem functions (Schindler 1974; Carpenter et al. 1998; MEA 2005; Dodds 2006). Land cover change within the United States has been extensive yet highly variable throughout the 20th century. Between 1973 and 2000, 16.6% of natural forested land was altered, and developed land cover expanded by 33% (Sleeter et al. 2013). Agricultural land cover decreased slightly during the same time frame, as intensified agriculture required smaller areas, and expanding urbanization created competition for land (Matson et al. 1997; Lambin et al. 2001). Additionally, over 100 million acres (about 50%) of natural wetlands were lost by the 1980s, and a net loss of wetlands continues to occur throughout the U.S (Dahl 2009). Among the most prominent outcomes resulting from conversion of natural forest and wetlands to agricultural and urban areas has been the increase in nutrient runoff, which subsequently leads to increased nutrient availability and eutrophication of surface waters (Vitousek et al. 1997; Alexander et al. 2000, 2008; Boyer et al. 2002). Although efforts to reduce nitrogen (N) and phosphorus (P) inputs to freshwater ecosystems have been ongoing since the 1970s, eutrophication and its associated negative effects are still a primary concern for freshwaters, and 42% of rivers and 66% of lakes in the US are negatively affected by excess N and P (EC and EPA 2009; Garnache et al. 2016).

Anthropogenic climate change is expected to alter temperature, precipitation, and duration of seasons in temperate regions (Crowley 2000; Rosenzweig et al. 2008; Stocker et al. 2013). Climate change throughout the Anthropocene has had, and will continue to have, many implications for freshwater ecosystems. Precipitation generally drives fluctuations in river discharge, overland runoff, and the input of water and pollutants from tributary streams and rivers to receiving bodies of water (Allan 1995; Nilsson et al. 2005). Seasonal variation in quantity and type of precipitation (i.e., rain or snow), as well as frequency of extreme weather events, play critical roles in riverine nutrient dynamics (Haith and Shoenaker 1987; Biggs 2000; Carpenter et al. 2015). Flushing of landscape-derived nutrients into streams during extreme weather events has significant effects on both total and relative abundances of nutrients in surface waters (Creed et al. 1996; Gergel et al. 2002; McClain et al. 2003; Mulholland et al. 2008). Further, nutrient processing within streams can drastically change among seasons and mediate the transport of nutrients from land to receiving waterbodies (Rosemond et al. 2000; Kincaid et al. 2020; Myrstener et al. 2020). Thus, climate and hydrology are particularly important for nutrient inputs to lakes and other terminal water bodies. To sustain and restore freshwater ecosystems, it is critical to have a detailed understanding of the spatial and temporal relationships among watershed characteristics, climate variation, and in-stream nutrients. The interconnected relationships among watershed characteristics and climate become increasingly important for massive water bodies that receive nutrients from hundreds to thousands of spatially diverse tributaries that experience drastic seasonal climate shifts.

The Laurentian Great Lakes of North America constitute one of the world's truly unique ecosystems. Together, the Great Lakes hold 85% of North America’s liquid freshwater, and their coastline, deemed the “Third Coast”, is 17,000 km long and receives water and pollutants from thousands of inflowing tributaries (Krushelnicki and Botts 1995). Not only do the separate basins of Lakes Huron, Ontario, Michigan, Erie, and Superior span an incredible range of watershed characteristics and spatially variability, they all experience dramatic seasonal climate shifts that alter everything from precipitation, to human activity, to in-lake hydrodynamics (Holland et al. 2001; Farrow 2002; Norton et al. 2019).

The ecosystem functions provided by the Great Lakes are essential for communities within the basin and provide over 30 million people with drinking water (US EPA 2020). Further, the lakes generate over $15 billion annually through tourism, recreation, and shipping (Allan et al. 2012). However, the ecosystem functions and services of the Great Lakes are threatened by several interacting stressors, with nutrient loading and eutrophication being a keystone issue (Smith et al. 2015, 2019; Allan et al. 2015). In an effort to sustain and restore these globally significant ecosystems, the ongoing Great Lakes Restoration Initiative (GLRI) in the U.S. has spent $2.3B from 2010-2017 to enhance ecosystem health (US EPA 2017). However, dynamic land cover change and seasonal climate variability will continue to alter the state of the Great Lakes, increase nutrient loading, and degrade coastal ecosystems (Magnuson et al. 1997; Wolter et al. 2006; Kundzewicz et al. 2008; Milly et al. 2008; Radeloff et al. 2012; Wuebbles et al. 2019; Mahdiyan et al. 2020). Thus, a detailed understanding of the spatiotemporal drivers of nutrient inputs and their direct influence on coastlines is needed to restore and sustain their valuable and necessary functions.

Within the Great Lakes region, the Lake Michigan basin captures the full range of land cover, from heavily forested northern watersheds to highly urbanized areas, with variable amounts of agriculture across the forest-urban spectrum. Lake Michigan’s approximately 300 tributaries range from small, 1st order streams with catchments of just 2 km^2 to 6th order rivers with catchments as large as 16,000 km^2 (Forsyth et al. 2016). Additionally, the Lake Michigan shoreline shows a wide range of watershed characteristics and nutrient dynamics arising from differences in watershed land use, atmospheric N deposition, nutrient limitation (N vs. P), and population density (Danz et al. 2007; Han and Allan 2008, 2012; Robertson and Saad 2011; Han et al. 2012; Cooper et al. 2015). Despite efforts to alleviate non-point inputs, nutrient loads to Lake Michigan have proven difficult to reduce, and coastal waters often exceed target concentrations (EC and EPA 2009; Yurista et al. 2015). Thus, the Lake Michigan basin provides an ideal system to study how seasonal variability and watershed characteristics, such as land cover, watershed size, and geologic properties, influence tributary nutrient dynamics.

The primary goal of my dissertation was to determine how spatial and temporal variability influenced tributary nutrient concentrations, loads, and yields throughout the Lake Michigan basin. In chapter one, I used a snapshot, comprehensive sampling effort combined with modeled discharge to characterize total loads, yields, and dominant forms of nutrients for nearly every flowing tributary of Lake Michigan. In chapter two, I combined multi-year, synoptic seasonal sampling with modeled discharge for ~100 tributaries to determine how seasonality mediated watershed drivers of nutrient concentrations, loads, and yields. In the first part of chapter three, my co-authors and I used a similar approach as chapter two, but we instead focused on how seasonality and watershed characteristics influenced carbon quantity and composition for ~100 Lake Michigan tributaries. Finally, for the second part of chapter three, we coupled a three-dimensional, continuous hydrodynamic model with time-varying pollutant loads from 11 different tributaries for four years to determine how in-lake physics controlled the fate of watershed-derived pollutants in Lake Michigan. The results presented and discussed in the first three chapters of my dissertation highlight several critical components and patterns of nutrient inputs that will greatly benefit current and future efforts to restore and preserve coastal ecosystems throughout the Great Lakes – from whole-lake scales down to small bays, segments of coastline, and individual inflows.

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Chapter 1

A day in the life of a Great Lake: Outsized nutrient contributions from small tributaries

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Abstract

Excessive nitrogen (N) and phosphorus (P) loading is one of the greatest threats to aquatic ecosystems in the Anthropocene, causing eutrophication of rivers, lakes, and marine coastlines worldwide. For lakes across the U.S., eutrophication is driven largely by non-point nutrient sources from tributaries that drain surrounding watersheds. Decades of monitoring and regulatory efforts have paid little attention to small tributaries of large waterbodies, despite their ubiquity and potential local importance. We used a snapshot of nutrient inputs from nearly all tributaries of Lake Michigan – the world's fifth largest freshwater lake by volume – to determine how land cover and dams alter nutrient inputs across watershed sizes. Loads, concentrations, stoichiometry (N:P), and bioavailability (% dissolved inorganic nutrients) varied by orders of magnitude among tributaries, creating a mosaic of coastal nutrient inputs. The six largest of 235 tributaries accounted for ~70% of the daily N and P delivered to Lake Michigan. However, small tributaries exhibited nutrient loads that were high for their size and biased toward dissolved inorganic forms. Higher bioavailability of nutrients from small watersheds suggests greater potential to fuel algal blooms in coastal areas, especially given the likelihood that their plumes become trapped and then overlap in the nearshore zone. Our findings reveal an underappreciated

role that small streams may play in driving coastal eutrophication in large water bodies. Though they represent only a modest proportion of lake-wide loads, expanding nutrient management efforts to address smaller watersheds could reduce the ecological impacts of nutrient loading on valuable nearshore ecosystems.

Significance

Excessive nutrient inputs from tributary streams and rivers contribute to harmful algal blooms and coastal ecosystem degradation worldwide. However, the role that small tributaries play in coastal nutrient dynamics remains unknown because most monitoring and regulatory efforts focus only on the largest tributaries. We combined a 6-day sampling effort with discharge modelling to characterize nutrient inputs from nearly all watersheds draining to the world's fifth largest lake. We found that streams are particularly likely to promote eutrophication in coastal ecosystems because they deliver water with higher concentrations of nutrients that are readily available to algae. Thus, our findings indicate that efforts to control nutrient loading could be enhanced by looking beyond the largest tributaries to include smaller streams.

INTRODUCTION

Eutrophication arising from anthropogenic nutrient inputs has impaired lakes and reservoirs worldwide, leading to reduced water quality, altered ecosystem functions, and increased vulnerability to species invasions and harmful algal blooms (1–4). Following reductions in point-sources of nutrient pollution since the 1970's, non-point sources have become the major drivers of eutrophication (5–7). Tributary streams and rivers are conduits from watersheds to receiving waterbodies, and are often focal points for directing on-the-ground nutrient management because they are strongly influenced by land cover patterns (8–10). Monitoring and regulatory efforts typically focus on the largest tributaries of lakes and marine coastlines because they dominate hydrologic inputs (hydraulic loads) and likely deliver the largest fraction of nutrients by virtue of their high discharge. Notably, the absence of consistent monitoring in small- and mid-sized watersheds has prevented understanding of the role that small tributaries play in overall nutrient delivery (11) and, more importantly, local eutrophication along coastlines (12–15).

The Laurentian Great Lakes (hereafter Great Lakes) are a globally significant ecosystem that features the world’s longest freshwater coastline (17,000 km), offering an ideal setting for examining tributary inputs to large waterbodies. These lakes receive nutrients from thousands of watersheds that vary widely in attributes that affect the quantity and form of fluvial nutrients, including the presence of dams, stream order, catchment area, and land cover. The Great Lakes experience frequent algal blooms that have been linked to inputs from large tributary rivers, such as the Maumee River in Lake Erie, Fox River in Green Bay of Lake Michigan, and St. Louis River in western Lake Superior (16–19). These observations have fostered the expectation that large watersheds are responsible for the majority of watershed nutrient loading to the Great

Lakes. As a result, almost all long-term monitoring of nutrient inputs in the Great Lakes is done on 3rd order rivers or larger, providing loading measurements for only the largest watersheds in the basin. For example, even though Lake Michigan has approximately 300 inflows (20), loads have been monitored for just 37 tributaries (21–23) and modeled for tributary inputs with watersheds >150 km^2 (8). Consequently, large tributaries have been prioritized for interventions to reduce nutrient inputs to the lakes. The lack of comparable monitoring of the abundant smaller tributaries yields substantial uncertainty about the overall magnitude, variability, and geography of aggregate nutrient inputs to the Great Lakes (11) and other large water bodies.

Given the surge in the number of freshwater ecosystems experiencing frequent and sustained algal blooms (3), a strategic approach is needed to direct management interventions toward watersheds where load reductions are both feasible and likely to alleviate local eutrophication hotspots (15, 24). There are several reasons why nutrient inputs from smaller tributaries might warrant greater attention. First, small stream channels can have vastly different nutrient profiles than larger rivers (25–27). Second, after entering a receiving water body, plumes from small streams are more easily trapped in the littoral zone, thus increasing the likelihood that they will affect coastal ecosystem services (28). Third, overlapping plumes from multiple tributaries, which can occur readily among small tributaries with nearby inflows, magnify the adverse effects of watershed pollution on ecosystem services (29). Finally, while there are always challenges in implementing best management practices (BMPs) for nutrient control, they may be minimized in small watersheds with relatively simple land ownership patterns (30, 31). Thus, we posit that the lack of attention given to small- and mid-sized tributaries has led to overlooking important sources of nutrient loading and algal blooms in large receiving waterbodies such as the Great Lakes.

The objectives of this study were to characterize total loads, yields (load per unit drainage area), and dominant forms of nutrients for every flowing tributary of Lake Michigan. Through this effort we sought to evaluate the contribution that small tributaries make to lake-wide nutrient loads, and which watershed characteristics drive variation among tributary inputs. We integrated measurements of total nutrient and dissolved inorganic nutrient concentrations with modeled discharge to estimate loading from nearly all perennial tributaries of Lake Michigan for a six-day period in July 2018. Our snapshot approach at summer baseflow was designed to maximize the spatial extent of sampling while minimizing confounding temporal variation, thereby elucidating spatial patterns of nutrient concentrations, bioavailability, loads, and yields across a wide range of tributary sizes and land uses.

RESULTS

Gross differences in nutrients across the tributary size spectrum

Nutrient concentrations, stoichiometry (N:P), and bioavailability (defined here as the dissolved inorganic to total nutrient fraction (32)) varied by orders of magnitude among Lake Michigan's tributaries. Total nitrogen (TN) concentrations ranged from 0.22 to 9.53 mg N/L (Fig. 1 *A*, SI Appendix, Fig. S1), ammonium ranged from below detection (< 0.003 mg/L) to 1.05 mg N/L, and nitrate + nitrite varied from 0.003 mg/L to 9.48 mg/L. The proportion of TN composed of bioavailable dissolved inorganic nitrogen (DIN; nitrate + nitrite + ammonium) ranged from 1.8 to 100%. Total phosphorus (TP) concentrations varied from below detection (< 0.003 mg/L) to

0.59 mg P/L (Fig. 1 *B*, SI Appendix, Fig. S1), while soluble reactive phosphorus (SRP) ranged from below detection (< 0.003 mg/L) to 0.53 mg/L. SRP represented between 2.7 and 100% of TP.

The vast differences in tributary nutrient profiles reflect spatial variation in land cover and watershed size (Fig. 2 *A* and *B*), and are also mediated by the presence of dams. TN and DIN concentrations both increased with agricultural and urban land fraction and decreased with watershed size, while TN increased slightly with wetland coverage (Table 1). The proportion of TN composed of DIN increased with percent agriculture and decreased as both watershed area and wetland percentage increased. TP concentrations were primarily driven by land cover, with agriculture, wetland, and urban coverage all leading to increased TP. SRP concentrations also reflected land cover differences; but there were multiple interactions among agricultural development, watershed size, and presence of dams (Table 1). Additionally, SRP increased with urban development and wetlands, regardless of watershed size or dams. Similar to DIN/TN, the proportion of TP composed of SRP increased with percent agriculture and decreased as watershed area increased. The differences in controls on TN and TP led to high spatial variability in tributary nutrient stoichiometry (N:P, SI Appendix, Fig. S2), though several important relationships emerged. The N:P of tributary nutrients decreased (i.e., P was enriched relative to N) with percent urban or agricultural development, and as watershed size increased. In contrast, presence of dams within watersheds increased tributary N:P.

Large tributaries deliver a majority of tributary-derived nutrients

Tributary TN and TP loads were positively correlated with watershed area (Table 1), and several other watershed characteristics also influenced nutrient loads. Wetland extent and presence of dams within watersheds reduced TP load, and an interaction between agricultural development and watershed area suggested that the increase in TP load with watershed area is exacerbated by agricultural land use. TN loads decreased with wetland and urban extent, regardless of watershed size.

Small tributaries delivered only a modest fraction of the total tributary-derived nutrient load to Lake Michigan. Based on the sites we sampled, the comprehensive tributary TN and TP loads for Lake Michigan in mid-July 2018 were approximately 56.7 Mg/d and 2.9 Mg/d, respectively. The six largest tributaries by watershed area (Fox, Grand, St. Joseph, Menominee, Muskegon, and Kalamazoo Rivers, Fig. 1 *A* and *B*) accounted for nearly 70% of tributary-derived TN and TP (SI Appendix, Fig. S3). During this sampling period, the Fox River alone delivered 30% of the total daily TP load and the St. Joseph River provided 28% of the total daily TN load. In contrast, the 184 sampled tributaries that drain watersheds <150 km^2 together accounted for less than 5% of the total tributary-derived TN and TP (SI Appendix, Fig. S3). Those same 184 tributaries were responsible for 7.6 and 8.3% of DIN and SRP daily loads, respectively.

The large disparities in watershed area among Lake Michigan's tributaries (<2 to over 16,000 km^2) resulted in estimated discharges varying by four orders of magnitude. Even though nutrient concentrations varied by approximately two orders of magnitude, the much larger range in watershed area and discharge generally trumped the influence of land cover on loading rates. However, high N and P concentrations resulted in smaller tributaries (1st to 2nd order) having similar loads to mid-sized tributaries (3rd to 4th order), and there were numerous watersheds that produced comparable daily loads through disparate combinations of discharge and nutrient concentrations (Fig. 3 *A* and *B*). For example, high TN concentration in Lily Bay Creek (2.59 mg/L, 44°50'51.5580", -087°16'03.7776") led to delivery of the same 45 kg TN daily load as the Bark River (45°34'22.6380", -087°14'36.3588") from just 30% of the discharge.

Nutrient yields highlight potentially problematic inputs from small tributaries

Like nutrient concentrations and loads, nutrient yields exhibited wide variation across Lake Michigan's tributaries. TN yields ranged from 0.03 to 3.65 kg/d/km^2, and TP yields ranged from <0.001 to 0.64 kg/d/km^2. TP yields decreased with wetland development and presence of dams. (Table 1). Just as for TP loads, there was a positive interaction between watershed area and agriculture: TP yields decreased as watershed size increased, but the decrease in yield associated with larger watersheds was not as strong in watersheds with high agricultural land use. TN yields were negatively correlated with watershed size; smaller tributaries typically had higher TN yields than their larger counterparts. Additionally, TN yields decreased with wetland and urban extent, regardless of watershed size.

In parallel with comparing nutrient yields, we calculated TP and TN loading efficiencies (the proportion of aggregate tributary nutrient inputs relative to the proportion of aggregate tributary discharge) to assess which tributaries generate nutrient loads that are disproportionate to their hydrological inputs. We found that, in general, small tributaries with high nutrient concentrations deliver high TN and TP loads relative to their contribution to the lake-wide hydraulic load (Fig. 4 *A* and *B*).

DISCUSSION

Despite the importance of rivers in fueling lake and coastal eutrophication, most monitoring and regulatory efforts have overlooked nutrient inputs from abundant small tributaries. Our July snapshot around the ~2,000 km perimeter of Lake Michigan gives insight into the important role that smaller tributaries have in coastal eutrophication in Lake Michigan, and potentially, other large receiving waterbodies. A few of the largest tributaries delivered a substantial majority of lake-wide nutrient loads, reflecting relatively high discharges from their expansive watersheds. However, we also found that small watersheds play a special role in nutrient loading through elevated nutrient yields, loading efficiencies, bioavailability, and N:P. These disparities suggest that nutrient inputs from small watersheds are likely to have outsized ecological impacts on the coastal zone by creating local hotspots of nearshore nutrients that could fuel algal blooms and eutrophication.

Differences in land cover, watershed size, and dams among watersheds all played significant roles in N and P dynamics of Lake Michigan's tributaries. Unsurprisingly, agricultural development was particularly influential—driving increased TP, TN, SRP, and DIN concentrations, bioavailability of N and P, and reduced N:P ratios. These are common patterns throughout the world, as use of land for intensive agriculture leads to increased particle-bound N and P (33), runoff of inorganic N and P from fertilizer application (25), and differential cycling of particulate versus dissolved forms of nutrients (34, 35). The effect of agricultural development on SRP concentrations was mediated by watershed size and presence of dams, and our results suggest that the increase in SRP that occurred with agriculture is exacerbated in large watersheds but dampened by dams. We presume that this multi-level pattern reflects the greater probability of larger watersheds having large dams, and the fact that river impoundment promotes processing and retention of nutrients – especially in agricultural watersheds (36). Urban land cover was associated with elevated TP, TN, DIN, and SRP, consistent with other studies that have shown urbanization can cause increases in most forms of N and P (35).

The fraction of TN and TP loads composed of DIN and SRP, respectively, shifted across the spectrum of tributary sizes, suggesting fundamental differences in nutrient processing between small and large rivers. Small rivers have shorter flow paths from land to water as well as within the channel, resulting in land use having stronger and more direct effects in small watersheds (27). In the specific case of agricultural watersheds, fertilizer-derived inorganic nutrients can travel quickly from land to stream to lake in smaller watersheds. Additionally, increased wetland coverage within a watershed tended to decrease the fraction TN composed of DIN, which could be due to increased denitrification in wetland sediments, which permanently removes inorganic nitrogen (37). Our results suggest that variation in anthropogenic land development and watershed size have important roles in mediating nutrient dynamics among coastal inputs, especially for waterbodies with hundreds of highly variable tributaries.

The disparities in N and P loading profiles among watersheds of Lake Michigan are likely to create a mosaic of algal communities and eutrophication risk along the coast. Across tributaries, total nutrient concentrations spanned the range associated with the oligotrophic-eutrophic spectrum of ecosystem productivity (38), while N:P ranged from values indicating extreme N limitation to extreme P limitation for algae in freshwater ecosystems (39, 40). There were also sharp differences in nutrient bioavailability (Fig. 2 *A* and *B*). Collectively, tributary inflows could create local variation in algal communities along the coastline by shifting the relative availability of different nutrients, thereby granting competitive advantage to particular taxa (41, 42). For example, N-fixing cyanobacteria typically dominate in low N:P waters when P concentrations are relatively high (43). Some stretches of the coast received inputs from multiple watersheds with similar nutrient profiles, but other regions featured adjacent tributaries that were markedly different. For example, there are only 4 km of coast between the three rivers (Ogontz, Little, and Big Rivers) that flow into Ogontz Bay in Michigan (45°51'20.4264", -086°45'28.3752"), yet their TN and TP concentrations varied by an order of magnitude, and the dissolved proportions of TN and TP ranged from 7 to 29% and 13 to 82%, respectively.

The diversity of nutrient conditions expected to arise around the mouths and adjacent shorelines of these hundreds of tributaries surely extends the range of nutritional environments available to algae and microbes. In this way, tributaries may support niches that enhance aggregate ecosystem biodiversity. Though we usually conceptualize large water bodies as stable environments compared to the flow and thermal variation of tributaries, the diversity of river mouth conditions could in fact offer ecological refugia as prevailing conditions in the lake fluctuate seasonally. In that scenario, specialized taxa that are sustained by local tributary inputs could become the foundation for blooms whenever favorable conditions arise within the larger waterbody. Though speculative, the diversity of environmental conditions engendered by differences in tributary inputs represents an important ecological extension of our findings.

Due to their increased dissolved inorganic nutrient concentrations, smaller tributaries made a greater contribution to the lake-wide loads of DIN and SRP (~7.6% of DIN and 8.3% of SRP) compared to TN and TP (~4.8 % of TN and 4.0% of TP), respectively. Particulate and organic N and P become available to primary producers only after mineralization or other transformations (44), and as much as 70% of particulate nutrients may be deposited and permanently buried in lake sediments rather than becoming bioavailable (45). Thus, tributaries that deliver water with either greater concentrations of dissolved inorganic nutrients or a higher fraction of nutrients in bioavailable forms are more likely to produce nearshore algal blooms during the summer growing season (19). While other factors also affect localized coastal nutrient availability and eutrophication risk within Lake Michigan and the other Great Lakes, such as littoral nutrient retention by invasive dreissenid mussels (46, 47) and rising water temperatures (19, 48), bioavailable nutrient inputs often serve as an essential trigger for coastal eutrophication, especially in summer (49). Synergies among these various influences are likely to mediate coastal eutrophication, hence understanding the geography of highly bioavailable nutrient inputs in conjunction with other spatially and temporally variable drivers represents a critical frontier in efforts to conserve valuable coastlines (50).

The ecological consequences of nutrient inputs across the size spectrum of tributaries may be further amplified by coastal mixing processes. The hydraulic power of high-discharge plumes from large rivers enables them to transport their nutrient load further offshore than smaller inflows. Small plumes typically lack the coherence and momentum to reach the pelagic zone, and instead are retained along the shoreline (51). Because inflows from small tributaries tend to get trapped near shore and have high total and inorganic concentrations of N and P, these small systems should be particularly effective at locally fertilizing the coast. Given that the littoral zone is a hotspot for both human-lake interactions (52, 53) and aquatic biodiversity (54), tributary loads that differentially affect nearshore water quality are particularly concerning. Further, lake physics can strongly mediate the distribution of tributary-derived pollution from watersheds. When lake hydrodynamics cause tributary plumes to be trapped and intermingled, the detrimental effects on coastal water quality and ecosystem services could be magnified (29).

Focusing on aggregate nutrient loading rates has made it easy for environmental management to overlook small watersheds, but our findings reveal a need to reconsider these systems due to their outsized biological and ecological effects on the coastal zone. Prioritizing watersheds with high nutrient yields (Fig. 3 *A* and *B*) or whose contribution to lake-wide loading is disproportionately large relative to their hydrological input (Fig. 4 *A* and *B*) would identify new opportunities for strategic nutrient load management. Best management practices (BMPs), such as cover crops and wetland restoration (55), are often applied successfully and with high return-on-investment in small, high-yielding watersheds (56–58). This logic is implicitly embraced when BMPs are targeted toward high-yielding subcatchments nested within larger, high-loading tributaries (i.e., the Fox River of Lake Michigan and the Maumee River of Lake Erie) in an attempt to reduce their loads. Our results suggest that extending this approach by applying BMPs to smaller watersheds that flow directly into large waterbodies could offer a cost-effective means of reducing local eutrophication engendered by inputs of highly bioavailable nutrients.

Our snapshot of tributary nutrients provides the most spatially comprehensive view of nutrient loading available for a large water body, but has important limitations. We used extensive one-time sampling to ensure that load estimates among tributaries were comparable in terms of seasonal inputs and discharge dynamics. This level of temporal control comes at the cost of missing high-flow events that produce substantially higher loading rates in short pulses (59). To put our snapshot into perspective, the Fox River in Wisconsin has some of the largest annual nutrient loads to Lake Michigan at 5,000,000 kg TN and 400,000 kg TP per year (8), but a simplistic extrapolation of our one-day summer estimate to the entire year represents only 60% and 75% of the actual annual load. Thus, our estimates should not be treated as proxies for annual loads. Additional complexity could arise from disparities in hydraulic and nutrient load responses to storms due to watershed size or parent geology. The six largest tributaries accounted for ~52% of aggregate discharge to Lake Michigan during our summer assessment period but would contribute ~61% of all water flow if all sampled tributaries were flowing at their respective maximum discharge during 2018. Additionally, spatial variation in geology creates differences in soil depth and hydraulic conductivity that shape watershed flowpaths and thus the movements from land to stream (60–62). While complex interactions among land cover, geology, and stream chemistry are challenging to identify with synoptic sampling (63), especially when geological properties are highly collinear with land cover (SI Appendix, Fig. S5), such effects might emerge in response to different hydrologic conditions and have differential effects on bioavailability or amounts of N and P delivered to the lake (63–65).

Our approach sacrificed temporal representation in favor of spatial representation to gain insights into the watershed correlates of nutrient inputs, with the premise that disparities in nutrient loads and yields across tributaries of large water bodies are poorly known compared to well-documented statistical distributions of daily loads and discharge through time (66, 67). Our results reveal that nutrient loads vary even more widely than discharge across the spectrum of tributary size, thereby complementing well-known patterns of temporal variation in loading from watersheds of any given size. There is surely much to learn from testing how the spatial patterns illustrated here shift with time in response to seasonal precipitation and storm events. Such spatiotemporal integration will be necessary in order to fully resolve the role of small tributaries in coastal nutrient dynamics along the extensive coasts of large lakes and oceans.

Reducing inputs of nutrients to sensitive coastal environments remains a key management priority worldwide, particularly where harmful algal blooms and other symptoms of cultural eutrophication are evident (15, 68–70). Our findings indicate that efforts to control coastal nutrient loading can be enhanced by looking beyond the largest watersheds. Though aggregate tributary inputs of N and P are dominated by large rivers, we expect outsized ecological consequences of loading from small- and mid-sized tributaries due to their combination of increased dissolved inorganic nutrients, greater bioavailability, limited capacity to transport their loads away from the shoreline, and likely overlaps of plumes from nearby streams. Small watersheds may also be more feasible targets for management interventions because they are overseen by fewer land owners and political jurisdictions, on average, than larger counterparts (31). To help protect the irreplaceable ecosystems services from the Great Lakes—such as $15B annually from drinking water, recreation, fisheries, and shipping (52, 53)—hundreds of watershed organizations have mobilized to seek environmental improvements in their own backyard (71). Such vested interests have the capacity to improve local management of nutrients, and the collective influence of citizens and communities as advocates for healthy coastal ecosystems may help to persuade regional and federal authorities to act. Our results suggest abundant opportunities to advance lake-wide management goals by addressing nutrient loading from small watersheds of Lake Michigan, and this model is likely to be applicable to many other large freshwater and marine ecosystems.

Methods

Study system

The Lake Michigan basin provides an ideal ecosystem to estimate comprehensive nutrient loads and determine the spatial variability of nutrient profiles across the tributary size spectrum. The basin captures a wide range of tributary watershed size and land covers (SI Appendix, Fig. S4) found in the Great Lakes region, from undeveloped northern watersheds to highly urbanized areas, with variable amounts of agriculture across the natural-urban spectrum. The size of the basin paired with its high development results in Lake Michigan having the second highest total nutrient input out of all the Great Lakes, second only to Lake Erie (8). Lake Michigan's approximate 294 tributaries range from small, 1st order streams with catchments of just 3 km^2 to 6th order rivers with catchments as large as 16,000 km^2. Over 250 of its tributaries are 1st, 2nd or 3rd order streams with areas of 150 km^2 or less (20).

Tributary water collection

Between 10-15 July 2018, we sampled 235 of Lake Michigan's 294 tributaries. All sampling took place under low- to moderate-flow conditions when streams were below their 30th percentile of discharge for 2018. We visited an additional 26 tributaries that were not flowing and thus not contributing to the total nutrient input during the sample period (but may during times of year with higher discharge). We were unable to sample 33 tributaries (which accounted for approximately 3% of the Lake's basin) that were inaccessible for various reasons. Surface water was collected at the road crossing nearest to the mouth via bridge sampling methods (72). Collected water was left unfiltered for TN and TP analyses or immediately filtered through a 0.45 µm glass fiber filter for DIN and SRP analyses. All samples were kept on ice in the field, and frozen within 10 hours of collection. Water samples remained frozen until nutrient analyses were performed.

Nutrient analyses

SRP and DIN concentrations were determined for all filtered water samples using an Astoria-Pacific Astoria II segmented flow autoanalyzer and standard colorimetric assays (73). TP and TN were determined using similar methods following a persulfate digestion. Specific protocols can be found at (https://lter.limnology.wisc.edu/research/protocols). If dissolved nutrient concentrations exceeded measured total nutrient concentrations, we assumed the discrepancy was due to sampling or measurement variability, and assumed that all nutrients were in the dissolved form.

The detection limit for total nitrogen was approximately 0.021 mg/L and the analytical range for the method extends to 2.5 mg/L. The detection limit for ammonium was approximately 0.003 mg/L and the analytical range for the method extends to 4.0 mg/L, and the detection limit for nitrate + nitrite is approximately 0.002 mg/L. For TP and SRP, the detection limits were 0.003 mg/L. Samples that extended beyond the maximum of each method were diluted until they were within the detectable range. Concentrations that were below detection limit were adjusted to half of the detection limit concentration of each analyte. Although this may not be the most accurate way to adjust low concentration samples, it seemed appropriate given the wide range of concentrations that occurred across our sample set.

Discharge estimates and load and yield calculations

Discharge was estimated for each sampling point location by the discharge-area ratio method. First, all USGS stream gauges within the US Great Lakes Basin states with at least 20 years of recorded data were downloaded, resulting in 3,997 stations. From these, a GIS feature was created using the latitude and longitude from each stream site. The gauges were then subset by those with a reported drainage basin area, and then intersected with an outline of the US Great Lakes Basin. Following intersection, 924 gauged streams in the Great Lakes basin remained. Daily discharge data for all gauges was then downloaded from the USGS National Water Information Service (NWIS) using its REST API interface coded within MATLAB for the period 1980 – 2018. From the 924 gauges within the Great Lakes Basin with reported catchment areas, 657 had discharge data within this time window. Discharge values were then binned into 5-day averages and divided by basin area to compute 5-day basin yield averages (runoff). These basin yield values were interpolated to our coastal sampling locations using a two-step interpolation procedure. For each binned period, basin yield values were first interpolated using nearest-neighbor linear interpolation. This method allowed extrapolation beyond the convex hull of observed basin yield locations but can sometimes produce spurious values both due to extrapolation and having too few nearby gauges. In those instances, a secondary interpolation using nearest neighbors was used. Finally, the interpolated basin yield values above or below observed minimum and maximum values were truncated. Following interpolation of basin yield, each sampling location was then multiplied by its catchment area to compute 5-day average discharge.

To validate this approach, we subset the 657 gauges into validation and observed subsets and predicted discharge at the validation locations using the observed location values. For this separate validation, 10% of the 657 gauges were selected as a validation subset, with the remaining 90% as observed values. The median RMSE of the 5-day average predicted discharge across the 65 validation sites was 11.0% of observed flow at each location. For 25% of sites, the RMSE was less than 5.02% of discharge, while at the high end of error 25% of sites had RMSE values greater than 23.6% of discharge. We used this validation procedure to select the discharge averaging period. For bin widths greater than 5 days, discharge prediction error did not appreciably decrease, while for shorter periods, discharge prediction errors increased significantly. This is the case because as this procedure uses time-varying basin yield values from a range of gauged catchment sizes, temporal responses to precipitation or snow melt events can vary significantly. Below 5 days, this source of error dominates discharge estimation. For 5 or more days, the short-term responses to precipitation events are averaged out, and instead error is dominated by differing land cover, soils, slopes, groundwater conditions, and other hydrogeological characteristics that vary across catchments.

Nutrient loads were calculated as the product of concentrations and discharge estimates. Discharge was represented by the 5-day mean around the actual sampling date for each tributary. Yields were calculated by dividing the nutrient load by the area of the corresponding watershed.

Spatial data and statistical analyses

Watershed area was determined using the Great Lakes Aquatic Habitat Framework (GLAHF) database, and presence of dams within watersheds were determined using the spatial database from Januchowski-Hartley et al. (74). Land cover proportions were determined using the National Land Cover Database (NLCD) for 2011.

All data met assumptions of parametric tests (after $\log_{10}$-transformation, in the case of nutrient loads, yields, concentrations, and watershed area). Multiple linear regressions were used to determine if land cover types (percent agriculture, percent urban, and percent wetland), watershed area, and presence of dams along the tributary had main effects and/or interactive effects on TN and TP loads and yields, TN and TP concentrations, DIN and SRP percent of TN and TP, respectively, and molar N:P. Forest land cover was removed prior to analyzing regression models to reduce collinearity among main predictor variables and ensure that the variance inflation factors were acceptable. Multiple linear regression models were selected using backwards Bayesian Information Criterion (BIC) model comparisons to ensure that our final models were parsimonious. All final models had a ΔBIC greater than 2. However, if the two most reduced models for a nutrient metric had a $\Delta\text{BIC} < 2$, we reported the more complex model, which occurred for TN concentration, TP load, TP yield, and N:P stoichiometry. We chose this approach because all models with $\Delta\text{BIC} < 2$ are often considered to be similar, and the more complex model has support to be considered as the final model (75–77). All statistical analyses were completed in R v. 3.2.2.

Data availability

All data and analytical scripts used in this manuscript have been deposited on GitHub (https://github.com/RobertJMooney/LMtribs).

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Author Contributions

RJM, PBM, PCE, and EHS designed the study. RJM and WCR collected and prepared all samples for analyses. ADK calculated discharge estimates. RJM performed statistical analyses and drafted the manuscript. All authors discussed results and edited the manuscript.

Competing Interests

This research has not been published and is not in consideration for publication elsewhere. We have no competing interests to disclose.

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Figures

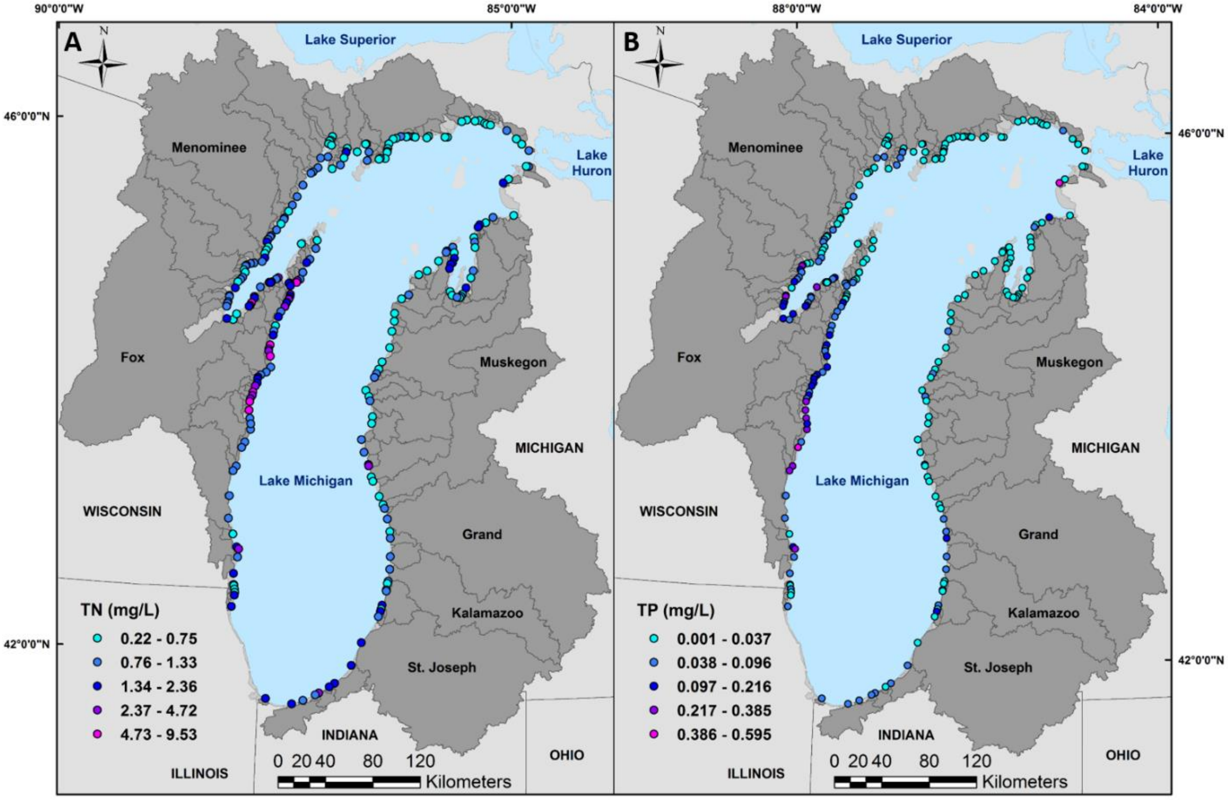


Figure 1. TN (*A*) and TP (*B*) concentrations for the 235 tributaries sampled between 10 – 15 July 2018. The dark grey polygons represent sampled tributaries, and the unsampled tributaries, dry tributaries (no flow), and interfluve areas (regions in the basin that do not have a tributary outflow) are represented by light grey polygons.

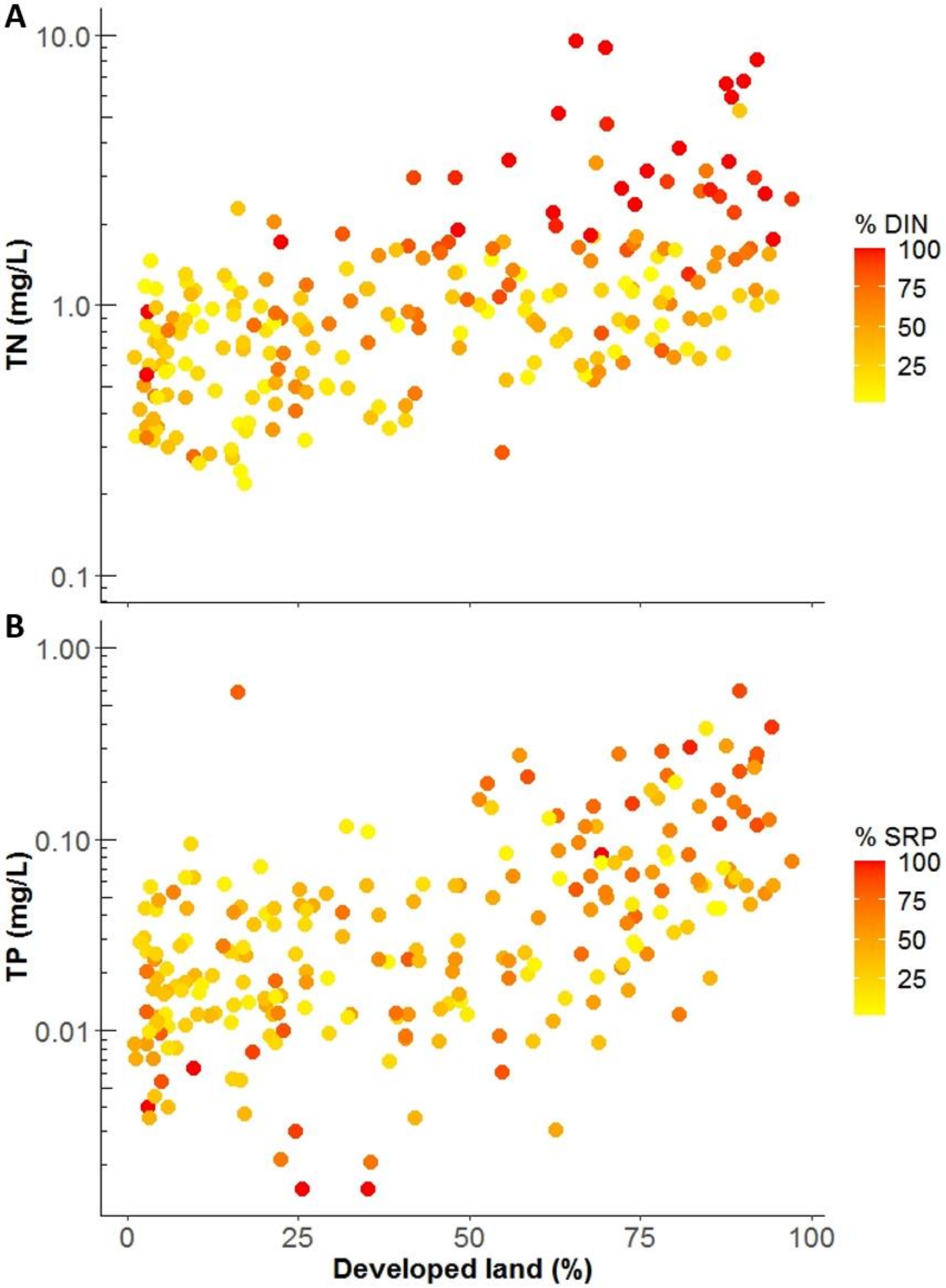


Figure 2. Tributary TN (*A*) and TP (*B*) concentrations and the proportion of TN and TP composed of dissolved inorganic N (DIN) and soluble reactive P (SRP, color of points), respectively. The 235 tributaries sampled between 10 – 15 July 2018 span a wide range of land development (combined agricultural and urban land cover).

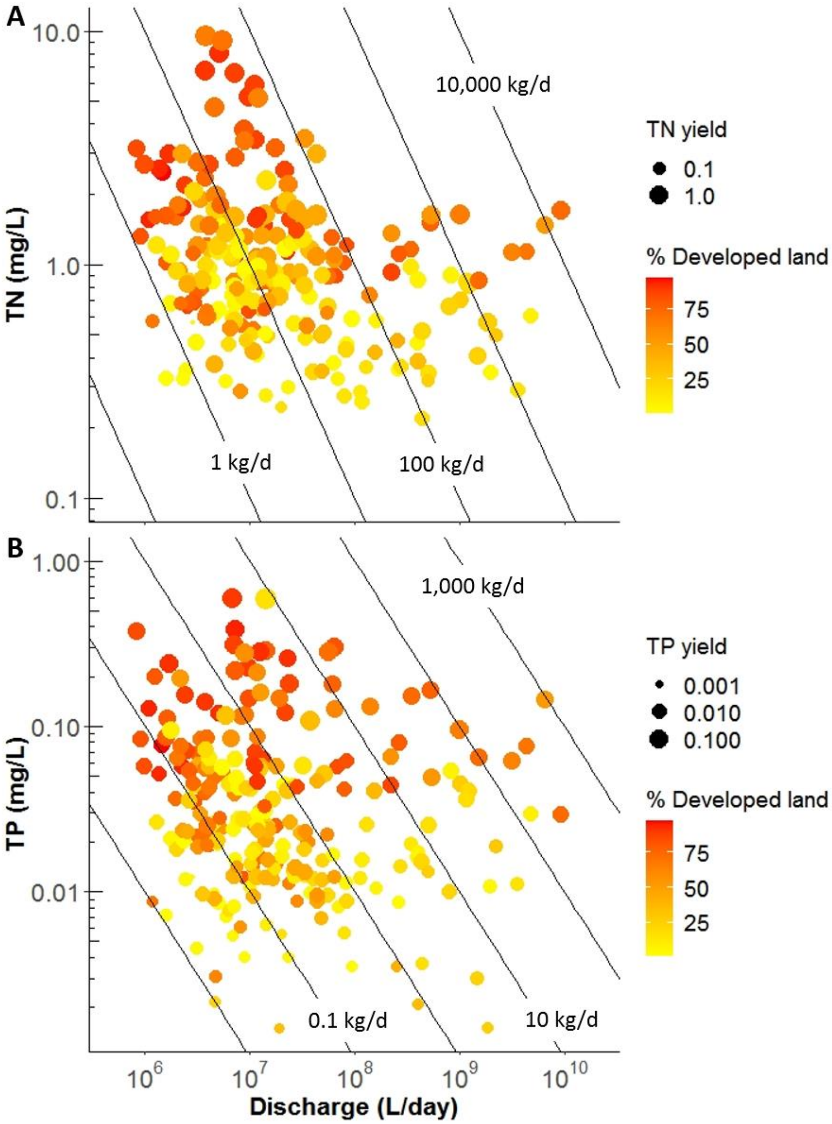


Figure 3. Combinations of discharge (L/day) and TN (*A*) and TP (*B*) concentrations responsible for estimated daily nutrient loads for 235 tributaries of Lake Michigan between 10 – 15 July 2018. Contour lines indicate TN or TP loading rates (kg/day) of the same order of magnitude. Point size is scaled to nutrient yield (kg/day/km^2), and point color represents the fraction of watershed area that has been developed (combined agricultural and urban percentage).

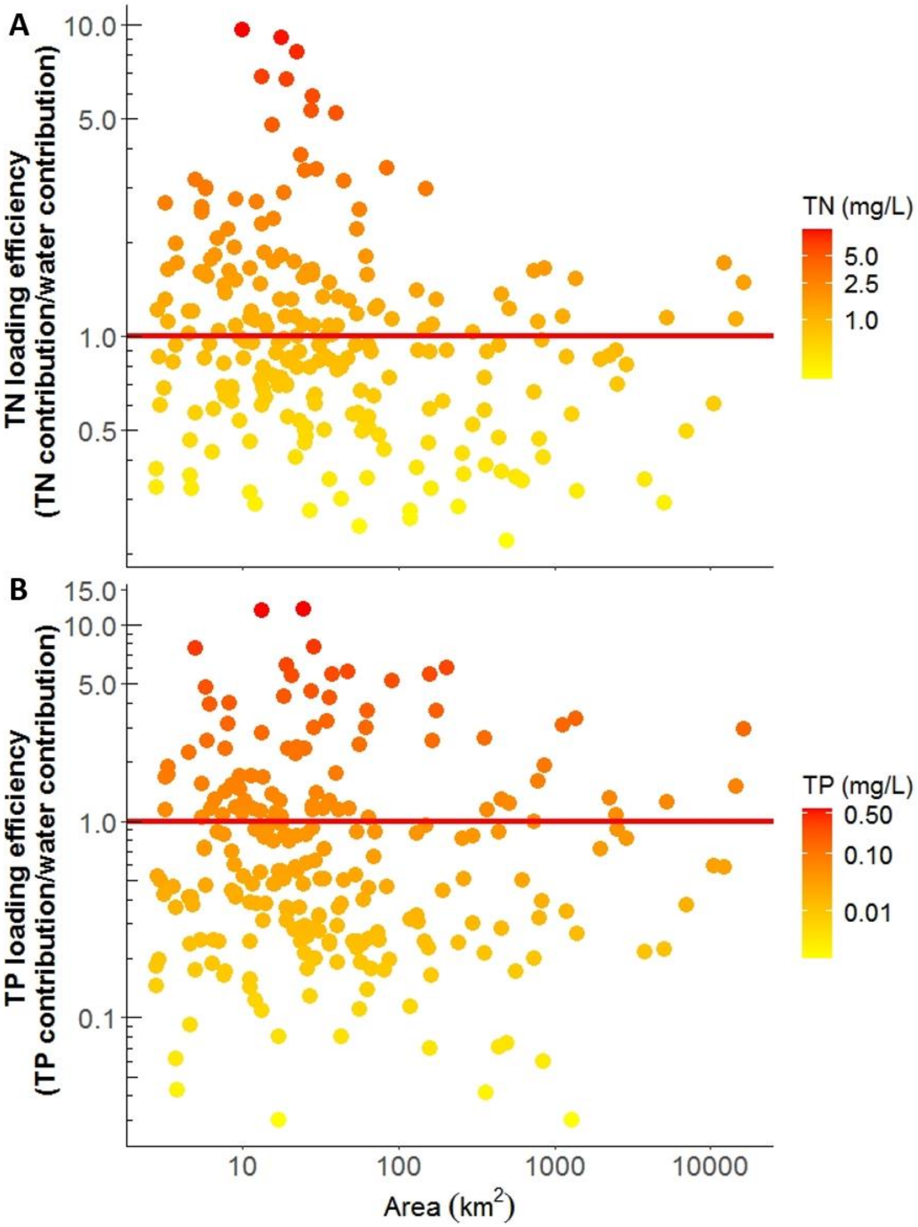


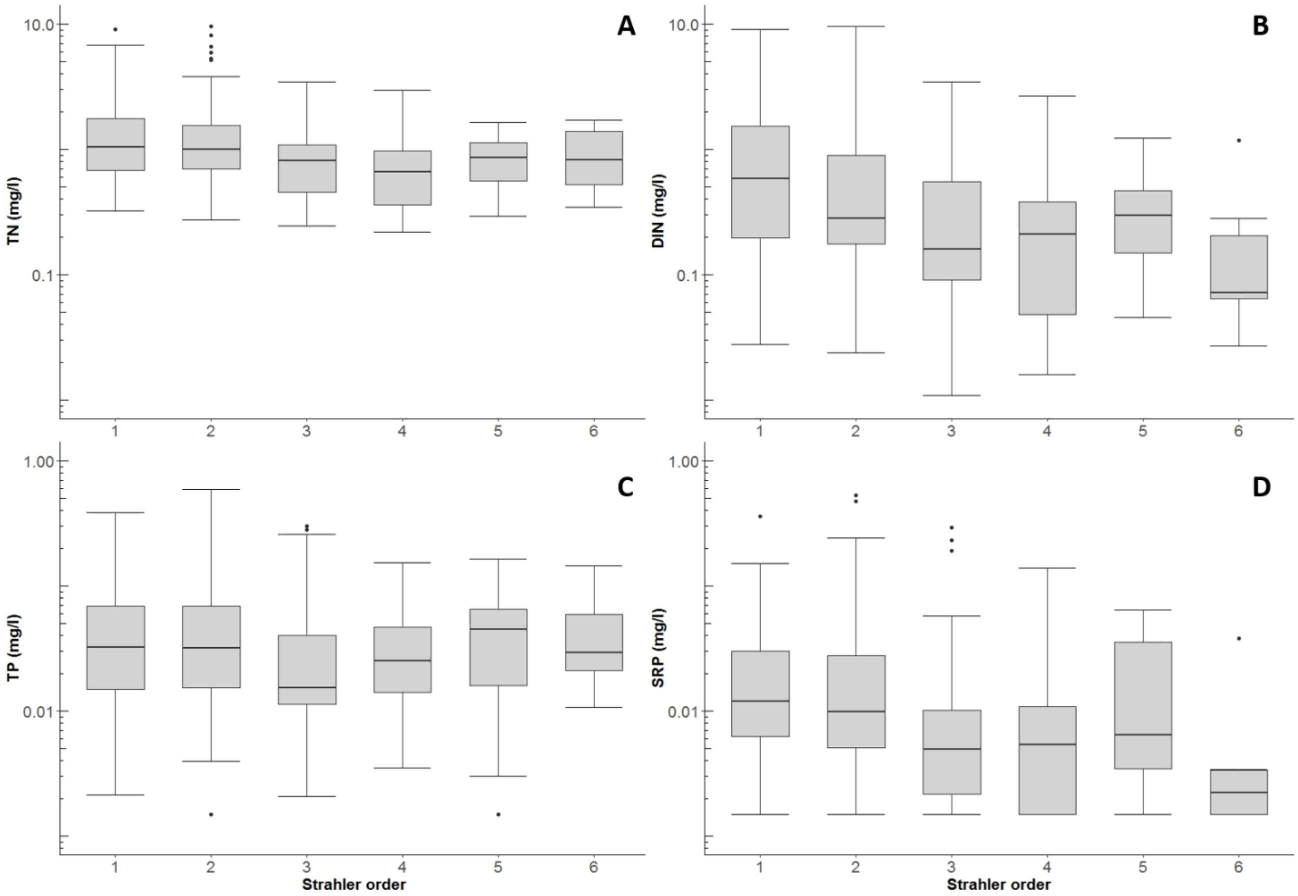
Figure 4. Scatterplot for 235 tributaries sampled between 10 – 15 July 2018 showing ratios between the contribution individual tributaries made towards the lake-wide N (A) or P (B) load with its contribution to the lake-wide hydraulic load. The horizontal red line represents a ratio of 1, where the nutrient load is directly proportional to the hydraulic load. Colors of points represent tributary TN (A) or TP (B) concentrations (mg/L).

Table 1. Multiple linear regression output for final models selected using backwards BIC model comparison. Independent variables represent main and interactive effects in the final selected model for each response variable. ΔBIC represents the difference in BIC values between the final selected model and the more complex candidate model from backwards selection.

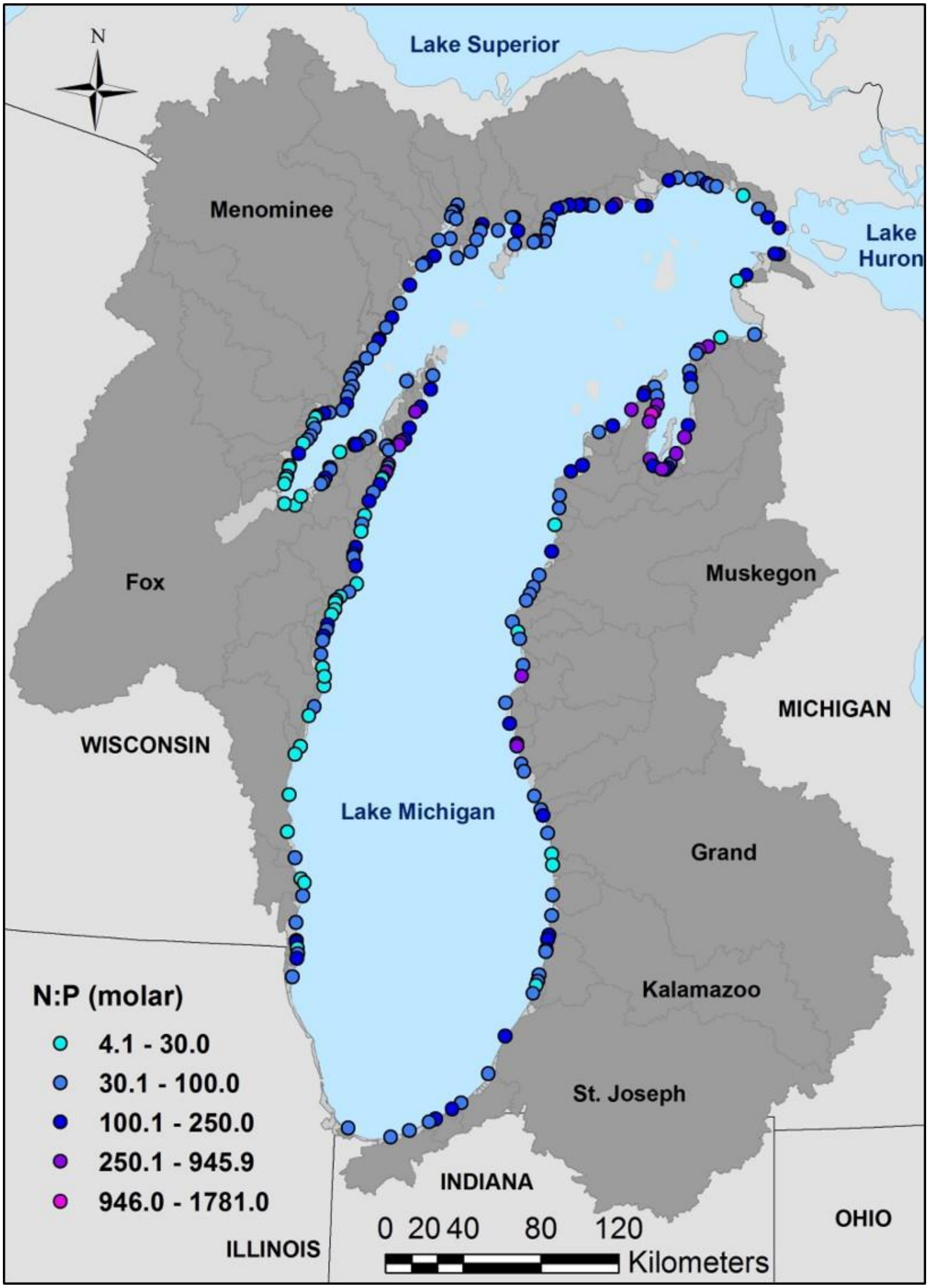
Nutrient metric (response variables)	Main and interactive effects (independent variables)	Coefficient	SE	ΔBIC	R^2
TP (mg/L)	Intercept	-2.18	0.098		
	% agriculture	0.0125	0.001		
	% wetland	0.0059	0.002		
	% urban	0.0113	0.002		
				2.03	0.350
TN (mg/L)	Intercept	-0.254	0.071		
	% agriculture	0.0075	0.001		
	% wetland	0.0025	0.001		
	% urban	0.0045	0.001		
	area (km^2)	-0.0669	0.019		
				4.31	0.388
SRP (mg/L)	Intercept	-2.4558	0.194		
	% agriculture	0.0077	0.004		
	area (km^2)	-0.1333	0.116		
	dams present	-0.5406	0.294		
	% wetland	0.0062	0.002		
	% urban	0.0089	0.002		
	% agriculture : area (km^2)	0.0060	0.003		
	% agriculture : dams present	0.0193	0.007		
	dams present : area (km^2)	0.2105	0.155		
	% agriculture : area (km^2) : dams present	-0.0115	0.004		
				3.69	0.397
DIN (mg/L)	Intercept	-0.6028	0.092		
	% agriculture	0.0097	0.001		
	% urban	0.0067	0.002		
	area (km^2)	-0.1918	0.041		
				4.72	0.273
%SRP of TP	Intercept	44.25	3.914		
	% agriculture	0.2945	0.057		
	area (km^2)	-5.4673	1.913		
				5.15	0.126
%DIN of TN	Intercept	65.337	6.078		
	% agriculture	0.189	0.079		
	area (km^2)	-9.631	2.202		
	% wetland	-0.412	0.108		
				2.50	0.206
TP load	Intercept	-1.751	0.103		
	% agriculture	-0.0003	0.002		

	area (km^2)	0.925	0.055		
	dams present	-0.177	0.070		
	% wetland	-0.003	0.002		
	% agriculture : area (km^2)	0.005	0.001		
				5.23	0.820
TN load	Intercept	0.023	0.060		
	area (km^2)	0.900	0.025		
	% wetland	-0.006	0.001		
	% urban	-0.004	0.001		
				2.59	0.861
TP yield	Intercept	-1.751	0.103		
	% agriculture	-0.0003	0.002		
	area (km^2)	-0.075	0.055		
	dams present	-0.177	0.069		
	% wetland	-0.003	0.002		
	% agriculture : area (km^2)	0.004	0.001		
				5.23	0.245
TN yield	Intercept	0.023	0.060		
	area (km^2)	-0.099	0.025		
	% wetland	-0.006	0.001		
	% urban	-0.004	0.001		
				2.59	0.170
Molar N:P	Intercept	2.169	0.077		
	% agriculture	-0.003	0.001		
	area (km^2)	-0.130	0.042		
	dams present	0.158	0.073		
	% urban	-0.005	0.002		
				3.13	0.102

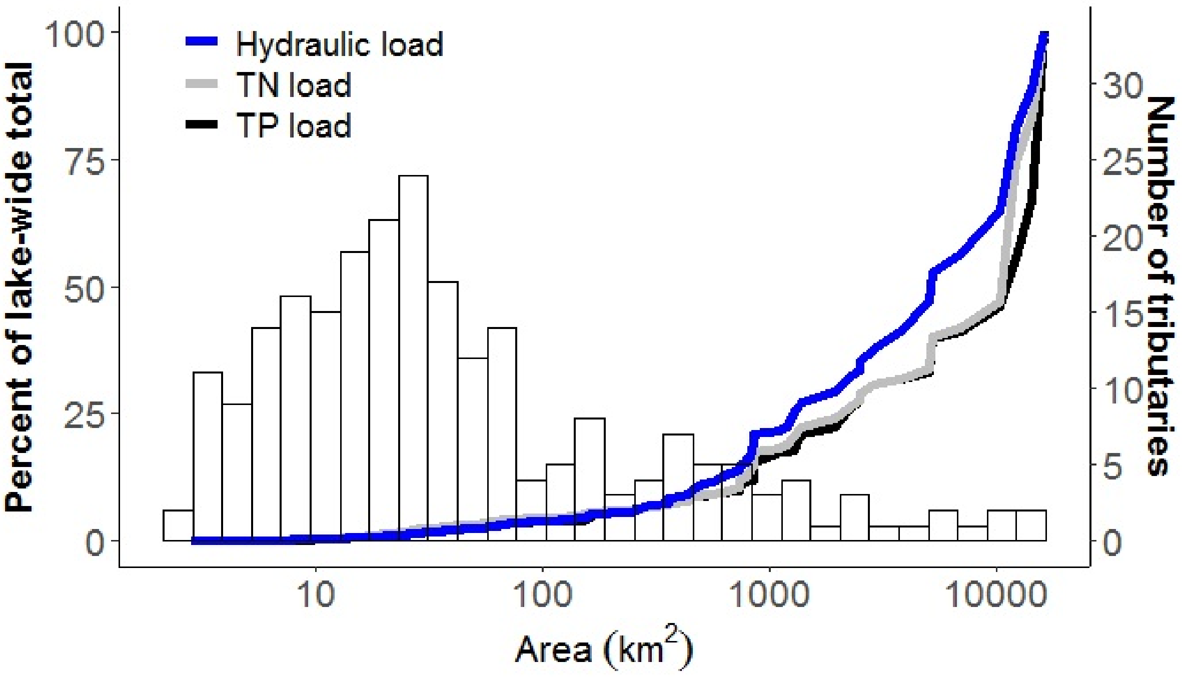
Supplementary information appendix



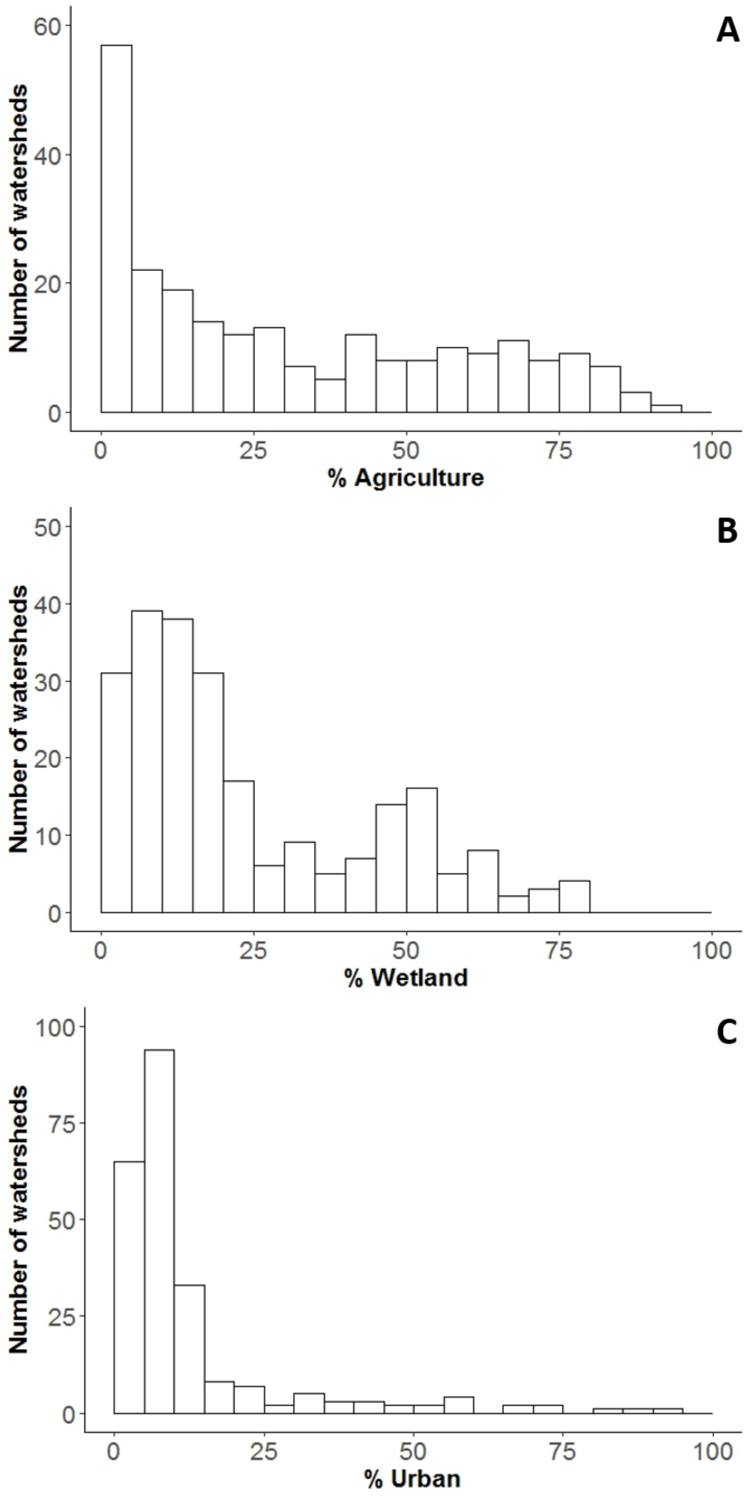
Supplementary Figure 1. Box plots showing the median and interquartile range for TN (A), DIN (B), TP (C), and SRP (D) concentrations (mg/L) for the 235 sampled tributaries. Whiskers represent 1.5 times above and below the interquartile range, and individual points represent outliers.



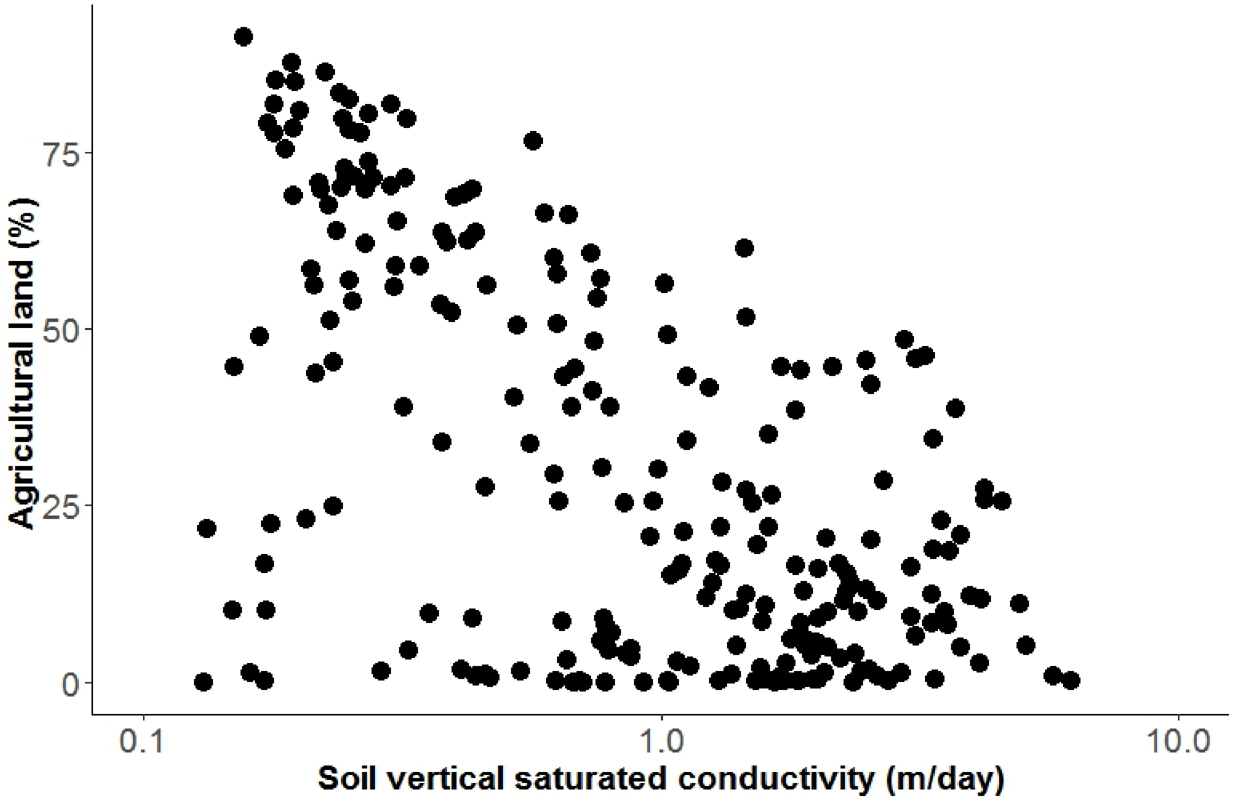
Supplementary Figure 2. Molar N:P based on total N and total P concentrations for 235 tributaries sampled between 10 – 15 July 2018.



Supplementary Figure 3. Cumulative curves for proportional contributions to hydraulic (blue), TN (grey), and TP (black) loads across all 235 sampled tributaries between 10 – 15 July 2018. The histogram shows the frequency distribution of watershed area (km^2) for the sampled tributaries.



Supplementary Figure 4. Frequency distributions of agriculture (A), wetland (B), and urban (C) land cover percentages for the 235 sampled watersheds.



Supplementary Figure 5. Patterns of agricultural land coverage (%) relative to soil vertical saturated conductivity (saturated k, m/day) for watersheds of all 235 tributaries sampled between 10 – 15 July 2018. The collinearity between agricultural land cover and soil is typical throughout the Great Lakes region.

Chapter 2

Seasonality mediates interacting watershed drivers of tributary nutrient inputs to a Great Lake

Being prepared for submission as: R. J. Mooney, E. H. Stanley, G. McKinley, L. Gloege, A. D. Kendall, and P. B. McIntyre. In prep. Seasonality mediates interacting watershed drivers of tributary nutrient inputs to a Great Lake

ABSTRACT

Nutrient inputs from tributaries cause coastal eutrophication in freshwater ecosystems throughout the United States. Yet, there remains uncertainty on how watershed characteristics interact to influence tributary nutrient dynamics throughout seasonal climate shifts – especially for smaller, abundant tributaries. We combined seasonal, synoptic sampling with modeled discharge for ~100 tributaries of Lake Michigan to identify the primary spatiotemporal drivers of nitrate and soluble reactive phosphorus (SRP) concentrations, loads, and yields. The largest tributaries generated the highest loads, but yields were highly correlated with concentrations. Further, multiple watershed characteristics influenced nitrate and SRP, but those relationships were further mediated by seasonality. Increases in SRP due to agriculture were exacerbated by soil conductivity, especially in the summer. Wetlands proved to be a critical driver of nitrate reduction in the winter when concentrations were otherwise elevated. The diverging spatiotemporal shifts in SRP and nitrate led to massive swings in nutrient stoichiometry. Our results highlight the importance of seasonality in mediating watershed controls of tributary inputs in large, temperate lakes.

INTRODUCTION

Nitrogen and phosphorus loads from inflowing tributaries continue to cause eutrophication in lakes throughout the United States despite efforts to reduce nutrient loading since the 1970s (IJC 1970; GLWQA 1978; Schindler 2012; Dolan and Chapra 2012). Eutrophication that arises from tributary nutrient inputs can alter ecosystem functioning and degrade valuable coastal ecosystem services, including fisheries, recreational opportunities, and drinking water availability (Michalak et al. 2013; Allan et al. 2015). Non-point source pollution, the primary source of excess nutrient loading to U.S. surface waters (Carpenter et al. 1998), is highly variable not only among tributary inputs (Mooney et al.; Robertson et al. 2006), but also within individual streams over time – especially in temperate regions that that experience seasonal climate shifts (Mulholland et al. 1985; Lin and Kao 2003; Kincaid et al. 2020).

Tributaries are a direct connection between surrounding watersheds and receiving waterbodies, and watershed characteristics, such as land cover, soil properties, and watershed size, can all play important roles in mediating stream nutrient dynamics. Notably, stream nutrients change across gradients of watershed land cover, especially as a result of anthropogenic land development (Alexander et al. 2000; Peterson et al. 2001; Stets et al. 2020). Nutrient concentrations and bioavailability (e.g., the proportion of total P composed of soluble reactive P) increase with agricultural land use due to wide-spread application of inorganic N and P fertilizer (Mooney et al.; Sharpley et al. 1994; Johnson et al. 1997; Daniel et al. 1998; Han et al. 2012; Han and Allan 2012). However, the effects that agricultural land practices have on stream nutrients can depend on underlying soil properties within a watershed, as hydraulic conductivity modulates the flow of water into and through the ground and thus the transport of overland flow into streams and groundwater (Bracken and Croke 2007; Hamlin et al. 2020). In urbanized areas with expansive impervious surfaces, storm water runoff and residential fertilizer application often increase nutrient concentrations in streams (Carpenter et al. 1998; Reynolds and Davies 2001). Conversely, while a shift to anthropogenic land use typically increases nutrient pollution, high nutrient processing rates in natural, wetland-dominated watersheds can reduce nutrient concentrations by various pathways, including settling of particulates, assimilation by primary producers, and denitrification (Howard-Williams 1985).

In temperate freshwater ecosystems, seasonality is an important factor for most biological and hydrological processes (Mulholland and Hill 1997; Doyle 2005; Ågren et al. 2007). Changes in temperature, flow, daylight length, riparian shading, and precipitation affect ecosystem metabolism, allochthonous carbon input, decomposition rates, transient storage, and primary production – all of which play major roles in nutrient uptake and processing (Newbold et al. 1982; Fisher et al. 2004; Tiegs et al. 2019; Coble et al. 2019; Blackburn and Stanley 2020). Further, seasonal weather patterns drastically modify flow rates and overland flow within a watershed, controlling the proportion of stream flow from groundwater, precipitation, and runoff (Hunt et al. 2016). In winter months, groundwater sources dominate tributary hydrology, whereas in the spring, summer, and fall, precipitation and runoff have increased importance (Pionke et al. 1999; Carpenter et al. 2015). Thus, seasonality can further mediate how watershed characteristics influence stream nutrients (Creed et al. 1996; Cross and Jacobson 2013; Van Meter et al. 2020).

The Laurentian Great Lakes receive water from thousands of tributaries which span a massive range of watershed size (<2 km^2 to > 20,000 km^2) and land cover (natural wetland or forest to highly developed) (Forsyth et al. 2016). Further, being temperate ecosystems, the tributaries that enter the Great Lakes are heavily influenced by seasonal climate and can have drastically different inputs throughout the course of a year. However, despite the important role that tributaries have in mediating coastal water quality, there remains uncertainty in the spatial and temporal drivers of nutrient inputs for the Great Lakes, especially for thousands of smaller tributaries that lack consistent nutrient data and discharge monitoring (Mooney et al.; Marcarelli et al. 2019). In addition to the already infrequent or absent monitoring of tributaries of all sizes, understanding of nutrient dynamics throughout the year (especially in winter) is lacking despite the fact that many inflows remain flowing throughout the year (Powers and Hampton 2016; Block et al. 2019; Coble et al. 2019).

There are several reasons why understanding how watershed characteristics influence tributary nutrient dynamics across seasons is critical for further reducing nutrient inputs throughout the Great Lakes. First, the role of land cover in mediating stream nutrient concentrations and loads changes spatially as a function of watershed size and soil properties, such as soil hydraulic conductivity (Lottig et al. 2011; Hamlin et al. 2020). Second, the mechanisms that drive spatial nutrient dynamics change among seasons (Coble et al. 2019), but seasonality can influence nitrogen and phosphorus differently (Goyette et al. 2019; Kelly et al. 2019; Van Meter et al. 2020). The spatial and seasonal shifts in both nitrate and SRP have the potential to produce stoichiometric swings in coastal inputs, which is highly relevant in the Great Lakes where coastal production can be either N, P, or co-limited (Paerl et al. 2014; Cooper et al. 2015; Schindler et al.

2016; Prater et al. 2017). Finally, seasonal shifts in lake temperature and hydrodynamics occur congruently with seasonal changes in tributary nutrient inputs. Because in-lake hydrodynamics distribute river plumes within the Great Lakes, adverse effects of pollutant loads can be magnified or reduced simply due to the time in which they enter the lakes and their potential to overlap (Gloege et al. 2020). While general patterns are expected to exist among land cover, seasonality, and tributary nutrient dynamics, watersheds within the Great Lakes basin are exceptionally spatially diverse, resulting in extreme N and P variation among inflows (Mooney et al.). Further understanding the complex spatial and seasonal drivers of nutrient inputs is necessary to identify tributaries that are likely to promote eutrophication and watersheds where remediation will be successful – two of the primary goals of watershed nutrient management (Howarth et al. 2003; Johnson et al. 2014; Scavia et al. 2017).

We combined multi-year, synoptic seasonal sampling with modeled discharge for ~100 tributaries of Lake Michigan to determine how watershed characteristics influenced nutrient concentrations, loads, and yields among seasons. We further wanted to assess the varying combinations of concentration, discharge, and watershed area that produced specific nutrient loads and yields to best identify problematic tributaries where on-the-ground management might be most effective. We hypothesized that tributary nutrient dynamics would show a strong signature of watershed land cover, but that those relationships would be mediated by other watershed properties, such as saturated soil conductivity (saturated K, m/day) and watershed size (Fig. 1). We expected the spatial controls to be further mediated by seasonality.

METHODS

Tributary sampling

We sampled ~100 tributaries around the perimeter of Lake Michigan in July, October, January, and March of 2016/17 and 2017/18 (Fig. 2). We used a synoptic sampling approach, and all sampling for a given season took place within 4, 6, or 8 consecutive days to minimize the potential influence of temporal variation within a single sampling event. Tributaries were selected using a stratified random design with stratification by watershed area and land cover to ensure representation of the full range of spatial conditions throughout the Lake Michigan basin. However, due to certain logistical complications, we were not able to sample all 100 tributaries during each sampling event. Water was collected from each tributary at road crossings upstream of the mouth via bucket sampling (EPA 2013). Water samples were immediately filtered in the field, stored on ice, and frozen within 6 hours of collection. All samples remained frozen until analyses.

Concentrations, loads, and yields

SRP and NO_2+NO_3-N (hereafter, nitrate) concentrations were determined for all filtered water samples using an Astoria-Pacific Astoria II segmented flow autoanalyzer and standard colorimetric assays. We chose SRP and nitrate as the focal nutrients because dissolved inorganic nutrients are immediately available to primary producers without prior transformations (Baker et al. 2014), and nitrate is typically the dominant form of dissolved, inorganic N throughout the Midwestern United States and Great Lakes regions (Stanley and Maxted 2008; Eimers and Watmough 2016). Specific nutrient analysis protocols can be found at (https://lter.limnology.wisc.edu/research/protocols).

Daily nutrient loads for each sampling event were calculated as the product of concentrations and discharge estimates. Discharge was represented by the 5-day mean around the actual sampling date for each tributary and was calculated using the discharge-area ratio method (SI appendix) (Mooney et al.). Yields were calculated by dividing the nutrient load by the area of the corresponding watershed.

Spatial data and statistical analyses

All spatial data was extracted using ArcMap. Land cover percentages were determined using the National Land Cover Database (NLCD) for 2011. Watershed areas were determined using the Great Lakes Aquatic Habitat Framework (GLAHF). Mean vertical conductivity for saturated soil was determined using Gridded Soil Survey Geographic (gSSURGO).

Data was transformed ($\log_{10}$, in the case of nutrient concentrations, loads, yields, N:P, watershed area, and saturated K) to improve normality. Multiple linear regression models were used to determine if land cover types (percent agriculture, percent urban, and percent wetland), watershed area, and saturated K had main effects and/or interactive effects on DIN and SRP concentrations, loads, yields, and molar N:P. Forest land cover was removed prior to analyzing regression models to reduce collinearity among main predictor variables and ensure that the variance inflation factors were acceptable. Multiple linear regression models were selected using backwards Bayesian Information Criterion (BIC) model comparisons to ensure that our final models were parsimonious. All final models had a ΔBIC greater than 2 and met parametric assumptions. Additionally, we used simple linear regression to determine if nutrient yields were significantly correlated with nutrient concentrations for individual seasons.

To further compare the spatial and seasonal variation for and between nitrate and SRP, we calculated coefficients of variation for each season across all tributaries (CVseasonal, equation 1) and for tributaries calculated across all four seasons (CVspatial; equations 2) (Berg et al.). Only tributaries that had samples representing all four seasons were included in this analysis.

CVseasonal = standard deviation of seasonal means / mean of entire data set * 100 (1)

CVspatial = standard deviation of tributary means / mean of entire data set * 100 (2)

RESULTS

Nutrient loads spanned multiple orders of magnitude not only among tributaries within a season, but also among seasons. Seasonal nitrate loads were lowest in the summer (0.003 – 8,000 kg N/Day) than in the fall (0.02 – 65,000 kg/Day), winter (0.07 to 73,000 kg/Day), and spring (0.03 to >30,000 kg/Day, Fig. S1). Similarly, SRP loading rates in summer (0.005 – 243 kg/Day), fall (0.005 – 275 kg/Day), winter (0.003 – 680 kg/day) and spring (0.001 – 244 kg/Day) showed high variation within and among seasons (Fig. S1). The massive range of watershed area (<2 km^2 – 16,000 km^2) inevitably resulted in discharge spanning several orders of magnitude, with larger watersheds having higher flow rates and, subsequently, elevated nutrient loads. However, there was considerable variability among loading rates for smaller tributaries (Fig. S2).

Like loads, SRP and nitrate yields spanned multiple orders of magnitude throughout the study period. SRP had a larger range in the summer (0.0001 – 0.34 kg/day/km^2) than in fall (0.0005 – 0.19 kg/day/km^2), winter (0.0006 – 0.115 kg/day/km^2), and spring (0.0003 – 0.173 kg/day/km^2). While nitrate yields also had the most variation in summer (0.0002 – 3.31 kg/day/km^2), the seasonal maximum nitrate yields were higher in the fall (0.004 – 6.99

kg/day/km^2), winter (0.003 – 5.61 kg/day/km^2), and spring (0.003 to 5.17 kg/day/km^2) than in the summer. We found that nutrient yields were highly correlated with nutrient concentrations across all seasons (Figs. S3 and S4).

Increased urban development and wetland coverage within a watershed was associated with decreased nitrate concentration in tributaries, but the effects were mediated by watershed area (Table 1), as these nitrate declines were more apparent in smaller watersheds. Further, the effects of wetlands on nitrate concentration were strongly mediated by seasonal variability as indicated by differences in the strength of the correlations between these variables among the four seasons (Fig. 3), regardless of watershed size. The reduction of nitrate due to wetlands was not as strong in the summer and spring as it was during fall and winter. Additionally, nitrate decreased with watershed size (Fig. 3, Table 1). Nitrate concentrations increased as saturated K and agriculture increased (Fig. S5). However, the interaction between agriculture and watershed size suggests that reduction in nitrate in larger watersheds isn't as apparent in agricultural watersheds.

SRP concentrations were highly variable across watersheds within and among seasons (Table 2). SRP increased with agricultural development, but the slope of that relationship was reduced as saturated K increased, especially in spring and summer (Fig. 4). Contrasting to the spring and summer, the reduction of the slope between agriculture and SRP was least evident in the winter. Additionally, the increase in SRP that occurs with agriculture was reduced in larger watersheds, regardless of season (Table 2). SRP increased as wetland coverage increased, but the slope of that relationship is reduced as watershed size increases (Table 2). Finally, regardless of season, SRP increased with urbanization within a watershed.

The differing watershed and temporal drivers of SRP and nitrate led to magnified variation in nitrate : SRP ratios (Figs. 5 and 6). N:P decreased with agricultural development (P enriched relative to N), but the slope of that relationship increased as area or saturated K increased (Table 3). Urban development reduced N:P, but this relationship was not as apparent as watershed area increased. Wetland coverage decreased N:P, but the effects of wetlands on N:P varied across watershed sizes and seasons (Fig. S7). The reduction in N:P as a result of increased wetland coverage was stronger in smaller watersheds. Seasonal constraints on the reduction of N:P due to wetland coverage were most notable in the summer and spring, with reduction of N:P being weakest in the summer and strongest in the spring (Fig. S7).

The large spatial and temporal ranges of nitrate and SRP among and within tributaries led to relatively high dispersion around seasonal and tributary means (Fig. S8). Nitrate had lower spatial and seasonal CVs (84.4 and 24.5%, respectively) than SRP (122.3 and 49.8%, respectively. Further, the difference in spatial and temporal CVs was lower for nitrate than for SRP.

DISCUSSION

Our synoptic, seasonal sampling approach revealed complex and interacting watershed and seasonal controls of tributary nutrient concentrations, yields, and loads. While the largest tributaries within the basin typically had the highest loads, nutrient yields were highly correlated with nutrient concentrations throughout the year. Nutrient concentrations, in turn, were influenced by land cover, watershed size, and soil properties – but those relationships varied as a result of seasonal climate variability (Fig. 1). In some cases, the interacting correlates had diverging effects on nitrate and SRP, leading to extreme stoichiometric variation among tributaries. Our results from the Lake Michigan basin suggest that even though land cover remains a driving factor for nutrient dynamics in tributaries, seasonality and watershed size play key roles in mediating nutrient inputs and, by likely extension, nutrient availability throughout coastal regions within the Great Lakes and other large receiving waterbodies.

Nutrient loads were highly variable throughout the Lake Michigan basin and, consistent with other studies, we found that the largest tributaries typically had the highest loads regardless of nutrient concentrations. Even though concentrations were sometimes relatively low, and the inflowing water was not conducive to immediate eutrophication, loads from large watersheds were generally high. For example, because of its size and high flow rates during our sampling events (50 to 135 m^3/s), the Menominee River would still have an SRP load greater than the vast majority of tributaries even with a 50% reduction in SRP concentration (21 to 53 kg/day).

Nutrient yields normalize loading rates by watershed area (Baker et al. 2014). Consequently, yields are used to identify tributaries that deliver high quantities of nutrients relative to their size and prioritize watersheds for on-the-ground management (Joosse and Baker 2011; Scavia et al. 2014). Targeting high yielding watersheds typically results in the best return on investment for watershed management and proves to be the best option for nutrient input reduction (Diebel et al. 2008; Dagnew et al. 2019). However, like loading rates, availability of discharge data is a limiting factor for yield measurements, as typically only the largest watersheds have consistent flow monitoring (Marcarelli et al. 2019). We posit that simple water quality tests can be used as a surrogate for targeting problematic nutrient inputs regardless of a watershed's size because of the tight correlation between yields and nutrient concentrations (Figs. S3 and S4). An approach using nutrient concentrations to identify problematic watersheds is appealing because it would allow for the inclusion of all tributaries when considering the prioritization of watersheds for management, regardless of consistent flow data availability or modeled discharge. Possibly more important is the fact that outside of the total nutrient loading context, dissolved nutrient concentrations and stoichiometry are often highlighted because they have direct biological relevance and limit short- and long-term primary and secondary production in most aquatic ecosystems (Elser et al. 2000, 2009; Sterner et al. 2002; Manning et al. 2020). Further, merges between comprehensive tributary sampling (e.g., Mooney et al.) and crowd-sourced science (Lowry et al. 2019) could be used to identify tributaries that have high yields or potentially outsized influence on water quality along stretches of coast, throughout individual bays, or adjacent to small inflows. While it may not be feasible to prioritize watersheds for management based solely on the concentrations of nutrients in tributary water, tributaries with elevated concentrations or that deliver nutrients that favor eutrophication (e.g., N:P < 32:1) should garner more attention, regardless of the total mass of N or P that deliver.

We found that watershed characteristics contributed to both increases and decreases in nitrate concentration, and that seasonality mediated the strength of some of those relationships. Unsurprisingly, agricultural land use was positively correlated with nitrate in streams. Larger watersheds typically had less nitrate than smaller streams, which is similar to findings from other studies (Dubrovsky et al. 2004; Van Metre et al. 2016), but that pattern was less apparent if larger watersheds were highly agricultural. Streams draining smaller watersheds that are primarily groundwater fed are typically high in nitrate, as nitrate is mobile and easily transported by groundwater sources (Pionke et al. 1999). This pattern becomes exacerbated when watersheds have agricultural activity (Hamlin et al. 2020), and the positive relationship between saturated K and nitrate we found further supports this relationship: the more easily water is transported through soil, the higher the nitrate concentrations in tributaries. However, for larger streams that are influenced by overland flow more frequently and are less dependent on groundwater inputs, nitrate concentration can be reduced via dilution (Fuhrer 1999) unless runoff carries nitrate into the stream – which is common with agriculture (Dubrovsky et al. 2004).

Both urbanization and wetland coverage were associated with lower nitrate concentrations. Though it may seem surprising that urbanization led to decreases in nitrate, a similar pattern throughout the Midwest shows that successful treatment of point sources in urban areas has been effective at removing DIN in receiving waterbodies (Stets et al. 2020). While the absence of a seasonal effect on the urban-nitrate relationship suggests year-round similarities in that mechanism, the reduction of nitrate in wetland-dominated watersheds varied seasonally. In general, nitrate concentrations throughout the Lake Michigan basin were highest in the winter and lowest in the summer (Table 1). Elevated winter nitrate is likely due to the combination of increasingly important contributions of groundwater to streamflow and low N processing rates. Conversely, low summer nitrate indicates lower inputs or higher N processing rates – or both. The seasonal-wetland interaction suggests that the wetland effect on N processing is present throughout the year, but other factors associated with summer nutrient dynamics (e.g., in channel processing, runoff, dilution) make the seasonal-land cover relationship blurrier. Taken together, our results suggest that wetlands play a critically important role in reducing nitrate, especially in the winter when high-nitrate groundwater dominates stream flow.

Anthropogenic land development was a primary correlate of tributary SRP concentration throughout the Lake Michigan basin, with increased urban and agricultural development leading to higher SRP. The increase in SRP in agriculturally dominated watersheds is undoubtedly caused by the use of inorganic fertilizer or manure on croplands, which is common throughout heavily farmed regions of the world (Schindler 1977, 2006). However, we found that multiple factors influenced how agricultural development altered SRP within tributaries. Soil saturated K mediated the effect of agriculture such that the increase in SRP in agricultural watersheds is reduced in more conductive soils – but that relationship was least apparent in the winter and strongest in the spring. In porous soils with elevated saturated K, hydrology tends to control the amount of biofiltration that occurs, with transport of water to biogeochemical hotspots in the soil being reliant on increased flow (Vervier et al. 1992; Claret and Boulton 2008). Thus, watersheds with elevated K would be expected to have more microbial processing under higher flow conditions. This pattern was apparent in our multiyear dataset, which suggested that in seasons with increased overland flow, high saturated K reduced the effect that agriculture had on tributary SRP. However, the direct effect of soil properties can be hard to identify because, throughout the Midwest, soils with lower saturated K (to a point) that retain water more are well-suited for rainfed agriculture. While disentangling the effects of land cover and soil can be challenging with synoptic sampling (Wayland et al. 2003), our seasonal approach identified important temporal controls on interacting watershed characteristics.

In addition to the complex seasonal, soil, and land cover interactions, the reduced agriculture-SRP relationship in larger watersheds further suggests that the variability of flowpaths between watershed and stream drive stream nutrient concentrations. Smaller watersheds typically have shorter flowpaths between the land, stream, and receiving waterbodies, and thus reflect land cover activity more strongly than larger watersheds (Lottig et al. 2011). Our results from the Lake Michigan basin highlight how the complex watershed controls of stream SRP are highly reliant on seasonal climate shifts, further complicating the challenging task of managing nutrient inputs.

The complex and diverging controls of N and P throughout the Lake Michigan basin led to drastic swings in tributary stoichiometry, covering five orders of magnitude and representing values that imply extreme N and P limitation (Rhee 1978; Elser et al. 2009). In the summer, N:P was reduced in agricultural watersheds with high SRP. However, in the winter, those same watersheds experienced drastic increases in N:P presumably due to sharp declines in overland flow and, subsequently, SRP inputs to channels (Reddy et al. 1999). However, that pattern may be contrary to N as dissolved inorganic N is highly mobile and readily gets into groundwater aquifers, leading to high nitrate concentrations when groundwater is the dominant water source (Hamlin et al. 2020). The importance of spatiotemporal variability in mediating tributary stoichiometry was further supported by the coefficients of variation for SRP and nitrate. Even though both nitrate and SRP had more spatial than temporal variation, the temporal variation was higher for SRP than nitrate, suggesting that seasonal shifts have a greater influence on tributary SRP. The spatial and temporal shifts in N:P are important because not only does algal nutrient limitation range from being N, P, and co-limited throughout coastal regions in the Great Lakes

(Cooper et al. 2015), but BMPs reduce N and P differently, with certain approaches better suited for either N or P reduction (US EPA 2007; Chesapeake Bay Program 2018). In order to most efficiently reduce the potential for eutrophication and restore coastal ecosystems, identifying the spatiotemporal intersections among nutrient limitation, tributary stoichiometry, and the potential influence of inflowing plumes should be prioritized.

Our results further suggest that small tributaries have an underappreciated importance in coastal nutrient dynamics in the Great Lakes, regardless of their low loads relative to large rivers. Not only do watershed characteristics influence stream nutrients more in smaller watersheds, but their loads are easily trapped along the shore (Churchill et al. 2003; Rao and Schwab 2007; Rodriguez et al. 2018) and likely have outsized ecological effects on the coastal region (Mooney et al.). The trapping of small plumes is further compounded in the winter and spring before the onset of horizontal stratification, as vertical stratification prevents mixing between coastal and pelagic waters (Holland et al. 2003; Makarewicz et al. 2012; Gloege et al. 2020). Unfortunately, even though SRP is reduced in high-agriculture watersheds during the time of the year when plumes become trapped, low agriculture watersheds with high SRP and those with elevated N deliver water that is likely to set up algal blooms during the spring and the onset of summer. That is an especially critical time of year, as March, April, and May nutrient inputs can dictate eutrophication for the year (Stumpf et al. 2016). The relationships among seasonality and tributary inputs are further muddled in Lake Michigan, which spans nearly 6° latitude, as the southern tip of the basin experiences seasonal shifts at different times and magnitudes than the northern tip.

Nutrient loads and yields will always be a focal point for nutrient management given the direct links between total nutrient loading and eutrophication, and yields and BMP success (Alexander et al. 2000; Dubrovsky et al. 2004). However, the interconnectedness of loads, discharge, concentrations, and yields should not be overlooked. In considering the variability of nutrient loads and yields, loads are correlated with discharge, and yields are highly correlated with concentrations. The tributaries of Lake Michigan span a wide range of seasonal discharge-concentration combinations that produce loads within the same order of magnitude – from high-yielding tributaries with low discharge and high concentration, to low-yielding tributaries with low concentration and high discharge (Figs. 8 and 9). The relationships among nutrient loads, yields, and concentrations suggest that detailed understanding of the drivers of nutrient concentrations is critical to pinpoint potentially problematic tributaries throughout the year.

By using synoptic sampling across multiple seasons, we highlighted the complex dynamics of the expansive basins that drain into Lake Michigan. Understanding the seasonal and spatial controls on tributary nutrient inputs becomes increasingly important as land cover development and anthropogenic climate change continue to occur and drastically influence tributaries that deliver water and pollutants into receiving water bodies. Our multi-year study offers insights into the challenges of managing seasonal nutrient inputs to the Great Lakes, which each have hundreds to thousands of diverse tributaries, and highlights the importance of including all tributaries when attempting to reduce eutrophication risk throughout dynamic coastal regions.

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FIGURES

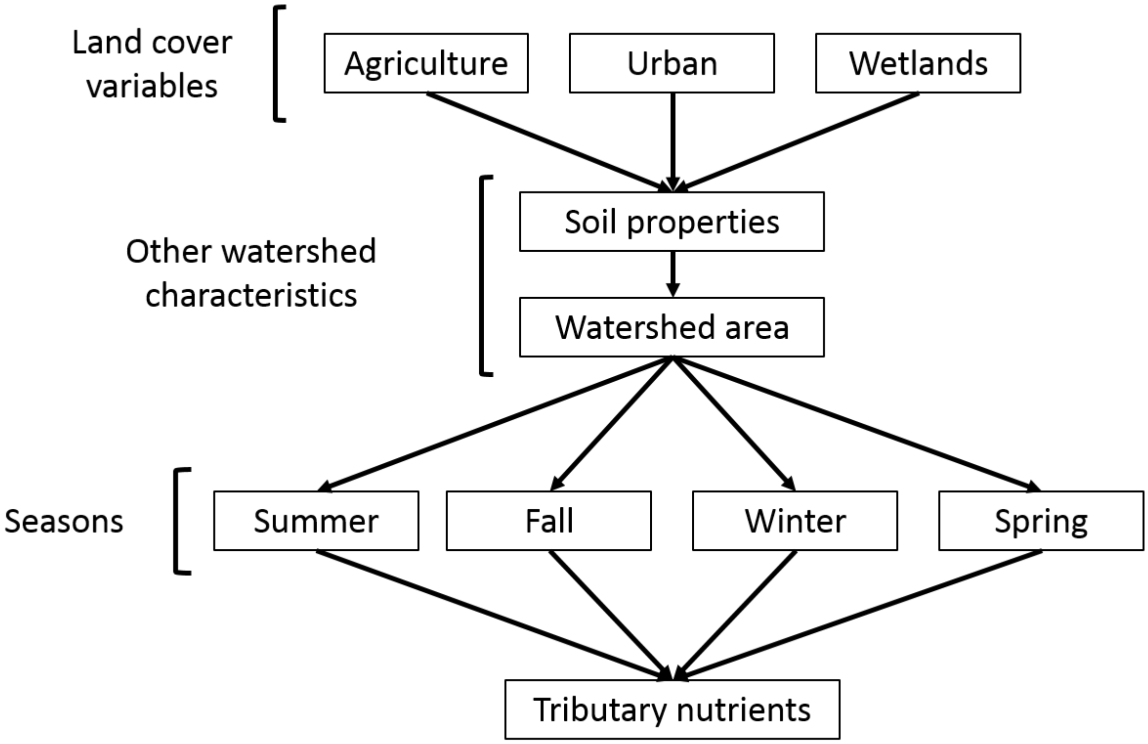


Figure 1. Conceptual diagram showing the various pathways land cover, watershed characteristics, and seasonality might influence tributary nutrients. Land cover variables have direct effects on stream nutrients, but those effects may be further mediated by other watershed characteristics. The spatial drivers of nutrients may be further modified by seasonal climate. Each box in the diagram likely serves as a specific "filter" to modify tributary nutrients. The effects of each filter could be further modified by subsequent filters, eventually leading to high spatial and temporal variability of tributary nutrients.

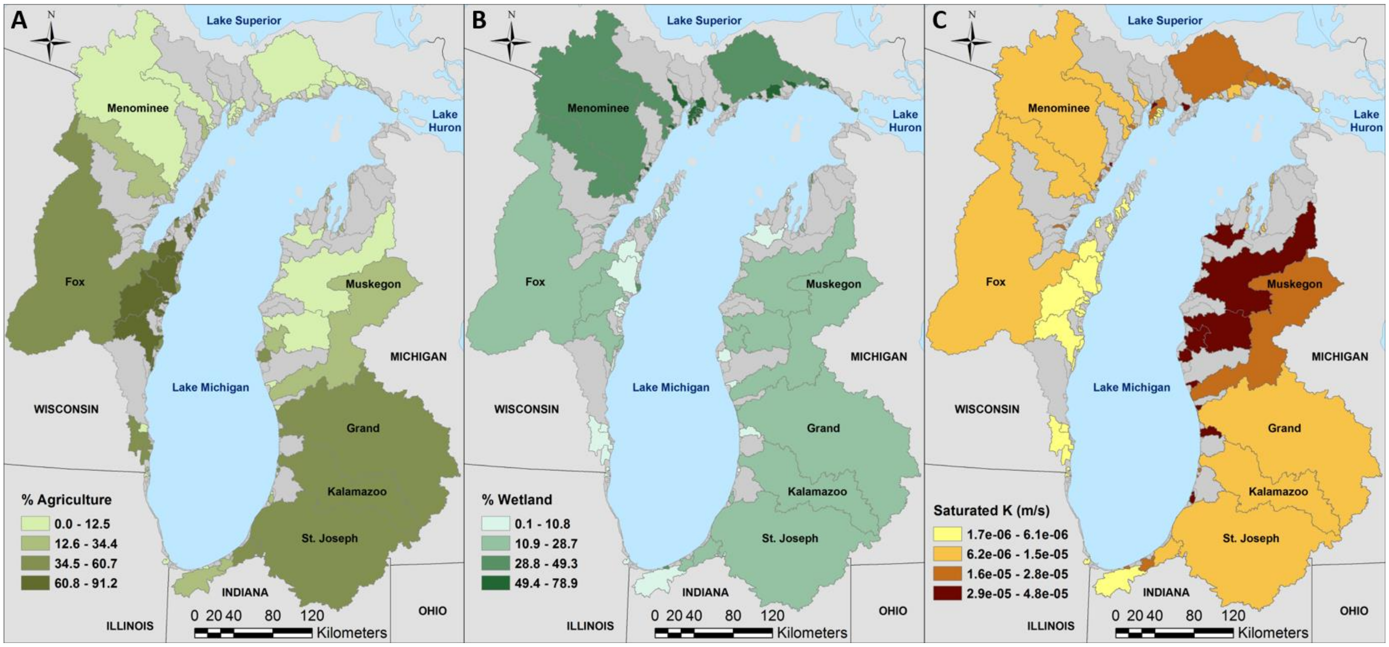


Figure 2. Agricultural development (%, A), wetland coverage (%, B), and mean watershed saturated K (m/s, C) for the 100 tributaries included in our seasonal sampling regime. Watershed sizes of the sampled tribuatires span the range within the basin, and grey polygons represent unsampled tributaries within the basin.

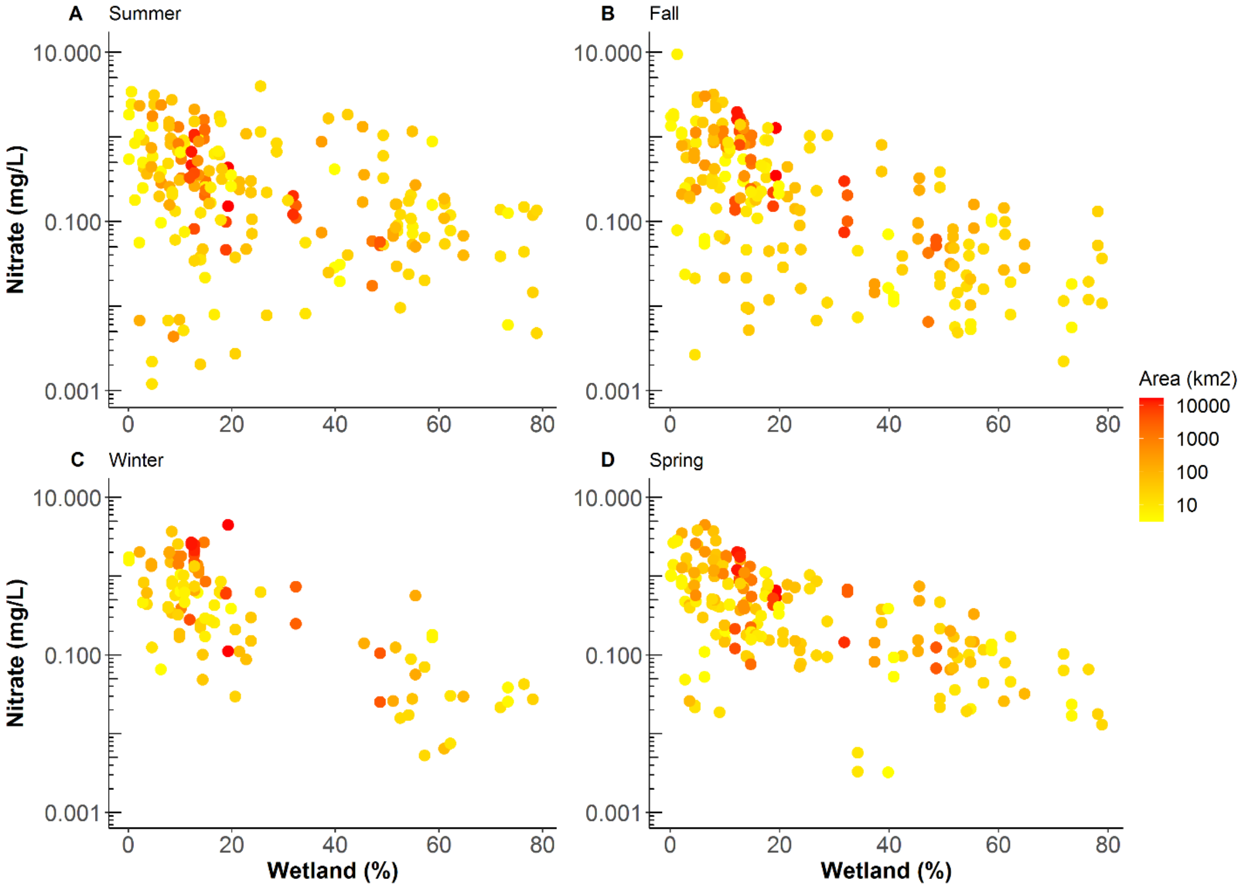


Figure 3. Nitrate concentrations (mg/L) and wetland coverage (%) within the watershed for tributaries sampled in summer (A), fall (B), winter (C), and spring (D) of 2016/17 and/or 2017/18. Individual points represent an individual tributary in the given season for a single year. The color of the points represents watershed area (km^2).

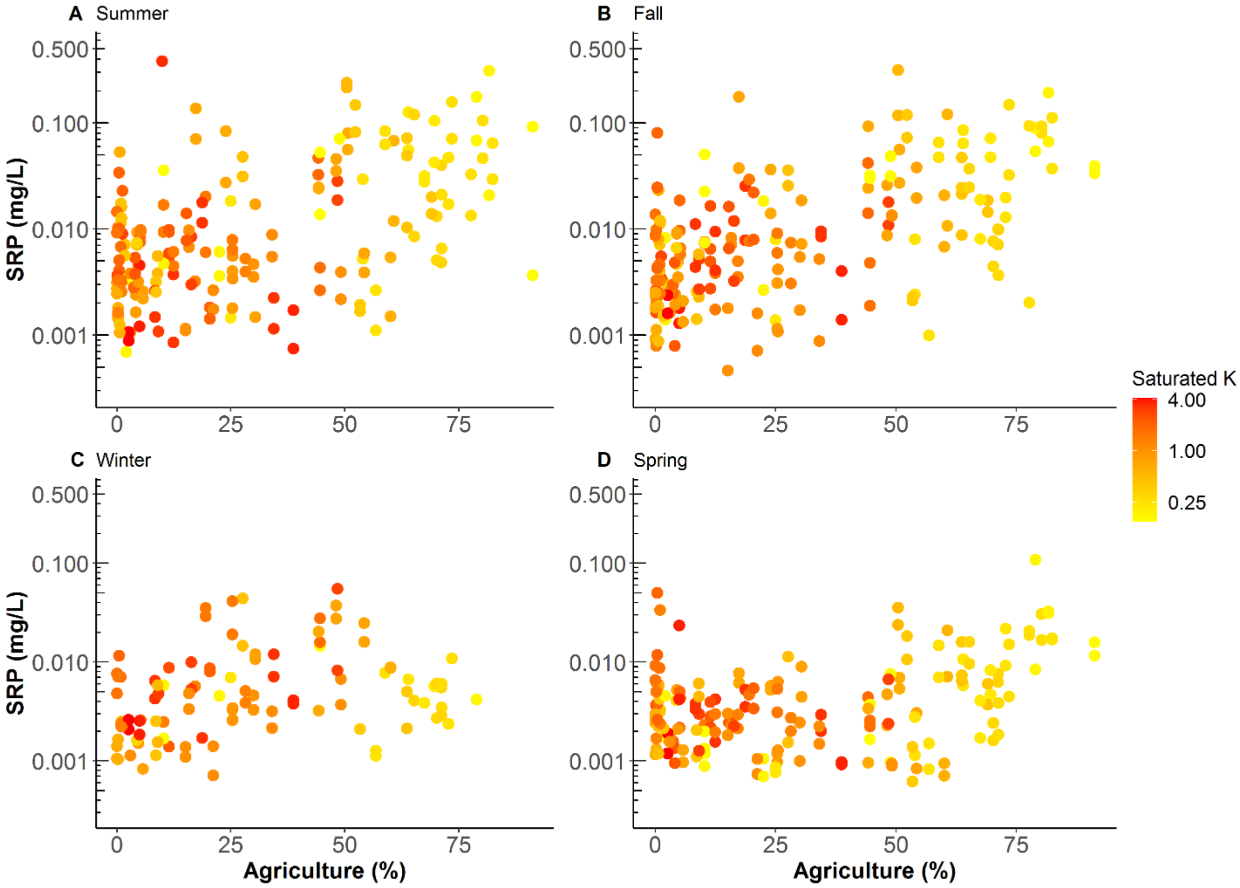


Figure 4. SRP concentrations (mg/L) and agricultural development (%) within the watershed for tributaries sampled in summer (A), fall (B), winter (C), and spring (D) of 2016/17 and/or 2017/18. Individual points represent an individual tributary in the given season for a single year. The color of the points represents mean saturated K (m/Day) of the soil within the watershed.

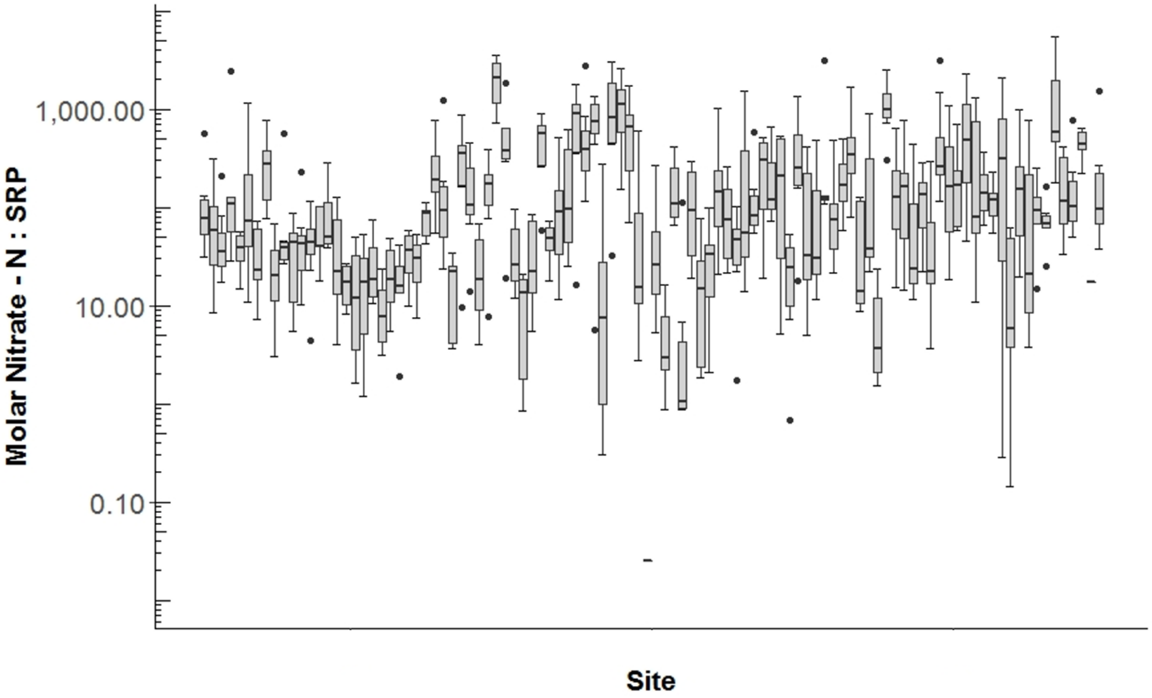


Figure 5. Box plots showing the median and interquartile ranges for Nitrate – N : SRP for individual tributaries sampled in 2016-2018. Whiskers represent 1.5 times above and below the interquartile range, and individual points represent outliers.

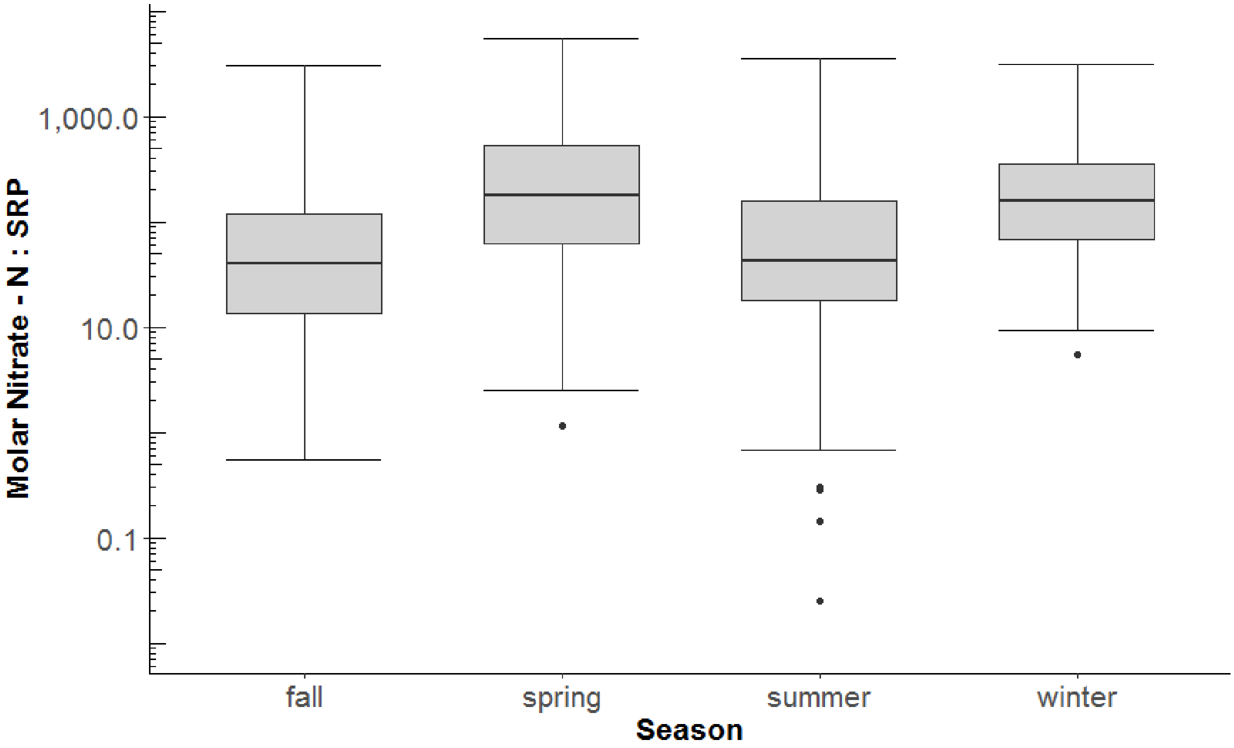


Figure 6. Box plots showing the seasonal median and interquartile range for Nitrate – N : SRP for all tributaries sampled in each season from 2016-2018. Whiskers represent 1.5 times above and below the interquartile range, and individual points represent outliers.

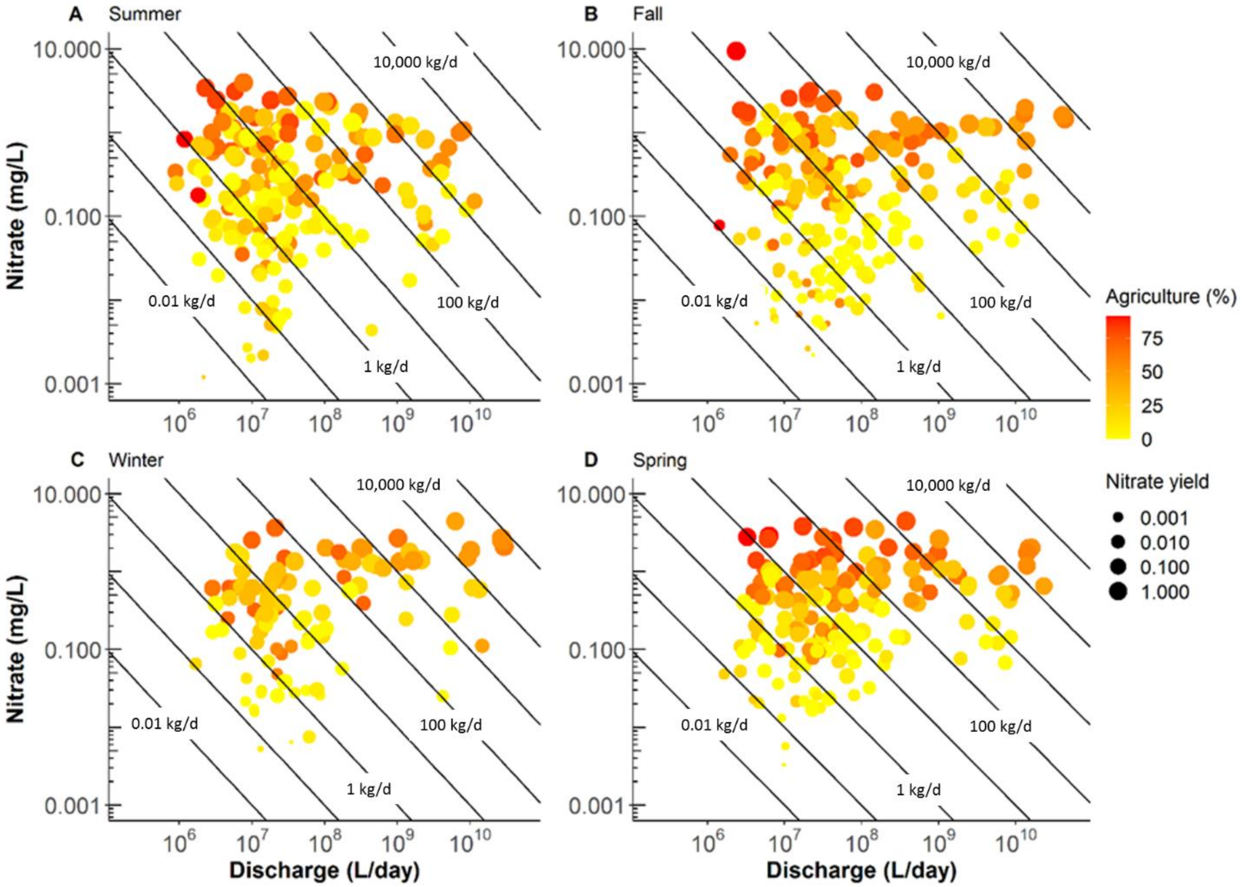


Figure 7. Combinations of discharge (L/day) and nitrate concentrations (mg/L) responsible for estimated daily nitrate loads for tributaries sampled in summer (A), fall (B), winter (C), and spring (D) of 2016-17 and/or 2017-18. Contour lines indicate nitrate loading rates (kg/day) of the same order of magnitude. Point size is scaled to nitrate yield (kg/day/km^2), and point color represents the fraction of watershed area that is considered agricultural.

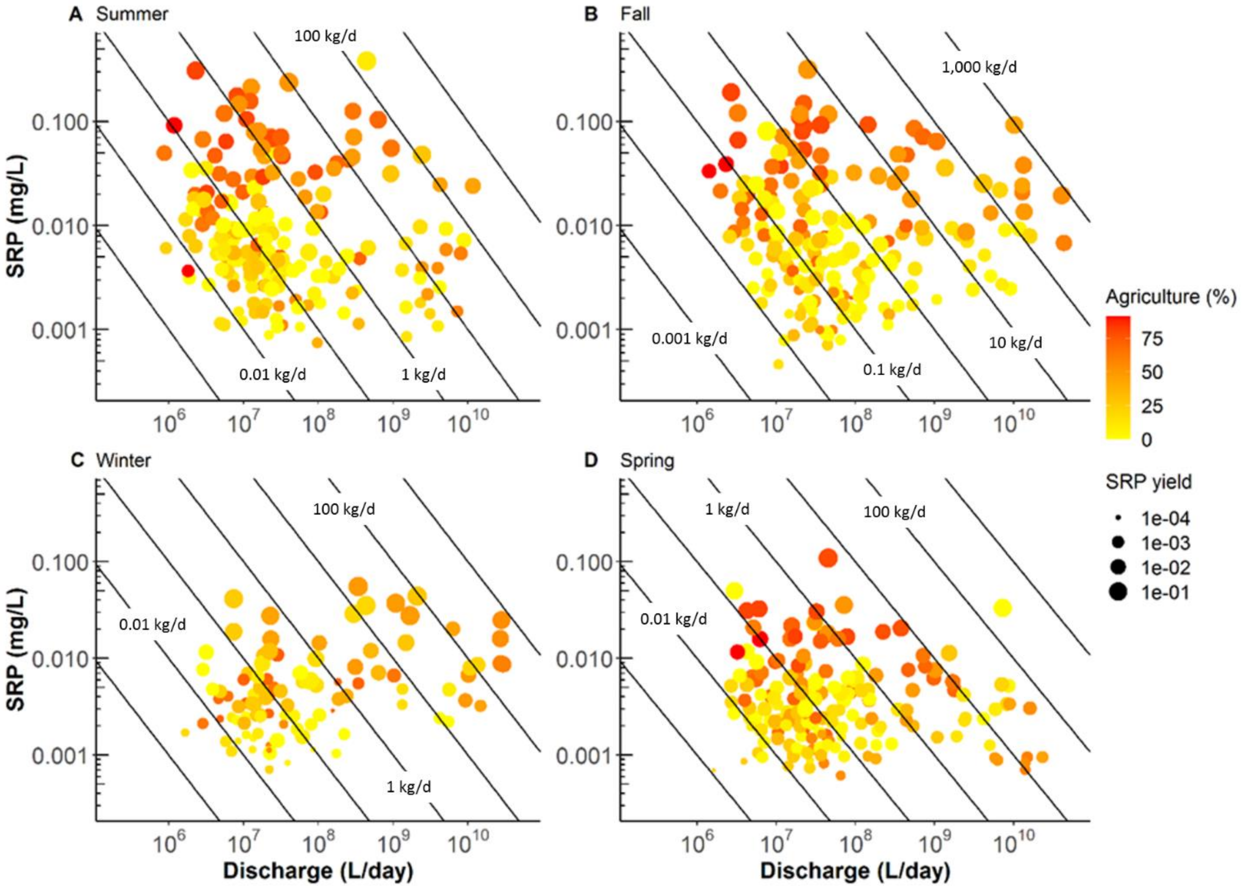
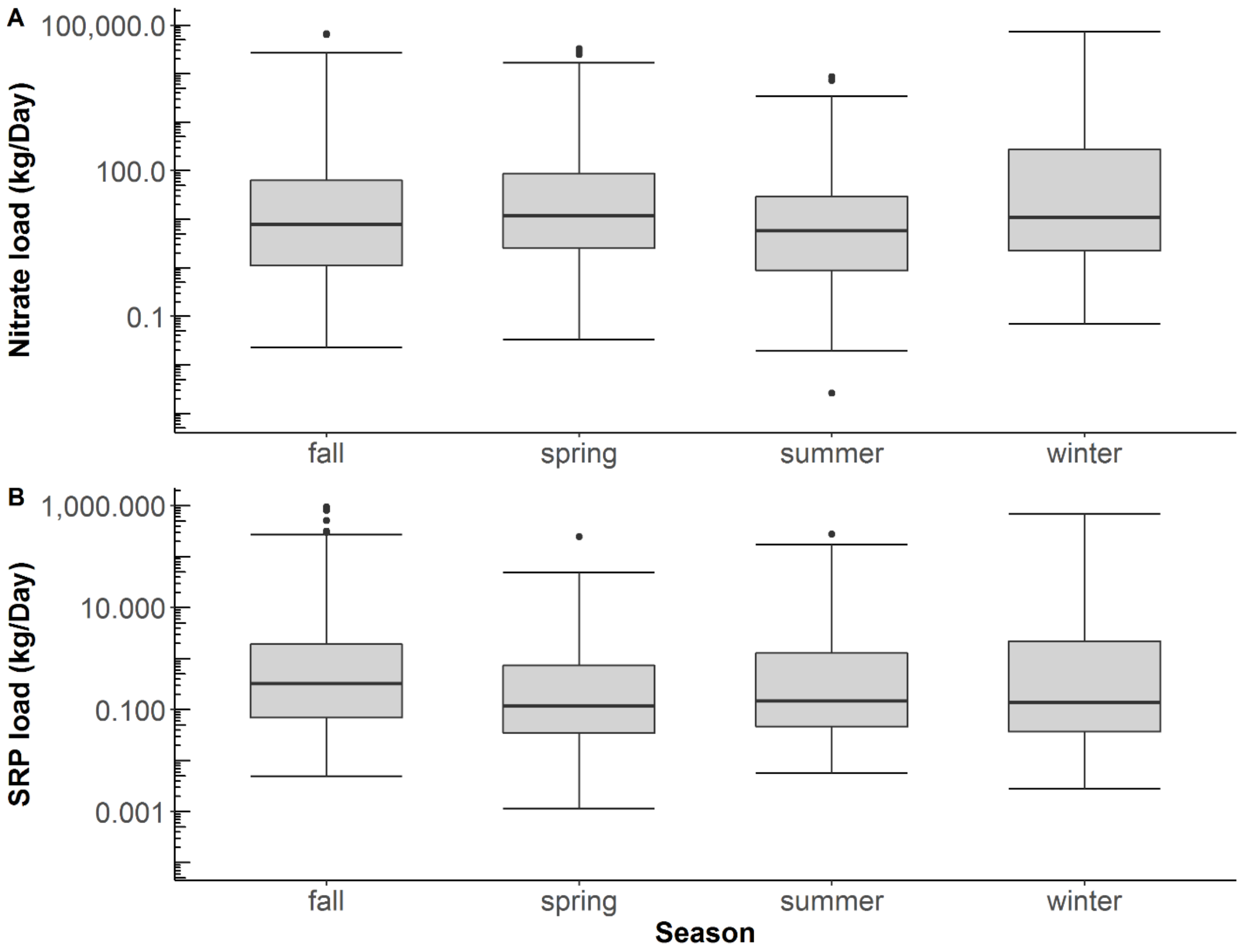
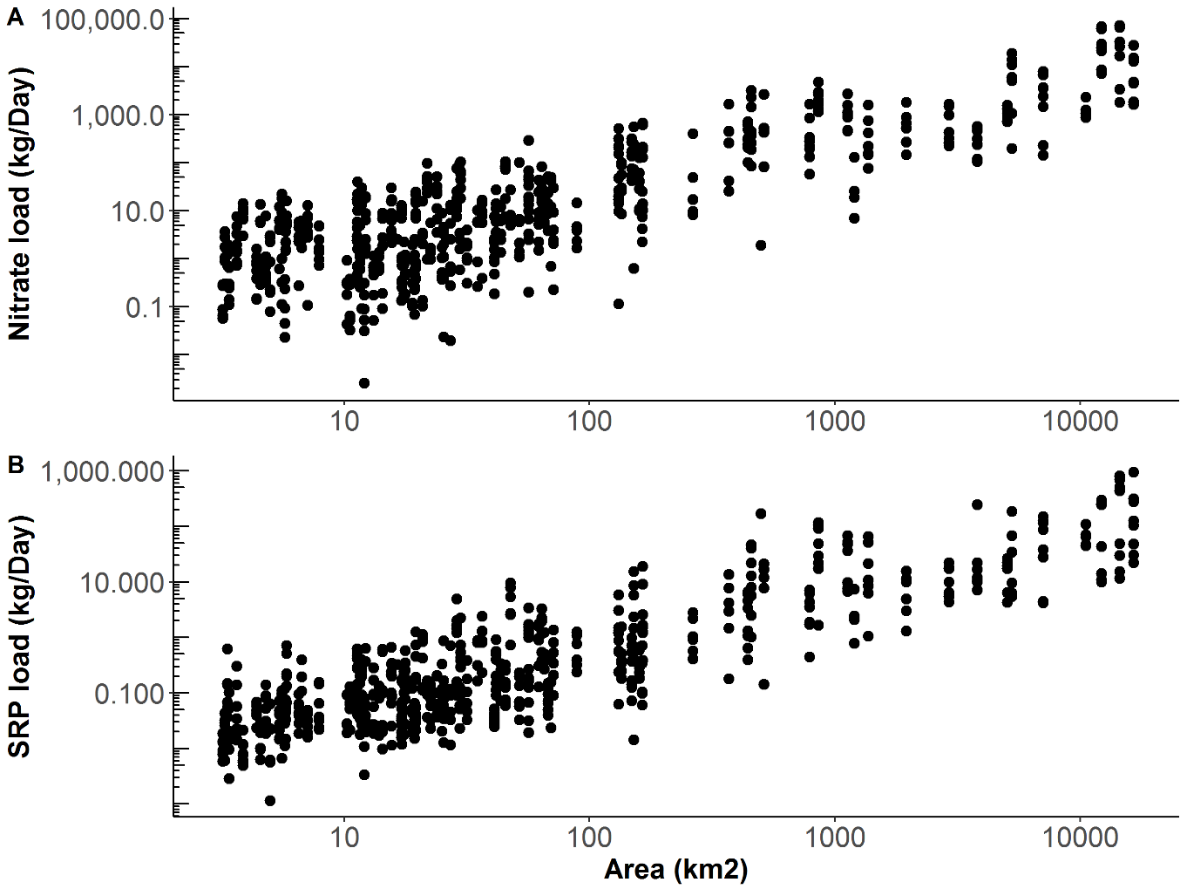


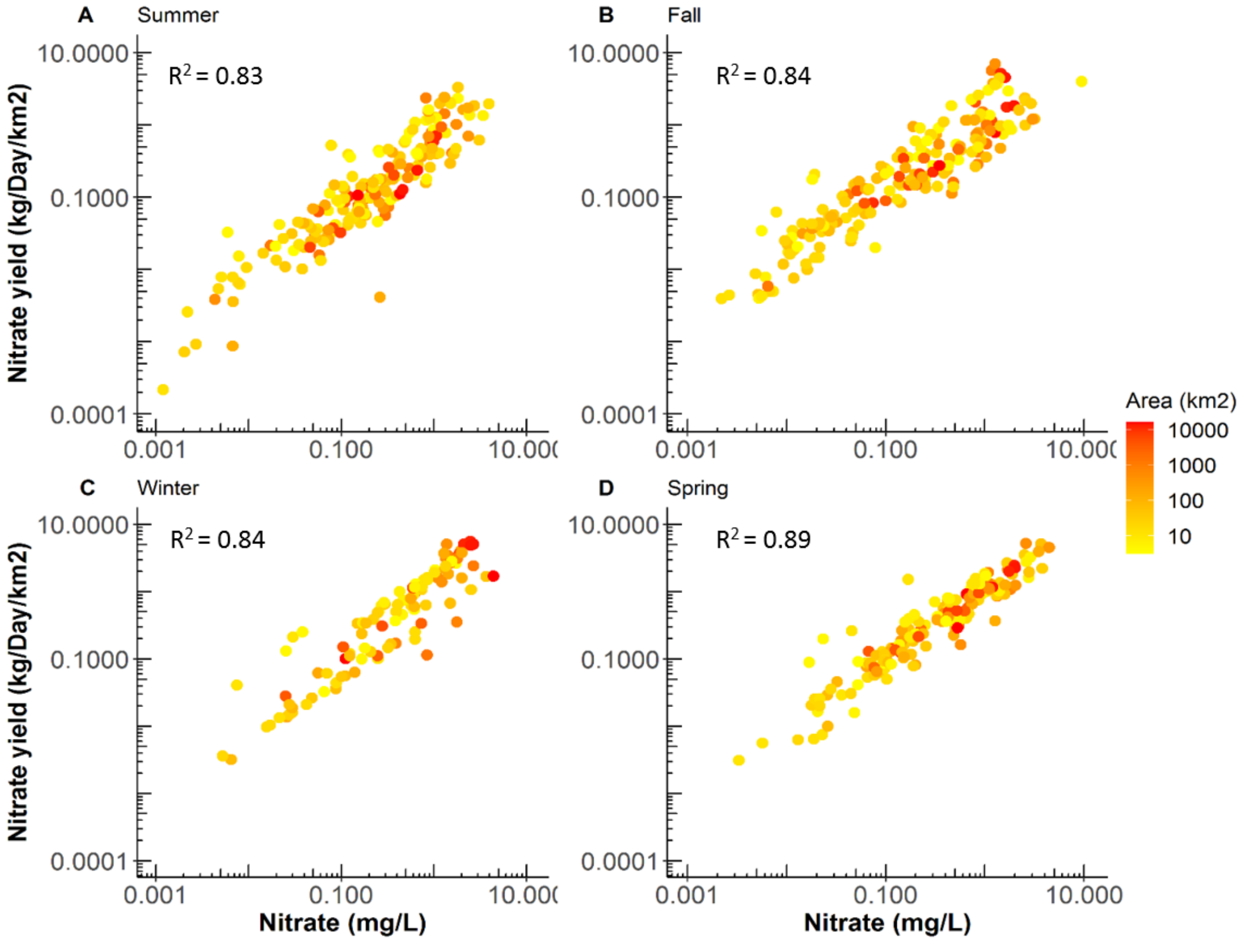
Figure 8. Combinations of discharge (L/day) and SRP concentrations (mg/L) responsible for estimated daily nitrate loads for tributaries sampled in summer (A), fall (B), winter (C), and spring (D) of 2016-17 and/or 2017-18. Contour lines indicate nitrate loading rates (kg/day) of the same order of magnitude. Point size is scaled to nitrate yield (kg/day/km^2), and point color represents the fraction of watershed area that is considered agricultural.



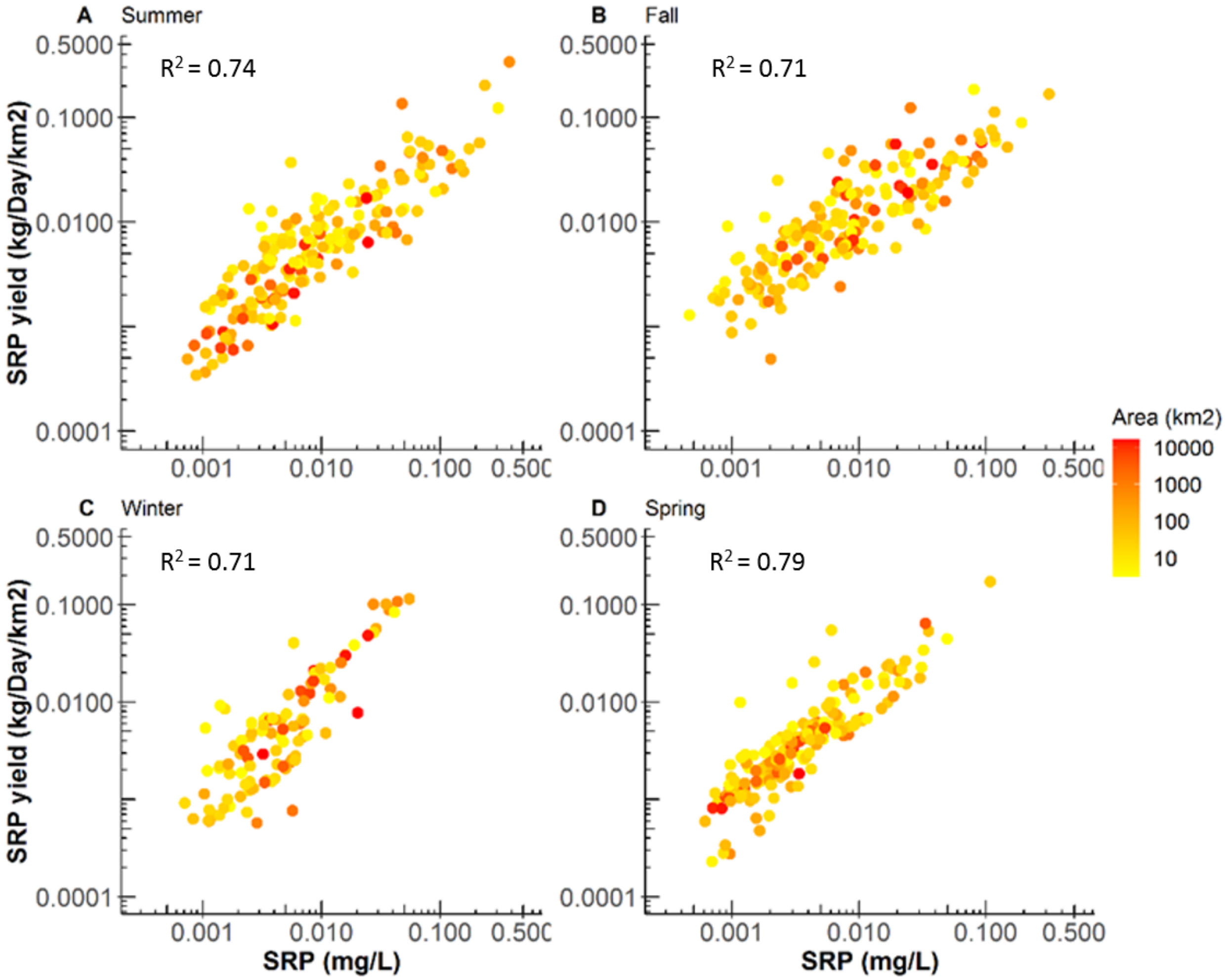
Supplementary figure 1. Box plots showing the seasonal median and interquartile range for nitrate (A) and SRP (B) loads (kg/Day) for all tributaries sampled in each season from 2016-2018. Whiskers represent 1.5 times above and below the interquartile range, and individual points represent outliers.



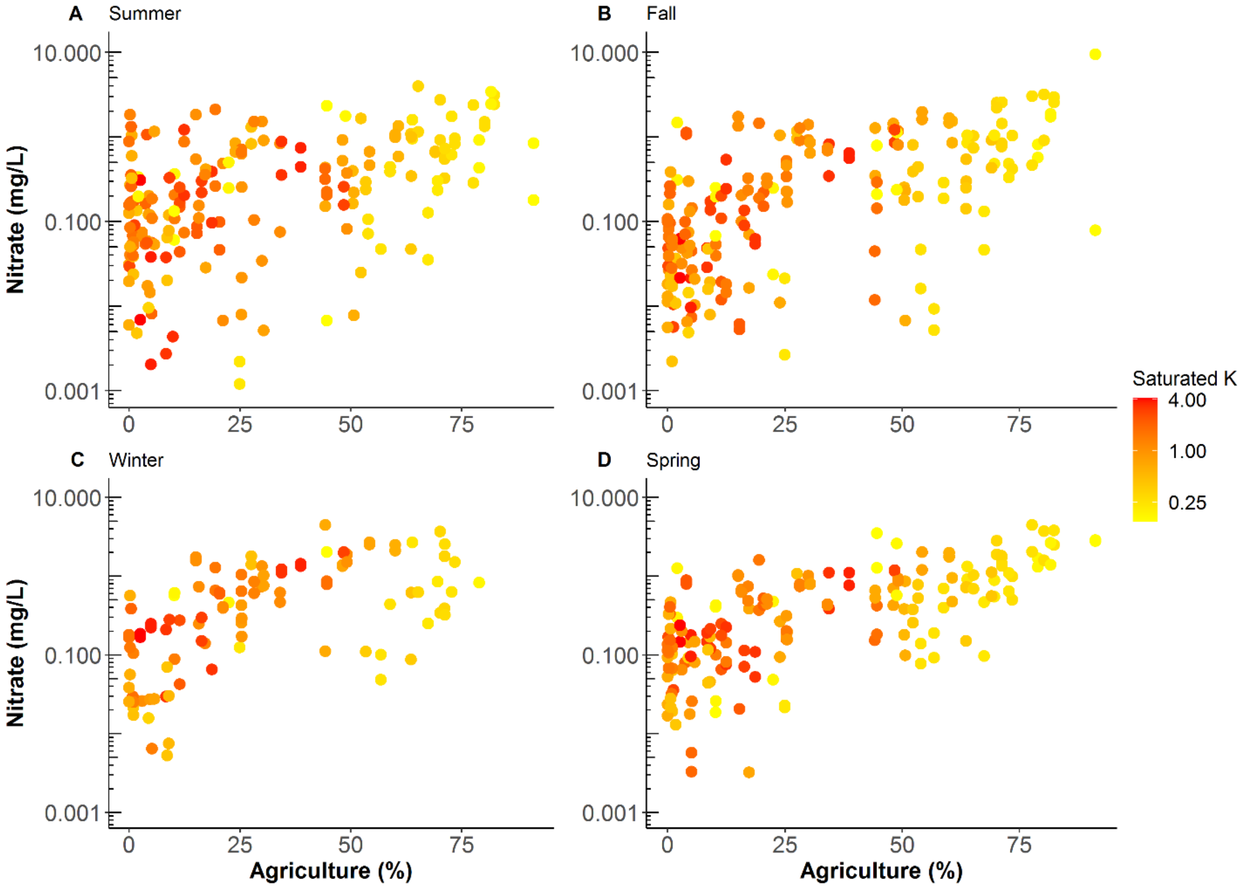
Supplementary figure 2. Nitrate and SRP loads (kg/Day) and watershed area for all sampled tributaries from summer, fall, winter, and spring 2016-2018.



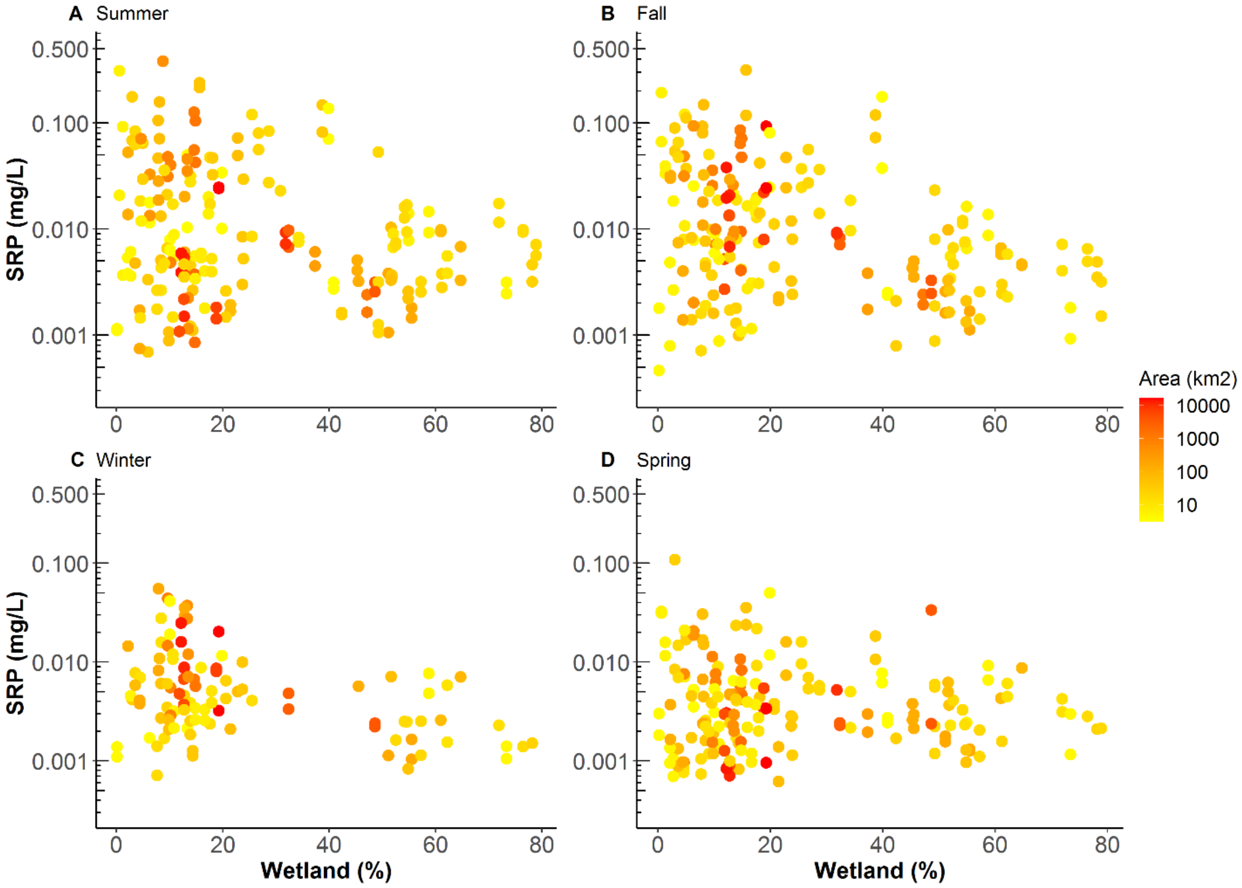
Supplementary figure 3. Nitrate yields (kg/Day/km^2) and concentrations for tributaries sampled in summer (A), fall (B), winter (C), and spring (D) 2016-2018. Individual points represent an individual tributary in the given season for a single year. The color of the points represents watershed area (km^2).



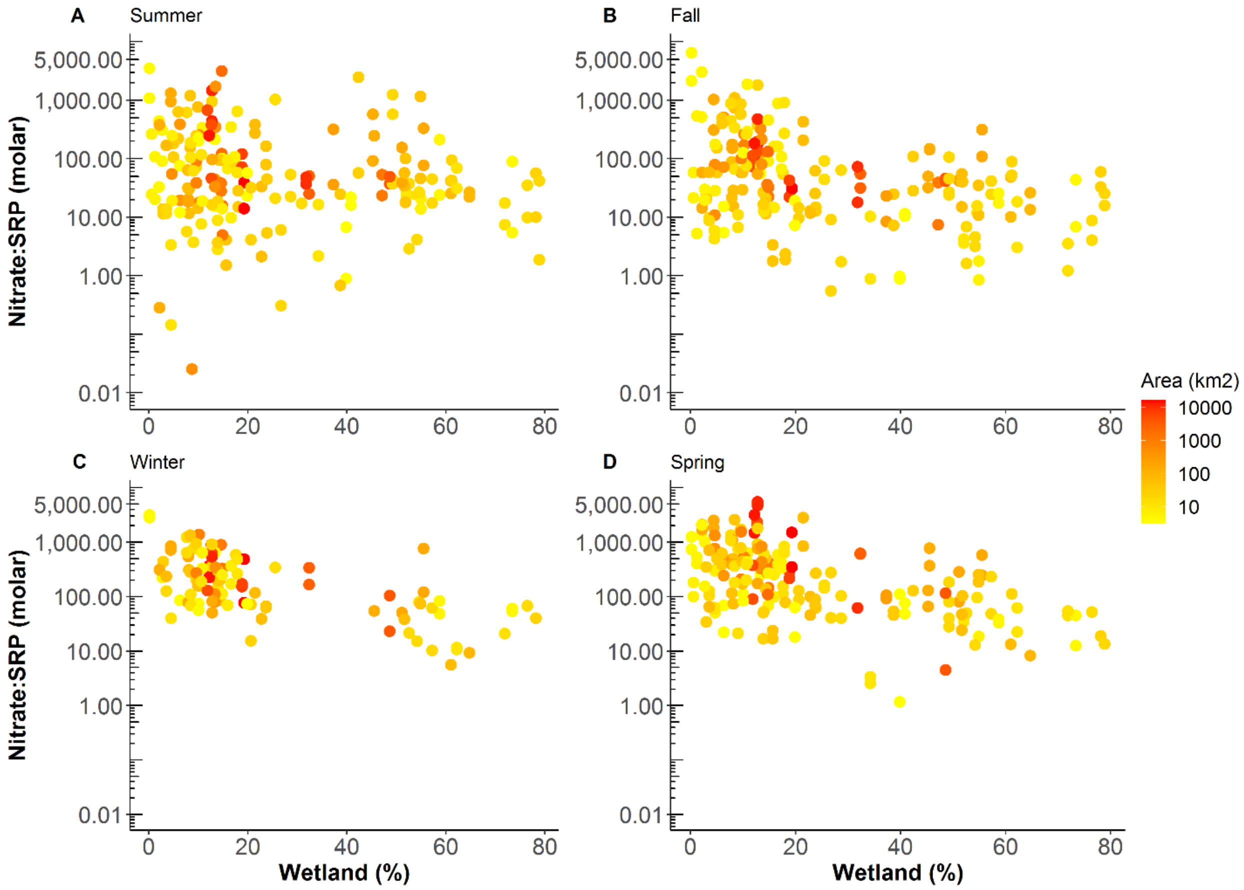
Supplementary figure 4. SRP yields (kg/Day/km^2) and concentrations for tributaries sampled in summer (A), fall (B), winter (C), and spring (D) 2016-2018. Individual points represent an individual tributary in the given season for a single year. The color of the points represents watershed area (km^2).



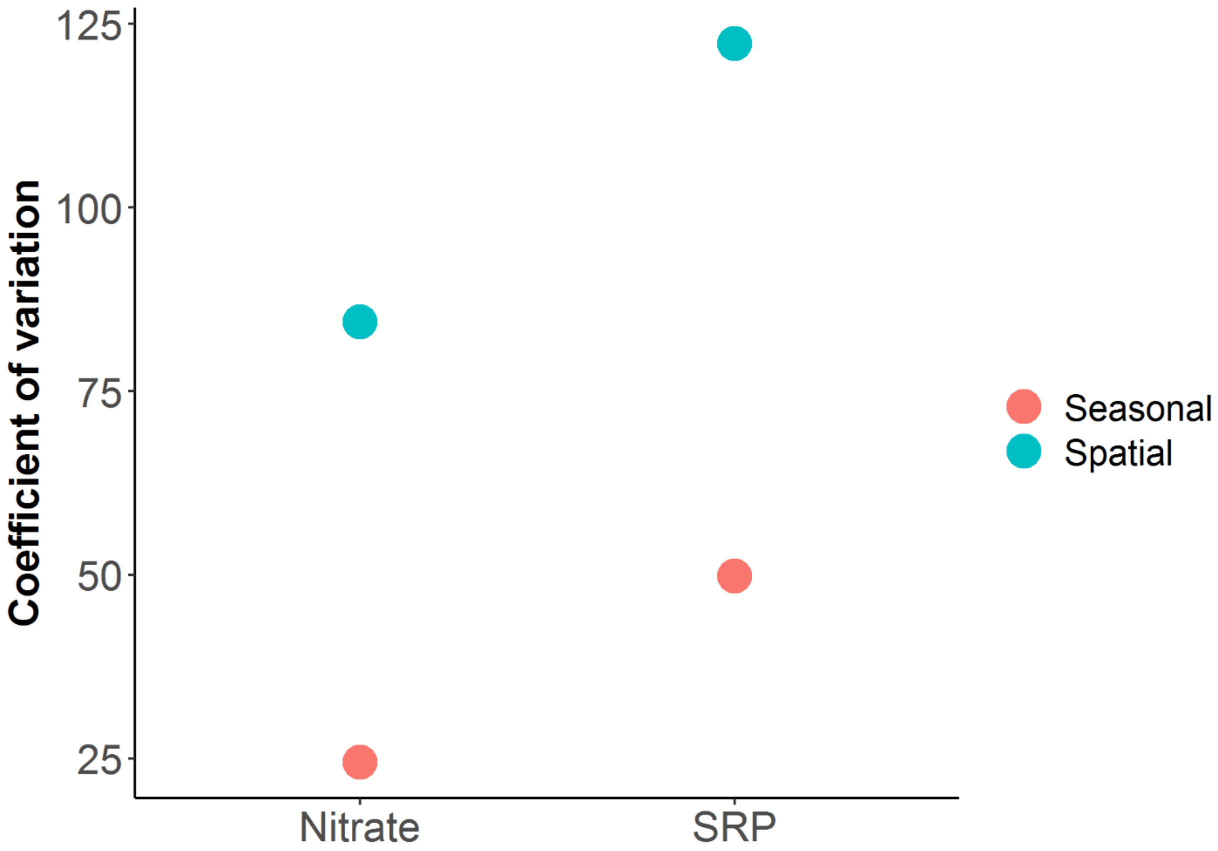
Supplementary figure 5. Nitrate concentrations (mg/L) and agricultural development (%) within the watershed for tributaries sampled in summer (A), fall (B), winter (C), and spring (D) of 2016/17 and/or 2017/18. Individual points represent an individual tributary in the given season for a single year. The color of the points represents mean saturated K (m/Day) of the soil within the watershed.



Supplementary figure 6. SRP concentrations (mg/L) and wetland coverage (%) within the watershed for tributaries sampled in summer (A), fall (B), winter (C), and spring (D) of 2016/17 and/or 2017/18. Individual points represent an individual tributary in the given season for a single year. The color of the points represents watershed area (km^2).



Supplementary figure 7. Molar nitrate : SRP ratios and wetland coverage (%) within the watershed for tributaries sampled in summer (A), fall (B), winter (C), and spring (D) of 2016/17 and/or 2017/18. Individual points represent an individual tributary in the given season for a single year. The color of the points represents watershed area (km^2).



Supplementary figure 8. Coefficients of variation (%) for standard deviation of nitrate and SRP means from each season across all tributaries (Seasonal CV) and for means of each tributary calculated across all four seasons (Spatial CV).

Table 1. Multiple linear regression output for the final Nitrate (mg/L) model (R^2 = 0.475) selected using backwards BIC model comparison.

Main and interactive effects	Coefficient	SE
Intercept	-0.196	0.167
Agriculture	0.005	0.002
Wetland	-0.026	0.003
Urban	-0.022	0.004
Spring	0.121	0.083
Summer	-0.213	0.083
Winter	0.289	0.097
Area (km^2)	-0.300	0.090
K saturation	0.127	0.075
Wetland*Spring	0.004	0.002
Wetland*Summer	0.012	0.002
Wetland*Winter	-0.002	0.002
Area*Wetland	0.007	0.002
Area*Urban	0.013	0.003
Area*agriculture	0.003	0.001

Table 2. Multiple linear regression output for the final SRP (mg/L) model (R^2 = 0.376) selected using backwards BIC model comparison.

Main and interactive effects	Coefficient	SE
Intercept	-3.08	0.136
Agriculture	0.021	0.003
Wetland	0.013	0.003
Urban	0.008	0.002
Spring	-0.162	0.075
Summer	0.079	0.072
Winter	-0.176	0.091
Area (km2)	0.235	0.073
K saturation	0.496	0.173
Agriculture*spring	-0.010	0.002
Agriculture*summer	-0.003	0.003
Agriculture*winter	0.001	0.003
K saturation*spring	0.612	0.189
K saturation*summer	-0.021	0.185
K saturation*winter	0.065	0.237
Area*K saturation	-0.270	0.078
Agriculture*K saturation	-0.001	0.004
Area*wetland	-0.005	0.002
Area*agriculture	-0.004	0.001
Agriculture*spring*K saturation	-0.016	0.005
Agriculture*summer*K saturation	-0.004	0.005
Agriculture*winter*K saturation	0.015	0.007

Table 3. Multiple linear regression output for the final nitrate : SRP model ($R^2 = 0.338$) selected using backwards BIC model comparison.

Main and interactive effects	Coefficient	SE
Intercept	2.82	0.202
Agriculture	-0.007	0.003
Wetland	-0.031	0.004
Urban	-0.026	0.005
Spring	0.698	0.101
Summer	-0.163	0.100
Winter	0.514	0.118
Area (km2)	-0.309	0.109
K saturation	-0.295	0.119
Wetland*Spring	-0.004	0.003
Wetland*Summer	0.009	0.003
Wetland*Winter	-0.001	0.004
Area*Wetland	0.008	0.003
Area*Urban	0.010	0.003
Area*agriculture	0.004	0.001
Agriculture*Saturated K	0.010	0.003

Supplementary information

Discharge estimates and load and yield calculations (from Mooney et al., in press)

Discharge was estimated for each sampling point location by the discharge-area ratio method. First, all USGS stream gauges within the US Great Lakes Basin states with at least 20 years of recorded data were downloaded, resulting in 3,997 stations. From these, a GIS feature was created using the latitude and longitude from each stream site. The gauges were then subset by those with a reported drainage basin area, and then intersected with an outline of the US Great

Lakes Basin. Following intersection, 924 gauged streams in the Great Lakes basin remained. Daily discharge data for all gauges was then downloaded from the USGS National Water Information Service (NWIS) using its REST API interface coded within MATLAB for the period 1980 – 2018. From the 924 gauges within the Great Lakes Basin with reported catchment areas, 657 had discharge data within this time window. Discharge values were then binned into 5-day averages and divided by basin area to compute 5-day basin yield averages (runoff). These basin yield values were interpolated to our coastal sampling locations using a two-step interpolation procedure. For each binned period, basin yield values were first interpolated using nearest-neighbor linear interpolation. This method allowed extrapolation beyond the convex hull of observed basin yield locations but can sometimes produce spurious values both due to extrapolation and having too few nearby gauges. In those instances, a secondary interpolation using nearest neighbors was used. Finally, the interpolated basin yield values above or below observed minimum and maximum values were truncated. Following interpolation of basin yield, each sampling location was then multiplied by its catchment area to compute 5-day average discharge.

To validate this approach, we subset the 657 gauges into validation and observed subsets and predicted discharge at the validation locations using the observed location values. For this separate validation, 10% of the 657 gauges were selected as a validation subset, with the remaining 90% as observed values. The median RMSE of the 5-day average predicted discharge across the 65 validation sites was 11.0% of observed flow at each location. For 25% of sites, the RMSE was less than 5.02% of discharge, while at the high end of error 25% of sites had RMSE values greater than 23.6% of discharge. We used this validation procedure to select the discharge averaging period. For bin widths greater than 5 days, discharge prediction error did not appreciably decrease, while for shorter periods, discharge prediction errors increased significantly. This is the case because as this procedure uses time-varying basin yield values from a range of gauged catchment sizes, temporal responses to precipitation or snow melt events can vary significantly. Below 5 days, this source of error dominates discharge estimation. For 5 or more days, the short-term responses to precipitation events are averaged out, and instead error is dominated by differing land cover, soils, slopes, groundwater conditions, and other hydrogeological characteristics that vary across catchments.

Chapter 3

Relevant co-authored papers* that investigated spatiotemporal variability of tributary nutrient dynamics and their potential impact on the coastal region of Lake Michigan

*Full co-authored manuscripts are included in appendix 1 of the dissertation document

Part I: Seasonal and spatial variability of carbon concentration and composition in Lake Michigan tributaries

In review as: S. M. Berg, **R. J. Mooney**, M. B. McConville, P. B. McIntyre, and C. K. Remucal. In review. Seasonal and spatial variability of carbon concentration and composition in Lake Michigan tributaries.

Abstract

Within a watershed, quantity and quality of dissolved forms of carbon are heavily influenced by landcover and vary seasonally. Understanding these dynamics is important because the amount and forms of carbon play critical roles in overall water quality and contaminant fate. In particular, dissolved organic matter (DOM) exists as a complex mixture of many organic compounds and the composition affects numerous reactions in the environment. Here, we determine how land cover variability and seasonality influence DOM concentration and composition, via ultraviolet-visible spectroscopy, in approximately 100 tributaries of Lake Michigan, one of the world's largest lakes. Wetland landcover has the largest effect on DOM, and correlates with high concentrations and more allocthonous DOM. The size of the watershed influences the composition of DOM but no effect is observed for concentration. We find that organic carbon composition in the tributaries is more sensitive to temporal variation

than concentration of either organic or inorganic carbon. Overall, we conclude that environmental processing of DOM is a more important control of composition than it is for concentration.

Part II: Lake hydrodynamics intensify the potential impact of watershed pollutants on coastal ecosystem services

Published as: L. Gloege, G. A. McKinley, **R. J. Mooney**, J. D. Allan, M. W. Diebel, P. B. McIntyre. 2020. Environmental Research Letters, 15: 064028

Abstract

Watersheds deliver numerous pollutants to the coastline of oceans and lakes, thereby jeopardizing ecosystem services. Regulatory frameworks for stressors often focus on loading rates without accounting for the physical dynamics of the receiving water body. Here, we use a three-dimensional hydrodynamic model to simulate the transport of a tributary-delivered pollutant within Lake Michigan based on the location and timing of loading. Simulating pollutant plumes from 11 rivers, and their intersections with coastal ecosystem services, reveals strong mediation of potential impacts by lake physics. Trapped pollutants accumulate in nearshore waters during spring peak flows, and become diluted by spreading offshore during the summer. The threat to coastal ecosystem services posed by pollutant loading differs sharply among rivers; high potential impact arises from the spatiotemporal coincidence of tributary input rates, lake mixing dynamics, and multiple human uses of the shoreline. Simultaneous pollution from multiple rivers yields overlapping plumes, creating a second way in which lake hydrodynamics

can amplify potential impacts on coastal ecosystem services. Our simulations demonstrate that the physical dynamics of large water bodies can create a dynamic stressor landscape arising from multiple independent sources of non-point-source pollution. The design and implementation of pollution regulations rarely account for spatial and temporal complexities of load processing in receiving waters, yet the resulting variability is likely to strongly mediate impacts on society. As hydrodynamic models improve, our analytical framework could be applied to a wide range of pollutants and waterbodies to enhance the sustainable use of coastal ecosystems.

Dissertation introduction for chapter four

Motivation plays a critical role in student success across all fields of study in higher education (Christophel 1990). Increased intrinsic motivation, or the internal desire to reach a goal or objective, has been found to significantly improve performance in educational settings (Sansone and Harackiewicz 2000). One of the most important components of a curriculum that leads to high intrinsic motivation is autonomy, which is a form of voluntary action or the feeling of individual choice (Núñez and León 2015, 2016). Students with high perceived autonomy generally have greater competence in the classroom, higher performance, and lower anxiety (Black and Deci 2000; Kusurkar et al. 2011). Additionally, when students thought their instructors displayed relatively high autonomy support, their performance in the class improved, especially for students that joined the class for required reasons, like meeting a degree or minor requirement (Black and Deci 2000). Providing structured guidance, communicating value in "less" interesting topics, giving students choices whenever possible, and incorporating student responsibility can help increase autonomy in the classroom and student motivation, thus improving overall student learning (DeLong and Winter 2002).

Extrinsic motivation, which is driven by external rewards, can further help students reach course learning objectives (Deci and Ryan 2001). However, the critical linkage between extrinsic motivation and student learning is entirely dependent on motivators, such as grades and assessments, being well-aligned with learning outcomes (Angelo 1993; Sundberg 2002; Miller et al. 2008). Curriculum alignment occurs when assessments of appropriate activities accurately reflect whether or not a student met the set learning outcomes. Misaligned outcomes and assessments often lead to conflicts between course material, student preparation and motivation, and instructor intentions and expectations (Biggs 1996; Leber et al. 2018). For example, if the learning objective is of higher order (e.g., synthesis) (Bloom 1956) but the assessment only tests for basal level learning (e.g., ability to recall), the instructor cannot properly evaluate if the students reached a desired learning outcome (Bloom 1956; Biggs and Tang 2011). Similarly, students can become frustrated if they prepared for higher order assessments but were only tested on their ability to recall information (i.e., downward misalignment). Downward misalignment often interacts with extrinsic motivation and leads to a "backwash effect" where students adjust their learning strategies for the assessment rather than the learning objective (Watkins et al. 2005; Parker et al. 2013). Because extrinsic motivation is often driven by grades, student preparation and learning are dependent on assessment type and its alignment with the course goals. Learning outcomes, activities, and assessments must be properly aligned for extrinsic motivation to be effective in student learning (Ausubel 1960; Biggs 1996; Wijngaards-de Meij and Merx 2018)

Some of the most common forms of assessment in biology laboratory classes are practical exams (Colosi and Zales 1998). Practical exams tend to be high-stakes, summative assessments given infrequently throughout a course (e.g., midterm and final practical exams) (Dixson and Worrell 2016). However, infrequent high-stakes exams do not promote continuous learning throughout the duration of a course and often fail to accurately reflect a student's knowledge (Madaus and Clarke 2001; Hofstein and Lunetta 2004). Intermittent assessments, however, can better promote continuous learning for diverse classes, reduce the weight of final exams, and allow students to change their learning habits and adapt throughout the duration of a course (Noble 2004).

Additionally, intermittent assessment allows instructors to evaluate themselves and alter their teaching and learning intervention strategies to teach more effectively (Miller et al. 2008).

One of the primary goals of the Ecology of Fishes Laboratory (ZOO 511) course at the University of Wisconsin – Madison is to teach anatomy and taxonomy of Wisconsin fishes. Throughout the semester, students gain experience identifying fishes to family, genus, and species using dichotomous keys to differentiate specimens using external anatomical features. In the past, the primary assessment of student taxonomy knowledge was a summative lab practical at the end of the semester. Many questions on the practical were composed of two parts: a preserved fish specimen and a question regarding its taxonomy (e.g., "What is the species of this fish?"). Although some students did well on the practical, they acknowledged that it was mostly memorization and that they lacked intrinsic motivation to learn and understand fish taxonomy, identification, and relatedness. Excerpts from past student evaluations suggested that the prior lab curriculum and assessments emphasized low-level learning and promoted memorization. For example, the two student comments below were common in course evaluations:

"Too much memorizing, especially for the final exam where we were expected to have many scientific names memorized."

"There was quite of bit of memorizing and for the final, if you didn't pretty much memorize all the material you were told to know, you were kind of out of luck."

The previous ZOO 511 taxonomy curriculum had misalignment of learning outcomes, activities, and assessments, resulting in the inability to evaluate if students were meeting the set learning outcomes. These issues also led to downward misalignment and reduced intrinsic motivation for students. Thus, I made several substantial changes to improve the curriculum and promote student learning (Fig. 1) by various mechanisms (Table 1). I felt the substantial curriculum revision was highly necessary, especially because the course, like many upper-level biology and ecology courses, can serve a pipeline to internships and jobs in environmental disciplines for students after graduation. While chapter four of my dissertation does not explicitly focus on all of the changes that I made and implemented to the ZOO 511 curriculum, it highlights an innovative, inquiry-based learning activity that I developed based on pedagogical theory after thorough self-reflection regarding the shortcomings of the course.

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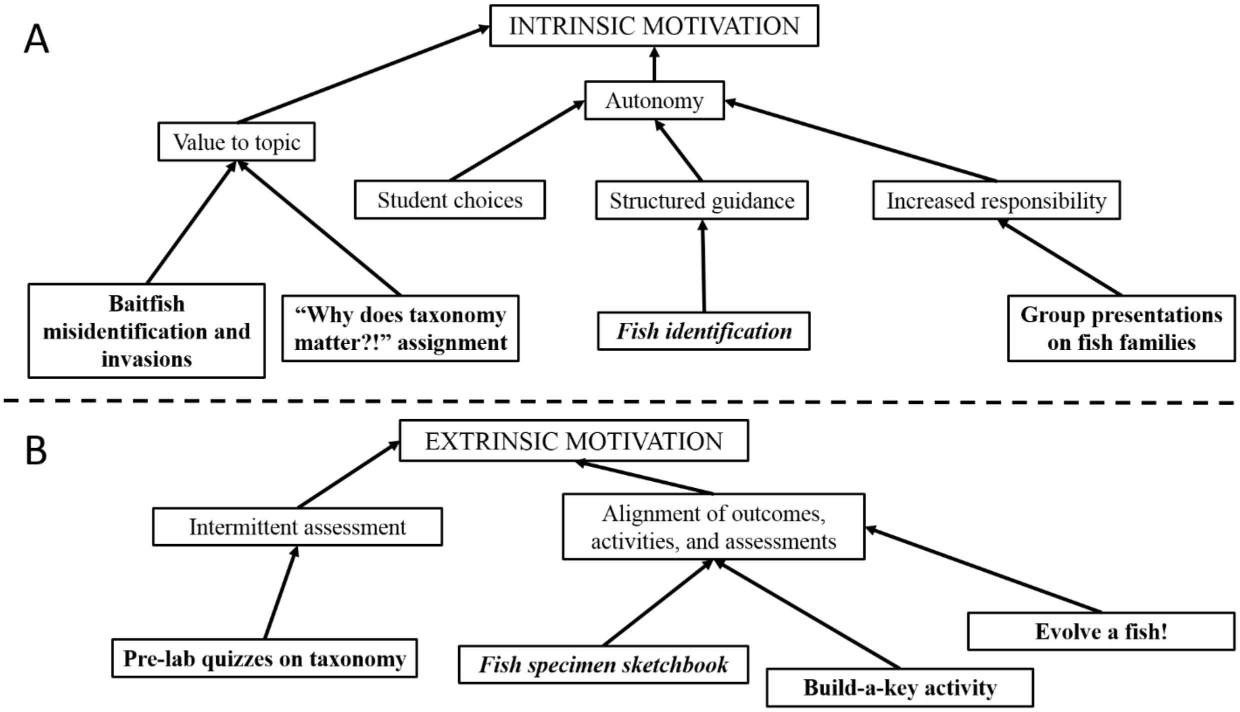

Figure 1. Additions (bold) and modifications to previous activities (bold, italicized) I incorporated to the ecology of fishes lab at UW-Madison to promote student intrinsic motivation (A) and ensure that extrinsic motivators (B) were properly aligned with the course learning outcomes.

Table 1. Learning outcomes, assessments, and added or modified associated activities for the ZOO 511 curriculum. I implemented these changes in spring semester 2019, the third semester I directly taught the course.

Activity	Learning outcome	Newly integrated mechanism to improve student learning
Baitfish misidentification and invasions	Highlighted in chapter 4	Highlighted in chapter 4
Why does taxonomy matter?!: Students selected and read 1 of 4 provided short papers to read that focused on the role that taxonomy has in broader fields of study	Students should recognize the role of taxonomy and organism identification in the fields of ecology, evolution, and conservation science	Intrinsic motivation – value to subject material, increased autonomy (student choice)
Fish identification (modified from earlier version): Each week, while working in groups, students would identify fishes to species base on external anatomy	Students should be able to use a dichotomous key to first identify a known fish and then unknown fishes, to species	Extrinsic motivation – alignment of course objectives Intrinsic motivation – structured guidance with the instructor serving as a facilitator
Fish family presentations: Groups of students prepared and give short presentations about 2 fish families, including identifying characteristics, ecological notes, and how functional morphology	Students should be able to explain and differentiate the identifying characteristics of 22 fish families	Extrinsic motivation – alignment of course objectives Intrinsic motivation – increased individual responsibility and accountability to a learning community
Weekly lab quizzes: students take a low stakes quiz on fish identification prior to each lab Fish sketchbook (modified from earlier version): students identified, sketched, and noted identifying characteristics of fishes	Students should be able to identify (without a scientific key) and recall the scientific names of certain fish species that are common throughout the state of WI	Extrinsic motivation – alignment of course objectives Formative assessment – improve instructor methods, give students weekly checkpoints
Build a key activity: Students select three fish and reverse engineer a	Students should be able to create a dichotomous key and apply it to three different	Extrinsic motivation – alignment of course objectives

multi-tier dichotomous key for those three fishes	specimens, showing they understand how a dichotomous key works. Their lab partners then try and use the produced key to identify the fishes	Intrinsic motivation – structured guidance with the instructor serving as a facilitator
Evolve a fish!: Students were randomly assigned a fish species, and had to "evolve" that fish to survive in a specific habitat. Lab group members all had the same habitat, but not necessarily similar fish. Students presented their process of evolution to the class	Students should be able to relate fish morphology to how the fish functions in its environment. Further, students should identify how specific characteristics are advantageous in certain environments	Extrinsic motivation – alignment of course objectives Intrinsic motivation – individual and group accountability

Chapter four

An inquiry-based activity for teaching taxonomy in college-level courses

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ABSTRACT

Despite the importance that taxonomy and species identification have in our current understanding of ecology, evolution, and conservation of organisms, it is a challenging topic to teach. One of the primary reasons for this challenge is the lack of student motivation to learn organism classification and identification, which is often reinforced by curricula that do not show the practical value of taxonomic knowledge. Here we provide an inquiry-based learning activity designed to show students the real-world value of organism identification. In this activity, students relate the misidentification of baitfish to the spread of invasive species via the baitfish industry. Students role play as fish ecologists and help a bait shop owner identify the specimens in their baitfish supply and subsequently develop a strategy to ensure that the business is not contributing to the spread of invasive species. By relating the field of taxonomy to species invasions, instructors can show students that they are learning information and gaining skills that have utility outside of the classroom. We found this to be an appealing alternative to other species identification activities, which typically focus on low-level learning, and we are excited to share our approach with the other instructors that deal with similar issues while developing their course curricula.

INTRODUCTION

The field of taxonomy, which focuses on species classification, relatedness, and identification, is critical to our current and continued understanding of evolution, ecology, and conservation of organisms (Winsor 2009; Tsang et al. 2016). Over the last 20 years, despite the historical and current importance of taxonomy, the natural sciences have entered a "taxonomic impendent" in which resources and number of experts have been steadily decreasing, leading to gaps in taxonomic knowledge (Lipscomb et al. 2003; Wheeler et al. 2004). Two primary reasons for the apparent decline of taxonomy are the lack of funding and employment opportunities for strict taxonomists (Coleman 2015). In academic settings, the disinterest and lack of motivation from students to learn taxonomy and organism identification is reciprocated by instructors and has contributed to the decline of taxonomy (Leather & Quicke 2010; Lucas Cajaiba 2014; Pisupati 2015). Teaching organism classification and species identification has multiple challenges, with fostering motivation and promoting higher levels of learning (e.g., application and evaluation) being central issues for many instructors (Gotelli 2004; Baum et al. 2005; Scott et al. 2012; Yamanoi et al. 2012).

Inquiry-based learning (IBL) can significantly promote and improve student autonomy and intrinsic motivation by emphasizing the role that students have in the classroom (Sansone & Harackiewicz 2000; Deci & Ryan 2001; Fink 2003). IBL activities allow students to critically think about posed questions and use provided materials to reach their own conclusions, with the instructor serving primarily as a facilitator (Ebert-May et al. 2003). The independence and feeling of ownership that students gain from IBL activities, when compared to traditional lectures, significantly improves overall student learning in biology courses (AAAS 2011; Kusurkar et al. 2011). Additionally, undergraduates typically want to collect and analyze their own data and apply their findings and conclusions to real-world problems (AAAS 2011). Although there are many examples of excellent IBL activities for biological and ecological courses (e.g., Heinrich et al. 2017; Bartlow & Vickers 2020) they are quite rare for taxonomy curricula, especially those with a strong species identification component.

Here we provide an IBL activity designed to show students the real-world value of taxonomic knowledge and organism identification. The activity revolves around societal, economic, and ecological issues that arise when organisms are misidentified. Specifically, students use a role-playing activity to relate the misidentification of baitfish to the spread of invasive species by the baitfish industry.

Using baitfish to show the importance of organism identification

Baitfish provide an excellent opportunity to link organism identification with real-world environmental issues. Fish species used as bait are often categorized as "target" and "non-target" baitfish (Drake & Mandrak 2014), with target species being legal to use as bait and non-target species being illegal. Non-target baitfish include invasive species as well as native species that should not be used as bait, including gamefish. Non-target baitfish are typically used as bait when the specimen is misidentified as a target baitfish or when there is no effort to properly identify a specimen before using or selling it as bait. Further, most baitfish, such as certain minnow, darter, and sucker species, are relatively small-bodied and can be notoriously challenging to identify and differentiate (Schroeder 2006). Misidentification of non-target species as target baitfish, when paired with the accidental or purposeful release of unused baitfish into lakes and rivers by anglers, can result in the spread of invasive species (Litvak & Mandrak 1993; Drake & Mandrak 2014).

Species invasions are some of the greatest ecosystem threats in the Anthropocene and can result in species extinctions, reduced ecosystem service value, and even societal conflict (Vander Zanden et al. 1999; MEA 2005; Estévez et al. 2015). By relating the importance of proper organism identification to this current environmental issue, instructors can show students that they are learning information and gaining skills that have utility outside of the classroom. We found this to be an appealing alternative to other species identification activities, which typically focus on low-level learning (e.g., remembering and recall) and result in students learning how to identify organisms for the sole purpose of doing well on summative assessments (Crowe et al. 2008; Pisupati 2015).

Objectives and student learning outcomes

Our activity is designed to promote intrinsic motivation and assign real-world value to taxonomy and species identification by relating the misidentification of baitfish to the spread of invasive species via the fishing industry. After the activity, students should be able to 1) identify fish species using a dichotomous key, 2) classify specimens as target or non-target baitfish, and 3) explain environmental consequences of organism misidentification.

ACTIVITY OVERVIEW AND MATERIALS

Class Design

In this activity, students work in small groups (3-5) and role play as a group of fish ecologists and environmental consultants. Students will be assisting the new owner of a bait shop with the identification of the baitfish being sold (provided by the instructor) and help them develop a strategy to ensure that they are not contributing to the spread of invasive species (detailed in the "role-playing scenario" portion of the "student handout material" section).

This laboratory activity is designed for a college-level biology course that has a strong organism identification component. We implemented the activity in two sections of a lab-based fish ecology course, with 24 students in each section. For each lab section, the activity took 3.5 hours to complete. However, because many courses do not have extended labs, the activity can be split across multiple class periods, as there are multiple distinct components: 1) background information and introduction to the activity from the instructor and 2) the role-playing activity, which consists of a) baitfish identification and classification and b) developing a strategy a bait shop owner can implement to prevent spreading invasive fishes. Alternatively, various aspects can be adjusted to complete the activity in a single, shorter class period. For example, instructors can reduce the number of specimens students identify and assign the written portion of the activity as homework to be completed as a group and turned in at a later time.

Instructor preparation

We recommend that the instructor reads the 4 following papers while developing their specific lesson plan. The following papers provide useful background information on the baitfish industry and species invasions, as well as the negative environmental consequences of species invasions.

- Litvak & Mandrak 1993 – "Ecology of freshwater baitfish use in Canada and the United States"
- Drake & Mandrak 2013 – "Ecological risk of live bait fisheries: A new angle on selective fishing"
- Pimentel, Zuniga, & Morrison, 2005 – "Update on the environmental and economic costs associated with alien-invasive species in the United States"
- McKinney & La Sorte, 2007 – "Invasiveness and homogenization: synergism of wide dispersal and high local abundance"

The instructor should determine specific details of the role-playing activity they will be implementing. One key consideration is where the role-playing scenario will take place. Our hypothetical scenario took place in Wisconsin (the state our university is in) because it is legal to use certain live fishes as bait throughout the state. However, if an institution is located in a state where baitfish use is prohibited, the instructor may want to have their scenario take place in a different state or region to ensure the activity remains realistic. The instructor should make a list of target baitfish and possible invasive fish species in the state in which the scenario is taking place. We have provided example baitfish lists for Wisconsin and Minnesota which can be used if the instructor chooses either of those states for the scenario (table 1). Descriptions of baitfish regulations, target (legal) baitfish, and invasive fishes can be found in state fishing regulation handbooks, which are typically available anywhere fishing licenses are sold or on State Department of Natural Resources websites (WI DNR 2019; MN DNR 2020).

Table 1. Common fishes in Wisconsin and Minnesota that may or may not be target (legal) baitfish. Note that there are differences in species that can be used as bait between the two states, and this is not an exhaustive list of species that are non-target baitfish. *Not all species in the Cyprinidae family are target baitfish. Goldfish and Common Carp are in the family Cyprinidae but are illegal to use as bait and are invasive.

	Wisconsin		Minnesota	
Fish species or group	Target baitfish?	Invasive species?	Target baitfish?	Invasive species?
Species in Cyprinidae*	Yes	No	Yes	No
Suckers	Yes	No	Yes	No
Mudminnow	Yes	No	Yes	No
Madtom	Yes	No	Yes	No
Stonecat	Yes	No	Yes	No
Killifish	Yes	No	No	No
Topminnow	Yes	No	No	No
Silverside	Yes	No	No	No
Sticklebacks	Yes	No	No	No
Trout-perch	Yes	No	No	No
Darters	Yes	No	No	No
Sculpins	Yes	No	No	No
Bullhead	No	No	Yes	No
Cisco	No	No	Yes	No
Lake Whitefish	No	No	Yes	No
Mooneyes	No	No	Yes	No
Goldeyes	No	No	Yes	No
Goldfish	No	Yes	No	Yes
Common Carp	No	Yes	No	Yes
Round Goby	No	Yes	No	Yes
Largemouth Bass	No	No	No	No
Northern Pike	No	No	No	No
Brook Trout	No	No	No	No
Channel Catfish	No	No	No	No

Finally, the instructor should ensure that all needed materials are accounted for – the baitfish samples (detailed below) can take up to two weeks to prepare and organize, especially if the instructor is unable to purchase baitfish and has to collect all of their own specimens.

Materials

- Becker, 1983 – "Fishes of Wisconsin" (or regionally appropriate dichotomous key)
- Hand lenses or magnifying glasses
- Nitrile gloves
- Wash bottle filled with tap water
- Paper towels
- Glass jars with preserved baitfish (detailed in "Baitfish samples" of this section)
- Plastic trays
- Student activity worksheet (which should include the "role-playing scenario" and "student instructions, prompts, and questions" sections below)
- List of target baitfish species and invasive species that students might find
- Data collection sheet (table 2)

Table 2. Data sheet for students to complete while identifying baitfish specimens. We provide 6 examples of potential target and non-target baitfish specimens found in a baitfish sample.

Species	Target baitfish?	Invasive species?	Identifying characteristics	# in sample
Fathead Minnow	Yes	No		15
Common Carp	No	Yes		1
Largemouth Bass	No	No		2
Goldfish	No	Yes		1
Brook Stickleback	No	No		2
Common Shiner	Yes	No		3

Baitfish samples

Glass jars with at least 24 preserved baitfish specimens (or fewer if there are time constraints) will be distributed to each group (1 jar per group). Having baitfish collected from a relatively local bait shop is a particularly appealing aspect of this activity, as it provides students with additional intrinsic motivation to engage. However, we realize that this may not possible everywhere. In these locations, collecting minnow and other small-bodied fish species with an institutional collection permit will serve the same purpose. We purchased fish from a store in Wisconsin that offered a "minnow mix" baitfish selection. Fish were preserved initially in 10% formalin and transferred to 70% ethanol for permanent preservation (Kumar & Hassan 2015). Because we were able to purchase a "minnow mix", which included target bait species and non-target baitfish, we did not add additional specimens to the baitfish jars before distributing them to students. However, because certain regions do not permit the sale of "minnow mixes", different species (e.g., Fathead Minnows, Golden Shiners, and Creek Chubs) can be purchased separately and mixed together prior to the activity to serve the same purpose. Preserved specimens of invasive species (e.g., small Common Carp or Round Gobies) or native species not intended for baitfish use (e.g., Northern Pike or Largemouth Bass) can also be added to the baitfish jars before students begin the activity. Adding additional specimens ensures that students will identify species not intended for bait use and shows the utility of taxonomic knowledge and proper identification in the fishing industry. Although adding specimens to the baitfish jars takes away some realism of the activity, if students only identify two or three species of target baitfish, the activity loses its primary purpose of demonstrating potential transport of invasive species. Finally, we recommend having an even distribution of both the number of species and the number of specimens in each jar. Although there will still be inherent variability among student groups, this minimizes the chances of groups having vastly different species and numbers of specimens to identify. The instructor should go through the baitfish that will be distributed to the students to be sure they know which species are present. This will ensure the instructor can play the role of facilitator and properly guide students when they have questions or become confused while identifying specimens.

We had the necessary Institution of Animal Care and Use Committee (IACUC) and state scientific collectors permit necessary to collect, preserve, and use fish specimens for teaching purposes. The instructor must obtain the necessary institutional permits to preserve and use vertebrate specimens in a classroom setting.

Beginning the activity

In the beginning of class, the instructor should give an overview of the relationship between the recreational baitfish industry and the spread of invasive species. Additionally, giving a brief description of the negative ecological and environmental consequences of species invasions will help set the stage for the activity. The instructor should also go over baitfish regulations and target (legal) and non-target (illegal) baitfish in their state. Even though students will be given a list of target baitfish, this will introduce students to specimens they might have in their baitfish sample.

Depending on the students' experience identifying fishes, it may be necessary to cover general characteristics of common baitfish species in the area. Fathead Minnows, Golden and Common Shiners, darters, and suckers tend to be common baitfish species throughout the United States (Drake & Mandrak 2014). However, if students have a firm grasp on external anatomy of fishes and appropriate terminology, a well-written dichotomous key (such as Becker, 1983 – "Fishes of Wisconsin") will suffice.

Implementing the role-playing activity

After going through background information and explaining the activity, students should get into their groups of 3-5 and receive their baitfish sample (the jar of baitfish), a plastic tray, a dichotomous key, magnifying glasses, wash bottle, and, if desired, gloves. Initially, students will remove all baitfish from their jar. Before attempting to identify specimens, we recommend that students sort fish into broad groups based on body shape and general appearance (figure 1). It can be overwhelming to students when they first remove dozens of fishes onto their trays, so initially sorting them into broad groups can help alleviate some of that stress. All fishes should stay wet (tap water is fine) throughout the identification process to avoid desiccation. As previously mentioned, these fishes can be challenging to not only identify, but also differentiate among species. Fish identification can be a frustrating process for students, so it is important for the instructor to normalize the struggle of identification to ensure students that they are not alone in the challenge. Walking through the dichotomous key with students when they begin to misidentify specimens can be extremely helpful and shows students that it can be a tedious process – and that is OK!

Figure 1. An example of what students might see when they remove the baitfish specimens from their jars. Fathead Minnows (A), Golden Shiners (B), and Brook Sticklebacks (C) are target baitfish in Wisconsin. Common Carp (D), however, are invasive minnows.

While identifying specimens, students should fill out their data sheet (table 2) while referencing the list of target and invasive species. Specimens will be categorized as: target baitfish; non-target baitfish but a native species; or non-target baitfish and an invasive species. For simplicity, we assumed that all non-native fish species had the potential to be an invasive species. After identification and classification, students should work together in their groups to answer questions 1-5 on their handout. However, if there are time constraints, the questions on the handout can be assigned to students as homework.

STUDENT HANDOUT MATERIAL

Role-playing scenario

A bait shop called "instructor should use creative freedom to come up with a name" in "state or specific region of the instructor's choice" has been sold to a new owner and is now under new management. The new owner, like many baitfish retailers, is aware of the threat that baitfish use and transport can have on recipient aquatic ecosystems. The owner is less than impressed with the current organization of baitfish being sold from the store. The bait shop currently has a single, aerated tank labeled "minnow mix" that houses all of the baitfish. The owner also noticed that there are multiple species in the tank. The owner and management team want to change how they organize baitfish in the store to ensure that they are not contributing to the spread of invasive species. The new owner, wanting the expert advice of fish ecologists, decides to hire outside consultants (you and your group of colleagues) to identify the specimens and make a recommendation on how to best proceed to reduce potential impacts of their baitfish on recipient ecosystem.

Student instructions, prompts, and questions

1. Remove the baitfish specimens from your random grab sample of baitfish and identify them to species. Which species are currently in the "minnow mix" baitfish tank? Are any of the fishes invasive? Which species, when misidentified as target baitfish, are most concerning from an ecological standpoint? Complete your data sheet as you go.

2. How do you recommend the new shop owner and management team organize their baitfish to ensure they are not contributing to the spread of invasive species? What training might the management team or employees need to take to make sure the organization remains consistent?

3. While completing your survey of baitfish, you talk with 3 different anglers that are purchasing bait from the store. You ask them where they plan to use the baitfish. What would you tell each angler about their plans to use baitfish during their trips? What recommendations about their baitfish use would you give each of them?
    1) Angler 1 is going to fish in a small, private lake that is nearby but has very few fish species.
    2) Angler 2 is going to fish in a river for a day in the same county as the bait shop but is then going to a river 6 hours away and plans on using the same baitfish.
    3) Angler 3 is passing through town on their way to fish in a different state, and just figured they would stop and get baitfish at the shop.

4. Based on your baitfish survey and interactions with the anglers, you also decide to make a recommendation to the new store owner about resources that should be provided to anglers when they purchase bait. What resources would you recommend?

5. What are some of the potential ecological and environmental consequences of misidentification of baitfish species?

Potential student responses

Student responses will likely vary among groups in a single class and among classes at different institutions. Here we provide some ideal student responses with explanations, as well as common responses that we received while implementing this activity.

Potential responses to the questions on the student handout:

1. Answers for this question will be highly variable based on location of the bait shop, the fish that are native to the region, and if the instructor adds additional specimens to the baitfish jars. However, students will likely identify a mix of target and non-target baitfish, as well as invasive specimens. Students should recognize that the misidentification of invasive species as target baitfish is the most concerning misidentification.

2. Students should state that the new bait shop owner should have separate tanks for individual species, and that the specimens should be sorted and identified properly before being sold. Some of our students noted that the processes of identifying every specimen would be very tedious and time consuming. Those students then recommended that the bait shop hire a part-time employee to specifically ensure that fishes are properly identified and sorted.

   Students should identify the need for bait shop employees to be properly trained on how to differentiate the fishes that commonly get put into their tanks – both target and non-target baitfish species. A common response from our students was that the owner should provide a dichotomous key for the fishes that are only commonly found in the tanks, as opposed to a comprehensive key for all fishes in the region. Similarly, some students suggested that, at a minimum, employees be trained on how to identify common invasive species. We thought these were especially great responses because it showed a balance of the students' recognition of the importance of taxonomy and the challenges associated with identification.

3. Angler 1: Students should identify that this angler can use the baitfish they purchased on the small, local lake. However, they should also note that the angler should not intentionally release their live baitfish when they are done fishing because they could introduce species that, although native to the area, may not be found in that specific lake.

   Angler 2: Similar to angler 1, students should recognize that the angler can use their baitfish in the relatively local river but should not release their baitfish. However, students should also say that they would tell the customer to not use the same baitfish in the river 6 hours away. They should suggest that the angler purchase different bait at a bait shop near the second river.

   Angler 3: Students should tell angler 3 that they should not purchase bait this far away from their fishing destination and recommend that they find a bait shop closer to the waterbody.

4. Students will likely come up with various suggestions for the bait shop owner. Many of our students recommended that the bait shop employees distribute cards or flyers with pictures and identifying characteristics of non-target baitfish to customers. They noted that many anglers will want to make their purchase quickly and leave the store, and so it wouldn’t be feasible to give them an in-depth lesson about fish identification. But, providing anglers with information about the risk of releasing misidentified baitfish and material to help them

recognize certain non-target baitfish would provide another line of defense beyond the bait shop employees.

5. Students should recognize that misidentification of baitfish can result in the spread of invasive species and lead to major ecological issues, including biotic homogenization and extinction of native species. Ideally, students should be able to give a correct response to this question after the assigned pre-reading and the activity introduction from the instructor. However, we chose this to be the last question on the worksheet to emphasize the importance of taxonomy and reinforce the practical, real-world value of organism classification. This question served as a good reminder for the students after completing a challenging activity.

CONCLUSION

The activity we designed includes multiple lesson plan characteristics recommended by AAAS (2011). Specifically, it used an IBL approach that demonstrated the real-world value of the topic being covered. Additionally, it allowed students to collect their own data and apply it to a realistic, hypothetical problem a business owner might encounter. By implementing this activity, we were able to show students that being able to properly identify species is an important skill to have and that misidentification of organisms can lead to environmental crises. In turn, we believe this activity promoted student motivation and has the capability to improve student learning in biology courses that have at least a small portion devoted to taxonomy and identification. We found this activity to be a helpful tool to increase student motivation, and we are excited to share our approach with the readers of *The American Biology Teacher*.

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Dissertation conclusion

The body of research presented in my dissertation showcases the extensive variability of tributary streams and rivers that flow into Lake Michigan, and offers insight into the challenges of understanding, monitoring, and managing nutrient inputs from the thousands of tributaries that drain into the Great Lakes. Chapter one showed that, while they may not contribute much to total lake-wide nutrient loads, nutrient inputs from small watersheds are likely to have outsized ecological impacts on the coastal zone by creating local hotspots of nearshore nutrients that could fuel algal blooms and eutrophication. Chapter two showed that even though land cover remains a driving factor for nutrient dynamics in tributaries, seasonality and watershed size should not be overlooked when it comes to nutrient management, as they play key roles in mediating loads, yields, and concentrations of bioavailable nutrients in Lake Michigan's tributaries. Part one of chapter three further highlighted the spatial and temporal variability of Lake Michigan's tributaries, this time showing that seasonal variation is more important for carbon composition than it is for carbon concentration, while watershed variability drives carbon concentration. Part two of chapter three showed that in-lake hydrodynamics play a critical role in distributing riverine pollutants, and offered new insights for management by merging riverine pollutant loads and three-dimensional lake hydrodynamics with ecosystem service geography.

Understanding the linkages among spatial and temporal drivers of tributary nutrient inputs, carbon dynamics, and tributary plume distribution throughout the coastal regions of the Great Lakes is entirely necessary to preserve and restore the lakes, especially in the face of continued Anthropogenic land development and climate change. While my dissertation filled critical knowledge gaps on the spatiotemporal drivers of tributaries and their potential influence on the coastal regions of Lake Michigan, it also showed that there is surely more to learn about how the extensive watersheds throughout the Great Lakes basin directly influence the coastal water quality, nutrient availability, and ecosystem functioning.

Appendix

Part I: Seasonal and spatial variability of carbon concentration and composition in Lake Michigan tributaries

In review as: S. M. Berg, **R. J. Mooney**, M. B. McConville, P. B. McIntyre, and C. K. Remucal. In review. Seasonal and spatial variability of carbon concentration and composition in Lake Michigan tributaries. Journal of Geophysical Research: Biogeosciences

Abstract

Within a watershed, quantity and quality of dissolved forms of carbon are heavily influenced by landcover and vary seasonally. Understanding these dynamics is important because the amount and forms of carbon play critical roles in overall water quality and contaminant fate. In particular, dissolved organic matter (DOM) exists as a complex mixture of many organic compounds and the composition affects numerous reactions in the environment. Here, we determine how land cover variability and seasonality influence DOM concentration and composition, via ultraviolet-visible spectroscopy, in approximately 100 tributaries of Lake Michigan, one of the world's largest lakes. Wetland landcover has the largest effect on DOM, and correlates with high concentrations and more allocthonous DOM. The size of the watershed influences the composition of DOM but no effect is observed for concentration. We find that organic carbon composition in the tributaries is more sensitive to temporal variation than concentration of either organic or inorganic carbon. Overall, we conclude that environmental processing of DOM is a more important control of composition than it is for concentration.

1. Introduction

Dissolved forms of carbon represent a significant portion of the global carbon pool [Cole et al., 2007]. Dissolved inorganic carbon (DIC), which exists as carbonate species in water bodies, exchanges with carbon dioxide in the atmosphere and can be converted to and from dissolved organic matter (DOM) through a variety of naturally occurring processes [*Granéli* et al., 1996; *Ward* et al., 2017]. DOM is a heterogenous mixture of biologically derived organic molecules that are diverse in their molecular composition, size, and properties. The source of DOM influences its composition. For example, allochthonous DOM originates from plant material on land, while autochthonous DOM is microbially-derived material that is produced within water bodies. Additionally, DOM composition can change during environmental processing via chemical or biological reactions.

DOM participates in many environmental processes. It is necessary for and influences microbial metabolism [*Lovley* et al., 1996; *Ward* et al., 2017] and provides an ultraviolet-filter to block irradiation within water columns [*Steinberg* et al., 2004]. DOM in the environment can also participate in reactions that affect the fate of metals and organic contaminants through physical, chemical and biological processes [*Aiken* et al., 2011; 2017; *Raeke* et al., 2017; *Zhao* et al., 2017]. For example, in surface waters, DOM can absorb sunlight and participate in reactions that degrade persistent chemicals in water bodies [*Remucal*, 2014]. Importantly, the composition of DOM affects the rates and extent of many of these reactions [*Berg* et al., 2019; *Maizel* et al., 2017]. The composition of DOM also represents an important component of water quality as a whole. DOM in drinking water sources can be problematic because reactions with disinfectants such as chlorine and chloramine form toxic disinfection by-products [Bulman and Remucal, 2020]. Evidence shows these reactions are selective and the composition of DOM in source water affects the by-products formed [*Lavonen* et al., 2013].

The Laurentian Great Lakes (hereafter Great Lakes) are among the largest lakes on the planet and hold 85% of North America's liquid freshwater [*Forsyth* et al., 2016]. However, tributaries influence water chemistry even in these large lakes that have significant dilution capacities and where precipitation can drive water inputs [*Marcarelli* et al., 2019]. Tributaries deliver nutrients (i.e., nitrogen, phosphorus, and carbon) and contaminants directly into lakes and have the capacity to alter characteristics of the nearshore zone [*Gloege* et al., 2020]· Observations of heterogeneity within the Great Lakes of nutrients and microbial metabolisms exist and are attributable to inputs from tributaries whose watersheds include wide ranges of land use and cover [*Marcarelli* et al., 2019*; Stephens and Minor,* 2010]· However, the spatial and temporal drivers of carbon quantity and quality remain unknown across the size spectrum of tributaries due to limited monitoring throughout the year, as well as lack of studies specifically including small tributaries.

The concentration of dissolved organic carbon ([DOC]) is commonly reported in surface waters. For example, previous research reports [DOC] in studies that take place over multiple years [*Jane* et al., 2017; *Strock* et al., 2017] as a result of spatial variability [*Frost* et al., 2006; *Mulholland and Hill*, 1997], as a function of season [*McCabe and Arnold*, 2016], or from a changing climate [*Freeman* et al., 2004; *Schelker* et al., 2012; *Weyhenmeyer and Karlsson*, 2009]. However, only a subset of existing [DOC] studies also include measurements of DOM composition which its reactivity in the environment ultimately depends on. These studies still provide useful data, but we believe that DOM composition is also important to include with [DOC] measurements.

The primary objectives of our study are to determine the spatial and temporal factors that influence not only dissolved organic and inorganic carbon concentrations, but also organic carbon composition. This study presents carbon concentration and composition data for >100 tributaries that drain into Lake Michigan. These tributaries are in watersheds that are highly diverse in terms of both their size and surrounding landcover types. GIS mapping is used to evaluate influences of surrounding landcover on carbon in the tributaries. Data from summer, fall, winter, and spring are included in order to evaluate seasonal variability in carbon. Our study is unique compared to existing literature because it includes compositional data as well as carbon concentration. Rather than considering only a single stream or even several streams, our study spans the circumference of Lake Michigan, likely making the relationships discovered in this study more applicable to other sites.

2. Materials and Methods

2.1 Sample Collection.

Tributaries surrounding Lake Michigan were sampled in July (n = 97), and October (n = 112) of 2016 and January (n = 67) and March (n = 111) of 2017. The number of tributaries sampled during each season varied due to inaccessibility of tributaries during certain sampling events (e.g., ice cover during January). Surface water was collected at the road crossing closest to the mouth using bridge sampling methods [*Decker* et al., 2013]. Samples were immediately filtered through 0.45 µm nylon filters and stored in amber glass vials at 4 ºC. All chemical analyses were performed within a month of sample collection except where noted otherwise.

2.2 Materials.

All glassware was combusted at 450 ºC for 8 hours to mineralize any trace amounts of organic carbon. Potassium hydrogen phthalate (ACS grade) and sulfuric acid (concentrated, ACS grade) were purchased from Fisher Scientific and used as received. All dilutions or blanks were prepared with ultra-pure water from a Milli-Q water purification system maintained at 18.2 MΩ cm.

2.3 Analytical Techniques.

A Shimadzu total organic carbon analyzer was used to measure [DOC]. Each sample was injected four times and the results of the last three injections were averaged. It was necessary to rerun some samples that had been collected in the spring due to instrument malfunction. These samples had been frozen and thawed. To determine the effects of freezing and thawing on DOM analysis, 15 samples that had been successfully analyzed for [DOC] in the spring were rerun after freezing and thawing and compared to their original concentrations. A linear regression was performed that was then applied to the samples that only had their concentrations quantified after freezing and thawing. Further details and a demonstration of no preferential loss of carbon is included in **Supporting Information Text SI**.

Alkalinity, which is a proxy for the dissolved inorganic carbon concentration ([DIC]), was quantified by measuring the amount of 0.1 N H_2SO_4 required to reach an endpoint of pH = 4.5 and is reported as $CaCO_3$ equivalents in the sample [*Yakushev,* 1999]. Ultraviolet-visible (UV-vis) spectroscopy was used to measure the amount of light absorbed by the sample from 200 – 800 nm. Water samples were referenced to ultra-pure water with absorbance from 700 – 800 nm subtracted. Samples whose absorbance values exceeded 1.5 at any wavelength were diluted with ultra-pure water. E_2:E_3 was calculated by taking the ratio of the absorbance at 250 nm to the absorbance at 365 nm [*Helms* et al., 2008]. $SUVA_{254}$ (specific ultraviolet absorbance at 254 nm) was calculated by dividing the absorbance at 254 nm by the concentration of dissolved organic carbon [*Weishaar* et al., 2003].

Here we use of ultraviolet-visible (UV-vis) spectroscopy to characterize DOM composition in tributaries of the Great Lakes. This technique is relatively simple and inexpensive compared to other methods, allowing us to consider differences in DOM composition across our entire large data set [*Minor* et al., 2014]. Additionally, UV-vis spectroscopy is the most commonly used technique for evaluating DOM composition making our results easily comparable to other studies. Furthermore, relationships between more complex DOM characterization and UV-vis measurements have been developed making UV-vis analysis even more informative [*Kellerman* et al., 2015; *Nebbioso and Piccolo*, 2013].

2.4 Data Analysis.

ArcGIS was used to determine watershed area, % agricultural, % barren, % herbaceous, % forest, % shrubland, % urbanized, and % wetland. A multiple linear regression (MLR) model was built to describe four carbon parameters including [DOC], alkalinity, $SUVA_{254}$, and E_2:E_3. Prior to any analysis, all values were $\log_{10}$ transformed to increase normality. The model was built in the R programming language and includes terms for watershed area and landcover types as continuous in dependent variables, and the season of sample collection as a categorical independent variable. Only those tributaries that were sampled in all four seasons were included in this analysis (n = 56, 59, 55, and 53 for [DOC], E_2:E_3, $SUVA_{254}$, and alkalinity, respectively) and only three landcover types, % agricultural, % urban, and % wetland were included in the MLR to avoid excess collinearity. Interactions between each land cover type and both the watershed area and season were also considered. Variance inflation factors (VIF) for each model input were equal to 1 with the exception of those involving seasons, which are categorical. Bayesian information criterion (BIC) was used for parsimonious model reduction and only those main effects and interactions with statistical significance were used in the reduced model. All p-values reported are based upon a 95% confidence interval. Simple linear regressions between all landcover types and the four parameters were also plotted in order to make our results comparable across other studies and to enable comparison of all landcover types beyond the three used in the MLR. Box and whisker plots where the middle of the bar represents the median, the upper and lower limits of the bar represents the first and third quartile, respectively, and the lower and and upper points represent the minimum and maximum values of the particular season, were constructed to display seasonal variation among the parameters. Statistically significant differences between the seasons are noted through the results of the MLR.

3 Results and Discussion

3.1 Watershed information.

The watersheds surrounding Lake Michigan are diverse in terms of their size, predominate landcover types, and geology. The percentage of landcover type in each watershed ranges widely and includes urban (1.6 - 79.1%), barren (0 – 8.6%), forest (0.9 – 63.1%), shrubland (0 – 6.1%), herbaceous (0 – 21.4%), agricultural (0 – 91.2%), and wetland (0.1 – 78.9%). Generally, the watersheds most dominated by wetlands are located on the northwestern side of the Lake Michigan, while agriculture and urban landscapes dominate the southeastern side (**Figure 1**). Additionally, the geographical areas of the sampled watersheds are diverse, ranging from 3.1 km^2 to 16,469 km^2.

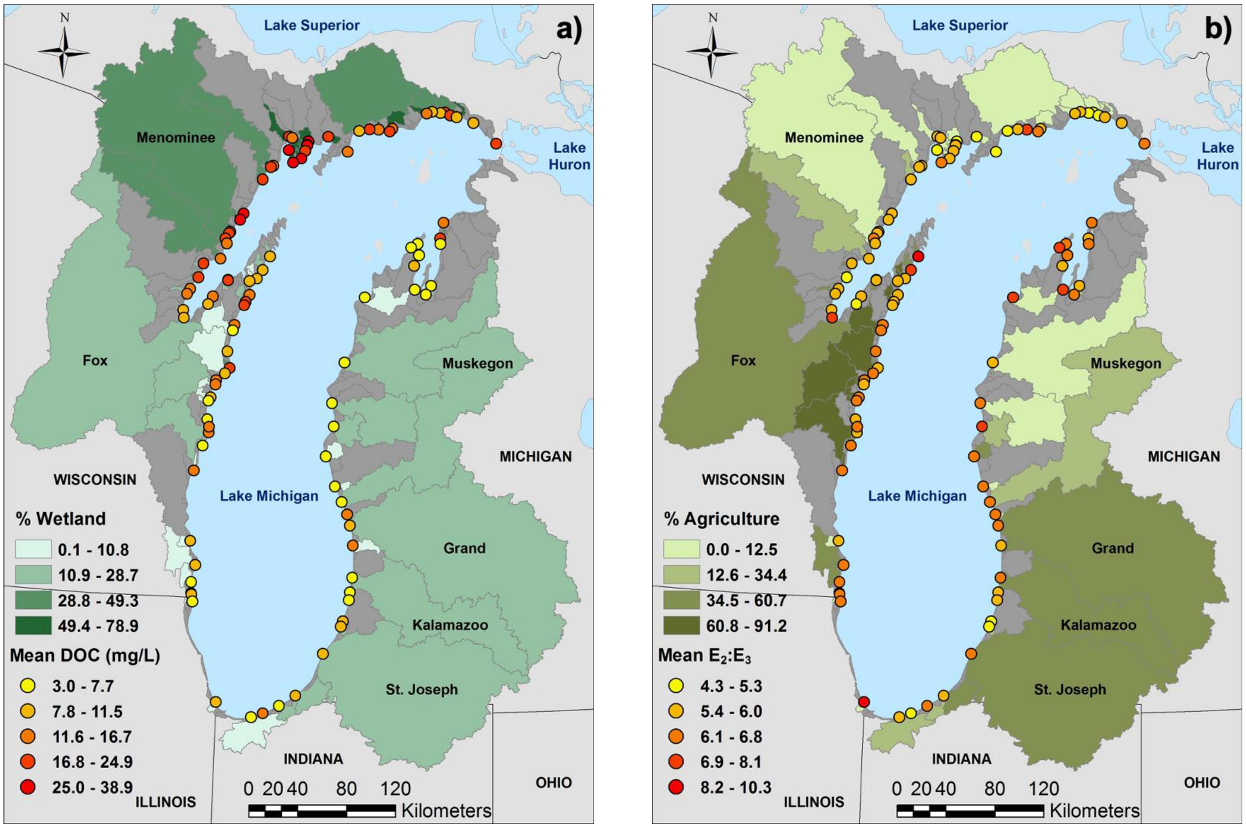

Figure 1. Map of Lake Michigan tributaries and watersheds. Points represent tributaries sampled where the color represents mean values of a) [DOC] in mg-C L^{-1} and b) E_2:E_3, for all samples collected. Shading of the watersheds represents the % landcover of a) wetlands and b) agriculture.

3.2 [DOC]

3.2.1 Spatial Variability

Dissolved organic carbon concentrations measured in the tributaries vary in space and by season. The mean [DOC] of the entire data set is 13.1 mg-C L^{-1} (n = 382), with individual values ranging from 1.6 to 48.4 mg-C L^{-1}. Generally, the highest [DOC] values are observed in the tributaries draining into the northwestern side of the lake (**Figure 1a**). These concentrations of DOC are relatively high for surface waters but fall within ranges of other measurements made in

Lake Michigan tributaries [*Frost* et al., 2006; *McElmurry* et al., 2014], as well as [DOC] in tributaries to other Great Lakes [*Berg* et al., 2019; E. *Minor and Stephens*, 2008].

Multiple linear regressions on [DOC] show that both landcover type and the season of sample collection influence [DOC] in tributaries. Our reduced model includes terms for % agriculture, % urban, and % wetland in the watershed, as well as season (**Table S1**). The % wetland in the watershed has the most significant positive effect on [DOC] (**Figure 2a**; **Table S1**). Variables for % urban and % agriculture have estimates that are nearly an order of magnitude less than that of % wetland (**Table S1**). It is also clear that % wetland in the watershed affects [DOC] the most. In fact, simple linear regressions of any landcover type observed in this study and [DOC] besides % wetland yield negative slopes (**Figure S3**), likely because increases in other landcover types correspond to decreases in % wetland. The area of the watershed is not a significant predictor of [DOC] in the tributaries (**Table S1**).

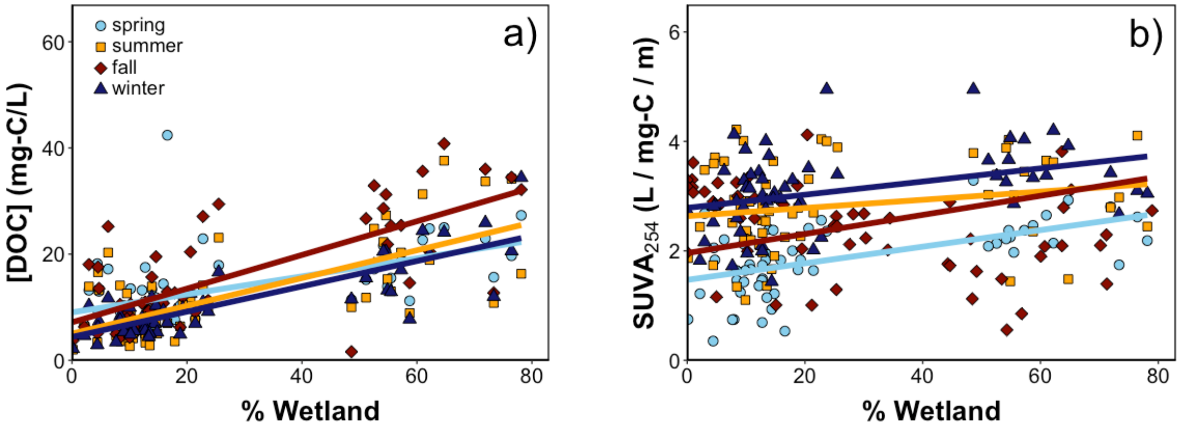

Figure 2. a) [DOC] and b) SUVA$_{254}$ versus % wetland in the watershed. Colors indicate season. Only tributaries sampled in all four seasons are included in this plot.

Wetlands show the strongest and most consistent positive trends to [DOC] in this data set and in the literature [*Cawley* et al., 2014; *Clark* et al., 2004; *Dillon and Molo*t, 1997; *Eckhardt and*

Moore, 1990; *Flint and McDowell*, 2015; *Frost* et al., 2006; *Hanley* et al., 2013; *Mattsson* et al., 2005; *Xenopoulos* et al., 2003]. This is unsurprising given that the water flowing through wetlands provides a mechanism for directly transferring terrestrial carbon into the dissolved phase. In contrast, conflicting relationships are observed with other landcover types. The positive relationships with [DOC] and % agriculture observed in this study in the MLR model agree with some studies [*Graeber* et al., 2012; *Shang* et al., 2018], but disagree with others [*McElmurry* et al., 2014]. Similarly, the positive relationship we report with [DOC] and % urban in the MLR is observed in some data sets [*Aitkenhead-Peterson* et al., 2009; *Alvarez-Cobelas* et al., 2012; *Hosen* et al., 2014] and not in others [*McElmurry* et al., 2014]. The MLR in this study does not consider % forest, but a scatter plot shows no clear trend with [DOC] (**Figure S3**). In other studies % forest has been both positively [*McElmurry* et al., 2014] and negatively correlated to [DOC] [*Frost* et al., 2006; *Graeber* et al., 2012]. Inconsistent trends in the literature is unsurprising given that data sets include vastly different study sites. For example, McElmurry *et al.* [2014] sampled surface runoff and therefore trends may not be transferrable to other water types. In addition, the types of statistics applied across data sets vary substantially with some groups using simple linear regressions [*Aitkenhead-Peterson* et al., 2009; *Cawley* et al., 2014; *Eckhardt and Moore*, 1990] and others using MLRs [*Alvarez-Cobelas* et al., 2012; *Clark* et al., 2004; *Dillon and Molot*, 1997; *Flint and McDowell*, 2015; *Frost* et al., 2006; *Graeber* et al., 2012; *Hanley* et al., 2013; *Mattsson* et al., 2005; *McElmurry* et al., 2014; *Shang* et al., 2018; *Xenopoulos* et al., 2003]. Even among the studies including MLRs, the input variables vary widely and likely affect the results.

Increases in [DOC] may be attributable to increased inputs from either terrestrial or microbial sources. For example, the increase in [DOC] observed with % wetland or % agriculture could be due to increased terrestrial inputs from runoff through vegetation across that landscape.

Alternatively, excess nutrients in agricultural runoff may stimulate autotrophic organisms which produce organic carbon within the water column. Without considering the composition of DOM, it is not possible to distinguish between these or other possibilities.

3.1.2 Seasonal Variability

Seasonality is also an important factor for $\log_{10}$ [DOC]. Mean [DOC] in the tributaries increases in the order of winter < summer < spring < fall with values of 10.6, 11.9, 13.5, and 15.5 mg-C L^{-1}, respectively (**Figure 3a**). It is interesting to note that the order of [DOC] does not follow a chronological order with the seasons. Results of the MLR indicate that [DOC] in the summer and winter is lower than in fall ($p = 4.75 \times 10^{-4}$ and 1.33×10^{-4}, respectively; **Table S1**). The different slopes between [DOC] and the landcover types show the importance of seasonal variability of [DOC] (**Figure 2a**), with steeper slopes corresponding to greater seasonal variation. In particular, the steepest slope for [DOC] versus % wetland is observed for the fall samples, while more shallow slopes are observed for the other seasons (**Figure 2a**).

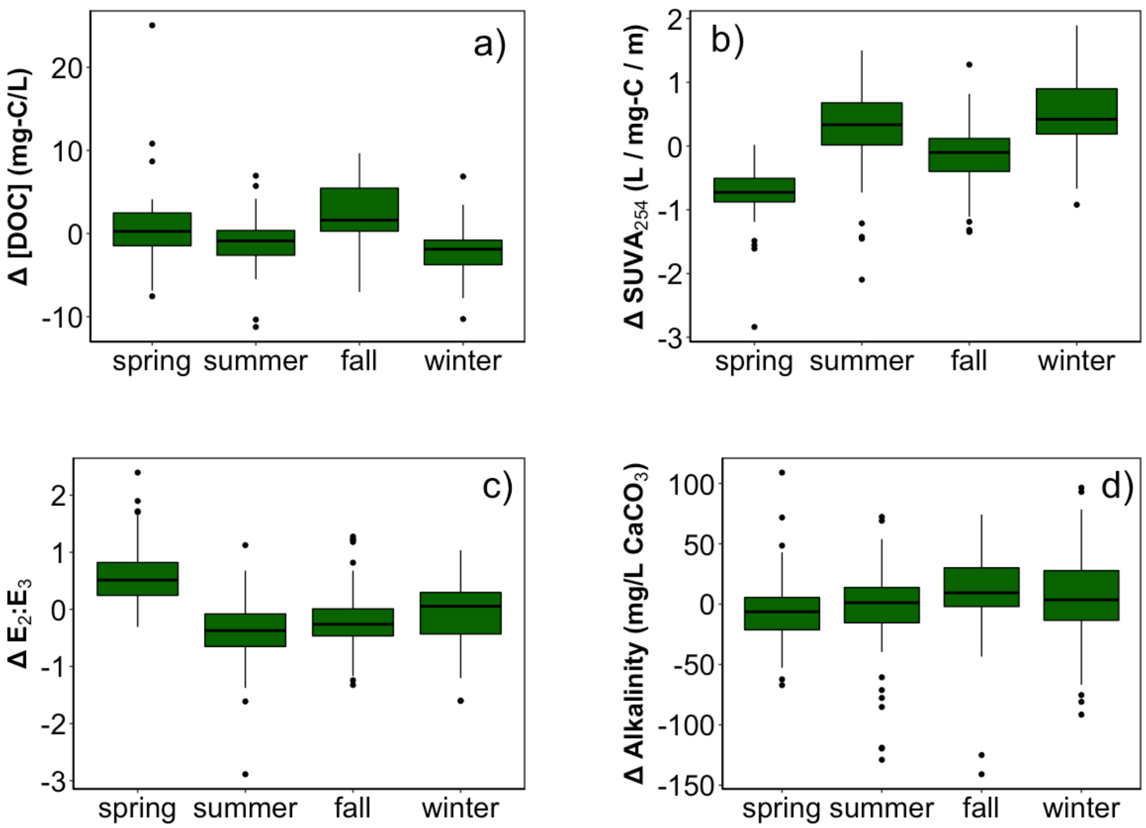

Figure 3. Box and whisker plots for differences (Δ) between the value measured in a particular season and the mean across all four seasons for that tributary for a) [DOC], b) SUVA$_{254}$, and c) E$_2$:E$_3$ and d) alkalinity. Only tributaries sampled in all four seasons are included.

Elevated [DOC] is frequently observed in the fall [*Aulló-Maestro* et al., 2017; *Dawson* et al., 2011; *Flint and McDowell*, 2015; *Liu* et al., 2014; *Mattsson* et al., 2015; *McCabe and Arnold*, 2016; *Mulholland and Hill*, 1997; *Oni* et al., 2014], which may be attributable to organic matter leaching from increased leaf litter. It has also been proposed that detritovores are most active in the fall and release [DOC] to the water column [*Mulholland and Hill*, 1997]. Increases in the relative amount of terrestrial DOM is consistent with these hypotheses but cannot be assessed fully considering [DOC] alone. The smaller amount of [DOC] observed in the winter samples may be consistent with either lower terrestrial inputs during this season or decreased microbial activity from autotrophs during the colder months.

3.2 DOM Composition

3.2.1 Spatial Variability

Carbon quality is assessed by measuring the optical properties $SUVA_{254}$ and E_2:E_3. $SUVA_{254}$ is positively related to DOM aromaticity measured using nuclear mangetic resonance spectroscopy [*Weishaar* et al., 2003] and high-resolution mass spectrometry [*Maizel and Remucal*, 2017]. High $SUVA_{254}$ values are indicative of more terrestrially-sourced and less processed DOM [*Weishaar* et al., 2003]. $SUVA_{254}$ ranges from 0.35 to 4.95 L mg-C^{-1} m^{-1}. Generally, the highest $SUVA_{254}$ values are observed in tributaries draining into the northwest side of the lake (**Figure S4**). E_2:E_3 is inversely proportional to the average molecular weight of DOM determined using direct measurements such as sequential ultrafiltration [*Maizel and Remucal*, 2017] and size exclusion chromatograpy [*Helms* et al., 2008]. Higher E_2:E_3 values are indicative of more aquatically-sourced DOM or terrestrially-sourced DOM that has undergone extensive environmental processing [*Helms* et al., 2014]. E_2:E_3 ranges from 3.6 to 12.0, with high values observed on the East and West side of the lake (**Figure 1b**).

The reduced MLR for $SUVA_{254}$ includes the season, % agriculture, % urban, and % wetland, along with interaction terms between the watershed area and both % urban and wetland (**Table S2**). Wetland landcover type has the strongest positive effect on $SUVA_{254}$ (**Figure 2b**; **Table S2**). The model shows that agricultural and urban landcover types also increase $SUVA_{254}$, but the negative interaction terms specify that these relationships become less important as the size of the watershed increases (**Table S2**). Smaller watersheds may be less influenced by wetland landcover type, resulting in % agriculture and % urban having a greater effect because there is less overall area of wetland possible.

E_2:E_3 is primarily controlled by season, but the MLR does include terms for % wetland and watershed size as well (**Table S3**). There is a positive estimate for % wetland accompanied with a negative interaction term between % wetland and watershed area, which indicates that the effect of % wetland is reduced as the size of the watershed increases because other landcover types may become more influential (**Figure S7**; **Figure S8**; **Table S3**).

$SUVA_{254}$ and E_2:E_3 are generally inversely proportional to one another [Fichot & Benner, 2011]' and that is also true in this data set. With the exception of herbaceous landcover, all relationships of landcover type to $SUVA_{254}$ are inverse those of E_2:E_3 (**Figure S5**; **Figure S6**). However, since this landcover type was not included in the MLR, this observation is based on simiple linear regressions alone. This opposing relationship is not obvious considering the MLR results alone as the MLR for $SUVA_{254}$ and E_2:E_3 include differing terms (**Table S2**; **Table S3**). This result may be attributable to the fact that optical properties depend on both the source of the carbon and the extent of environmental processing the DOM has undergone.

Overall the optical properties describing the composition of DOM show less significant spatial variability than [DOC]. Overwhelmingly the literature supports our observation that terrestrially-sourced DOM is consistently and positively correlated to % wetland using UV-vis spectroscopy [*Hanley* et al., 2013] or fluorescence spectroscopy [*Graeber* et al., 2012; *Singh* et al., 2017; *Williams* et al., 2010]. This observation is due to the large amount of plant-derived (i.e., allochthonous) carbon present in wetlands that can be carried into the tributaries. In addition, this carbon is fresh and therefore has had little opportunity to undergo environmental processing, which generally results in decreased aromaticity [*Helms* et al., 2013; *Minor* et al., 2007]. Terrestrially-sourced DOM has also been correlated to other landcover types in the literature including % agriculture using UV-vis [*McElmurry* et al., 2014], and fluorescence spectroscopy [*Graeber* et al., 2012], as well as to % forest using UV-vis [*McElmurry* et al., 2014], and fluorescence spectroscopy [*Singh* et al., 2017]. Microbially-sourced (i.e., authochthonous) DOM or more environmentally processed DOM, which is represented with high E_2:E_3 values in this study, has been correlated to % forest with fluorescence spectroscopy [*Heinz* et al., 2015], to % urban with both UV-vis [*McElmurry* et al., 2014] and fluorescence spectroscopy [*Chen* et al., 2017; *Hosen* et al., 2014; *Lu* et al., 2014], and to % agriculture with UV-vis spectroscopy [*Shang* et al., 2018]·

3.2.1 Seasonal Variability

Seasonality has important effects on both $SUVA_{254}$ and E_2:E_3. Mean $SUVA_{254}$ values increase in order of spring < fall < summer < winter, with values of 1.98, 2.49, 2.95, and 3.10 L mg-C^{-1} m^{-1}, respectively (**Figure 3b**). The MLR for $SUVA_{254}$ similarly demonstrates that values in the spring are lower and values in summer and winter are higher than those in the fall (**Table S2**). Seasonal means for E_2:E_3 increase in order of summer < fall < winter < spring, with values of 5.70, 5.92, 6.02, and 6.71, respectively (**Figure 3c**). In the MLR, values in spring are lower than those in the fall (**Table S3**).

Compared to carbon concentrations, much more seasonal variation is observed in both of the optical properties measuring carbon composition. The lowest $SUVA_{254}$ and highest E_2:E_3 values are observed in the spring. While there are many studies that consider [DOC], far fewer data sets include information about DOM composition. A range of seasonal effects have been reported for DOM composition ranging from no effects observed using fluorescence spectroscopy [*Heinz* et al., 2015], to decreasing $SUVA_{254}$ over the warm months (i.e., spring to fall) [*McCabe* *and Arnold*, 2016; *Müller* et al., 2014] increasing absorbance during the spring snowmelt [*Cao* et al., 2016; *Macdonald and Minor*, 2013], and higher E_2:E_3 in the winter as compared to summer [*Yates* et al., 2016]. Likely, these mixed relationships are due to complex interactions between landcover types and seasonality, as well as the possibility that different frameworks may be necessary to describe DOM compositional dynamics in different climates.

Sources of DOM and environmental processing of DOM are often important drivers of compositional changes. High $SUVA_{254}$ values in the fall can be partially explained by increased leaching from leaf litter during this season [*Mulholland and Hill*, 1997]. This may also explain our observations of high E_2:E_3 and low $SUVA_{254}$ in the spring when vegetation is minimal in this region. Microbial activity also alters DOM composition in the environment. Generally, both heterotrophic respiration of DOM and autotrophic production of DOM produces DOM with higher E_2:E_3 and lower $SUVA_{254}$ [*Bai* et al., 2017; *Mulholland and Hill*, 1997; *Zhou* et al., 2019]. In the context of our data set, optical properties are consistent with both decreased terrestrial inputs and increased microbially activity in the spring. Photobleaching is another process that results in decreased $SUVA_{254}$ and increased E_2:E_3 [*Aulló-Maestro* et al., 2017; *Brinkmann* et al., 2003; *Cory* et al., 2007; *Helms* et al., 2008, 2014; *Macdonald and Minor*, 2013; *Minor and Stephens*, 2008; *Vodacek* et al., 1997], and rates may be fastest in the spring when there is little canopy cover to block solar irradiation within tributaries. However, if this were the only driving factor, low $SUVA_{254}$ and high E_2:E_3 would also be expected in the winter. Results from winter are interesting as relatively high values for both optical properties were observed in this season potentially due the presence of small, aromatic compounds or, alternatively, large compounds that are not aromatic.

3.3 Alkalinity

Alkalinity is a measurement for DIC because carbonate species are the main buffering components in natural waters [*Stumm*, 1996]. In this study, alkalinity ranges from 11.6 - 468 mg L^{-1} as $CaCO_3$, with a mean of 197 mg L^{-1} as $CaCO_3$. Tributaries on the southeastern side of the lake have typically higher alkalinity values (**Figure S9**).

Alkalinity appears to correlate with landcover types (**Figure S10**). The reduced model for alkalinity includes terms for % agriculture, % urban, area of the watershed, and an interaction term between % agriculture and area of the watershed (**Table S4**). Although not explicitly tested in this study, it is likely that geology plays an important role in alkalinity, particularly in tributaries that are impacted by groundwater. In our study, the highest alkalinity values are observed in the southeastern side of Lake Michigan (**Figure S9**), which is also the area where the most limestone beds are found [*Shedlock* et al., 1993]. Others have documented increased [DIC] in streams that flow over limestone sediments [*Mosher* et al., 2010]. Means for alkalinity increase in the order of spring < summer < winter < fall (**Figure 3d**). However, no seasonal effects are found to be significant via in the MLR, which is consistent with geology, rather than landcover type being the main driver of alkalinity (**Table S4**).

3.4 Spatial/Seasonal Comparison

One of the primary objectives of this study is to compare spatial versus seasonal effects on both carbon concentration and composition. From the MLRs, it is clear that spatial terms, or terms describing landcover type in the watershed, play a larger role in predicting concentration parameters (i.e., [DOC] and alkalinity), while seasonal terms are more important in predicting compositional parameters (i.e., $SUVA_{254}$ and E_2:E_3). In fact, only seasonal main effects are reported for the E_2:E_3 MLR when terms with complex interactions are not considered. To further analyze these interactions, we calculate coefficients of variation for standard deviation of means from each season across all tributaries ($CV_{seasonal}$) and compare them to coefficients of variation for means of each tributary calculated across all four seasons ($CV_{spatial}$; **equations 1 and 2**).

$CV_{spatial}$ = standard deviation of tributary means / mean of entire data set * 100 (**eq 1**)

$CV_{seasonal}$ = standard deviation of seasonal means / mean of entire data set * 100 (**eq 2**)

To prevent bias, only those tributaries that were sampled in all four seasons are included in this analysis. For all four parameters tested, $CV_{spatial} > CV_{seasonal}$ (**Figure 4**). However, the difference between these values is much smaller for the compositional parameters $SUVA_{254}$ and $E_2:E_3$. From this we conclude that seasonal variation is more important for DOM composition than it is for concentration.

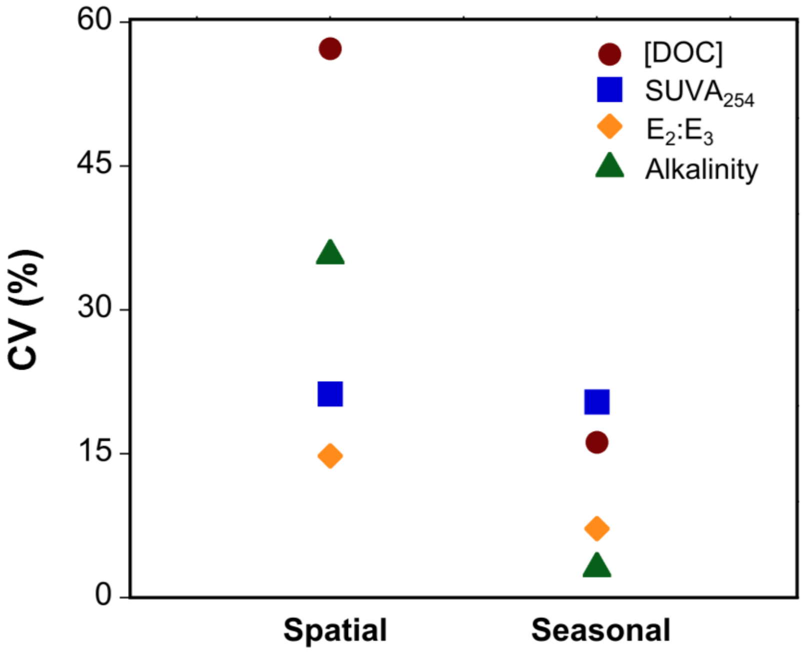

Figure 4. Coefficients of variation, $CV_{spatial}$ and $CV_{seasonal}$, for [DOC], alkalinity, $SUVA_{254}$, and $E_2:E_3$ measured in tributaries that were sampled in all four seasons.

Carbon source and environmental processing can both alter [DOC] and composition. In our study, landcover types do not vary temporally but notably, microbial activity and vegetation on these landcover types do vary throughout the year. Environmental processing, although not directly measured here, is likely represented through seasonal variation where observations of [DOC] and composition variability cannot be explained through differences in landcover types. For [DOC] and alkalinity, $CV_{spatial} >> CV_{seasonal}$, which indicates that landcover type is the largest controlling factor. The fact that values of $CV_{spatial}$ are much more similar to those of $CV_{seasonal}$ for the composition parameters $SUVA_{254}$ and $E_2:E_3$ indicates that environmental processing and the relative abundance of terrestrial plants, which can vary temporally in the context of our study, play a larger role for these parameters. Changes in carbon concentration require either removal through processes such as gaseous fluxes and sedimentation or through redox reactions involving reduction of carbonate species or complete mineralization of DOM. In contrast, multiple biological or chemical reactions can convert one form of DOM to another, which would alter composition but not overall [DOC], and may explain why seasonality has a larger effect on DOM composition than concentration in this study.

4. Conclusions

Both concentration and composition of carbon forms vary widely in Lake Michigan tributaries. Our results show that landcover type plays a strong role in dictating carbon concentrations, as well as composition. Seasonal variation influences $SUVA_{254}$ and $E_2:E_3$ (i.e., composition terms) more significantly than it influences [DOC] or alkalinity (i.e., concentration terms). The highest [DOC] values are observed in watersheds with high wetland landcover in the fall, while the lowest [DOC] values are observed in watersheds with minimal wetland landcover in the winter. $SUVA_{254}$ also increases with increasing wetland landcover while relationships for

E_2:E_3 are more complex. Our unique data set also demonstrates that complex interactions exist between watershed attributes and seasons that only become clear in large data sets. Furthermore, our data set shows that both spatial and seasonal variation can be important and that interpreting one without the other may yield conclusions that are not transferrable.

Understanding carbon dynamics in the environment has important implications for many global cycles, as well as reactions that dictate contaminant fate. Increasingly, attention is being paid to carbon fluxes between surface waters [*Cory* et al., 2014; *Jaffé* et al., 2008; *Ward* et al., 2017]. These reactions take place via oxidation through both chemical pathways, such as photooxidation, and heterotrophic biological pathways. Importantly, both processes are affected by the composition of DOM [*Cory and Kaplan*, 2012; *Lusk and Toor*, 2016a, 2016b; *Parr* et al., 2015]. For example, waters with higher SUVA$_{254}$ values are more susceptible to photobleaching due to greater overlap with the solar spectrum [*Brinkmann* et al., 2003; *Helms* et al., 2014].

Complicating all these relationships is the fact that landscapes across the globe are changing rapidly and this comes with important implications for carbon in the environment. In this study, we observe that landcover types affect [DOC] and DOM composition. Therefore, as urbanization increases, we should expect to see corresponding changes in DOM and optical properties. Based on this study, decreases in concentration, color, and molecular size are expected to accompany urbanization. Our large data set reveals how spatial and seasonal variability influence DOM concentration and composition. The diverse samples included in our study likely make our conclusions transferrable to other study sites within similar climates.

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Supplementary information

Text S1.

Due to instrument malfunction, the [DOC] in sites 1-69 from the Spring samples were not measured and too little volume was left to measure again. Frozen archive samples were saved and these samples were thawed, re-filtered through 0.45 um (nylon, Agilent) filters and rerun on the instrument. However, it remained unclear if the thawing and re-filtering would have an effect on [DOC]. To determine this, we also thawed and re-filtered 20 samples from the October sampling trip to compare to their original [DOC] (Figure S1). About 23% of [DOC] was lost during this process.

To determine if there was any preferential loss of [DOC] based on composition, we also compared E_2:E_3 values of 20 original October samples and from those that had been thawed and re-filtered (Figure S2).

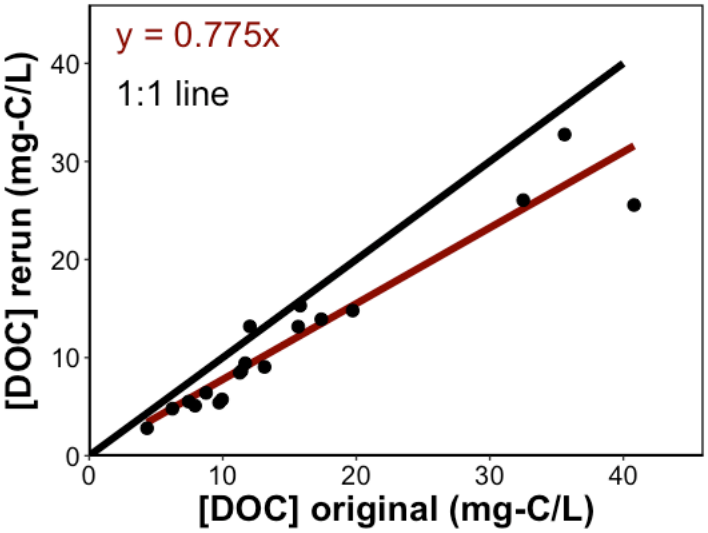

Figure S1. Comparison between [DOC] measured in October 2016 samples originally and in aliquots of the samples that had been thawed and re-filtered.

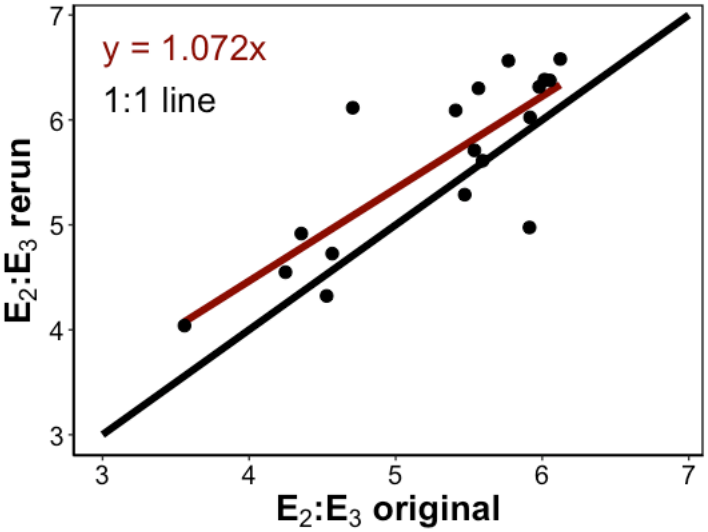

Figure S2. Comparison between E_2:E_3 measured in October 2016 samples originally and in aliquots of the samples that had been thawed and re-filtered.

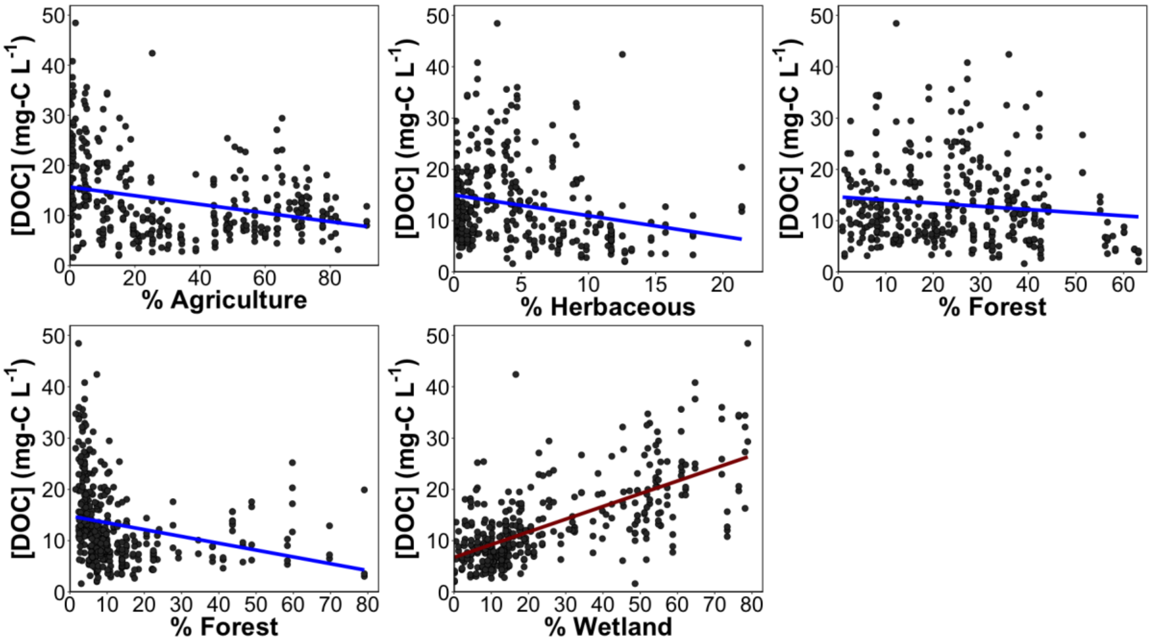

Figure S3. Scatter plots of [DOC] and landcover types for all samples collected. Blue regression lines indicate a negative slope and red regression lines indicate a positive slope.

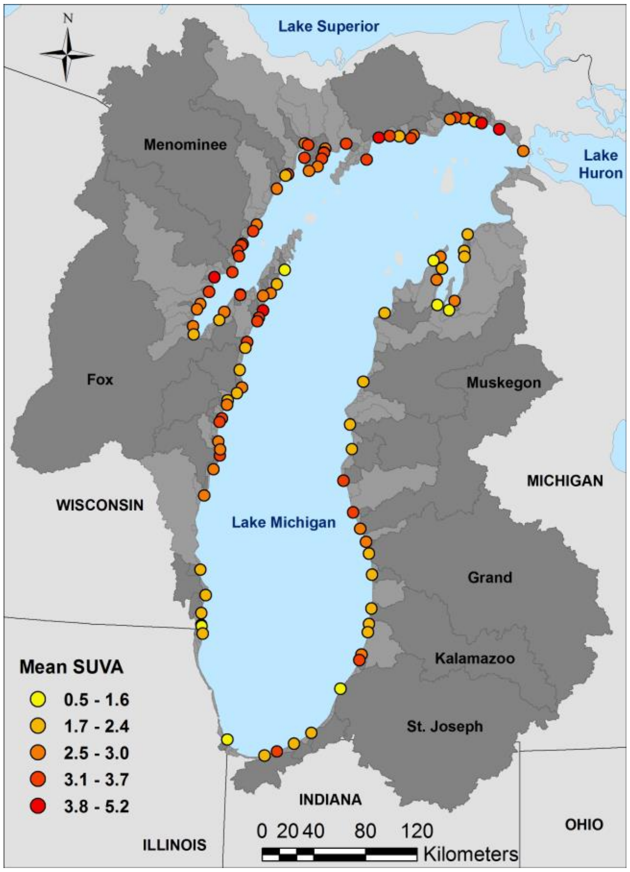

Figure S4. Mean SUVA$_{254}$ values in Lake Michigan tributaries for all samples collected.

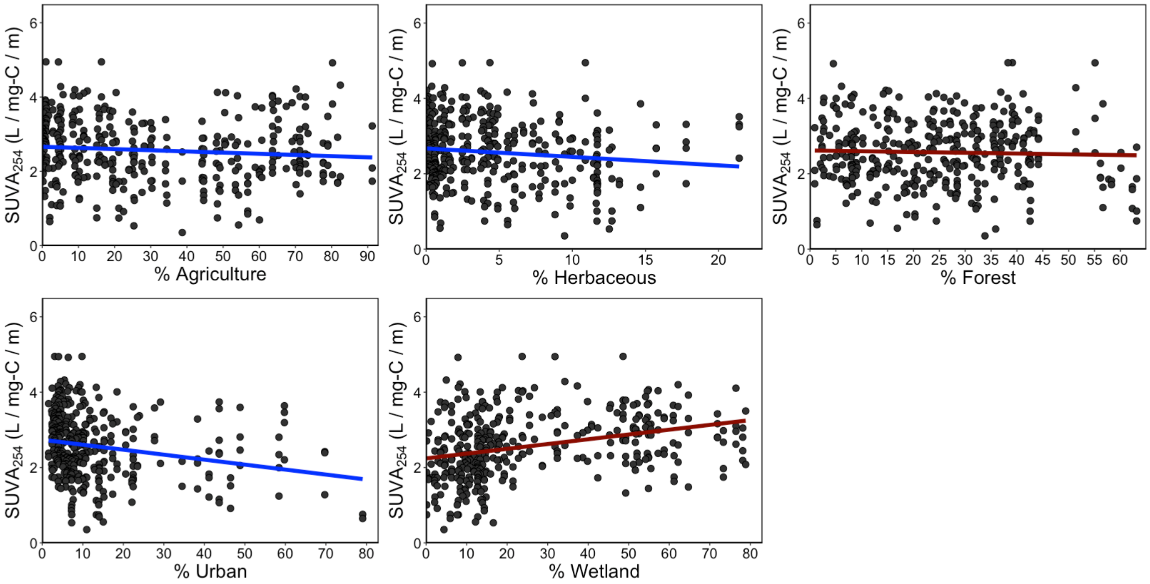

Figure S5. Scatter plots of SUVA$_{254}$ and landcover types for all samples collected. Blue regression lines indicate a negative slope and red regression lines indicate a positive slope.

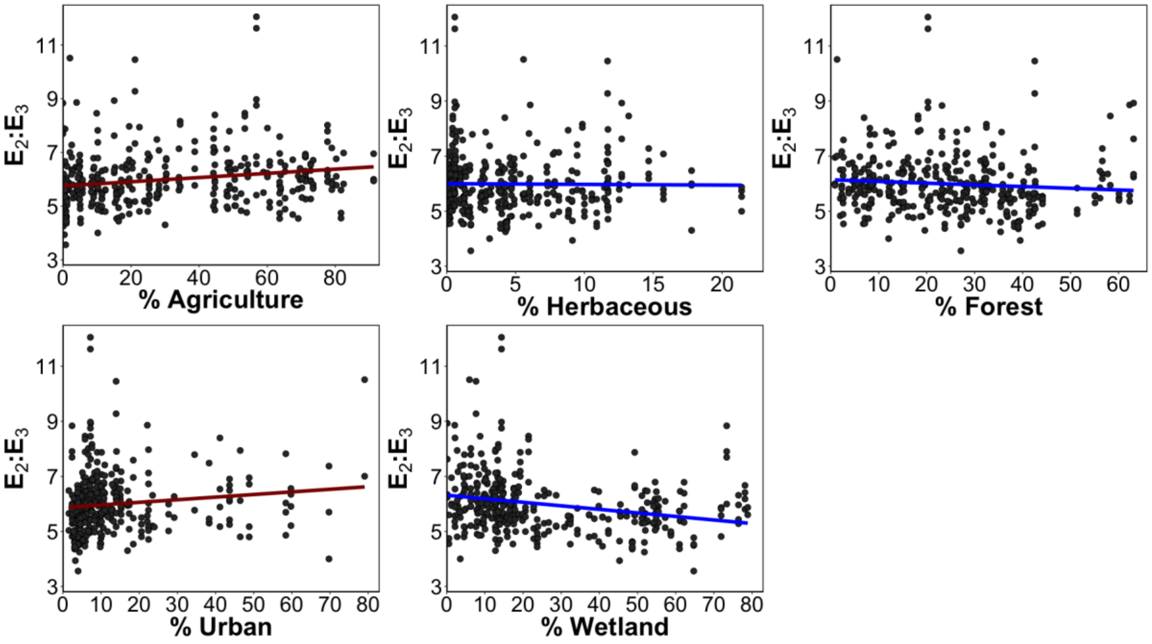

Figure S6. Scatter plots of E_2:E_3 and landcover types for all samples collected. Blue regression lines indicate a negative slope and red regression lines indicate a positive slope.

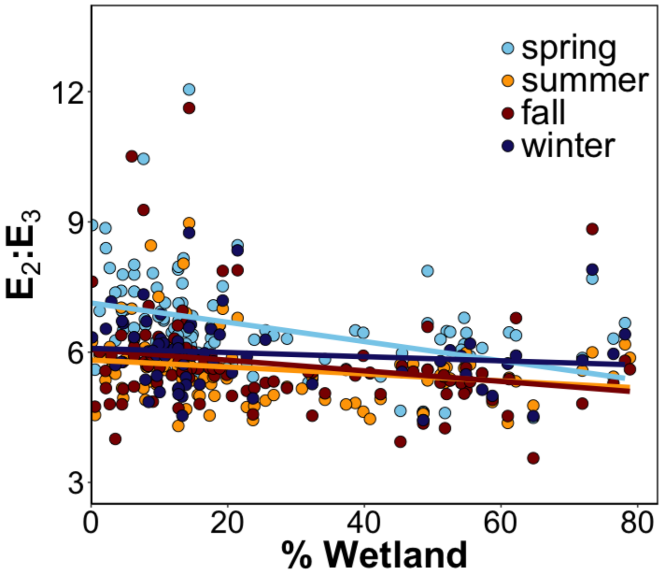

Figure S7. E_2:E_3 versus % wetland in the watershed. Colors indicate season. Only tributaries that were measured in all four seasons are included.

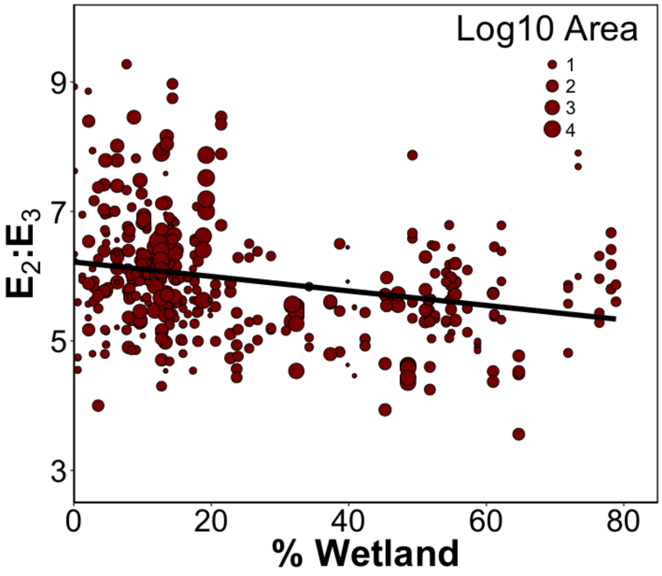

Figure S8. E_2:E_3 versus % wetland for samples collected in all 4 seasons. The size of the point is proportional to the size of the watershed.

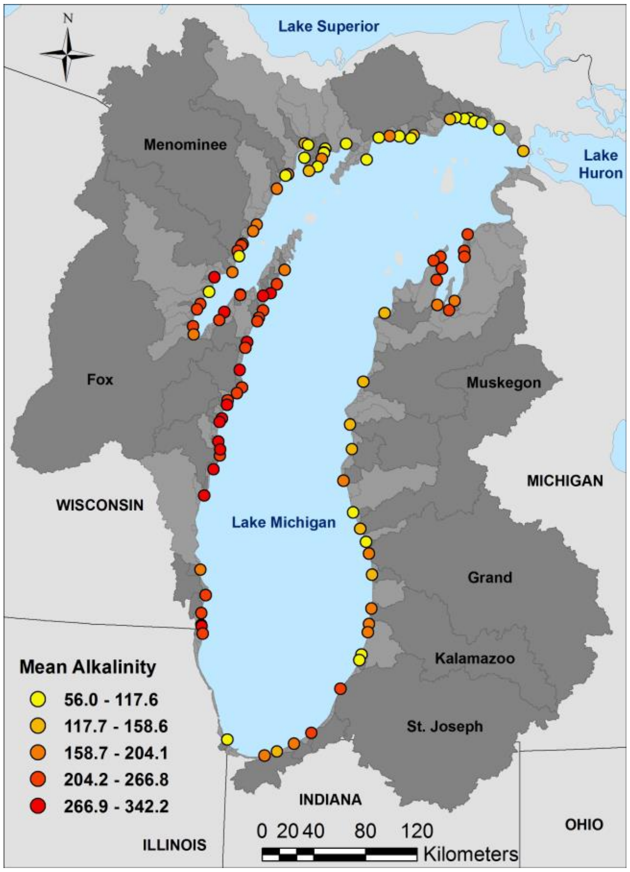

Figure S9. Mean alkalinity values in Lake Michigan tributaries for all samples collected. Alkalinity is reported in units of mg L^{-1} as $CaCO_3$.

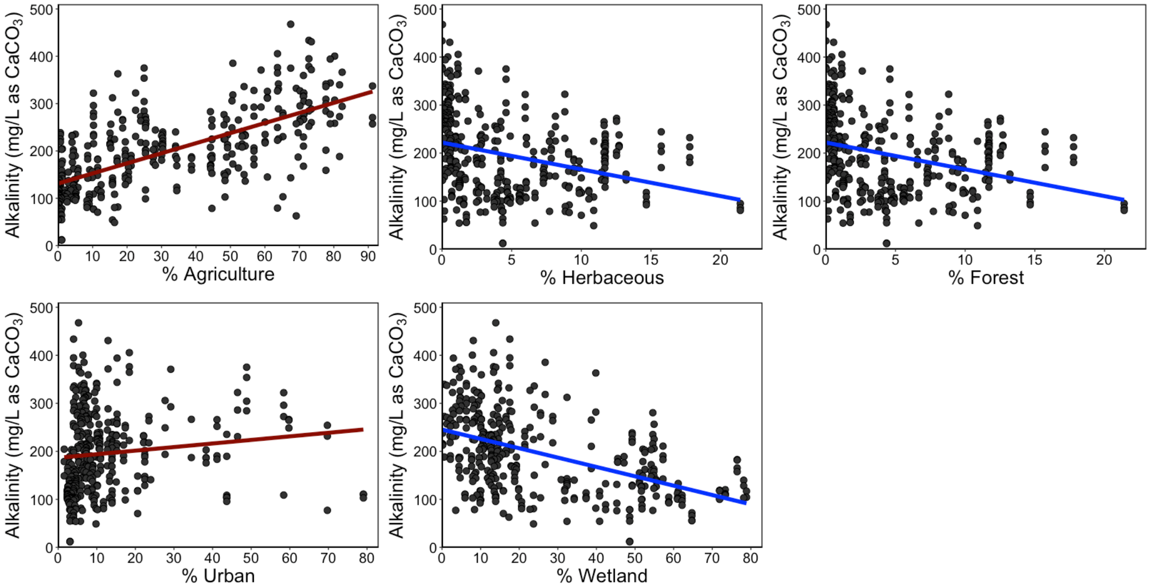

Figure S10. Scatter plots of alkalinity and landcover types for all samples collected. Blue regression lines indicate a negative slope and red regression lines indicate a positive slope.

Table S1. Results of [DOC] MLR. Multiple $R^2 = 0.5535$, Adjusted $R^2 = 0.5412$, $p < 2.2 \times 10^{-16}$.

	Estimate	**Std. Error**	**t value**	**p**
Intercept	5.72×10^{-1}	5.77×10^{-2}	9.90	$< 2 \times 10^{-16}$
% agriculture	4.10×10^{-3}	7.54×10^{-4}	5.44	1.42×10^{-7}
spring	-1.49×10^{-2}	3.56×10^{-2}	-4.18×10^{-1}	6.76×10^{-1}
summer	-1.26×10^{-1}	3.56×10^{-2}	-3.55	4.75×10^{-4}
winter	-1.38×10^{-1}	3.56×10^{-2}	-3.89	1.33×10^{-4}
% urban	6.42×10^{-3}	1.19×10^{-3}	5.39	1.85×10^{-7}
% wetland	1.22×10^{-2}	8.84×10^{-4}	13.8	$< 2 \times 10^{-16}$

Table S2. Results of $SUVA_{254}$ MLR. Multiple $R^2 = 0.4464$, Adjusted $R^2 = 0.4227$, $p < 2.2 \times 10^{-16}$.

	Estimate	**Std. Error**	**t value**	**p**
Intercept	9.54×10^{-2}	5.55×10^{-2}	1.72	8.74×10^{-2}
% agriculture	3.67×10^{-3}	9.92×10^{-4}	3.70	2.76×10^{-4}
$\log_{10}$ area	7.89×10^{-2}	2.09×10^{-2}	3.78	2.05×10^{-4}
spring	-1.06×10^{-1}	2.52×10^{-2}	-4.20	4.01×10^{-5}
summer	8.76×10^{-2}	2.52×10^{-2}	3.48	6.04×10^{-4}
winter	1.23×10^{-1}	2.51×10^{-2}	4.92	1.79×10^{-6}
% urban	5.20×10^{-3}	1.48×10^{-3}	3.52	5.29×10^{-4}
% wetland	3.51×10^{-3}	6.64×10^{-4}	5.30	2.99×10^{-7}
% agriculture: $\log_{10}$ area	-1.59×10^{-3}	4.46×10^{-4}	-3.58	4.29×10^{-4}
$\log_{10}$ area: % urban	-2.61×10^{-3}	9.36×10^{-4}	-2.79	5.72×10^{-3}

Table S3. Results of alkalinity E_2:E_3. Multiple $R^2 = 0.506$, adjusted $R^2 = 0.4965$, $p < 2.2 \times 10^{-16}$.

	Estimate	**Std. Error**	**t value**	**p**
Intercept	7.43×10^{-1}	1.50×10^{-2}	49.5	$< 2 \times 10^{-16}$
$\log_{10}$ area	2.75×10^{-2}	7.10×10^{-3}	3.88	1.39×10^{-4}
spring	5.69×10^{-2}	1.18×10^{-2}	4.80	2.85×10^{-6}
summer	-1.24×10^{-2}	1.19×10^{-2}	-1.04E	3.00×10^{-1}
winter	1.13×10^{-2}	1.19×10^{-2}	9.43×10^{-1}	3.47×10^{-1}
% wetland	1.05×10^{-3}	4.52×10^{-4}	2.33	2.08×10^{-2}
$\log_{10}$ area: % wetland	-1.29×10^{-3}	2.90×10^{-4}	-4.44	1.43×10^{-5}

Table S4. Results of alkalinity MLR. Multiple $R^2 = 0.506$, adjusted $R^2 = 0.4965$, p < 2.2 x 10-16.

	Estimate	**Std. Error**	**t value**	**P**
Intercept	2.19	3.77×10^{-2}	58.1	$< 2 \times 10^{-16}$
% agriculture	3.57×10^{-3}	9.13×10^{-4}	3.91	1.27×10^{-4}
$\log_{10}$ area	-1.02×10^{-1}	2.12×10^{-2}	-4.82	2.72×10^{-6}
% urban	3.30×10^{-3}	8.39×10^{-4}	3.93	1.16×10^{-4}
% agriculture: $\log_{10}$ area	1.34×10^{-3}	4.87×10^{-4}	2.74	6.61×10^{-3}

Text S.2. The S.1 file contains all raw data used in the models and for the figures. The variable names and units (if applicable) are:

Parameter	-the parameter measured. alk, doc, suva, and e2e3 correspond to alkalinity, [DOC], $SUVA_{254}$, and E_2:E_3, respectively.
Season	-the season the measurement was taken
Value	-the value of the measurement. Units are mg L^{-1} as $CaCO_3$, mg-C L^{-1}, L mg-C^{-1} m^{-1}, and unitless for alkalinity, [DOC], $SUVA_{254}$, and E_2:E_3, respectively.
Hydroid	-unique identifier code for the tributary used to make maps.
Urban	-the percentage of urban landcover in the watershed of the sampled tributary
Barren	-the percentage of barren landcover in the watershed of the sampled tributary
Forest	-the percentage of forest landcover in the watershed of the sampled tributary
Shrubland	-the percentage of shrubland landcover in the watershed of the sampled tributary
Herbaceous	-the percentage of herbaceous landcover in the watershed of the sampled tributary
Ag	-the percentage of agricultural landcover in the watershed of the sampled tributary
Wetland	-the percentage of wetland landcover in the watershed of the sampled tributary
Area	-the area of the watershed of the sampled tributary with units of km^2

Part II: Lake hydrodynamics intensify the potential impact of watershed pollutants on coastal ecosystem services

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Abstract

Watersheds deliver numerous pollutants to the coastline of oceans and lakes, thereby jeopardizing ecosystem services. Regulatory frameworks for stressors often focus on loading rates without accounting for the physical dynamics of the receiving water body. Here, we use a three-dimensional hydrodynamic model to simulate the transport of a tributary-delivered pollutant within Lake Michigan based on the location and timing of loading. Simulating pollutant plumes from 11 rivers, and their intersections with coastal ecosystem services, reveals strong mediation of potential impacts by lake physics. Trapped pollutants accumulate in nearshore waters during spring peak flows, and become diluted by spreading offshore during the summer. The threat to coastal ecosystem services posed by pollutant loading differs sharply among rivers; high potential impact arises from the spatiotemporal coincidence of tributary input rates, lake mixing dynamics, and multiple human uses of the shoreline. Simultaneous pollution from multiple rivers yields overlapping plumes, creating a second way in which lake hydrodynamics can amplify potential impacts on coastal ecosystem services. Our simulations demonstrate that the physical dynamics of large water bodies can create a dynamic stressor landscape arising from multiple independent sources of non-point-source pollution. The design and implementation of

pollution regulations rarely account for spatial and temporal complexities of load processing in receiving waters, yet the resulting variability is likely to strongly mediate impacts on society. As hydrodynamic models improve, our analytical framework could be applied to a wide range of pollutants and waterbodies to enhance the sustainable use of coastal ecosystems.

Introduction

The coastlines of oceans and large lakes are often severely stressed (Millennium Ecosystem Assessment 2005, Diaz and Rosenberg 2008, Halpern *et al* 2008, Allan *et al* 2013), in part due to chemical pollution from tributary watersheds. In parallel, human use of large water bodies is concentrated along the coasts, especially near inflowing rivers (Allan *et al* 2015). The spatial coincidence of tributary-delivered pollution and human reliance on coastlines raises the possibility of widespread impacts on key ecosystem services. Moreover, coastal ecosystems have less dilution capacity than deeper offshore waters, so pollution from watersheds can become concentrated when trapped or transported along the coast (Hoffman and Hittinger 2017). These mixing dynamics of coastal waters are highly dynamic in space and time (Holland and Kay 2003, Rao and Schwab 2007), as are the concentration and timing of pollutant inputs delivered by tributary rivers (Dolan and Chapra 2012).

Ideally, limits on pollutant loading to coastal waters should account for the spatial and temporal dynamics of both inputs from watersheds and processing within receiving water bodies. Under the United States' Clean Water Act, limits on pollutant loading are expressed as Total Maximum Daily Loads (TMDLs). While thousands of TMDLs have been developed in the United States (EPA 2019), few are developed for large lakes or marine coastal areas with complex hydrodynamics, with some exceptions such as Chesapeake Bay (EPA 2010). Many of these waters are under the jurisdiction of more than one state, which complicates selection of targets, allocation of pollutant limits, and coordination of technical development and implementation through regulatory programs. In addition, the complexity of modeling pollutant transport and its effect on ecosystem processes and human uses may delay or deter integrating it into regulatory frameworks. For example, the 2012 Great Lakes Water Quality Agreement (United States and Canada 2012) between the United States and Canada sets forth a goal of reviewing and updating the phosphorus loading targets for each Great Lake for the purpose of meeting multiple ecosystem objectives, most of which are related to eutrophication. As of 2019, targets have only been updated for Lake Erie, and the parties have recognized gaps in knowledge of the distribution and movement of nutrients between nearshore and offshore zones in Lakes Ontario, Huron, and Michigan (United States and Canada 2019a).

The Great Lakes of North America offer a particularly ideal setting for evaluating the implications of the physical dynamics of large receiving waters for TMDL-type regulatory paradigms. Along their extensive coastlines, there is enormous spatiotemporal variation in tributary pollutant inputs, hydrodynamics of the receiving water body, and reliance on ecosystem services. The stakes are high for managing pollution of these massive lakes, which hold 84% of North America’s surface fresh water (21% of the global total), support nearly 1.5 million jobs, and engender $8B in annual recreational expenditures (Vaccaro and Read 2011). For local communities, including many major cities, these coastlines offer potable water, fisheries, cooling water for power plants, and a wide range of aesthetic and recreational benefits (Allan *et al* 2015). Threats to these ecosystem services from harmful algal blooms, hypoxia, toxic chemicals, and species invasions inspired the ongoing Great Lakes Restoration Initiative (GLRI) in the United States, which spent $2.3B from 2010-2017 to enhance ecosystem health (EPA 2017). Nonetheless, closures of swimming beaches and municipal drinking water intakes remain a regular occurrence due to pollution from industrial facilities, agricultural landscapes, and urban centers.

TMDL-type regulatory paradigms often focus on the sources and dynamics of pollution, but they also have the potential to incorporate understanding of how lake physics mediate the propagation of pollutants in space and time within large aquatic ecosystems. The depth and thermal structure of lakes creates three-dimensional heterogeneity in water density that can foster either rapid dilution by mixing or the trapping of a pollutant entering from a particular location (Auer and Gatzke 2004, Makarewicz *et al* 2012, Yurista *et al* 2015). Each of the Great Lakes shows a pronounced annual cycle in its thermal structure (Boyce *et al* 1989, Beletsky and Schwab 2001), changing from vertically mixed in winter to vertically stratified and laterally mixed in summer. Prior to the onset of summer stratification, spring surface warming of the shallow water column along the coast separates it from cooler water offshore. The convergence zone between the inshore and offshore water masses occurs at the temperature of maximum density (~4°C), and this “thermal bar” (Holland and Kay 2003, Bai *et al* 2013) acts as a barrier to their mixing. As the surface continues to absorb radiation and warms, the thermal bar dissipates, and is replaced by stable vertical stratification across the lake during the summer and early fall. These strong vertical versus lateral gradients of water temperature—and thus density—modify circulation patterns within each Great Lake (Gbah and Murthy 1998, Auer and Bub 2004, Rao and Schwab 2007, Makarewicz *et al* 2012) and can influence ecological functioning (Scavia and Bennett

1980). Both observations and models have illustrated the importance of these hydrodynamic patterns for coastal trapping of nutrients and contaminants (Spain *et al* 1976, Boyce *et al* 1989, Auer and Bub 2004, Auer and Gatzke 2004).

The Great Lakes have been the subject of relatively comprehensive analyses of the geography of both stressors and ecosystem services. Examples of tributary derived stressors include non-point sources such as suspended sediments, nutrients, and combined sewer overflow events or chemical pollution such as mercury, copper, and polychlorinated biphenyl compounds (PCBs). A synthesis of 34 anthropogenic stressors shows that cumulative stress is highest in coastal areas with high levels of human activity on shore and in upstream watersheds (Allan *et al* 2013). Similarly, Great Lakes coastlines are the focal point for many aspects of human use, representing high but spatially variable reliance on ecosystem services (Allan *et al* 2015). Thus, the Great Lakes offer a unique opportunity to integrate realistic spatiotemporal dynamics of pollutant inputs and in-lake transport with ecosystem service distributions to evaluate whether potential impacts on ecosystem services are closely related to watershed loading rates. By accounting for patterns of human use value (Allan *et al* 2015), such an integrative approach could enable pollution control programs to direct their efforts toward watersheds where loading patterns and lake hydrodynamics create the highest potential societal benefits from reducing coastal ecosystem degradation.

Here, we simulate the fate of watershed-derived pollutants in Lake Michigan by coupling a three-dimensional advection-transport model of Lake Michigan with input time series of a passive tracer from 11 different tributaries (Figure 1). Lake Michigan has a drainage area of

118,000 km^2, a retention time of 99 years, an average depth of 85 m, and a volume of 4920 km^3. Tracer input time series are based on phosphorus, an important anthropogenic pollutant. However, we are not attempting to simulate phosphorus concentrations which are modulated by complex biological interactions. Instead, we use this time history to represent a generic tributary-derived pollutant. Within the lake, the pollutant is modeled as a generic, conservative tracer that could represent any contaminant entering the lake via time-varying river flows. large-scale stressor assessments in the Great Lakes have overlooked the spatial and temporal variability of watershed-derived stressors, despite emphasizing their contribution to aggregate ecosystem stress status (Allan *et al* 2013). After developing realistic watershed input estimates, we then evaluate whether the seasonal hydrodynamics of a large receiving body lead to trapping, dilution, or transport of pollution. In addition to testing how the capacity of the lake to attenuate pollutant concentrations varies with the location of the river mouth, we overlay the pollution plumes from all 11 watersheds. Finally, we intersect the aggregate pollution distribution with maps of summertime use of various coastal ecosystem services. These spatial comparisons enable us to quantify the cumulative stress to services based on the duration and spatial extent of overlap between elevated pollutant concentrations and coastal ecosystem service locations, thereby focusing on the potential implications of pollution rather than its intensity per se.

Materials and Methods

Hydrodynamic Model Description

We used the Massachusetts Institute of Technology general circulation model (MITgcm) (Marshall *et al* 1997a, 1997b) configured to the bathymetry of Lake Michigan (National Geophysical Data Center 1996). For computational efficiency, the lake is modeled as a closed basin with a horizontal resolution of 1 minute (approximately 2 km) and 28 vertical levels. The thickness of vertical levels increases from 5 m at the surface to 31 m at the bottom. Sub-grid-scale processes are simulated via the K-Profile Parameterization (KPP) vertical mixing scheme (Large *et al* 1994) and the Smagorinsky horizontal diffusivity scheme (Smagorinsky 1963). Further discussion of the physical model and its validation can be found elsewhere (Bennington *et al* 2010, Pilcher *et al* 2015). The model solves the tracer transport tendency equation at each grid cell (Equation 1)

$$\frac{\partial C}{\partial t} = -(U \ \cdot \nabla)C + S + I \quad Equation\ 1$$

where $(U \ \cdot \nabla)C$ represents advection of a tracer volume concentration (C) by the three-dimensional flow field (U), S includes convective mixing and sub-grid parameterizations of mixing, and I represents time-varying tracer input from 11 tributaries (Figure 1). The tracer is neutrally buoyant, biologically inert, and non-interactive with the atmosphere, suspended particles, and bottom substrate. This approach allows us to focus on pollutant trapping and redistribution via hydrodynamics.

The model is forced at the surface using meteorological and radiative fields with a temporal resolution of 3 hours. Atmospheric downward shortwave and longwave radiation, air temperature, specific humidity, and wind stress are imposed at surface from the North American Regional Reanalysis Project (NARR) (Mesinger *et al* 2006). Daily lake ice fractions are taken from the U.S. National Ice Center (U.S. National Ice Center 2010). There is an established warm bias in the physical model due to both the NARR forcing and the ice mask (Bennington *et al* 2010, Pilcher *et al* 2015). Despite this known bias, NARR is selected due to its higher spatial resolution relative to other choices. The model is spun up for two years by repeating 2007 forcing to achieve a repeating annual cycle (Pilcher *et al* 2015), after which it is run for a four-year period (2007-2011). We focus our analysis on surface concentrations between May and August (Figure 2).

Simulated pollutant inputs are based on estimated daily histories of total phosphorus export for 11 rivers (Supplementary Figure 1) from 2007- 2010. These estimates were derived from the weighted regressions of concentrations on time, discharge and season method (WRTDS, Supplementary Table 1) (Hirsch *et al* 2010). Tracer concentrations in the lake were reset to zero on 1 January of each year to reflect overturn during the cold season and to facilitate comparisons of tributary plume dynamics among years. This is necessary since the model does not include any tracer sinks. When compared to bi-weekly observations of surface phosphorus concentrations near Milwaukee, the model reasonably estimates the temporal and spatial variation of in-lake concentrations (r=0.7; Supplementary Figure 2), indicating that it broadly captures the input and redistribution of watershed pollutants. Our pollutant was simulated as being conservative, though we recognize that phosphorus is quite reactive. By making this comparison to data collected close to the input location, the effect of our neglect of phosphorus reactions is minimized. Pollutant concentrations arising from tributary loading were scaled by dividing by the expected background concentration from fully mixing the total annual load from all rivers into the entire lake volume (~1 μg L^{-1}). This allows regions above a well-mixed background concentration to be easily identified.

Ecosystem Services

Maps of ecosystem service delivery on a 2x2 km grid were drawn from the Great Lakes Environmental Assessment Mapping (GLEAM) Project (Allan *et al* 2013, 2015). These maps indicate the location-based usage of each service (municipal water intake, beaches, and marinas/boat launches) (Figure 3), but do not represent the economic value or supply-demand balance of each service. Following Allan *et al* (2015), each usage metric is $\log_{10}(x+1)$ transformed, and then linearly normalized between the maximum and minimum value. These time-invariant services maps are primarily representative of usage in the summer months (June-August).

In the GLEAM dataset, service location and usage are mapped separately for each service using publicly available data. Using data maintained by the Great Lakes Commission and individual state contacts, municipal water usage is quantified as the annual (2013 or 2014) water withdrawal amounts in millions of gallons per year from intake/outfall sites within 5 km of the shore. Beach locations are obtained from the US EPA BEACH Act Geospatial database. As a proxy for beach visitation, the InVEST model (Natural Capital Project 2013) counts the number of geo-tagged Flickr photos within a 500 m buffer of each beach location (see Wood *et al* (2013)). Marina/boat launch locations are identified from internet sites, governmental sources, tourist information publications, and from marinas that reported boat launch availability; locations are confirmed using Google Earth. Usage for marina and boat launches is obtained from marina websites, agency sources, and Google Earth imagery. Marina and boat launch usage is quantified as the number of boat slips and boat launch parking spaces, respectively.

Cumulative Stress Days (CSD)

Cumulative Stress Days (CSD) quantify the intersection of service usage and tributary-delivered pollutant concentrations, and is calculated by multiplying the number of days exceeding the background concentration (Exceedance Days, ED) by normalized service usage at adjacent grid cells. Our CSD metric is designed to quantify the cumulative stress to services caused by local exposure to elevated pollutant concentrations. Since the background concentration is equal to the annual load being well mixed throughout the entire lake, this identifies times and locations where pollutant concentrations are elevated due to in-lake hydrodynamics.

To calculate CSD, we first calculate ED separately for each river and for all the rivers grouped in the North, East, and West. ED is a proxy for potential stress to ecosystem services, and is defined as the period over which pollutant concentrations (C) exceed an estimated background concentration state (C_{bg}). At each location, and for each day of the year, a value of 1 is assigned if C is greater than C_{bg} and 0 otherwise. Then, for a particular nutrient load source, we tally these binary (0,1) scores for each grid cell over the M days in each month to get a monthly ED (Equation 2).

$$ED = \sum_{i=1}^{M} (C_i > C_{bg}) \quad \textit{Equation } 2$$

Finally, for each month, each service metric (Boating, Beaches, or Water) is weighted by ED at each of the N locations and summed to yield the CSD for that month and for the respective region or river (Equation 3).

$$CSD = \sum_{i=1}^{N} [(ED_i * Boating_i) + (ED_i * Beaches_i) + (ED_i * Water_i)] \quad \textit{Equation } 3$$

Large CSD values can arise by persistently high tracer concentrations within the region, many days of residence of the tracer plume on the shore, or the density of ecosystem services. Changes in service supply or demand associated with an excessive concentration are not accounted for with CSD. Other metrics that weigh the absolute concentration of nutrients from tributary loading more than persistence of the threshold were considered. Since both types of metrics give qualitatively similar results, we chose the simpler ED and CSD metrics.

Results

Seasonal barriers to mixing

Our simulations of time-varying tributary loads and lake mixing reveal that both strongly affect the spatial (Figure 1) and temporal (Supplementary Movie) propagation of pollutants arriving from each watershed. The strong lateral temperature gradient—the "thermal bar"—in May acts as a barrier to horizontal transport (Figure 2A), thereby trapping pollution near the coast and acting as a conduit for spreading along the coast (Figure 2B). As spring progresses, the lake surface warms everywhere and the lateral barrier is diminished. In its place, vertical thermal stratification develops (Supplementary Figure 3). The progression toward a laterally-uniform surface temperature (Figure 2C) allows the pollutant to spread offshore and become diluted (Figure 2D). During the late summer and fall, vertical stratification traps the pollution above the thermocline without constraining its lateral spread (Supplementary Figure 3).

When all 11 tributary plumes are overlaid, we find a highly heterogeneous distribution of aggregate pollutant concentrations (Figure 1, Figure 2BD). Peak concentrations generally represent regions where inputs from multiple tributaries coincide. Monthly average pollutant concentration is particularly elevated along the eastern coastline and within Green Bay (Figure 2AB, Supplementary Figure 4). Peak coastal concentrations occur in May due to the influence of both the thermal bar and high input rates associated with annual maximum discharge from each tributary (Figure 2B). Interannual variation in wind patterns creates substantial differences in the dispersal of tributary plumes from year to year (Supplementary Figure 4).

To represent the point beyond which aggregate pollutant concentrations might begin to threaten ecosystem services from the lake, we developed an Exceedance Days metric (ED, see Methods). ED is a tally of the number of days per year when local accumulation of the conservative pollutant leads to concentrations that exceed expectations from mixing the same total load throughout the lake. We find that ED is particularly high within Green Bay, but is also consistently higher in the nearshore zone than in open water. There is also substantial temporal variability in ED arising from the dynamics of plume location and concentration. For example, ED near the Sheboygan River is elevated in June as its pollution load remains trapped along the shore (Figure 3D), then drops sharply in July and August as the plume mixes laterally (Figure 3FH).

Potential stress on coastal ecosystem services

The distribution of coastal ecosystem service utilization (Figure 3) is no less spatially heterogeneous than that of tributary-derived pollution (Figure 1). Elevated pollutant concentrations intersect with many important ecosystem service sites during the summer (Supplementary Figure 5). To integrate across boating, beaches, and water intakes as potentially impacted services, we calculated a Cumulative Stress Days metric (CSD, see Methods) that sums the ED for each tributary plume that directly contacts coastal sites where these three ecosystem services are documented.

Ecosystem services in the North and East regions of Lake Michigan are exposed to more tributary-derived pollution than services in the West (Figure 4A). High values of CSD can arise from either of two distinct patterns: sustained high pollutant concentrations that overlap with a modest number of services, or intermittently high concentrations intersecting with a larger number of services. For instance, although Green Bay's load from the Fox River drives average summer pollutant concentrations higher in the North (5.1 μgL^{-1}) compared to the East (0.7-1.1 μgL^{-1}), the river plumes in the East overlap spatially with twice as many services (Supplementary Figure 5). These intermittent high concentrations at sites of multiple services leads to peak CSD in the East (Figure 4A). In contrast, high CSD values in the North are due to prolonged high concentration of pollution at a few service locations (Supplementary Figure 5).

Within each region, there is variability in CSD across the summer months that reflects the dynamic extent of river plumes in the vicinity of service sites (Figure 3). For example, low ED in June leads to minimal CSD at Washington Island (Figure 3E), while CSD generally increases later in the summer as plumes expand across the North region (Figure 3GI, 4A). In contrast, pollution tends to be trapped along the coast in the East (Figure 3A) and West (Figure 3D) during June, thereby creating elevated CSD at service sites (Figure 4A). In July and August, ED values are reduced (Figure 4A) in the East (Figure 3BC) and West (Figure 3FH) as river plumes are diluted by mixing with open water. However, high ED continues and expands within Green Bay throughout the summer due to its lack of dilution capacity and limited exchange with the open lake (Figure 3EH).

Calculating CSD separately for each river plume underscores the roles of both loading rates and ecosystem service distributions in governing potential impacts on societal use of Lake Michigan. CSD in the West region is predominantly driven by the Milwaukee River. However, in June the Sheboygan River plume spreads further along the shore (Figure 3D), and makes a greater contribution to CSD (Supplementary Figure 5). The number and spatial distribution of services is limited in the North compared to other regions (Figure 3, Supplementary Figure 5), but CSD is high due to high ED from persistent inputs of pollution from the Fox River (Dolan and Chapra 2012) into shallow Green Bay, which mixes slowly with the open lake. In the East, ED is dominated by the Grand, Kalamazoo, and St. Joseph Rivers (Figure 4A), each of which drives high CSD values as its plume overlaps with many service sites along the coastline (Figure 3, Supplementary Figure 5). These three river plumes spread along the shoreline in June due to the thermal bar (Figure 3A), giving rise to high CSD values (Figure 4A, Supplementary Figure 5). Moreover, elevated CSD values to the north of the Muskegon River reflect overlapping loading from four rivers that each discharge to a stretch of the Lake Michigan shoreline where coastal currents carry pollution to areas that people use regularly for boating, beaches, and water supplies (Supplementary Figure 6). The intensity of this joint pollution is alleviated by offshore mixing later in the summer, but not entirely eliminated (Figure 4A).

Discussion

Merging realistic riverine pollutant loading and three-dimensional lake hydrodynamics with ecosystem service maps offers a new perspective on pollution control strategies for large water bodies, which can lead to more effective coastal management approaches. Physical mixing within Lake Michigan yields extensive redistribution of watershed-derived pollution during our study period (2007-2010). Strong offshore temperature gradients, such as the thermal bar, in spring and early summer inhibit offshore mixing, thereby trapping pollution against the shore (Figure 2). Notably, the resulting high expected pollutant concentrations at that time are primarily an effect of in-lake physics rather than high loading rates, even though nutrient control measures often focus on load dynamics alone. We find that, regardless of the instantaneous loading rate, the thermal bar not only causes incoming pollution to accumulate in the vicinity of the river mouth, but also promotes its spread along the shoreline, where societal reliance on ecosystem services is greatest (Allan *et al* 2015). This pattern is readily visualized through an animation of the model results (see Supplementary Movie), including the transition from pollution being trapped by the thermal bar (April 1st) to spreading widely under vertical stratification as the lake surface becomes isothermal during the summer (August 1st).

Our findings illustrate the insights that can emerge from unifying spatial analyses of stressors and ecosystem service use with models of the hydrodynamics of the receiving water body. As mixing dynamics cause pollution to be trapped and spread throughout the nearshore zone (Figure 2), the risk that watershed-derived pollution will affect coastal ecosystem services becomes amplified. The effectiveness of this trapping, when it coincides with the locations of population centers and ecosystem service utilization, could lead to problems with harmful algal blooms, bacterial contamination, and other water quality problems even when the load arriving from the nearest tributary is not particularly high (Figure 4B). Indeed, the East region of Lake Michigan exemplifies this scenario; the likelihood of impacts on services arises from the overlap of multiple river plumes, each of which could only modestly increase pollutant concentrations in lake waters when considered in isolation.

Our incorporation of lake hydrodynamics into analysis of the spatial relationships between pollutant inputs and human use of Lake Michigan's shoreline is merely a start toward quantifying the impact of pollution on coastal ecosystem services (Dodds *et al* 2008, Wolf *et al* 2017), but it has clear implications for regulations in the Great Lakes. The first phosphorus loading goals for the Laurentian Great Lakes were expressed as total loads (International Joint Commission 1978), an approach that implicitly treated all sources and locations equally. Though overall phosphorus loads to Lake Michigan have decreased below the target concentration under the existing binational agreement (Dolan and Chapra 2012), problems with nuisance algae remain in many embayments and near-shore areas (Brooks *et al* 2015) due to elevated coastal phosphorus (Yurista *et al* 2015). Algal growth in the nearshore zone is exacerbated by invasive zebra and quagga mussels that capture planktonic nutrients and deposit them on the substrate (Hecky *et al* 2004, Mosley and Bootsma 2015, Pilcher *et al* 2017, Rowe *et al* 2017), but lake hydrodynamics plays a mediating role even in that process (Pilcher *et al* 2015). Indeed, the ironic state of Lake Michigan is that invasive filter feeders and reduced phosphorus loading have diminished open-water phytoplankton production to the point of undercutting the energetic basis for important pelagic fisheries (Rowe *et al* 2017), yet coastal ecosystems still suffer from widespread overabundance of benthic and planktonic algae (Brooks *et al* 2015). The contribution of temperature-driven trapping of watershed nutrient loads along the shoreline has received little attention, but our simulations suggest that it may be an important factor.

The continuing evolution of regulatory frameworks that set pollutant loading targets offers opportunities to incorporate the hydrodynamics of receiving bodies. A focus on total loads, even when specific to a particular tributary, can inadvertently overlook both pollutant accumulation in the nearshore (Yurista *et al* 2015) and advection to far-away sites that are critical for coastal ecosystem services (Hoffman and Hittinger 2017). An approach like ours can be used to estimate the spatial and temporal variation in the effective load to the coastal zone under a range of watershed management and climate scenarios, thereby enabling the next generation of regulatory load targets to account for seasonality of both inputs and in-lake processing. As the United States and Canada launch efforts to update phosphorus load targets for Lake Michigan and other Great Lakes in the next few years (United States and Canada 2019b), we hope that the growing evidence that lake hydrodynamics either trap or dilute tributary loads will be considered. While it would be too cumbersome to expect regulatory agencies to run sophisticated hydrodynamic models for every receiving body, our findings suggest that setting targets without accounting for mixing dynamics of large lakes and coastal oceans would undercut the objective of protecting public health and environmental quality.

Regulatory mandates are often framed around avoiding the impairment of human use of water bodies, and our spatial analysis of the intersection of aggregate pollution patterns with coastal ecosystem services represents a feasible approach for tackling this issue explicitly. However, we recognize that our Cumulative Stress Days (CSD) metric is a blunt instrument for translating pollutant concentrations into potential impact on services. Its strengths include integrating through time and across multiple services, but it focuses on exceedance of an estimated background concentration in a well-mixed system as a proxy for impact. Refining this approach could start with integrating the sensitivity of ecosystem service levels to the relative dosage of key pollutants, as well as differentiating between reactive and conservative behavior of pollutants. It also would be ideal to account for potential synergistic effects of multiple pollutants entering from the same tributary (Smith *et al* 2019).

As eutrophication and hypoxia continue to expand along the world's coastlines (Smith 2003, Diaz and Rosenberg 2008), it is critical to bear in mind both successes and limitations in managing loads of nutrients and other pollutants. The current paradigm in the United States of regulating loads from each watershed independently has unquestionably had positive effects over the last fifty years, yet hypoxia continues to plague commercial fisheries in the Gulf of Mexico (Scavia *et al* 2017) and nuisance algal blooms are expanding in lakes of all sizes (Dolan and Chapra 2012, Brooks *et al* 2015). These forms of environmental degradation threaten commerce and quality of life for coastal communities (Dodds *et al* 2008, Allan *et al* 2015, Wolf *et al* 2017), and partly reflect a failure to recognize that the internal dynamics of large water bodies often redirects pollutants. Our simulations of Lake Michigan illustrate the insights into nutrient management that can come from jointly accounting for spatiotemporal patterns of pollutant inputs, large-scale hydrodynamics, and human use of coastal ecosystems. This analytical approach is transferable to any large water body, and incorporating it into the next generation of regulatory loading targets is likely to enhance the protection of critical coastal ecosystem services.

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Data Availability

The model setup, tributary phosphorus fluxes, and analysis scripts are contained in the GitHub repository https://github.com/lgloege/MITgcm-Lake-Michigan-tracer. MITgcm can be downloaded at https://github.com/mitgcm. Meteorological and radiative forcing fields are available at https://doi.org/10.68084/m9.figshare.c.4222538.

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Figures and Tables

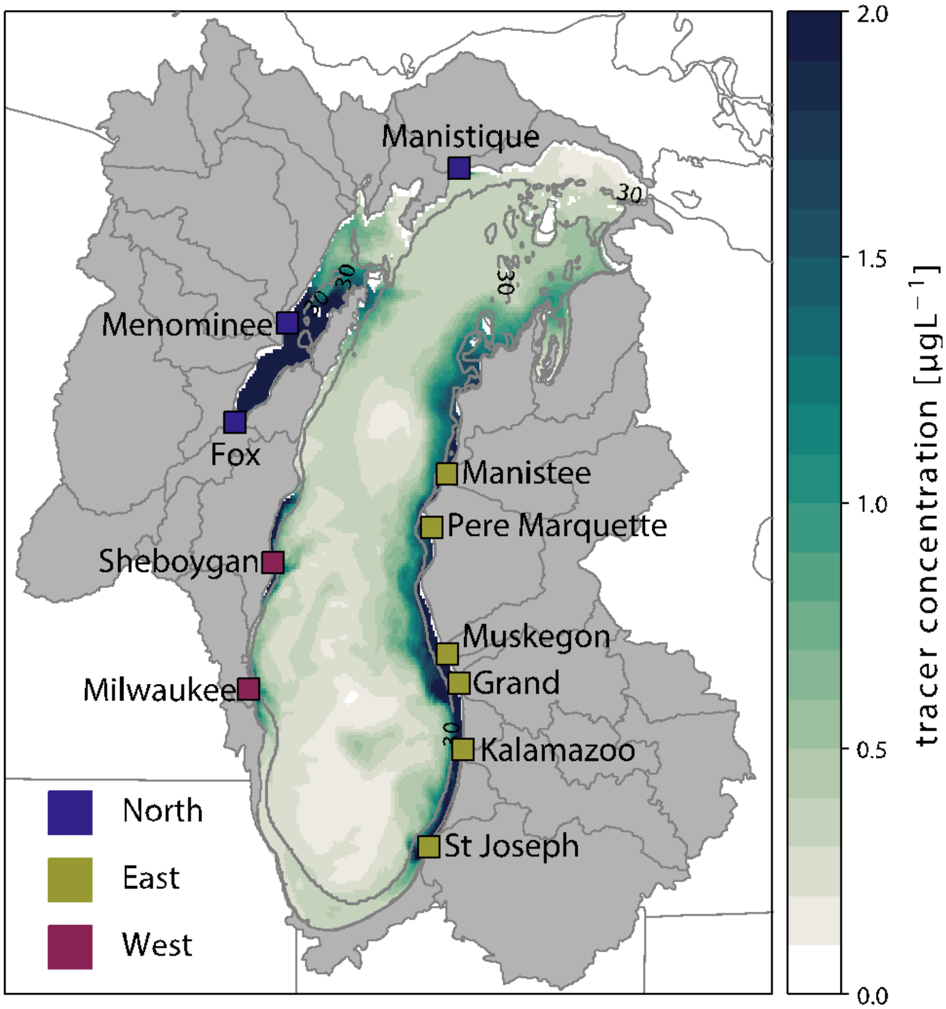


Figure 1. Maximum concentration (in µg L^{-1}), 2007-2010 average summer. The 11 rivers are marked and segregated in to North, East, and West groups. The watershed is shaded in dark gray with sub-basins delineated by hydrologic unit codes. The near-shore zone is delineated using the 30 m depth contour (gray), the definition used by National Coastal Conditions Assessment.

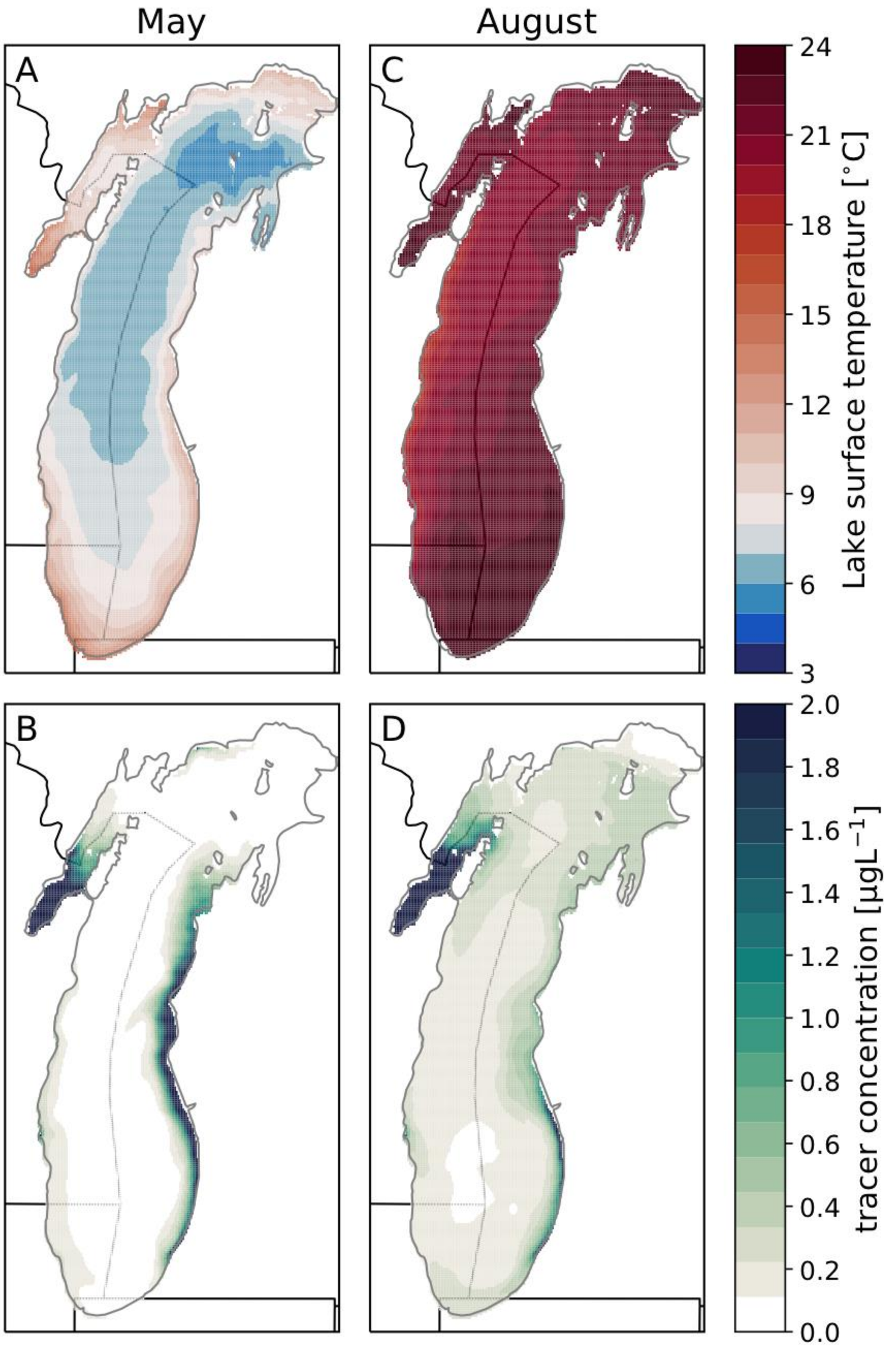


Figure 2. Average surface temperature in A) May and C) August. Average tracer concentration in B) May and D) August.

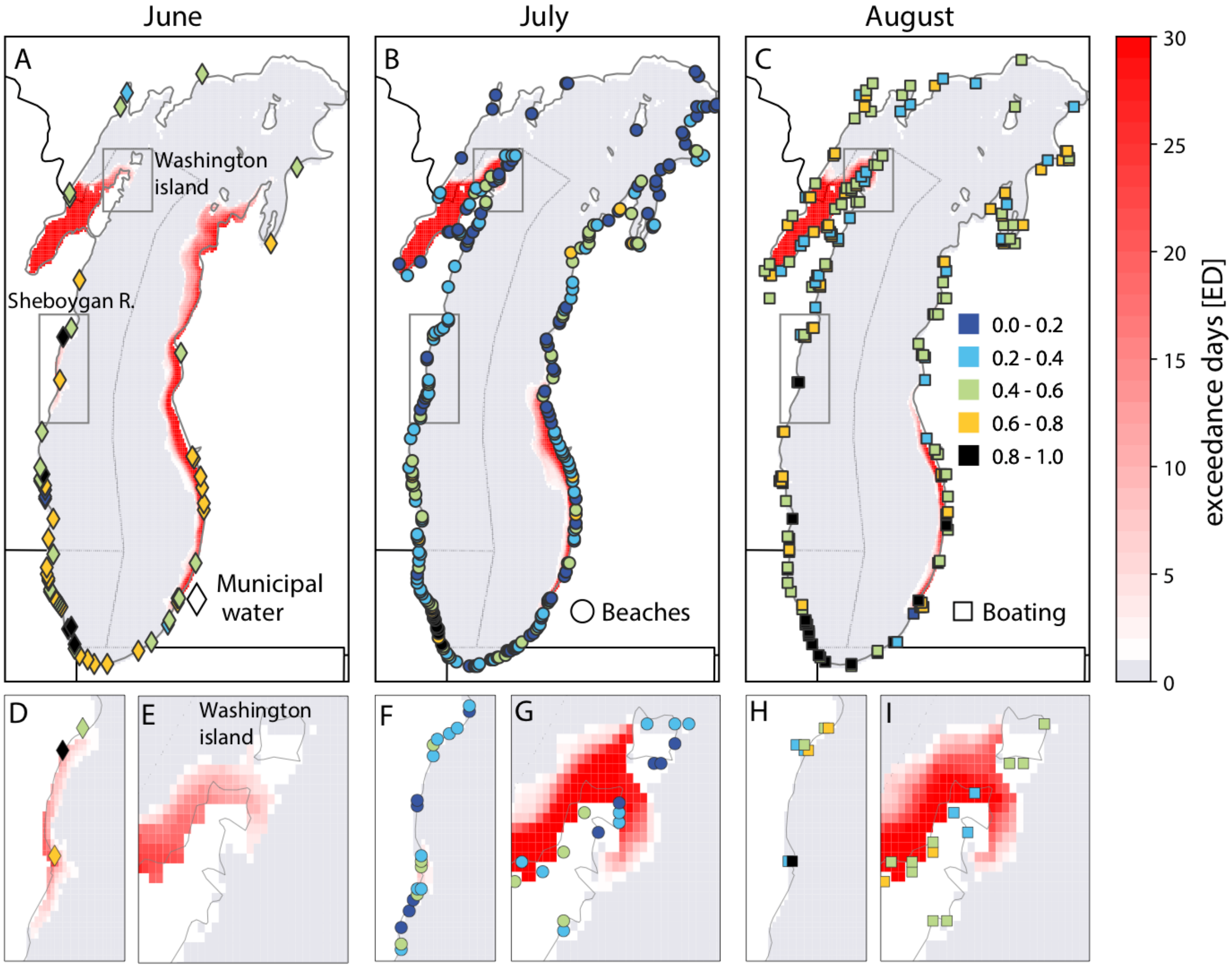


Figure 3. Time-invariant locations of a) municipal water intake sites b) beaches c) recreational boating. Symbol color represents normalized usage for each index. Red shading indicates the number of days a threshold of 1 μgL^{-1} is exceeded at each model point in a) June b) July and c) August. For clarity of presentation, time-invariant ecosystem services are plotted on the map only for a single month. The insets at the bottom of A), B), and C) magnify the Sheboygan river (D, F, H) region and Washington Island region (E, G, I) in June, July, and August, respectively.

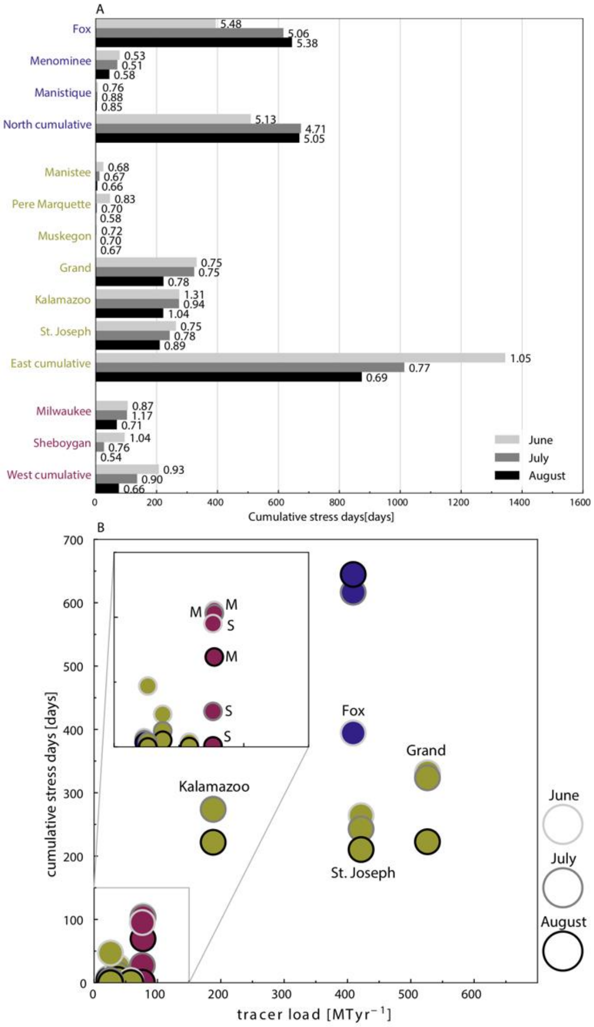


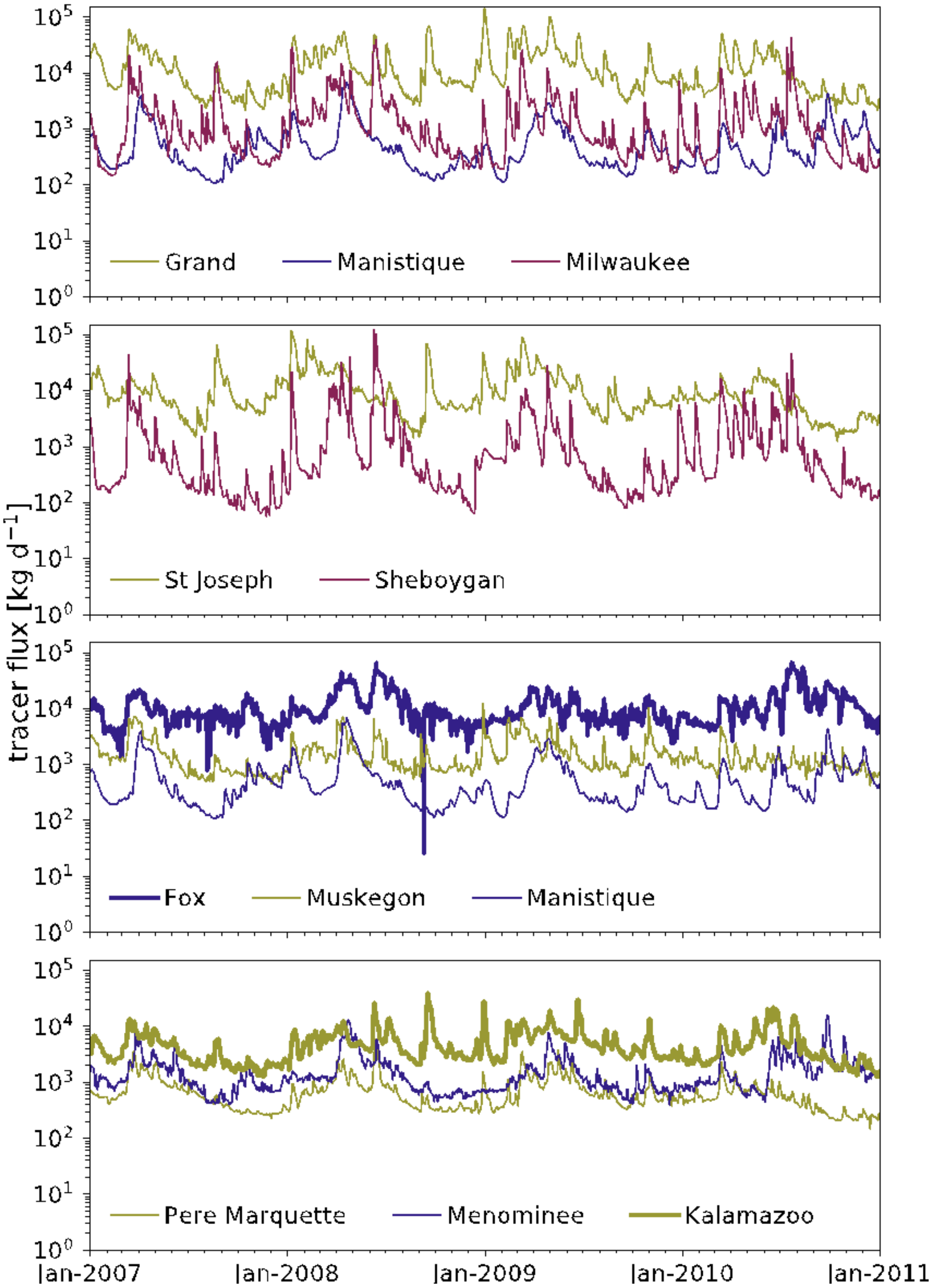
Figure 4. A: Cumulative Stress Days (CSD) for each summer month, calculated separately for each river plume in North (blue), East (green), West (purple) regions. Average tracer concentration within each tributary plume (in μgL^{-1}) shown beside each bar. B: Cross plot of Cumulative Stress Days and tracer load for each river. Color represents the region the river lies in (See Figure 1). The inset magnifies the tributaries with small loads. Rivers with the highest Cumulative Stress Days are named (S=Sheboygan and M=Milwaukee). Outline color represents the month Cumulative Stress Days is calculated for: light gray is June, medium gray is July, and black is August. Population is not a strong contributor to this relationship (Supplementary Figure 7).

Supplementary material

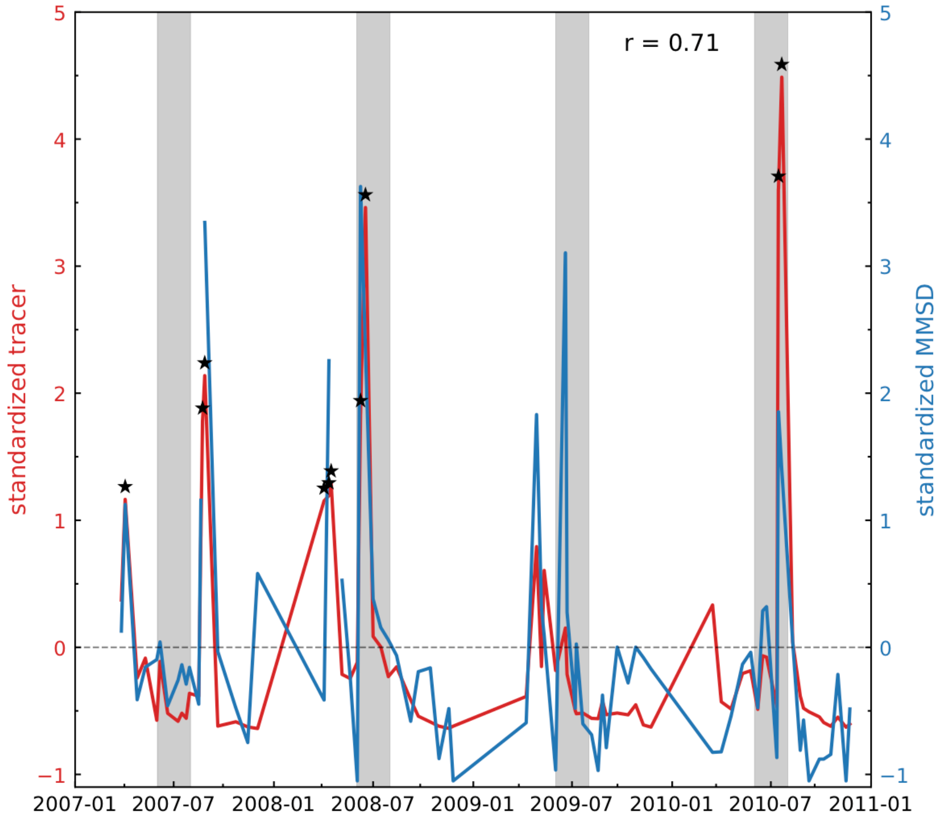
Supplementary Table S1. Water quality and discharge data sources for each river used to create WRTDS phosphorus flux histories. Flux histories were constructed from N samples in each period.

USGS chem ID*	USGS flow ID *	WDNR ID †	River	Period	N
04108660			Kalamazoo	2003-2016	255
04119400	04119000		Grand	2000-2016	253
04102080	04101500		St. Joseph	2002-2013	75
04122030	04121970		Muskegon	2002-2013	153
04057004	04056500		Manistique	2002-2013	78
04122500			Pere Marquette	2002-2013	79
04126010	04125550		Manistee	2002-2013	70
04085059	04084445	053210	Fox	1992-2017	257
04087000		413640	Milwaukee	1973-2017	634
04067500		383088	Menominee	1979-2017	307
04086000		603095	Sheboygan	1977-2017	543

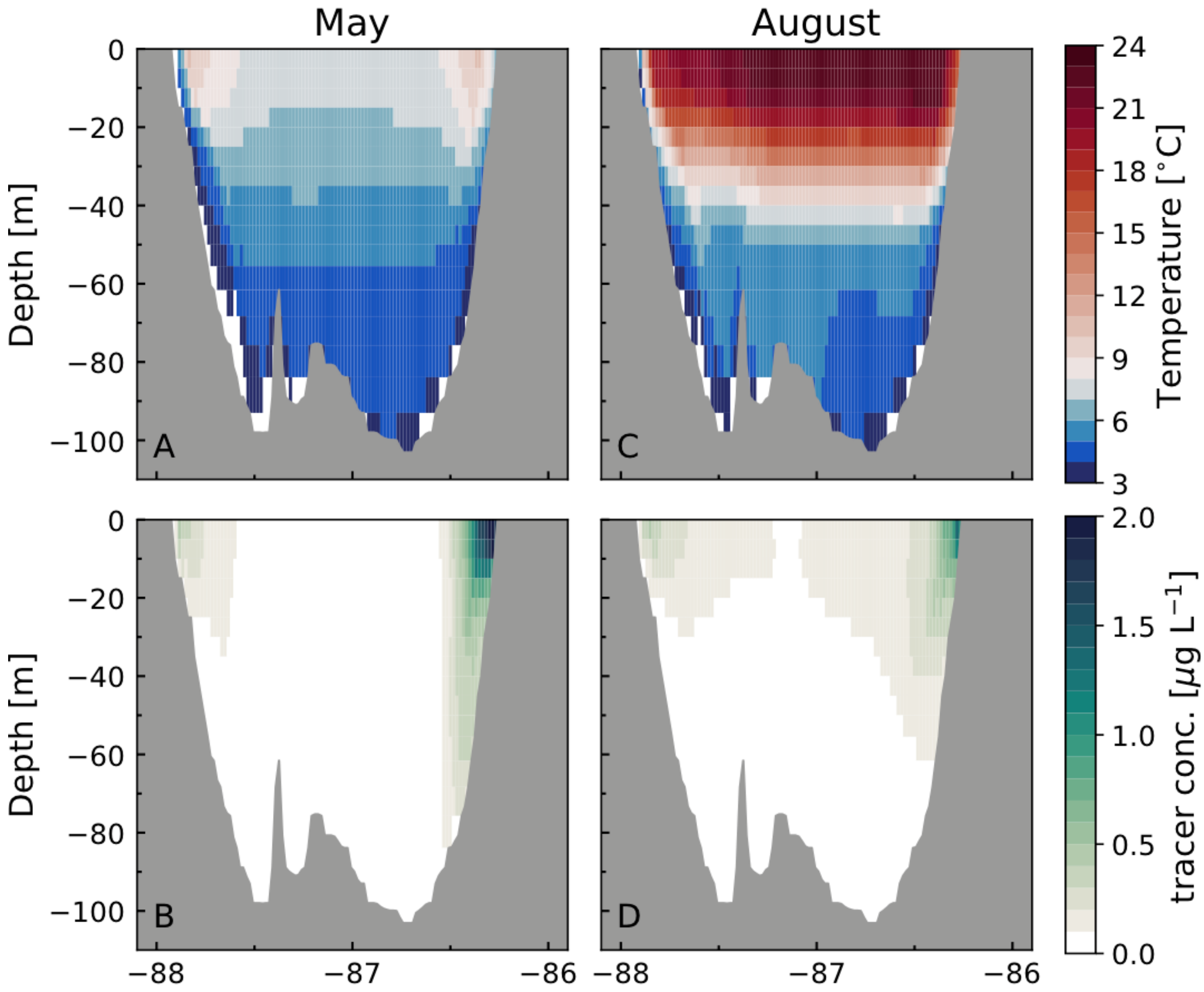
* USGS water quality and discharge data were downloaded from https://waterdata.usgs.gov/nwis
† WDNR water quality data were downloaded from https://prodoasint.dnr.wi.gov/swims/login.jsp



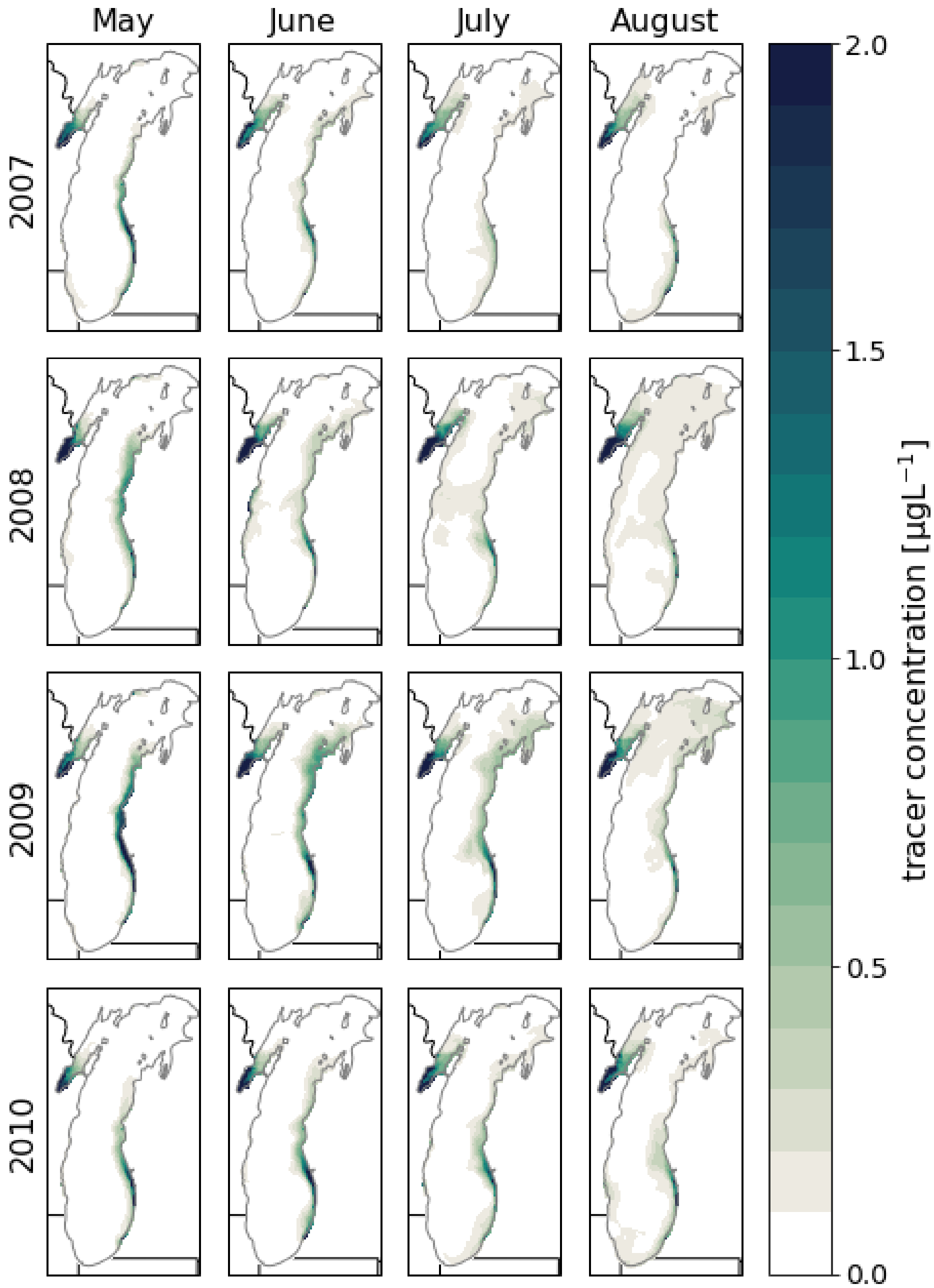
Supplementary Figure 1. Log$_{10}$ transformed tracer flux for each tributary. Color represents river location in the north, east, or west.



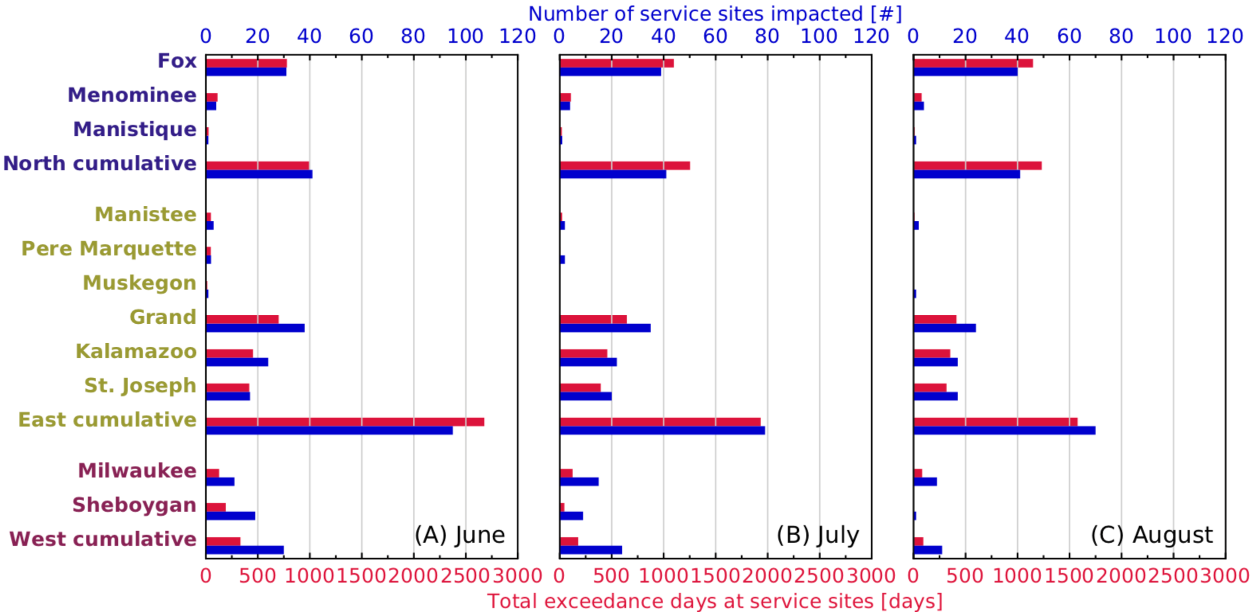
Supplementary Figure 2. Standardized tracer concentration (red) compared to standardized bi-weekly *in-situ* phosphorus concentration observations (blue). Gray bars highlight the analysis period (June-August) in this study and the stars indicate when the standardized tracer reaches above unity. The correlation between the standardized tracer and standardized observations is shown in the top right. Surface observations are from the Outer Harbor sampling survey, part of the Milwaukee Metropolitan Sewerage District (MMSD) monitoring program (data available at http://www.waterbase.glwi.uwm.edu/mmsd/). Data is collected during non-ice conditions near the Jones Island Wastewater Treatment Plant.



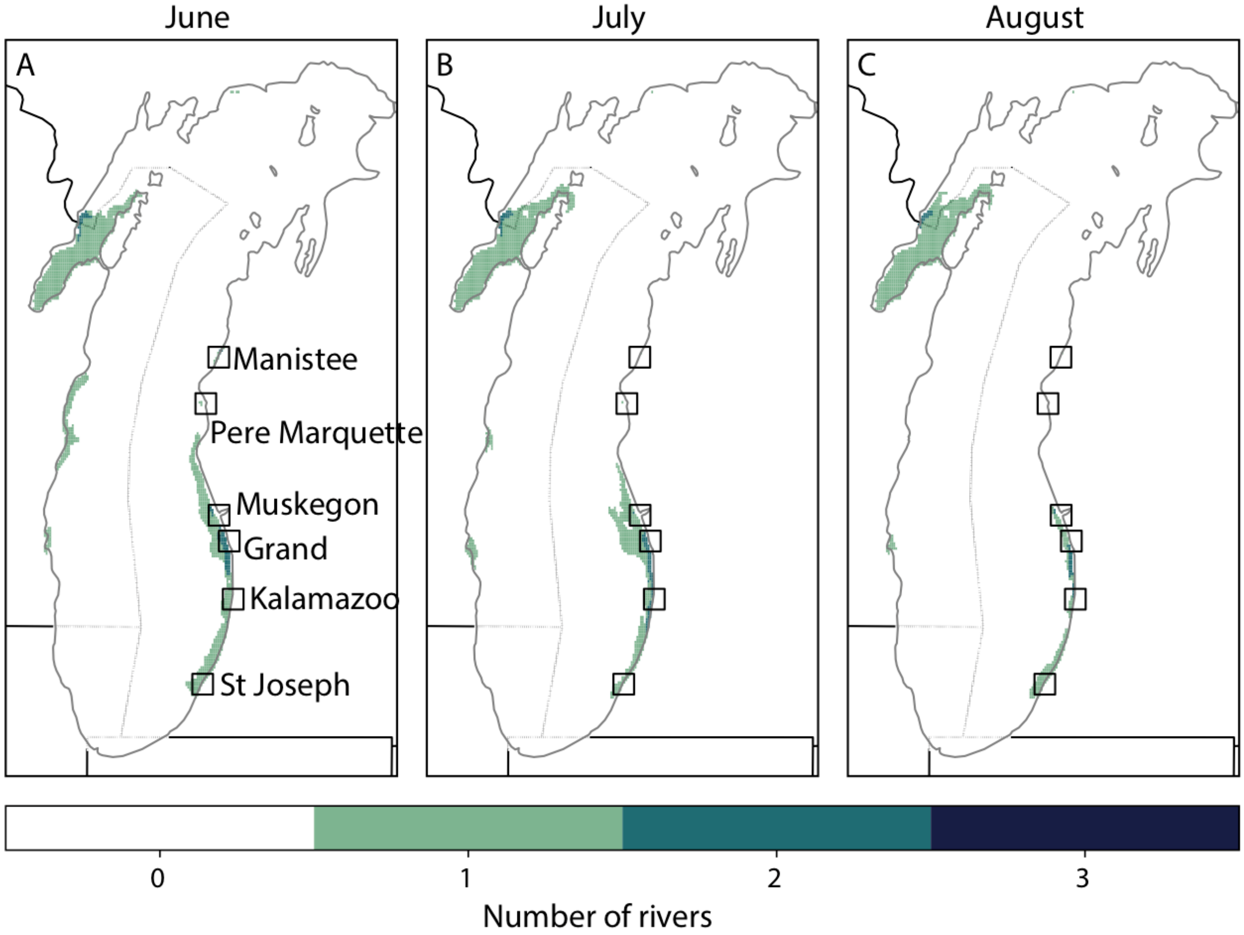
Supplementary Figure 3. Temperature and tracer concentration averaged between 42.8°N and 43.2°N in A, B) May and C. D) August. The latitude band is centered at the mouth of the Milwaukee River.



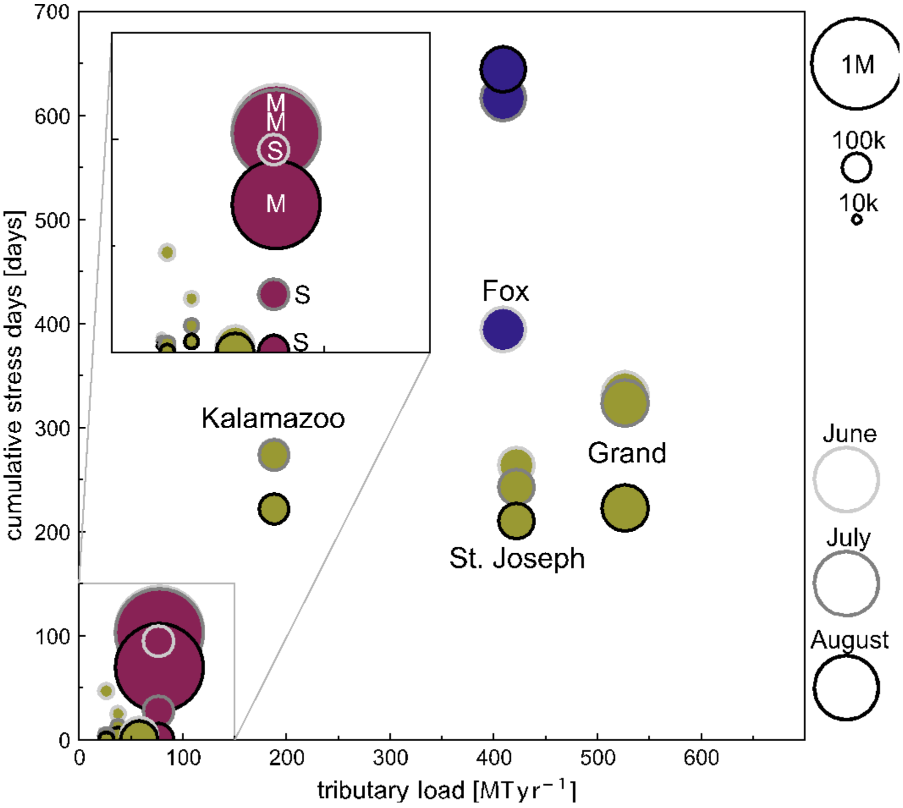
Supplementary Figure 4. Average tributary derived tracer concentration for May, June, July, and August for each simulated year (2007, 2008, 2009, and 2010).



Supplementary Figure 5. Total number of service locations within the phosphorous plume (Blue) and the cumulative number of Exceedance Days at all service locations within the tracer plume (Red) calculated separately for each river and in each month A) June B) July, and C) August.



Supplementary Figure 6. Color at each location indicates the number of individual rivers with Exceedance Days above the threshold concentration for A) June, B) July, and C) August.



Supplementary Figure 7. Cross plot of Cumulative Stress Days and tracer load for each river. Color represents the river's region (See Figure 1). Outline color represents the month Cumulative Stress Days is calculated for: light gray is June, medium gray is July, and black is August. The area of the circle displays the population of the county at the mouth of each river based on the 2010 census. The inset magnifies the tributaries with small loads.

Follow the link to access the movie: https://figshare.com/s/ee755da2aaf1ceb33b3f

Supplementary Movie 1. A passive tracer is released at the mouth of the St. Joseph River on either January 1st, April 1st, or August 1st of 2007. The color represents the concentration of the tracer relative to it being well-mixed throughout the entire basin. Blue is below well-mixed, white is completely well-mixed, and red is above well-mixed. The day of the year (DOY) is shown in each panel.