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Variation in particulate C:N:P stoichiometry across the Lake Erie watershed from tributaries to its outflow

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Abstract

Human activities can cause large alterations in biogeochemical cycles of key nutrients such as carbon (C), nitrogen (N), and phosphorus (P). However, relatively little is known about how these changes alter the proportional fluxes of these elements across ecosystem boundaries from rivers to lakes. Here, we examined environmental factors influencing spatial and temporal variation in particulate C:N:P ratios across the Lake Erie watershed from its tributaries to its outflow. Throughout the study, particulate nutrient ratios ranged widely (C:N 2.0–25.8, C:P 32–530, N:P 3.7–122.9), but mean values were generally lower than previous estimates from different aquatic environments. Particulate C:N ratios varied the least across all environments, but C:P and N:P ratios increased between tributaries and coastal areas and throughout the growing season in coastal environments. These ratios also differed temporally in offshore waters as particulate C:P and N:P were higher in the spring and summer and lower in the fall and winter. Particulate C:P ratios also increased between the western/central and eastern basins indicating differential nutrient processing across the lake. These stoichiometric changes were associated with unique environmental factors among ecosystems as tributary stoichiometry was related to terrestrial land use and land cover, coastal ratios were a product of mixing between riverine and offshore waters, and offshore patterns were influenced by differences in temperature and particulate nutrient loading among basins. Overall, by studying changes in particulate C:N:P ratios across the Lake Erie watershed, our study demonstrates the power of using mass balance principles to study nutrient transformations along the aquatic continuum.

Humans are responsible for significant changes to nutrient cycles at local, regional, and global scales (Vitousek et al. 1997; Kaye et al. 2006). Altered nutrient loading into aquatic ecosystems can result in eutrophication and serious degradation of ecosystem health in rivers, lakes, and estuaries along the

aquatic continuum from land to sea (Carpenter et al. 1998; Smith and Schindler 2009). Although increased watershed export of nitrogen (N) and phosphorus (P) would be expected to simply increase nutrient concentrations in receiving waters, differences in uptake and retention of these key biogeochemical elements can also lead to proportional changes in stoichiometric ratios across ecosystem boundaries (Vanni et al. 2011; Sitters et al. 2015). For instance, tributary particulate N:P ratios are typically much lower than those in downstream lakes suggesting differential nutrient processing between these environments (Frost et al. 2009; Vanni et al. 2011; Larson et al. 2016). But, while this pattern could result from a combination of many factors such as differences in the effects of terrestrial nutrient supplies (Arbuckle and Downing 2001; Vanni et al. 2001), abiotic and biotic variables (Hessen 2006), and physical characteristics such as ecosystem size and water residence times (Hecky et al. 1993; Sterner et al. 2008), little is known about the relative influence of these factors on particulate nutrient

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Special Issue: Headwaters To Oceans: Ecological and Biogeochemical Contrasts Across the Aquatic Continuum

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processing along the aquatic continuum. To this end, we examined environmental variables affecting suspended particulate carbon (C):N:P ratios across tributary, coastal, and offshore areas of Lake Erie.

Nutrient dynamics in Lake Erie have been extensively studied for decades. Over the years, the lake has experienced dramatic changes in external nutrient loading undergoing eutrophication events associated with point sources of P (DePinto et al. 1986; Joesse and Baker 2011), periods of lower productivity (Howell et al. 1996; Matisoff and Ciborowski 2005), and more recent re-eutrophication stemming from nonpoint source P (Kane et al. 2014; Scavia et al. 2014). Although most of the water flowing into the Lake Erie comes from the Detroit River (> 90%), a majority of N and P delivery is linked to tributary inputs from agricultural watersheds in the southwest (Kane et al. 2014; Stow et al. 2015). High nutrient inputs from these areas are associated with episodic harmful algal blooms and anoxic dead zones during summer months in the western and central basins of the lake (Watson et al. 2016). However, despite receiving the highest nutrient loads out of all of the Laurentian Great Lakes (Robertson and Saad 2011), Lake Erie's algal communities have nonetheless been found to experience seasonal nutrient limitation in the central and eastern basins (Guildford et al. 2005; Moon and Carrick 2007; North et al. 2007). In all, nutrient supplies are heterogeneous across the Lake Erie catchment, which likely causes significant spatio-temporal variation in particulate C:N:P ratios flowing into and through the lake.

Compared to dissolved and total N and P concentrations in Lake Erie, much less is known about its particulate elemental stoichiometry. Particulate P represents the majority of P delivery into the lake (Joesse and Baker 2011), and riverine total organic C: total P molar ratios are low across the Great Lakes basin (Larson et al. 2016) suggesting that tributary particulate C:P ratios are likely to be lower than mean lake values (Hecky et al. 1993; Guildford et al. 2005). Particulate P concentrations appear to remain high moving from tributaries into the western basin (Guildford et al. 2005; Watson et al. 2016), and particulate N:P ratios increase considerably between near-shore and offshore environments in the central and eastern basins and going from west to east across the lake (Watson et al. 2016) suggesting differential nutrient processing between these areas. Temporal patterns in Lake Erie stoichiometry also remain poorly understood, but surface water C:P and N:P ratios can show considerable seasonal and inter-annual variation (Watson et al. 2016), and tributary values are likely affected by seasonal differences in particulate P loading (MOE 2012; Chomicki et al. 2016). Thus, while we have a general idea of the extent of stoichiometric variation within and around Lake Erie, more data are clearly needed to complete this picture and more fully understand the general mechanisms influencing these patterns.

Particulate C:N:P ratios can be thought of as highly integrated ecosystem-level variables, which respond dynamically

to chemical, physical, and biological processes in aquatic environments. At a proximal level, particulate stoichiometry in rivers and lakes is partly controlled by terrestrial inputs, and C:N:P ratios can vary considerably with differences in dissolved nutrient supplies delivered from various land use types (Arbuckle and Downing 2001; Vanni et al. 2001; Larson et al. 2016). Transport of this material is strongly linked to discharge (Frost et al. 2009), which also affects internal nutrient processing along with other physical variables such as temperature resulting in distinct seasonal changes in particulate stoichiometry (Vanni et al. 2001; Hessen et al. 2005). For example, high N and P loading during spring runoff can fuel primary production and decrease particulate N:P ratios in lakes (Vanni et al. 2011; Michalak et al. 2013), but extensive bloom formation in warmer summer months may lead to elevated seston N:P ratios if algal biomass production is not matched by internal P supplies (Spilling et al. 2014). In addition to these producer mediated changes, aquatic consumer activity can also affect particulate stoichiometry by altering producer biomass and through differential nutrient uptake and recycling, which influences elemental fluxes into upper trophic levels and through ecosystems (Elser and Urabe 1999; Dickman et al. 2008). Overall, by observing changes in environmental parameters and particulate C:N:P ratios across Lake Erie, we can see how different factors combine to control nutrient processing and alter the mass balance of elemental flows across the aquatic continuum.

Our study documented variation in particulate C:N:P ratios flowing into and through Lake Erie. Several aspects of this large lake ecosystem make it ideal for examining particulate nutrient dynamics along the aquatic continuum. Given its extensive catchment area, Lake Erie has a greater diversity of inflowing rivers and higher variability in nutrient delivery compared to smaller lakes. Furthermore, Lake Erie's larger size means that we can capture important mixing processes, such as incomplete horizontal mixing, which can increase within lake heterogeneity. These properties combined with its relatively short mean retention time (~ 3 yr; Quinn 1992) allowed us to use mass balance principles to examine in situ particulate nutrient dynamics and to test the hypotheses that particulate elemental composition differs across the aquatic continuum and through time. We predicted that C:N ratios would vary little throughout the study but that C:P and N:P ratios would increase moving from rivers into coastal areas and west to east across the lake. We also expected to find seasonal changes with lower ratios during winter and spring months and higher ratios in the summer and fall. Finally, we predicted that the major environmental factors driving stoichiometric variation would differ along the continuum. Specifically, we expected that tributary stoichiometry would be strongly associated with land use and discharge, coastal areas would respond to a mixture of riverine and offshore influences, and offshore variation would be primarily driven by dissolved nutrient supplies and algal biomass. Thus, by studying

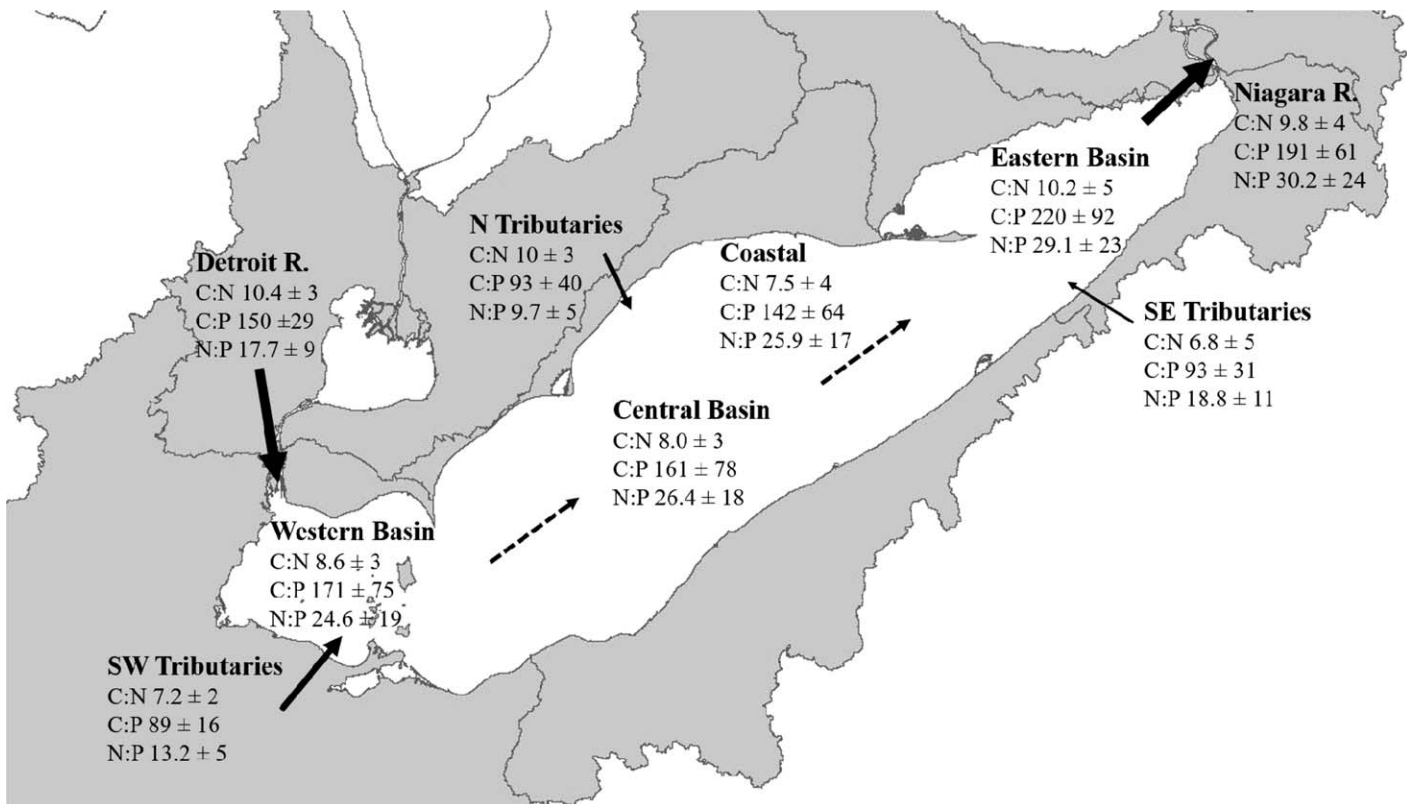


Fig. 1. Particulate stoichiometry in the Lake Erie basin. Means and standard deviation are given for particulate carbon:nitrogen (C:N), C:phosphorus (C:P), and N:P ratios measured within each major ecosystem type and region. Dark arrows represent proportional tributary inflows and outflows for the lake, and dotted lines depict the direction of water flow across the lake.

large lake ecosystems, we can gain novel information about the extent of stoichiometric variation across aquatic environments and relate these changes to watershed and lake characteristics.

Methods

Study sites

We sampled tributary, coastal, offshore, and outflow areas of Lake Erie (Supporting Information Fig. 1). Due to its much higher discharge and lower nutrient concentrations, we separated the Detroit River (collected upstream of the Detroit sewage treatment plant) from all other tributaries. These rivers ($n = 16$) drain $\sim 50\%$ of the watershed area for the entire lake watershed and were divided into three regions: southeast (Chautauqua Creek, Cattaraugus Creek, and the Buffalo River); northern (Grand River, Sandusk Creek, Lynn River, Big Creek, Big Otter Creek, Kettle Creek, Sturgeon Creek, and Cedar Creek); and southwest (River Raisin, Maumee River, Portage River, Sandusky River, and the Cuyahoga River). Coastal sites ($n = 18$) were defined as any location < 2 km from the mainland, and all other lake sites were considered offshore sites ($n = 24$). Offshore areas of the lake were further subdivided into western, central, and

eastern basins. The lake outflow was sampled in the Niagara River near Fort Erie.

Coastal samples were only collected in 2014 whereas samples were collected in tributary and offshore sites in 2014 and 2015 with additional offshore site sampling conducted in the winter of 2016. We collected samples 1–2x during each major growing season: spring, summer, and fall in the tributaries and coastal areas and across all four seasons in the offshore sites. The Detroit River was additionally sampled on a weekly basis from late March through early November in 2015. As a large amount of particulate P can be delivered into Lake Erie during winter storm events (MOE 2012), it is possible that we underestimated seasonal variation in the tributaries. However, we found no differences in particulate stoichiometry between weekly and seasonal samples from the Detroit River (t -test $p = 0.506$) indicating that our coarse tributary sampling regime provided representative estimates for mean stoichiometric values at each site.

Field measurements

We measured general limnological, chemical, and physical characteristics at each site (Table 1). Discharge, conductivity, and temperature measurements for the Detroit River were downloaded from a gauging station operated by the

United States Geological Survey (USGS). Temperature and conductivity measurements in all other tributaries were made using handheld meters (YSI, Yellow Springs, Ohio, U.S.A.). We estimated discharge at a subset of these sites using either field measurements of velocity and depth across the stream channel using a SonTek FlowTracker (YSI) or from data downloaded from gauging stations operated by the Grand River Conservation Authority, Water Survey of Canada, or the USGS. Temperature profiles at coastal sites were measured using a PUV-2500 probe (Biospherical Instruments, San Diego, California, U.S.A.), and conductivity was measured aboard the Lake Guardian vessel using an AMT profiling sonde (Analysenmesstechnik GmbH, Rostock, DEU). Temperature profiles and conductivity at offshore sites were measured aboard the CCGS Limnos (open water period) using a winch-deployed SeaBird 25 (Sea-Bird Electronics, Bellevue, Washington, U.S.A.) and aboard the CCGS Griffon ice breaker (winter period) using a hand held YSI EXO (YSI).

Water collection procedures

Detroit River water ($n = 39$ samples) was collected from a dock at the Great Lakes Institute of Environmental Research (GLIER). Integrated water samples from other tributaries ($n = 81$) and the outflow ($n = 10$) were collected in the thalweg of each site. Water samples were collected in coastal areas aboard the R/V Lake Guardian using glug-glug depth integrated sampling device (type 12; Wildco, Yulee, Florida, U.S.A.) to collect water samples 1 m below the surface and a beta bottle grab sampler (type 11; Wildco) to collect water 1 m above the lakebed ($n = 77$). Offshore sites were sampled depths of 1 m below the surface and 2 m above the lakebed aboard the CCGS Limnos using a Niskin sampling bottle (General Oceanics, Miami, Florida, U.S.A.) ($n = 135$). All water samples were transferred into acid washed 1 L carboys and transported back to the lab on ice ($\sim 4^{\circ}\text{C}$) for further processing.

Water sample processing

In the laboratory, we filtered and saved analytical samples ($n = 2$) for water quality analysis within 2–10 h of collection except for weekly Detroit River samples, which were processed within 1–2 d. To estimate total suspended solids (TSS) in the water column, we filtered whole water samples onto $0.7\ \mu\text{m}$ GF/F filters, which were dried at 60°C and stored at 20°C . We also preserved whole water samples for total phosphorus (TP) analysis in acid washed high density polyethylene (HDPE) bottles that were stored in the dark at 4°C until analysis. All remaining samples were pre-filtered through a $60\ \mu\text{m}$ nylon mesh. Water samples for total dissolved phosphorus (TDP), nitrate (NO_3), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC) were filtered through a $0.2\ \mu\text{m}$ polycarbonate filters and stored in the dark in either HDPE or pre-combusted amber bottles (for DOC) at 4°C . For particulate stoichiometry and algal biomass (chlorophyll *a*) analyses, we filtered suspended materials onto pre-ashed $0.7\ \mu\text{m}$ GF/F glass fiber filters (two separate CN, P, and Chl *a* analytical replicates), and all visible zooplankton were

carefully removed using forceps. Stoichiometry samples were then dried at 60°C and stored at 20°C while Chl *a* samples were frozen and stored at -20°C .

Water sample analyses

Coastal water quality parameters were measured at the Laboratory Services Branch of the Ministry of the Environment and Climate Change (MOECC, Toronto, Ontario, Canada) whereas water quality from the Detroit River, tributary, and offshore areas along with all particulate C, N, and P samples were analyzed at Trent University (Peterborough, Ontario, Canada). We made pH measurements on whole water samples using a handheld probe (Accumet Basic, Fisher Scientific, Ottawa, Ontario). Filters for TSS analysis were dried and weighed using a microbalance ($\pm 1\ \mu\text{g}$; Mettler-Toledo, Markham, Ontario, Canada). We analyzed TP, particulate P, and TDP samples by measuring P concentrations following persulfate digestions using a molybdate-blue colorometric method (APHA 1992) and a spectrophotometer (Cary-50, Varian, Palo Alto, California, U.S.A.). Particulate CN was measured using an elemental analyzer (Vario EL III, Elementar Mt. Laurel, New Jersey, U.S.A.). We determined NO_3 and TDN concentrations using a second derivative spectroscopy method (Crumpton et al. 1992). Water DOC concentrations were measured following sample acidification on an OI Aurora TOC analyzer (Xylem, College Station, Texas, U.S.A.). We thawed Chl *a* filters, extracted pigments using a cold/dark ethanol 24 h extraction (Marker et al. 1980), and measured Chl *a* concentrations using a fluorometer (Cary-Eclipse, Varian).

Land use

Watershed land use was quantified for four major land use types (developed, agriculture, forested, and wetland) using the Great Lakes Aquatic Habitat Framework (GLAHF). Tributary watersheds for individual rivers were delineated at a resolution of 30 m using the explorer tool (Goodspeed et al. 2016), and land use was classified according to the Great Lakes hydrography dataset (GLHD; Forsyth et al. 2016) comprised of harmonized 2010/2011 land use data derived from the National Land Cover Database (NLCD) and the Ontario Ministry of Natural Resources and Forestry (OMNRF). Coastal sites were snapped to the closest mainland point using ArcGIS (ESRI, Redlands, California, U.S.A.), and land use for all watersheds draining into a 50 km radius of each point was calculated. Land use for each major offshore basin was calculated in ArcGIS using the GLHD watersheds download package (Forsyth et al. 2016).

Statistical analyses

General differences in stoichiometric ratios across waterbody types and seasons were first compared using one-way analysis of variance (ANOVA). Prior to parametric analyses, we first tested for equal ratio variance using Levene's test. Then, we conducted individual ANOVAs for each ratio separately (C:N, C:P, and N:P) to examine spatial and temporal differences in particulate stoichiometry. Post hoc differences among

Table 1. Summary of water quality parameters collected across the aquatic continuum. The number of samples (N), mean, and standard deviation (SD) are shown for all parameters. Samples not applicable (n/a) or not collected (NC) in certain waterbody types are also indicated.

Parameter	Detroit River			Tributaries			Coastal			Offshore			Outflow		
	N	Mean	SD	N	Mean	SD	N	Mean	SD	N	Mean	SD	N	Mean	SD
Urban (%)	1	22.05*	n/a	16	11.14	10.15	18	10.93	7.69	24	21.99	16.73	1	11.36	n/a
Agriculture (%)	1	61.05*	n/a	16	66.92	20.56	18	68.89	17.60	24	55.23	16.26	1	65.37	n/a
Forest (%)	1	8.96*	n/a	16	14.78	15.52	18	12.03	9.40	24	14.32	3.09	1	7.57	n/a
Wetland (%)	1	6.22*	n/a	16	5.16	3.36	18	6.67	3.87	24	5.76	1.75	1	15.32	n/a
Discharge ($m^3 s^{-1}$)	39	5827.26	236.04	55	13.08	19.06	0	n/a	n/a	0	n/a	n/a	0	NC	NC
Temperature ($^{\circ}C$)	15	16.46	5.74	81	16.45	5.74	73	14.94	5.21	125	14.60	7.60	4	14.05	6.50
Conductivity ($\mu s cm^{-1}$)	15	230.46	27.59	81	605.74	164.63	73	302.69	100.15	120	264.98	28.56	6	287.13	6.02
DOC ($mg L^{-1}$)	39	2.37	0.80	77	5.68	2.47	77	2.48	0.96	135	2.55	1.03	5	2.29	0.36
NO ₃ ($\mu g L^{-1}$)	36	441.26	356.89	78	2713.27	4070.12	77	301.76	387.12	135	204.15	156.13	10	167.79	83.52
TDN ($\mu g L^{-1}$)	38	568.47	371.53	78	2790.13	3048.78	77	436.36	468.96	135	393.26	177.26	10	376.94	84.90
TDP ($\mu g L^{-1}$)	38	6.09	3.60	81	40.14 [†]	60.02	0	NC	NC	134	9.55	6.20	10	8.82	3.29
TP ($\mu g L^{-1}$)	36	24.44	13.60	81	104.77 [†]	113.92	77	16.84	23.72	134	19.80	25.03	10	12.42	5.23
TSS ($mg L^{-1}$)	38	8.78	7.25	81	22.38	29.23	77	4.54	4.06	135	4.91	8.68	5	1.68	1.36
Chl <i>a</i> ($\mu g L^{-1}$)	38	3.37	2.16	79	26.94	32.19	77	7.23	12.65	135	7.29	11.83	8	1.70	0.92
C:N (mol)	39	10.01	3.77	81	8.81	3.10	77	7.53	3.91	135	8.83	3.45	6	9.87	3.99
C:P (mol)	39	150.37	29.70	81	91.76	33.23	71	142.79	64.77	131	180.34	80.47	6	182.04	61.45
N:P (mol)	39	17.77	8.89	81	11.76	6.38	73	25.90	16.53	131	26.44	21.94	6	30.17	24.10

Chl *a*, chlorophyll *a*; C:N, particulate carbon : nitrogen ratio; C:P, carbon : phosphorus ratio; DOC, dissolved organic carbon; NO₃, nitrate; N:P, nitrogen : phosphorus ratio; TDN, total dissolved nitrogen; TDP, total dissolved phosphorus; TP, total phosphorus; TSS, total suspended solids.

* Landuse estimates for the Detroit River represent landuse for the immediate (Lake St. Clair) watershed only.

[†] Tributary phosphorus estimates do not include values from Sturgeon Creek due to anomalously high values ($>1 mg L^{-1}$) in this tributary.

all sites and seasonal differences within each waterbody type were determined using *t*-tests of least squared means adjusted for multiple comparisons. We also measured synchrony of seasonal changes in C:P and N:P ratios by transforming ratios to z-scores and examining Pearson correlations between values exhibiting seasonal differences (Patoine and Leavitt 2006).

In addition to examining spatial and seasonal effects, we separately compared the relative influence of individual water quality parameters (Table 1) on particulate stoichiometric ratios using partial least squares (PLS) regression analyses. Parameters were chosen to represent a consistent suite of land use and water quality variables that were collected across all sites and have been shown to affect resource stoichiometry in aquatic ecosystems. To focus on the effects of these variables, we *partially* controlled for spatio-temporal variation by excluding these terms as variables in the models and by constructing separate models for each major waterbody type. We built individual models for the Detroit River, tributaries, coastal, and offshore environments but did not create a model for the Niagara River outflow because it did not differ significantly from other sites in the eastern basin. Prior to model construction, all variables were tested for normality using Shapiro-Wilk's test, and variables that did not meet normality assumptions were either log or arcsine (land use and land cover only) transformed. We ran individual models for each ratio and waterbody type ($n = 12$ separate models) and used weights from the first two PLS factors to compare the relative strength and direction of correlations between individual water quality parameters and each stoichiometric ratio. The relative importance of predictor variables was compared using variable importance predictor (VIP) scores (Wold et al. 2001) where variables > 1.0 were considered strong predictors, variables 0.8–1.0 as moderately important, and variables < 0.8 as weakly important (Gudasz et al. 2012).

Results

Spatial variation

Particulate molar ratios ranged widely (C:N 2.0–25.8, C:P 32–531, N:P 3.7–122.9) and differed significantly across the Lake Erie watershed ($p < 0.001$; Fig. 1). All ratios were relatively low in inflowing waters, and mean values generally increased going from tributaries to coastal and offshore areas and between the western/central and eastern basins (Fig. 1). Stoichiometric variation also increased across the continuum as the Detroit River was generally less variable with a coefficient of variation (CV) of 28% compared to other tributaries (42%), coastal (54%), and offshore areas (56%). Particulate C:N ratios varied the least throughout the study (CV = 42%) followed by C:P (52%) and N:P ratios (83%). Other than the significantly lower C:N ratios seen in the coastal sites (mean = 7.5), C:N values did not differ systematically with location (Fig. 2). Particulate C:P and N:P ratios in the

Detroit River were generally higher than those in the other tributaries and were more similar to those in coastal and offshore areas. Both C:P and N:P ratios increased significantly going from tributaries into coastal environments (C:P $\Delta = 51$, N:P $\Delta = 14.1$; $p < 0.001$). Further, particulate C:P ratios were similar in the western and central basins but increased significantly in the eastern basin ($\Delta = 53$; $p < 0.001$). Outflow stoichiometry was not significantly different than that seen in the eastern basin.

Seasonal variation

Mean stoichiometric ratios in the Detroit River and other tributaries did not differ significantly through time (Fig. 3; $p > 0.5$), and particulate C:N ratios did not exhibit strong seasonal differences across the continuum. In contrast, C:P and N:P ratios in coastal environments differed considerably and were lowest in the spring and increased synchronously across the growing season (Pearson's $r = 0.35$; $p = 0.002$). Offshore particulate C:P and N:P ratios also exhibited synchronous temporal changes ($r = 0.37$; $p < 0.001$) with the lowest mean values occurring in the fall and winter and higher values in the spring and summer.

Environmental factors related to stoichiometric variation

Apart from these strong spatio-temporal effects, regression models explained $\sim 33\%$ of stoichiometric variation on average. But, the predictive ability of PLS models and of individual explanatory variables differed greatly for each elemental ratio and among aquatic environments (Fig. 4). In general, our models explained the most variation in C:P ratios ($R^2 = 38\%$), followed by N:P (36%) and C:N ratios (27%). We accounted for the most elemental variation in the Detroit River ($R^2 = 50\%$) followed by offshore (32%), tributary (28%), and coastal areas (24%). Total P and dissolved N and P were strongly related to particulate stoichiometry in all sites, but the relative importance of other predictor variables differed along the continuum (Fig. 4). Elemental variation in the Detroit River was mostly related to conductivity and discharge whereas particulate C:N:P in the other tributaries was associated with land use (urban) and land cover (wetlands). Conductivity and temperature were strongly related to particulate stoichiometry in coastal areas, and variation in offshore environments was tied to TSS, temperature, and Chl *a*.

Discussion

We documented considerable spatial and temporal variation in particulate stoichiometry along the aquatic continuum in the Lake Erie watershed. Particulate C:N ratios varied little throughout the study, which is a common pattern in aquatic environments as C and N appear to be more tightly coupled and vary less in organismal tissues compared to P (Sterner and Elser 2002; Sterner et al. 2008). Therefore, differences in particulate P content were largely responsible for systematic changes in C:P and N:P ratios across the

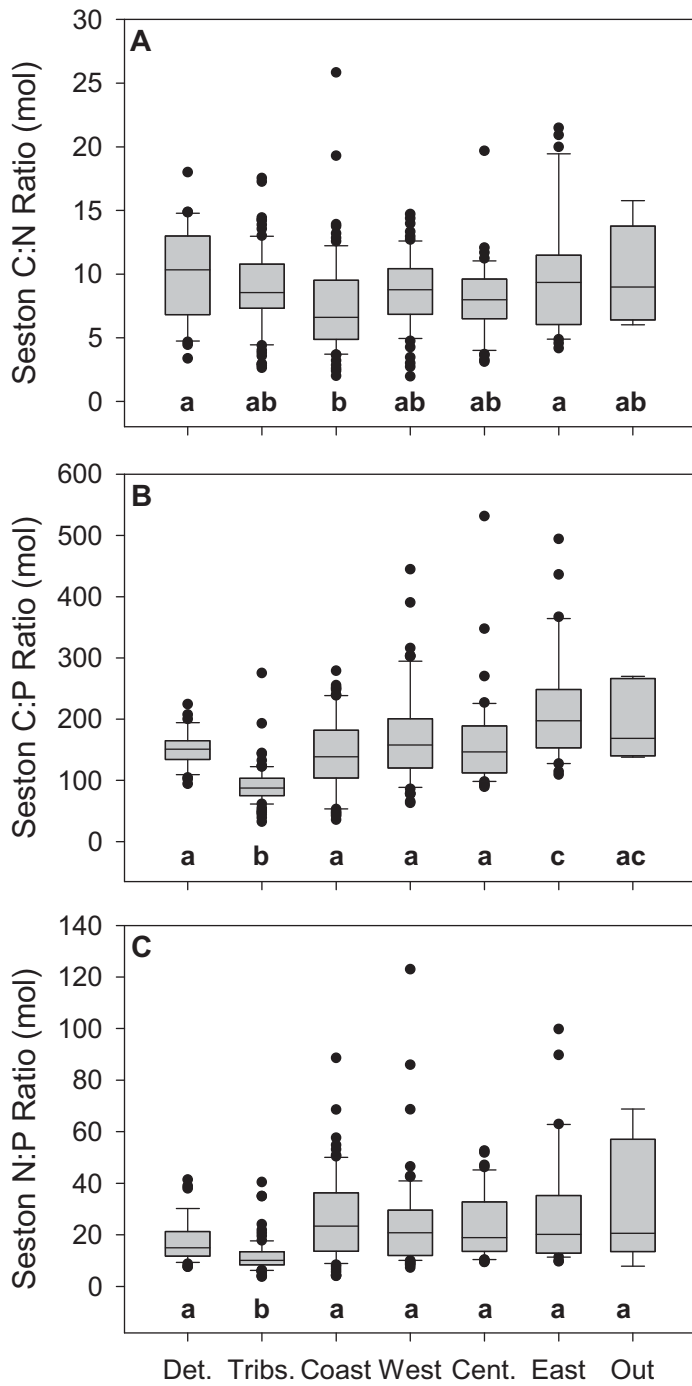


Fig. 2. Spatial differences in particulate stoichiometry across the Lake Erie basin. Boxplots depict medians, 25th and 75th percentiles (boxes), and 10th and 90th percentiles (error bars) for each stoichiometric ratio: (A) carbon:nitrogen (C:N), (B) C:phosphorus (C:P), and (C) N:P ratios. Letters denote significant differences ($p < 0.007$) across waterbody types: Detroit River (Det.), tributaries (Tribs.), coastal areas (Coast), offshore areas (Western, Central, and Eastern basins), and the outflow (Out) of the Niagara River.

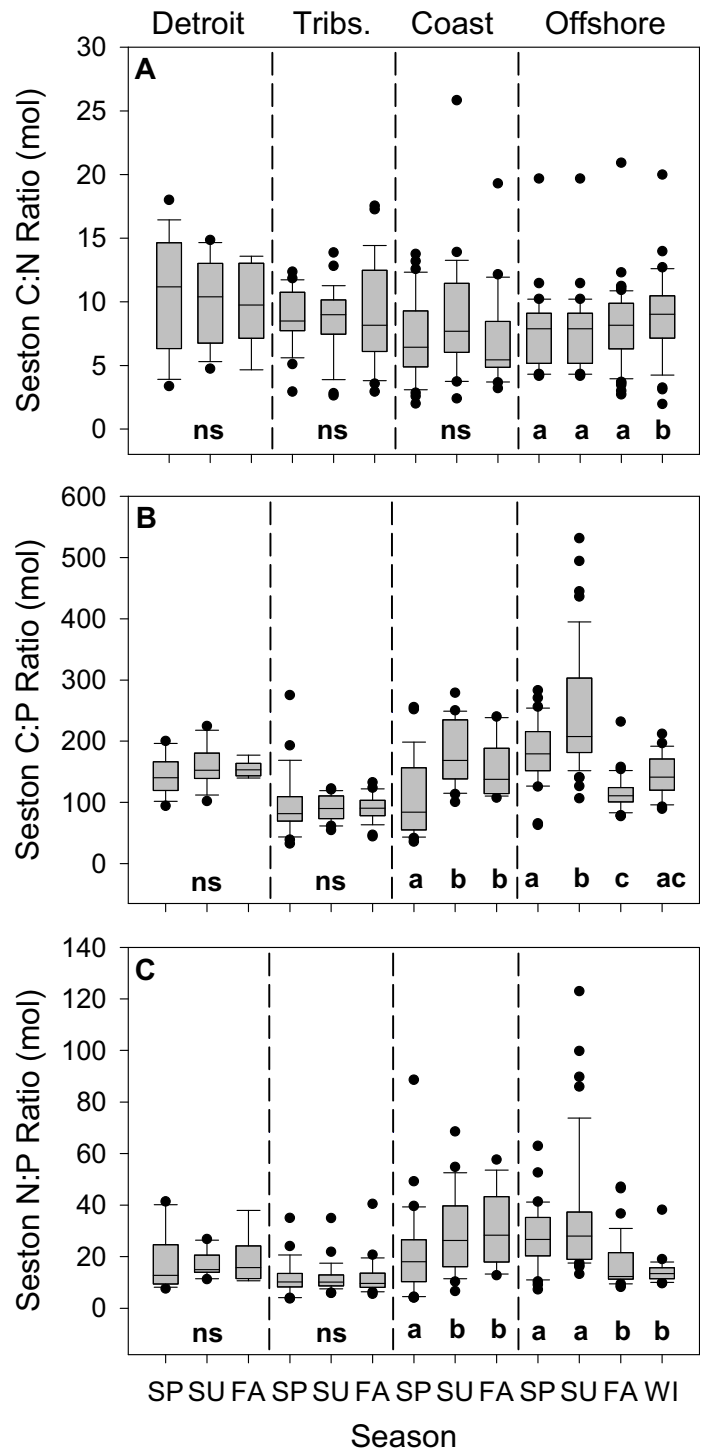


Fig. 3. Seasonal differences in particulate stoichiometry within the Detroit River, tributaries, coastal, and offshore areas of Lake Erie. Boxplots depict medians, 25th and 75th percentiles (boxes), and 10th and 90th percentiles (error bars) for each stoichiometric ratio: (A) carbon:nitrogen (C:N), (B) C:phosphorus (C:P), and (C) N:P ratios. Letters denote significant seasonal differences ($p < 0.017$ tributary and coastal; $p < 0.013$ offshore) in particulate stoichiometry within each waterbody type, and n.s. indicates no significant differences. Seasonal abbreviations include: FA, fall; SP, spring; SU, summer; WI, winter.

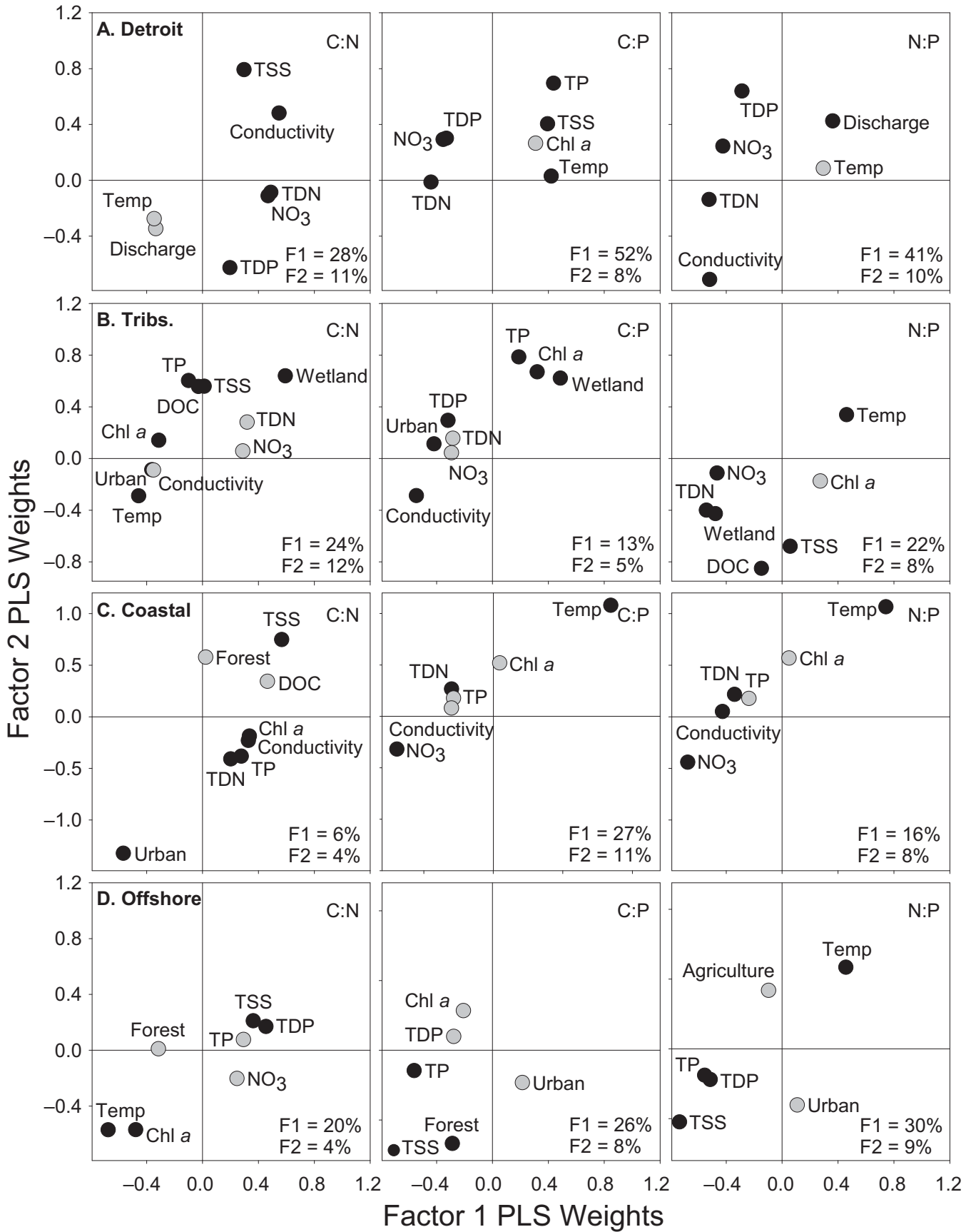


Fig. 4. Predictors of variation in particulate stoichiometric ratios in the Detroit River, tributaries, coastal, and offshore areas of Lake Erie. Scatterplots of PLS regression variable weights demonstrate positive and negative correlations between particulate ratios and individual predictor variables where variable weights are directly proportional to the amount of variance explained for each factor (1 and 2). Particulate ratios are shown in the top right of each figure, and the relative importance of each predictor according to variable importance scores (VIP) are indicated as: (●) highly important and (◐) moderately important. Weakly important variables are not shown. Particulate carbon : nitrogen (C : N), C : phosphorus (C : P), and N : P ratios, are shown for each waterbody type: (A) Detroit River, (B) tributaries (tribs.), (C) coastal, and (D) offshore areas. Abbreviations include: Chl *a*, chlorophyll *a*; DOC, dissolved organic carbon; NO₃, nitrate; TP, total phosphorus; TDN, total dissolved nitrogen; TDP, total dissolved phosphorus; Temp, temperature; TSS, total suspended solids.

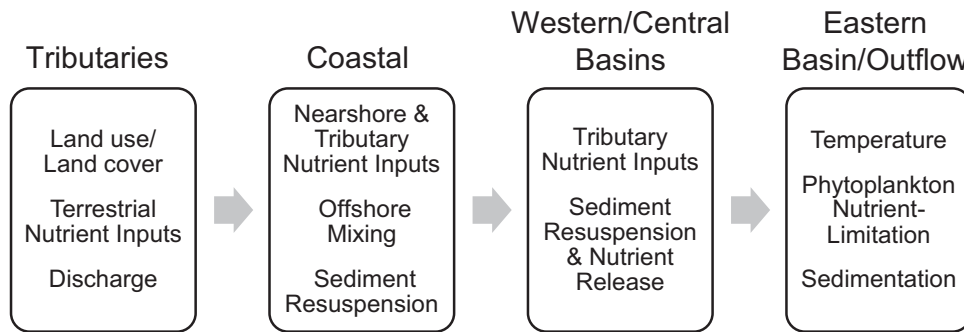


Fig. 5. Conceptual diagram of factors affecting particulate stoichiometry across the aquatic continuum in Lake Erie.

Lake Erie ecosystem. These ratios generally increased going from the tributaries, into coastal and offshore areas, and flowing out of the lake, but stoichiometric variation across the continuum was related to different environmental variables (Fig. 5). Particulate ratios did not differ seasonally in the Detroit River or other tributaries, but C:P and N:P ratios were synchronous across the growing season in coastal and offshore environments. Altogether, our results indicate considerable modification of elemental stoichiometry across different aquatic environments resulting largely from reduced water column particulate P relative to other elements in Lake Erie.

Particulate stoichiometry in the Detroit River and smaller tributaries

Compared to nearby smaller rivers, particulate C:P and N:P ratios in the Detroit River were elevated and more closely resembled lake values. One explanation for this pattern is that a majority of hydrological inputs into the Detroit River arrive directly from upstream lakes (i.e., Lake Huron and Lake St. Clair; Healy et al. 2008). Particulate material entering into Lake St. Clair is largely removed by sedimentation in delta or wetland areas and is replaced by autochthonous production that mixes with oligotrophic Lake Huron waters before being delivered into the Detroit River (Herdendorf et al. 1986; Griffiths et al. 1991; Healy et al. 2008). This shift from P-rich erosional materials to potentially nutrient-limited algal biomass likely explains the elevated particulate C:P ratios and N:P ratios in this major tributary. In addition, large amounts of particulate N delivered from surrounding urban areas during high rain events could account for the strong relationships between discharge/conductivity and C:N and N:P ratios in the Detroit River (Fig. 4). Altogether, elevated C:N:P ratios combined with relatively low overall particulate concentrations helps to explain the disproportionately small N and P loading rates from the Detroit River compared to smaller tributaries (e.g., the Maumee River; Robertson and Saad 2011).

Tributary particulate elemental ratios were lower on average than those in the Detroit River but fell within ranges reported for agricultural and forested streams (i.e., N:P 4–40; Vanni et al. 2001, 2011; Frost et al. 2009; Veldboom and Haro 2011). As predicted, mean tributary values (C:P 91 and

N:P 11.8) were also low compared to coastal and offshore areas of Lake Erie in addition to previous measurements collected across the aquatic continuum (Sterner et al. 2008). Low C:P and N:P ratios in particulate matter in Lake Erie tributaries are consistent with high nutrient loading from agriculture-rich catchments surrounding much of the lake (Kane et al. 2014; Wang et al. 2015). The sustained proportional delivery of agricultural nutrients could also explain the lack of seasonal variation in tributary stoichiometry despite contrasting discharge rates and dissolved nutrient concentrations within and among sites. This homogeneity differs from observations of temporal variation in stream particulate stoichiometry in less agriculturally intensive regions (Atkinson et al. 2009; Mehler et al. 2013) and reinforces the idea that land use and terrestrially derived nutrients may predominantly shape Lake Erie tributary stoichiometry. Interestingly, although it represents the largest land use category (mean land cover > 65%), agriculture was not an important predictor of stoichiometric variation in Lake Erie tributaries in PLS regressions. Instead, the urban land use (~ 11%) and wetland land cover (~ 5%) had proportionally larger effects on particulate ratios with urban areas providing a source of N and P and wetlands primarily serving as nutrient sinks.

Moving along the continuum: Coastal and offshore stoichiometry

Dissolved and particulate nutrient concentrations decreased and became more variable going from rivers into nearshore environments as previously documented throughout the Great Lakes basin (Dila and Biddanda 2015; Larson et al. 2016). Particulate C:N ratios were the lowest in coastal areas, but C:P ratios were intermediate between tributary and offshore values. Thus, coastal waters represented transitional zones, and particulate stoichiometry in these areas was likely influenced by many complex local factors including shoreline development, site proximity to tributaries and river plumes (e.g., conductivity, Fig. 4), and mixing dynamics of coastal and offshore waters (Rao and Schwab 2007; Chomicki et al. 2016; Larson et al. 2016). For example, rivers can discharge high amounts of particulate P (Scavia et al. 2014) and drive resuspension of benthic sediments, which can represent a

majority of suspended matter in some nearshore areas (Bridgeman et al. 2012; Matisoff and Carson 2014). Alternately, coastal C:P and N:P ratios were more similar on average to offshore sites, and temperature, which serves as a proxy for mixing between these areas (Chomicki et al. 2016) was positively related to coastal C:P and N:P ratios suggesting a strong influence of nutrient poor offshore waters in coastal environments.

Further offshore, stoichiometric ratios were generally higher than in coastal waters, and particulate C:P ratios increased across the lake. We expected to find lower nutrient ratios in the western and central basins due to high P loading rates from urban and agricultural catchments. As evidence of this mechanism, variables associated with eutrophication in these areas (e.g., Chl *a*, TP, and TSS; Richards et al. 2008; Conroy et al. 2014) were negatively related to C:P and N:P ratios. In contrast, C:P ratios were significantly higher in the eastern basin further away from nutrient sources. Lower nutrient inputs combined with a greater mixing depth in the eastern basin allows for increased P loss from surface waters increasing the likelihood of P-limited phytoplankton growth and elevated C:N:P ratios (Gacher et al. 1974; Lean et al. 1983; Guildford et al. 2005). Although we can only speculate about mechanisms behind reduced particulate P concentrations across offshore areas of the lake (e.g., sedimentation or consumer uptake), particulate C:N and N:P ratios stayed relatively stable while C:P ratios increased significantly in the eastern basin. This suggests that the eastern basin acts as a net P sink, relative to C and N, thus serving as an important modifier of particulate elemental composition in Lake Erie.

In addition to spatial differences, coastal and offshore changes in C:P and N:P ratios were synchronous across the growing season. Particulate ratios were low in the spring and increased in the summer and fall in coastal areas. These patterns were likely related to differences in particulate P supply, which is typically higher during spring runoff periods and decreases over the summer and fall (MOE 2012; Chomicki et al. 2016). Early seasonal patterns were similar in offshore areas with particulate C:P and N:P ratios also increasing from spring to summer following typical dynamics of temperate lakes (Elser et al. 1995; Hessen et al. 2005). These changes are consistent with seasonal differences in primary production as high light and temperatures can increase producer metabolic rates (i.e., C-fixation), and greater production combined with lower dissolved P concentrations could result in acute P-limitation (Rhee and Gotham 1981; Spilling et al. 2015) explaining the elevated C:P and N:P ratios in coastal and offshore areas during warmer months.

Contrary to our predictions, fall stoichiometric ratios were consistently lower across both years in offshore areas, and we observed considerable inter-annual differences in particulate C:P ratios in the winter and spring. Reduced fall C:P and N:P ratios differ from previous studies in smaller

temperate lakes (Elser et al. 1995; Kreeger et al. 1997), likely reflecting site-specific physical characteristics. For instance, Lake Erie has a comparatively shallower mixing depth and a longer fetch meaning that fall turnover is likely to happen earlier resulting in dissolved nutrient regeneration and high inputs of re-suspended C, N, and P (Gacher et al. 1974; Bloesch 1982). Differences in early season dynamics between years were also likely tied to climatic factors influencing temperature and light regimes. In particular, 2014 was one of the coldest winters on record (a.k.a., “polar vortex”), and the lake was completely ice-covered in 2014–2015 (GLERL 2014), which may have decreased particulate C:N:P ratios by influencing light levels (i.e., light nutrient hypothesis; Sterner et al. 1997). Furthermore, timing of ice off could have also affected the initiation of the spring phytoplankton bloom by influencing phytoplankton succession and nutrient physiology (Adrian et al. 1999; Özkundakci et al. 2016). Given this extensive temporal variation, a more complete understanding of seasonal nutrient dynamics in Lake Erie will require coupling knowledge of both biogeochemical and physical factors shaping nutrient processing in coastal and offshore environments (Lean et al. 1983; Guildford et al. 2005; Watson et al. 2016).

Conclusions

Overall, we documented considerable spatial and seasonal variation and identified areas of abrupt transitions in particulate stoichiometry among tributaries, coastal, and offshore areas of Lake Erie. In doing so, we found unique ecosystem-level processes shaping elemental dynamics in each environment, which likely combine to influence elemental flows from catchments to inland waters and ultimately to the sea. As our work represents a first-order examination of these stoichiometric patterns, we could only generally explore the underlying mechanisms controlling C:N:P ratios of particles at any one location. Nevertheless, our study highlights the utility of using mass balance principles to better understand stoichiometric nutrient transformations in aquatic environments, and this framework should be useful for future work examining environmental factors controlling the fluxes of key biogeochemical elements within and across ecosystem boundaries.

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Conflict of Interest

None declared.

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