Recent patterns in Lake Erie phosphorus

2 concentrations in response to changing loads

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13 KEYWORDS

14 chlorophyll *a*; Great Lakes; Maumee River; monitoring; phosphorus; SRP; TP

15 ABSTRACT

16 Despite the initial success of extensive efforts to reduce phosphorus (P) loading to Lake Erie as 17 part of the Great Lakes Water Quality Agreement, Lake Erie appears to be undergoing a re-18 eutrophication and is plagued by harmful algal blooms. To offer insights into potential lake 19 responses under differing Maumee River loads and reveal recent changes with time, we explored 20 patterns in phosphorus and chlorophyll *a* data from 2008–2018 collected in western Lake Erie near 21 the mouth of the Maumee River. We found high, but relatively stable Maumee River and lake 22 concentrations of total P (TP) and soluble reactive P (SRP) with no discernable annual or seasonal 23 patterns. Maumee spring TP load was not strongly related to lake TP, and lake SRP concentrations 24 were positively but weakly related to SRP loads. Lake TP was a strong predictor of chlorophyll a, 25 but the relationship was weaker at sites closer to the Maumee. These results highlight spatial 26 differences both in P concentration and the relationship between TP and chlorophyll a, and indicate 27 that spring phosphorus loads are a weak algal biomass predictor in the portion of the western basin 28 of Lake Erie represented by these sampling stations.

29 INTRODUCTION

30 In the 1960s Lake Erie became infamous for poor water quality and was widely reported to be dying (The Economist 1965, Sweeney 1993), generating concerns of irreversible damage 31 32 (Hartman 1972). In response, Canada and the United States established total phosphorus (TP) 33 load targets to mitigate the severe anthropogenic eutrophication conditions that were a problem 34 throughout the Great Lakes. Lake Erie's target TP load was 11,000 metric tonnes yr⁻¹, a 55% 35 reduction from the estimated 1976 load (International Joint Commission [IJC] 1978). Under 36 these new restrictions water quality improved, and the problem was considered solved (De Pinto 37 et al. 1986, Makarewicz and Bertram 1991, Ludsin et al. 2001). 38 Paradoxically, since the early 2000s, Lake Erie has again become plagued by harmful 39 algal blooms (HABs) despite the fact that TP loads have met the target in most years (Baker et 40 al. 2014). In 2011, for example, Lake Erie experienced a record bloom despite meeting the 1978 41 target (Michalak et al. 2013). Subsequently, in 2014 the city of Toledo, Ohio issued a do-not-42 drink advisory when toxins found in treated water were traced back to high toxin concentrations 43 in the intake water due to a *Microcystis* bloom (Steffen et al. 2017). Furthermore, in the past few 44 years both Michigan and Ohio have declared the open waters of western Lake Erie as impaired 45 due to HABs as per the Clean Water Act (Davis et al. 2019). Recognizing the resurgent problem, 46 Canada and the United States proposed lower phosphorus targets, which became effective in 47 2016. These new targets focus on inputs from the Maumee River (Figure 1), considered the main 48 driver of HABs in Lake Erie's western basin, and include spring (March–July) limits for both 49 total phosphorus (860 metric tons) and dissolved reactive phosphorus (186 metric tonnes) 50 (Annex 4 Report 2015).



To better understand the response of western Lake Erie to yearly differences in spring

52 phosphorus load we analyzed phosphorus and chlorophyll *a* concentration data collected over an 53 approximately 300 km² region (Figure 1) near the mouth of the Maumee River by the National 54 Oceanic and Atmospheric Administration Great Lakes Environmental Research Laboratory 55 (NOAA GLERL) and the University of Michigan Cooperative Institute for Great Lakes Research 56 (CIGLR). These data reveal changes during the recent period of re-eutrophication and, when 57 compared with Maumee River data, offer insights into the effect of differing phosphorus inputs. 58 Our results will help guide expectations as management actions are implemented throughout the 59 watershed to meet the new phosphorus targets.

60 MATERIALS AND METHODS

Maumee River data collection. Maumee River flow and nutrient concentration data have been collected nearly continuously by the National Center for Water Quality Research (NCWQR) at Heidelberg University and the USGS since 1974. NCWQR collects water 5.6 km upstream of the USGS stream gage at Waterville (USGS #04193500). Details on lab analysis for Maumee River samples can be found in Baker et al. (2014).

66 Western Lake Erie data collection. We collected surface (0.75 m) samples at set stations

67 (Table 1, Fig. 1) from western Lake Erie from spring (April-May) until fall (October-

68 November) from 2008–2018. Additional "bloom chasing" samples were collected in 2008–2013

69 to target large *Microcystis* blooms. Weekly sampling stations were not set until 2009, so we

70 present the 2008 data plus the bloom chasing samples as site "other" and do not include it in the

violin plots showing concentration data over time at set sampling stations. Samples were taken

- 72 with a modified clean Niskin bottle (Fahnenstiel et al. 2002), poured into acid-washed 4 L
- 73 Nalgene containers, stored in coolers, and brought to GLERL for immediate processing.

74 Chlorophyll *a* (chl *a*) samples were filtered onto Whatman GF/F filters (0.7 μm nominal

pore size) and frozen until extraction the next day. Two replicate filters were extracted with N,
N-dimethylformamide (Speziale et al. 1984) and analyzed on a Turner Designs fluorometer
calibrated with commercial chl *a* standards.

Two replicate raw water samples for total phosphorus (TP) were collected from each site.
Total phosphorus samples were digested by the persulfate oxidation method and stored at room
temperature until analysis. Two replicates were filtered through a 0.2 µm nylon filter for soluble
reactive phosphorus (SRP) and frozen until analysis. TP and SRP concentrations were
determined on a SEAL QuAAtro or AA3 autoanalyzer (SEAL Analytical Inc., Mequon, WI
USA) using standard colorimetric procedures (APHA 1998) as detailed by the instrument
manuals.

85 Statistical analysis. We estimated multilevel/partially pooled Bayesian hierarchical models of Maumee River loads vs. lake P and chl a vs. TP where slope and intercept differed by station 86 87 using the 'rstanarm' package (Goodrich et al. 2018) in R (R Core Team, 2018). Partial pooling 88 combines information from all stations such that parameters for a given station can be estimated 89 when only a few observations are available (Stow et al. 2009, Qian 2017). We used diffuse 90 normal prior distributions with a mean of zero. We ran three chains for 10,000 iterations and 91 discarded the first half as warm-up to obtain 15,000 simulations for analysis. We confirmed 92 convergence using Gelman-Rubin statistic (R-hat <1.01; Gelman and Hill 2006) and by 93 examining traceplots. None of the models had influential outliers as assessed by leave-one-out 94 cross-validation ('loo') in the 'rstan' package (Stan Development Team 2018).

95 **RESULTS**

96	Maumee River TP concentrations were highly variable by about an order of magnitude,
97	but fairly consistent in range and average from 2009–2018 (Figure 2, top panel). For every year
98	except 2012, the median (160–250 μ g L ⁻¹) and average (200–280 μ g L ⁻¹) daily TP concentrations
99	were similar. A higher frequency of low concentrations was observed in 2012 than for other
100	years resulting in a lower median (140 μ g L ⁻¹) and average (180 μ g L ⁻¹). There was no
101	discernible monthly pattern; in some years the highest concentrations occurred in March and
102	April (e.g., 2009, 2012, 2013) while in some years March and April exhibited the lowest
103	concentrations (e.g., 2010, 2017, 2018).
104	Lake TP concentrations were variable within a year but showed only slight year-to-year
105	variability, although data at some sites was insufficient to draw any conclusions regarding
106	changes with time (Figure 2, bottom panel). Concentrations were generally related to distance
107	from the mouth of the Maumee River; the highest average concentrations occurred at Sites
108	WE06 (average \pm SD = 114 \pm 129 µg L ⁻¹) and WE09 (158 \pm 119 µg L ⁻¹), which are 6.9 and 4.5
109	km, respectively, from the river mouth (Table 1, Figure 1). Conversely, the lowest TP
110	concentrations occurred at sites WE03 (27.4 \pm 12.9 μg $L^{\text{-1}}$), WE04 (24.0 \pm 15.4 μg $L^{\text{-1}}$), and
111	WE05 (28.1 \pm 17.5 µg L ⁻¹), which are 25.0, 27.1, and 21.0 km, respectively, from the river
112	mouth. There were no discernable patterns with lake TP and sampling month (Figure 2, bottom
113	panel).
114	Maumee River spring TP loads ranged from 393–2,318 metric tonnes (2012 and 2011,
115	respectively; Figure 3). Lake TP concentrations ranged from 1.8–2,482 μ g L ⁻¹ . The relationship
116	between spring TP load and lake TP across all sites and years was likely positive, though the

117 95% credible interval included negative values (slope = 0.008 [-0.009, 0.026]; mean and 95%

118 credible interval [CRI]; Figure 3). The slopes differed among sites, but there was high

uncertainty in the model. Only three sites (WE06, WE08, and WE09) had strictly positive CRIs(Figure 3).

121	Maumee River SRP concentrations varied over two orders of magnitude, but had no							
122	discernable inter-annual patterns from 2009–2018 (Figure 4, top panel). Similar to TP, 2012 had							
123	lower average (37 μ g L ⁻¹) and median (35 μ g L ⁻¹) SRP than the annual medians (45–87 μ g L ⁻¹)							
124	and averages (45–86 μ g L ⁻¹) from all other years. There was no discernable monthly pattern; in							
125	some years the highest concentrations happened in March and April (e.g., 2011, 2012), whereas							
126	in March and April had the lowest concentrations in other years (e.g., 2015, 2017).							
127	Lake SRP was variable across sites and among years, with no consistent temporal							
128	patterns (Figure 4, bottom panel). Sites WE06 (average \pm SD = 19.7 \pm 27.9 μg $L^{\text{-1}}$) and WE09							
129	$(29.7\pm29.5~\mu g~L^{\text{-1}})$ had the highest average SRP concentrations, similar to what was observed in							
130	TP. The lowest concentrations were at sites WE03, WE04, and WE05 (average \pm SD of 1.9 \pm							
131	2.4, 2.5 \pm 3.4, and 2.0 \pm 2.8 μ g L ⁻¹ , respectively). There were no consistent patterns in SRP							
132	concentrations and sampling month.							
133	Spring SRP loads ranged from 64–610 metric tonnes (2012 and 2015, respectively;							
134	Figure 5) and lake SRP concentrations ranged from 0.04–135 μ g L ⁻¹ . Across all sites and years							
135	there was an overall positive relationship between spring SRP load and lake SRP (slope = 0.021							
136	[0.004, 0.037]; Figure 5). Unlike TP, the site-specific slope estimates were all positive (Figure							
137	5), although most 95% credible intervals included negative values. Five sites (WE02, WE06,							
138	WE08, WE09, and WE12) had strictly positive CRIs. Sites WE06 and WE09 had the strongest							
139	relationships with SRP spring load (slope = 0.052 [0.037 , 0.676] and slope = 0.066 [0.046 ,							
140	0.086], respectively), and sites WE03 (slope = 0.006 [-0.012, 0.029]), WE04 (slope = 0.004 [-							
141	0.011, 0.018], and WE05 (slope = 0.008 [-0.014, 0.030]) the weakest (Figure 5).							

142	We observed a large range of chl <i>a</i> and TP concentrations, and sites with higher TP
143	tended to have higher chl a (Table 1). We found support for a strong, positive relationship
144	between chl a and TP for all sites together (slope = 0.793 [0.563, 1.035]; Figure 6), and at
145	individual sites (Figure 6, inset). The credible intervals were generally overlapping, indicating
146	weak differentiation among stations. The relationship was strongest at sites WE08 (slope = 1.257
147	[1.024, 1.497]) and WE15 (slope = 1.191 [0.747, 1.667], Figure 6). Site WE15 is the farthest site
148	from the Maumee (Table 1), while WE08 is closer to the River Raisin than most sites.
149	Conversely, sites WE06, WE09, and WE12 had lower slopes and a higher intercept, suggesting
150	higher TP and chl <i>a</i> overall (Table 1), but a weak response of algal biomass to TP (Figure 6).
151	These three sites lie almost directly at the mouth (WE09 and WE06), or along the southern shore
152	(WE12, Figure 1). The bloom-chasing ("other") samples were very similar to the overall
153	estimates (Figure 6).

154 **DISCUSSION**

155 The establishment of phosphorous load targets to control eutrophication was 156 revolutionary in the 1970s, arising from a body of work by Richard Vollenweider that produced 157 the "phosphorus loading concept". This concept is based on the premise that P loading influences 158 lake P concentrations, and higher P concentrations lead to higher primary production 159 (Vollenweider and Dillon 1974). We found that, despite large differences in Maumee River 160 spring loads, western Lake Erie exhibited highly variable phosphorus concentrations from 2008-161 2018 with no discernable trends. While our results did demonstrate a consistent positive 162 relationship between lake TP and chlorophyll a, the overall weak relationship between load and 163 lake phosphorus concentration indicates that spring phosphorus loads are a poor algal biomass 164 predictor in this portion of western Lake Erie.

165 Our results highlighted spatial differences in phosphorus concentration; sampling stations 166 generally reflected Maumee River concentrations based on proximity to the river mouth. Larson 167 et al. (*in revision*) showed a similar pattern, reflecting the gradient between very low 168 concentrations entering from the Detroit River to the north and the high Maumee River 169 concentrations from the south. The high Maumee phosphorus concentrations may promote 170 western basin cyanobacterial dominance. The probability of cyanobacteria becoming dominant 171 in experiments increases to about 80% at TP of 0.1 mg L⁻¹ (Downing et al. 2001), and experimental *Microcystis* growth plateaus at 0.22 mg L⁻¹ TP with sufficient light and nitrogen 172 173 (Baldia et al. 2007). In our analysis, Maumee River concentrations were on average $\sim 0.2 \text{ mg L}^{-1}$ 174 TP in the spring, and the lake sites closer to the Maumee (e.g., WE06 and WE09) frequently had 175 TP concentrations in this range.

176 The relationship between TP and algal biomass (as chl a) also depended on proximity to 177 the Maumee River. Stations WE06 and WE09, near the mouth of the river, which exhibited the 178 strongest TP load to lake TP concentration-response (Figure 4), exhibited the weakest chl a - TP179 relationship (Figure 6). Conversely, stations farther away (e.g., WE04 and WE05), which had 180 minimal TP load-response relationships had stronger, better defined chl a – TP relationships. 181 This decoupling at stations closer to the Maumee could result from several factors: vertical 182 migration of cells/colonies not captured by sampling at 0.75 m, light limitation, the relative 183 proportion of non-organic particulate vs. soluble P, shorter residence time, or a lack of nutrient 184 limitation near the river mouth. However, the consistently positive relationship suggests that 185 phosphorus concentration decreases should promote lower primary productivity (Stow and Cha 186 2013).

187

Western Lake Erie's algal biomass, since the late 1990s, has been correlated with

188 Maumee River spring phosphorus load (Stumpf et al. 2012, Obenour et al. 2014), which may 189 seem to contrast our result of only modest relationships between phosphorus load and lake 190 concentration. However, the algal biomass reported in these studies is an estimate for the entire 191 western basin, which captures the spatial extent of the bloom, not necessarily local 192 phytoplankton intensity. Higher spring loads result largely from higher river flow, which carries 193 phosphorus farther into the lake where variable circulation patterns can widely distribute 194 phosphorus resulting in a more spatially extensive bloom. Thus, when evaluating the effect of 195 fluctuating loads it is important to differentiate the bloom spatial extent, which is strongly 196 determined by Maumee River flow (Stumpf et al. 2012), from phytoplankton density, which is 197 influenced by local phosphorus concentration.

198 These results have important implications for monitoring conducted to evaluate Lake 199 Erie's response to management actions to meet the new load targets and for guiding public 200 expectations. Higher loads will continue to cause spatially extensive blooms, but these result 201 largely from annual differences in precipitation, temperature, and antecedent soil moisture, 202 which are independent of phosphorus management activities. Thus evaluating yearly load 203 changes over time may not clearly reflect phosphorus mitigation activities in the basin. 204 Additionally, both precipitation (USGCRP 2018) and Maumee River flow have been increasing 205 (Stow et al. 2015) which may obscure, or even partially offset, the effect of phosphorus 206 management efforts. To separate these, Choquette et al. (2019) presented methods to track load 207 changes by removing the effect of changing river flow. However, effective watershed 208 management actions should eventually lower Maumee River phosphorus concentrations 209 sufficiently to reduce western basin phosphorus and chlorophyll a concentrations. Assessing

- 210 these responses in the lake requires a large-scale monitoring network to effectively document
- 211 both changes in the spatial extent of the bloom and local phosphorus concentrations.

212 FIGURES







Figure 2. Total phosphorus (TP) in the Maumee River as daily flow-weighted mean concentrations (top panel) and lake concentrations at regularly monitored sites (bottom panel). Months are represented in different colors. For each violin, the horizontal line shows the median, and the black

- squares show the average for a year. Only regularly sampled stations with more than one year of
- 220 data are included.



222	Figure 3. Maumee River spring (1 Mar–30 Jul) loads vs. lake concentrations for total phosphorus
223	(TP) 2008–2018 in Lake Erie. (A) Regularly sampled sites (Figure 1) and extra samples ("other")
224	are depicted in inset with estimated regression plus 100 posterior draws (gray lines). The larger
225	figure depicts the intercepts and slopes estimated for each station (gray lines) and overall
226	regression (black line). Each point represents an average of all samples from a site within a year.
227	(B) Coefficient means with 50% (thick line) and 95% (thin lines) credible intervals for the model.



Figure 4. Soluble reactive phosphorus (SRP) in the Maumee River as daily flow-weighted mean
concentrations (top panel) and lake concentrations at regularly monitored sites (bottom panel).
Months are represented in different colors. For each violin, the horizontal line shows the median,

- and the black squares show the average for a year. Only regularly sampled stations with more than
- 234 one year of data are included.



Figure 5. Maumee River spring (1 Mar–30 Jul) loads vs. lake concentrations for soluble reactive phosphorus (SRP) 2008–2018 in Lake Erie. (A) Regularly sampled sites (Figure 1) and extra samples ("other") are depicted in inset with estimated regression plus 100 posterior draws (gray lines). The larger figure depicts the intercepts and slopes estimated for each station (gray lines) and overall regression (black line). Each point represents an average of all samples from a site within a year. (B) Coefficient means with 50% (thick line) and 95% (thin lines) credible intervals for the model.



- Figure 6. Chlorophyll *a* (chl *a*) vs. total phosphorus (TP) from 2008–2018 in Lake Erie. (A)
- 245 Regularly sampled sites (Fig 1) and extra samples ("other") are depicted in inset with estimated
- 246 regression plus 100 posterior draws. The larger figure depicts the intercept and slopes estimated
- for each station (gray lines) and overall regression (black line). (B) Coefficient means with 50%
- 248 (thick line) and 95% (thin lines) credible intervals for the model.

TABLES.

 Table 1. Site descriptions including years sampled, number of samples collected (n), and coordinates, and the average and range

 (min-max) of phosphorus and chlorophyll samples from the western basin of Lake Erie.

Site	Years	n ¹	Latitude	Longitude	Distance ² from Maumee	Total phosphorus ($\mu g L^{-1}$)		Soluble reactive phosphorus ($\mu g L^{-1}$)		Chlorophyll a (µg L ⁻¹)	
					(km)	avg	range	avg	range	avg	range
WE01	2009–2011	32	41.88265	-83.32794	24.0	44.2	(16.6–107.0)	2.9	(0.3–12.7)	27.7	(3.1–109.0)
WE02	2009–2018	167	41.76217	-83.33000	13.7	62.9	(13.9–334.0)	10.9	(0.04–118.0)	28.2	(0.7–194.0)
WE03	2009–2011	34	41.85920	-83.26237	25.0	27.4	(12.3–74.7)	1.9	(0.04–9.0)	22.0	(1.8–115.0)
WE04	2009–2018	164	41.82667	-83.19317	27.1	24.0	(5.9–99.7)	2.5	(0.04–20.6)	15.0	(0.4–120.0)
WE05	2009–2011	35	41.79967	-83.25732	21.0	28.1	(9.4–81.1)	2.0	(0.08–9.4)	14.4	(0.6–44.7)
WE06	2009–2018	166	41.70517	-83.38533	6.9	114.0	(1.8–1468.0)	19.7	(0.08–135.0)	49.4	(0.7–532.0)
WE07	2009–2011	34	41.73428	-83.40275	7.0	56.7	(19.8–132.0)	9.3	(0.4–47.6)	24.9	(5.4–99.3)
WE08	2009–2018	167	41.83400	-83.36383	17.8	80.5	(14.9–2482.0)	7.8	(0.1–52.6)	74.7	(0.8–6784.0)
WE09	2009–2018	93	41.71765	-83.42378	4.5	158.0	(31.8–807.0)	29.7	(0.4–117.0)	42.0	(4.4–183.0)
WE12	2014–2018	98	41.70317	-83.25433	17.7	63.6	(9.9–224.0)	11.1	(0.1–70.4)	22.1	(1.9–190.0)
WE13	2014–2018	94	41.74100	-83.13617	28.0	35.1	(4.0–182.0)	4.4	(0.05–26.1)	17.6	(1.6–173.0)
WE15	2015-2018	48	41.61667	-83.00933	39.1	39.4	(11.3–128.0)	4.9	(0.4–30.1)	30.5	(1.2–221.0)
WE16	2018	15	41.65968	-83.14287	27.3	31.1	(17.1–61.1)	4.8	(1.5–18.3)	14.4	(1.8–26.9)
Other ³	2008–2013	164	Various	Various	—	59.2	(10.4–380.0)	4.0	(0.03–20.9)	33.8	(0.1–180.0)

¹All data are from surface samples collected at 0.75 m.

²The distance from the Maumee River was calculated as the straight line distance between the Maumee River mouth and each lake site.

³ 'Other' includes sites that were sampled for only one season (n = 65) as well as opportunistic samples collected during algal blooms n = 99).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This publication is contribution #xxxx from the Cooperative Institute for Great Lakes Research,

University of Michigan under the NOAA Cooperative Agreement NA17OAR4320152.

ACKNOWLEDGMENTS

We thank the captains and crews of the research vessels and the technicians at GLERL. Funding was provided by the Great Lakes Restoration Initiative.

ABBREVIATIONS

Chl *a*, chlorophyll *a*; CRI, credible interval; GLWQA, Great Lakes Water Quality Agreement; HAB, harmful algal bloom; SRP, soluble reactive phosphorus; TP, total phosphorus.

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