Routine monitoring of Western Lake Erie to track water guality 1

changes associated with cyanobacterial harmful algal blooms 2

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19 Abstract

The western basin of Lake Erie has a history of recurrent cyanobacterial harmful algal blooms 20 21 (HABs) despite decades of efforts by the United States and Canada to limit phosphorus 22 loading, a major driver of the blooms. In response, the National Oceanic and Atmospheric 23 Administration (NOAA) Great Lakes Environmental Research Laboratory (GLERL) and the 24 Cooperative Institute for Great Lakes Research (CIGLR) created an annual sampling program 25 to detect, monitor, assess, and predict HABs in western Lake Erie. Here we describe the data 26 collected from this monitoring program from 2012 to 2021. This dataset includes observations 27 on physico-chemical properties, major nutrient fractions, phytoplankton pigments, microcystins, 28 and optical properties for western Lake Erie. This dataset is particularly relevant for creating 29 models, verifying and calibrating remote sensing algorithms, and informing experimental 30 research to further understand the water quality dynamics that influence HABs in this 31 internationally significant body of freshwater. The dataset can be freely accessed from NOAA 32 National Centers for Environmental Information (NCEI) at https://doi.org/10.25921/11da-3x54 33 (Cooperative Institute for Great Lakes Research, University of Michigan; NOAA Great Lakes 34 Environmental Research Laboratory, 2019).

35 Introduction

36 Lake Erie is situated on the international boundary between the United States and 37 Canada and is the smallest by volume of the five Laurentian Great Lakes. It is ecologically. 38 culturally, and economically significant to the approximately 12.5 million people who live in the 39 watershed. Each year Lake Erie supports nearly 14,000 tonnes of commercial and traditional 40 fisheries, over 33,000,000 tonnes of freight, and over \$1.5 million in recreation and tourism 41 business (Sterner et al., 2020). Lake Erie has endured multiple anthropogenic stressors since 42 European settlement in the area, most notably the draining of coastal wetlands for development 43 of agricultural lands in the late 18th century (Allinger and Reavie, 2013). Currently, the 44 ecological state of Lake Erie is considered poor, partially due to excess nutrient input that 45 supports harmful algal blooms (HABs; ECCC and US EPA, 2022). These seasonal HABs are 46 typically dominated by toxin producing cyanobacteria, causing concern for public and 47 ecosystem health (Watson et al., 2016). Humans can be exposed to cvanotoxins through 48 ingestion of contaminated fish and drinking water and through inhalation and dermal exposure 49 during recreational events such as swimming and boating (Carmichael and Boyer, 2016; Buratti 50 et al., 2017). Cyanotoxins can also cause illness and death in aquatic and terrestrial animals 51 (Carmichael and Boyer, 2016). The economic cost of HABs impacts in Lake Erie is estimated to 52 be hundreds of millions of dollars each year (Smith et al., 2019).

To combat the deteriorated state of Lake Erie water quality, bi-national water resource management policies alongside scientific research and water quality monitoring efforts have been underway for decades. The Great Lakes Water Quality Agreement (GLWQA), first signed in 1972, was a commitment between the US and Canada in response to degraded water quality throughout the Great Lakes ecosystem (GLWQA, 2012). Phosphorus was found to be the key nutrient that was promoting excess phytoplankton growth (Charlton et al., 1993), and thus the GLWQA sought to limit total phosphorus input to the lakes in an attempt to reduce

60 phytoplankton growth and biomass (Steffen et al., 2014). The 1972 Clean Water Act (CWA) was similarly enacted to regulate point-source pollution discharge, including phosphorus, into 61 62 navigable waters in the United States. After the signing and implementation of the phosphorus 63 load reduction practices outlined in the GLWQA and CWA, the water quality of Lake Erie 64 improved and the lake experienced a period of restoration (Makarewicz and Bertram, 1991). 65 This success was attributed to upgrades to sewage treatment plants and industrial discharges 66 which reduced phosphorus loading from point sources by 50% within ten years of peak levels 67 observed in 1968 (Charlton et al., 1993; Joosse and Baker, 2011; Steffen et al., 2014).

68 While the water quality of Lake Erie rebounded in the 1980s and early 1990s, by the mid 69 1990s and early 2000s annual HAB events were occurring in Lake Erie again, particularly in the 70 warm, shallow western basin (Allinger and Reavie, 2013; Kane et al., 2015; Watson et al.,

71 2016). Total phosphorus loading has been relatively stable in Lake Erie from the 1980s onward 72 (Dolan and Chapra, 2012; Watson et al., 2016), and although point-source phosphorus loading 73 controls had been a successful mitigation measure at one point, several anthropogenic 74 stressors within the watershed were exacerbating the issue of poor water quality. An increase in 75 agricultural sources of biologically available soluble nutrients, legacy phosphorus in the Lake 76 Erie watershed, altered nutrient cycling by invasive dreissenid mussels, and climate change are 77 thought to be primarily responsible for the HABs resurgence (Vanderploeg et al., 2001; Conroy 78 et al., 2005; Bridoux et al., 2010; Michalak et al., 2013; Matisoff et al., 2016; Huisman et al., 79 2018; Van Meter et al., 2021).

The post-recovery period HABs have predominantly been composed of the cyanobacteria species *Microcystis aeruginosa* along with genera *Anabaena, Aphanizomenon, Dolichospermum,* and *Planktothrix* (Steffen et al., 2014; Watson et al., 2016). These cyanobacteria can produce an array of several types of phycotoxins, with the most common being a suite of hepatotoxins known as microcystins (MCs). Microcystins primarily affect the liver but can also cause adverse health effects on the kidneys, brain, and reproductive organs

86 (Carmichael and Boyer, 2016). Phycotoxins are commonly present during Lake Erie HABs, and
87 in August 2014 the city of Toledo, OH drinking water supply was contaminated with MCs,

leaving >400,000 without clean drinking water (Steffen et al., 2017).

89 To understand HAB events in US waterways, Congress authorized the Harmful Algal 90 Bloom and Hypoxia Research and Control Act in 1998 (HABHRCA; Public Law 115-423) which 91 mandated the National Oceanic and Atmospheric Administration (NOAA) to "advance the 92 scientific understanding and ability to detect, monitor, assess, and predict HAB and hypoxia 93 events". Under HABHRCA, the NOAA Great Lakes Environmental Research Lab (GLERL), NOAA National Centers for Coastal Ocean Science (NCCOS), and the Cooperative Institute for 94 95 Great Lakes Research (CIGLR; formerly CILER - Cooperative Institute for Limnology and 96 Ecosystems Research) developed an ecological forecast to predict HAB events in Lake Erie. 97 Starting in 2008, researchers at these institutes began using remote sensing to monitor 98 seasonal HABs, created a seasonal forecast system based on spring P loads, and developed 99 models to predict short-term bloom changes to alert stakeholders and the public (Rowe et al., 100 2016). Products from these efforts, known as Lake Erie Harmful Algal Bloom Forecasts, are 101 freely available during the bloom season at https://coastalscience.noaa.gov/research/stressor-

102 <u>impacts-mitigation/hab-forecasts/lake-erie/</u>.

103 In-situ sampling of the bloom was necessary to calibrate and validate the remote 104 sensing images and models as well as measure microcystin concentration. Sampling events 105 were led by personnel at GLERL and CIGLR starting in 2008 and were designed to collect 106 discrete samples within the extent of the bloom area. At first, samples were taken 107 opportunistically within the bloom and sampling locations and analytical parameters were 108 inconsistent. In 2009, regular sampling stations were identified based on spatial patterns of the 109 bloom. From 2009 to 2011, in addition to opportunistic samples, nine main stations in the 110 western basin of Lake Erie were sampled intermittently from June through October (Bertani et 111 al., 2017; Rowland et al., 2020). While these sampling efforts initially began to complement

existing research products, the experimental nature of the 2008 to 2011 sampling cruises also
provided insight into creating a regular monitoring program that would support critical research
and product development related to western Lake Erie HABs.

115 In 2012, researchers at GLERL and CIGLR, with support from the Great Lakes 116 Restoration Initiative (GLRI), formalized a sampling regimen to monitor the spatial and temporal 117 variability of seasonal HAB events in western Lake Erie (WLE). The establishment of this 118 monitoring program corresponded with increased federal emphasis on evaluating trends and 119 drivers of WLE HABs and water quality. Four monitoring stations were identified and regular 120 surface samples were collected from May to September and analyzed for nutrient, pigment, and 121 particulate microcystin concentrations (Figs. 1 & 2). In following years, the monitoring program 122 evolved and expanded. New stations were added to better characterize the bloom and 123 complement other observing systems. Sampling parameters were adjusted and added based on 124 the needs of current research (Table 1). Results of these sampling cruises were compiled and 125 distributed informally upon request until 2019 when the data were organized and archived on 126 the NOAA National Centers for Environmental Information (NCEI) open-access data repository 127 (https://www.ncei.noaa.gov/).

128 Long term monitoring of WLE is fundamental to the continual assessment of water 129 guality changes in response to both stressors and water guality management efforts (Hartig et 130 al., 2009, 2021). The GLERL/CIGLR monitoring data has been used by numerous researchers 131 to develop and assess models (Rowe et al., 2016; Weiskerger et al., 2018; Fang et al., 2019; 132 Liu et al., 2020; Qian et al., 2021; Wang and Boegman, 2021; Hellweger et al., 2022; Maguire et 133 al., 2022), to calibrate remote sensing algorithms (Sayers et al., 2016, 2019; Avouris and Ortiz, 134 2019; Bosse et al., 2019; Vander Woude et al., 2019; Pirasteh et al., 2020; Xu et al., 2022), and 135 to elucidate ecological mechanisms and complement experimental data (Cory et al., 2016; 136 Reavie et al., 2016; Berry et al., 2017; Steffen et al., 2017; Kharbush et al., 2019, 2023; Newell

et al., 2019; Den Uyl et al., 2021; Smith et al., 2021, 2022; Hoffman et al., 2022; Marino et al.,
2022; Yancey et al., 2022a, b).

The objective of this paper is to inform users of the dataset "Physical, chemical, and biological water quality monitoring data to support detection of Harmful Algal Blooms (HABs) in western Lake Erie, collected by the Great Lakes Environmental Research Laboratory and the Cooperative Institute for Great Lakes Research since 2012" by describing the data generated from this monitoring program and detailing how samples were collected and analyzed. This paper contextualizes this long-term data set so that it can continue to be used to benefit our collective ecological knowledge of western Lake Erie.

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Table 1. Description of stations sampled in western Lake Erie from 2012 to 2021. Latitude and
longitude (decimal degree) coordinates for each station are target locations as the boat was
allowed to drift at each site during *in-situ* sampling.

Station	Latitude	Longitude	Avg. Depth (m)	Years Monitored
WE02	41.762	-83.330	5.4	2012-2021
WE04	41.827	-83.193	8.4	2012-2021
WE06	41.705	-83.385	2.9	2012-2021
WE08	41.834	-83.364	4.8	2012-2021
WE09	41.718	-83.424	2.7	2016-2021
WE12	41.703	-83.254	6.6	2014-2021
WE13	41.741	-83.136	8.9	2014-2021
WE14	41.720	-83.010	9.3	2015
WE15	41.617	-83.009	4.5	2015-2017
WE16	41.660	-83.143	6.2	2018-2021

152 Methods

153 Study Site

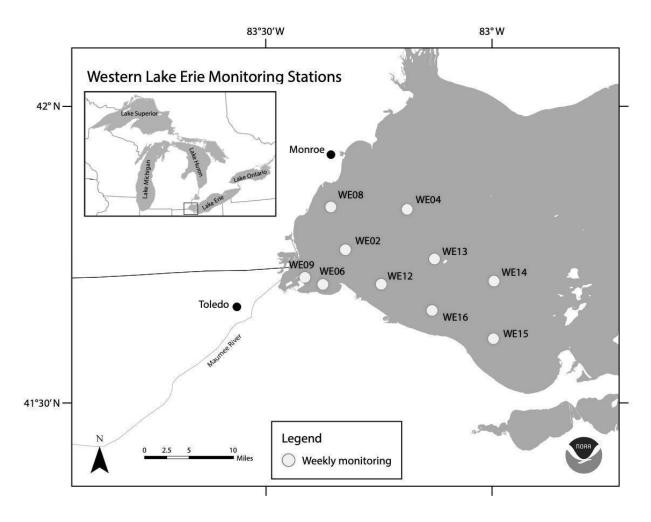
154 Based on the lake's bathymetry, Lake Erie can be divided into the eastern, central, and 155 western basins which in turn influence physical and biological processes (Allinger and Reavie, 156 2013). The data presented in this paper were collected from the western basin, which 157 encompasses the western part of the lake to Point Pelee, ON, Canada and Cedar Point, OH, 158 USA (Fig. 1). The well-mixed western basin is the shallowest (maximum average depth of 11 159 m), warmest, and most productive of the three basins. Although it's typical for temperate WLE to 160 have ice cover in the winter (Jan to Mar), summer (Jul to Sep) surface water temperatures often 161 reach or exceed 25 °C. The western basin receives 95% of its hydraulic inflow from the Detroit 162 River, which connects Lake Erie hydrologically to Lake Huron via the St. Clair River and Lake 163 St. Clair (Cousino et al., 2015). Among the other tributaries to WLE (including River Raisin, 164 Portage River, Ottawa River, Stony Creek, Swan Creek, and Sandusky River), the Maumee 165 River discharges into the western basin near the city of Toledo, Ohio and contributes a 166 significant amount of sediments and nutrients to the entire Lake Erie basin (Baker et al., 2014a, 167 b; Rowland et al. 2020; see NCWQR 2022 for Maumee River water quality data). Nutrient and 168 sediment loads from the Maumee River can vary with precipitation, where stormwater runoff can 169 provide a pulse of nutrients into the basin, potentially altering cyanobacteria dynamics (Baker et 170 al., 2014a; King et al., 2022). Land use in the Lake Erie watershed is 75% agricultural and 11% 171 urban, both of which contribute to the large amounts of soluble reactive phosphorus into the 172 basin (Mohamed et al., 2019; Myers et al., 2000).

173 This dataset includes water quality data from ten monitoring stations on the United 174 States side of WLE that were sampled from 2012 to 2021 (Figs. 1 & 2, Tables 1 & 2). The

175 average depth of monitoring stations ranged from 2.7 m at WE9 to 9.3 m at WE14. These sites 176 were chosen to reflect the various nutrient and hydrologic inputs and gradients into WLE, as 177 well as represent areas of the basin that are prone to HABs. The Maumee River inflow was a 178 major consideration in determining these sites. The initial 4 stations sampled in this program 179 (WE02, WE04, WE06, and WE08) were selected because they were consistently within the 180 WLE blooms occurring at the time. Additional sites were later added to better represent the 181 spatial extent of HABs and to augment existing data provided by moored buoy continuous 182 monitoring systems, advanced monitoring technologies, such as Environmental Sample 183 Processors (Den Uyl et al., 2022), and other monitoring programs in WLE.

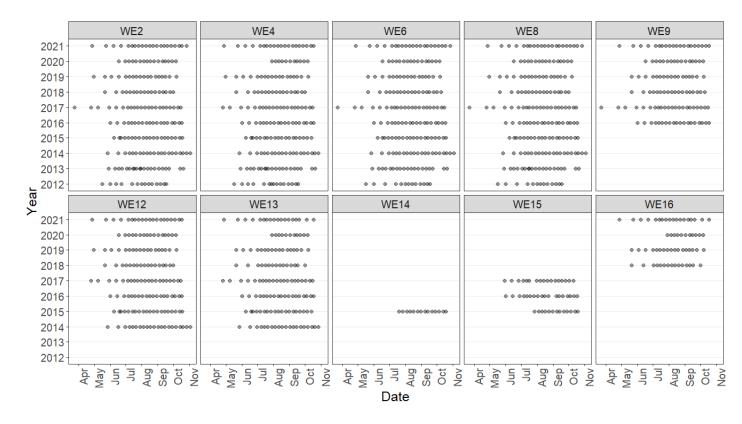
184 Field Sampling

185 Western Lake Erie discrete field sampling was accomplished using NOAA GLERL 186 research vessels. Sampling took place during ice-free months and aimed to quantify the 187 environmental conditions prior to, during, and at the end of the bloom (Fig. 2). Sampling stations 188 represent approximate locations (Table 1; Fig. 1); in situ measurements and sampling were 189 collected once the boat reached the targeted location and then proceeded to drift during 190 sampling. The frequency and timing of those cruises varied over the first few years but has been 191 consistent since 2017 (Fig. 2). Sampling was disrupted in 2020 due to the global COVID-19 192 pandemic and resulting public health restrictions. In 2020, sampling was initiated in mid-June at 193 a reduced number of sites for select water quality parameters. In July, sampling stations and 194 parameters were expanded and all stations and parameters were sampled and measured by 195 August 2020. The prior standard sampling schedule resumed in April 2021.



196

- 197 Figure 1. Location of western Lake Erie water quality monitoring stations. This map was
- 198 provided by NOAA for use in this publication.



199

Figure 2. Sampling frequency for each monitoring station for years sampled between 2012 to2021.

203 In-situ measurements for conductivity, temperature, dissolved oxygen (DO), beam 204 attenuation, transmission, and photosynthetically active radiation (PAR) were taken with a Sea-205 Bird 19plus V2 conductivity, temperature, and depth (CTD) profiler attached to a hydraulic 206 crane. Data were collected on the downcast and were reported as the mean of recorded values 207 within ± 0.5 m of the discrete sample depth. In 2012, sample temperature was taken on the boat 208 with a Vee Gee Scientific IP67-rated digital thermometer. Sky conditions were recorded at the 209 discretion of the field technician at each station during the sampling cruise. A Secchi disk was 210 lowered into the water on the shaded side of the boat at each station and the depth at which the 211 Secchi disk was no longer visible was recorded (Wetzel and Likens, 2000). 212 Water column samples were collected using a 5 L vertical Niskin bottle (General

213 Oceanics model 1010). Niskin casts were evenly distributed between one or more high-density

214 polyethylene bottles that were rinsed with site water and stored in a cooler. Three to four Niskin 215 casts were used to fill the bottles, such that each bottle is a composite sample of the water 216 collected. Surface samples were taken 0.75 m below the water's surface, mid-column samples 217 were taken at approximately 4.25 m below surface, and benthic or bottom samples were taken 218 at approximately 0.5 m above the lake bottom at each station. Surface samples were taken at 219 all stations while mid-column and benthic sample collection varied between sites and years. 220 Scum samples of dense cyanobacterial accumulation on the surface of the water were collected 221 opportunistically using a 2 L modified Van Dorn water sampler. Sampling times were reported 222 as Eastern Daylight Time (UT -4:00). Upon arrival at the laboratory, raw water samples were 223 immediately subsampled and preserved until analysis.

224 Wind speed and wave height data were obtained from moored buoy continuous 225 monitoring systems in proximity to sampling stations for a timestamp that corresponded to the 226 time samples were collected at that station. Wave height data for all stations were obtained from 227 the Toledo Intake Buoy (owned and maintained by Limnotech Inc.). Wind speed data for 228 stations WE02, WE06, WE09, WE12, WE14, WE15, and WE16 were also collected from this buoy. Data for this buoy is available through the Great Lakes Observing System (GLOS; 229 230 platform ID 45165, https://seagull.glos.org/data-console/71). Wind speed data for stations 231 WE04, WE08, and WE13 were obtained from the Toledo Harbor Light no. 2 buoy (Station 232 THLO1, owned and maintained by GLERL). Data for this buoy is available through NOAA's 233 National Data Buoy Center (https://www.ndbc.noaa.gov/station realtime.php?station=THLO1). 234

235 Laboratory analysis of samples

236 Water collected from WLE was subsampled to make a range of analytical

237 measurements in the laboratory (Table 2).

- 239 Table 2. Summary of parameters reported in the dataset. Wind speed and wave height data are
- collected from moored buoy continuous monitoring systems which provide the data in Imperial
- 241 units.

Parameter	Years monitored	Method			
Surface samples (n=1296)	2012-2021	n/a			
Mid-column samples (n=19)	2015	n/a			
Benthic samples (n=512)	2015-2021	n/a			
Station depth (m)	2012-2021	Sea-Bird 19plus V2 CTD profiler			
Time of sampling (Eastern Daylight Time UTC -4:00)	2012-2021	n/a			
Latitude (decimal degree)	2012-2021	n/a			
Longitude (decimal degree)	2012-2021	n/a			
Wind speed (knots)	2015-2021	Moored buoy continuous monitoring systems			
Wave height (ft)	2012-2021	Moored buoy continuous monitoring systems			
Cloud cover (sky)	2012-2021	Qualitative description			
Secchi depth (m)	2012-2021	Wetzel and Likens (2000)			
Sample temperature (°C)	2012	Vee Gee Scientific digital thermometer			
CTD temperature (°C)	2013-2021	Sea-Bird 19plus V2 CTD profiler			
CTD specific conductivity (µS cm ⁻¹)	2013-2021	Sea-Bird 19plus V2 CTD profiler			
CTD beam attenuation (m ⁻¹)	2013-2021	Sea-Bird 19plus V2 CTD profiler			
CTD transmission (%)	2013-2021	Sea-Bird 19plus V2 CTD profiler			
CTD dissolved oxygen (DO; mg L ⁻¹)	2013-2021	Sea-Bird 19plus V2 CTD profiler			
CTD photosynthetically active radiation (PAR; μ E m ⁻² s ⁻¹)	2013-2021	Sea-Bird 19plus V2 CTD profiler			

	-	
Turbidity (NTU)	2013-2021	EPA Method 180.1
Particulate microcystins (µg L ⁻¹)	2012-2021	Wilson et al. (2008)
Dissolved microcystins (µg L ⁻¹)	2014-2021	Wilson et al. (2008)
Phycocyanin (µg L ⁻¹)	2012-2021	Horvath et al. (2013)
Chlorophyll <i>a</i> (µg L ⁻¹)	2012-2021	Speziale et al. (1984)
Total phosphorus (TP; µg L ⁻¹)	2012-2021	Standard Method 4500-P
Total dissolved phosphorus (TDP; μg L ⁻¹)	2012-2021	Standard Method 4500-P
Soluble reactive phosphorus (SRP; μ g L ⁻	2012-2021	Standard Method 4500-P
Ammonium-N (µg L ⁻¹)	2012-2021	Standard Method 4500-nh3-nitrogen (Ammonium)
Nitrate-N + Nitrite-N (mg L ⁻¹)	2012-2021	Standard Method 4500-no3-nitrogen (nitrate)
Urea-N (µg L ⁻¹)	2016-2017	Milvenna and Savidge (1992), Goeyens et al. (1998), Chaffin and Bridgeman (2014)
Particulate organic carbon (POC; mg L ⁻¹)	2012-2021	Hedges and Stern (1984)
Particulate organic nitrogen (PON; mg L ⁻¹)	2012-2021	Hedges and Stern (1984)
Colored dissolved organic material (CDOM; m ⁻¹)	2014-2021	Binding et al. (2008), Mitchell et al. (2003)
Dissolved organic carbon (DOC; mg L ⁻¹)	2012-2017	APHA Standard Method 5310 B
Total suspended solids (TSS; mg L ⁻¹)	2012-2021	APHA Standard Method 2540
Volatile suspended solids (VSS; mg L ⁻¹)	2012-2021	APHA Standard Method 2540

243 Optical properties

Turbidity was measured on raw samples using a Hach 2100AN Turbidimeter following
US EPA method 180.1 (1993). Colored dissolved organic material (CDOM, also defined as
chromophoric dissolved organic matter) was determined by filtering lake water through an acid

rinsed 0.2 µm nuclepore polycarbonate filter into acid-washed and combusted borosilicate vials.

248 Optical density of the filtered samples was then measured using a Perkin Elmer UV/VIS

Lambda 35 spectrophotometer at wavelengths from 300-800 nm. CDOM absorption was

calculated at 400 nm (Mitchell et al., 2003; Binding et al., 2008).

Dissolved organic carbon (DOC) concentrations were determined following American
Public Health Association (APHA) Standard Method 5310 B. Briefly, lake water was filtered
through 0.45 µm polyvinylidene difluoride membrane filters into combusted borosilicate glass
vials and frozen at -20°C until analysis. The filtrate was acidified with HCl and sparged with air
for 6 min before being analyzed on a Shimadzu total organic carbon analyzer.

256 Duplicate samples for particulate organic carbon (POC) and particulate organic nitrogen 257 (PON) were collected onto pre-combusted glass fiber filters and analyzed following Hedges and 258 Stern (1984) Samples were stored at -20 °C until analysis. The filters were then acidified by 259 fumigation with 10% HCl and dried at 70°C for 24 h before being quantified on a Perkin Elmer 260 2400 or a Carlo-Erba 1110 CHN elemental analyzer.

Total suspended solids (TSS) and volatile suspended solids (VSS) were determined via gravimetric analysis following APHA Standard Method 2540. A known volume of lake water was filtered through a pre-combusted, pre-weighed Whatman GF/F glass fiber filter. The filters were then dried at 60° C for at least 24 h and reweighed. The difference in mass between the preweighed and processed filter was reported as TSS. Volatile suspended solids concentrations were quantified by combusting the filters used for TSS analysis at 450 °C for 4 h, weighing the combusted filters, and calculating the mass lost.

268 Nutrient fractions

Total phosphorus (TP) and total dissolved phosphorus (TDP) samples were collected in duplicate by subsampling 50 mL (2012 to 2019) or 20 mL (2020 to 2021) of lake water into acid washed glass tubes and by filtering 20 mL of lake water through a 0.2 µm membrane filter and

272 collecting the filtrate, respectively. Samples for TP and TDP were refrigerated until samples were digested with potassium persulfate solution and autoclaved at 121°C for 30 min, modified 273 274 from APHA Standard Method 4500-P. Digested TP and TDP samples were stored at room 275 temperature until concentrations were measured on a Seal QuAAtro continuous segmented flow 276 analyzer (SEAL Analytical Inc.) from 2012 to 2019 and a Seal AA3 from 2020 to 2021 using the 277 ascorbic acid molybdenum method as detailed by the instrument manual and APHA Standard 278 Method 4500-P. Analytical detection limits for the analyses were taken from the instrument 279 manufacturer's documentation.

280 Soluble reactive phosphorus (SRP), ammonium, nitrate + nitrite, and urea were each 281 determined by filtering 12 mL of lake water through a 0.2 µm membrane filter into 15 mL 282 centrifuge tubes during field sampling. Sample filtrates were stored at -20 °C upon receipt at the 283 laboratory. Soluble reactive phosphorus, ammonium, and nitrate + nitrite concentrations 284 were determined simultaneously on a Seal AA3 continuous segmented flow analyzer. Soluble 285 reactive phosphorus concentrations, like TP and TDP concentrations, were measured using the 286 ascorbic acid molybdenum method as detailed by the instrument manual and APHA Standard 287 Method 4500-P. Ammonium concentrations were measured using Bertholet reactions 288 according to the instrument manual and APHA Standard Method 4500-nh3-nitrogen. Nitrate + 289 nitrite concentrations were measured using copper-cadmium reduction methods according to 290 the instrument manual and APHA Standard Method 4500-no3-nitrogen. Analytical detection 291 limits for these inorganic nutrient analyses were taken from the instrument manufacturer's 292 documentation. Urea samples were measured by adding diacetyl monoxime and 293 thiosemicarbazide to the filtrate and briefly vortexing to mix, followed by adding sulfuric acid and 294 ferric chloride to the solution and briefly vortexing to mix. Samples were then incubated in the 295 dark for 72 h at room temperature before absorbance at 520 nm was read on a Perkin Elmer 296 UV/VIS Lambda 35 spectrophotometer. Urea concentrations were then quantified using a 297 standard curve (Mulvenna and Savidge, 1992; Goevens et al., 1998; Chaffin and Bridgeman,

2014). The detection limit was calculated using the standard deviation of repeatedmeasurements.

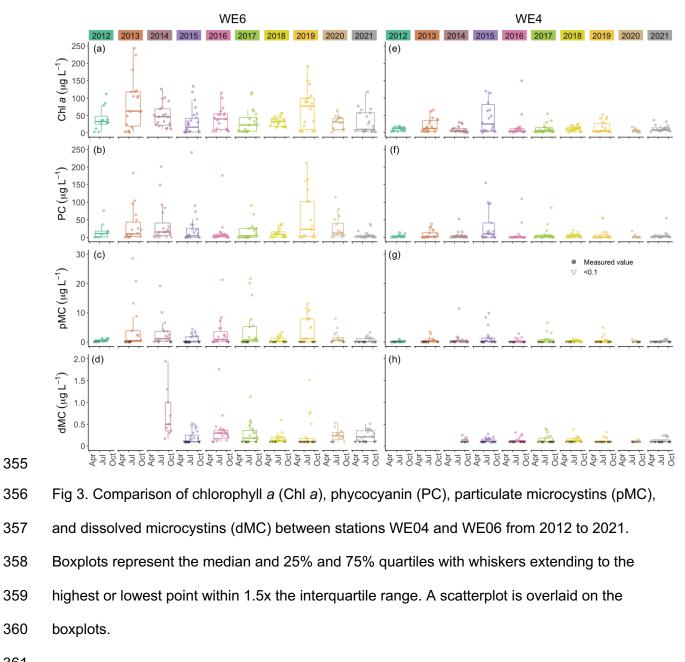
300 Photopigments and microcystins

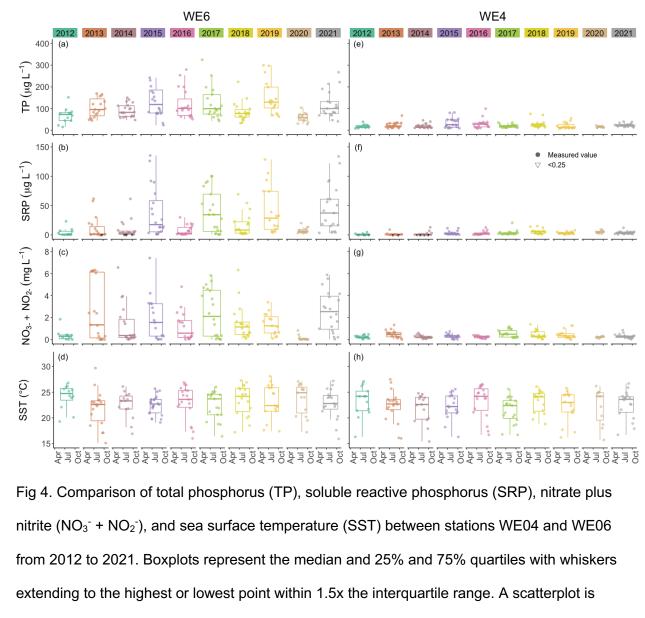
301 Particulate phycocyanin and chlorophyll a concentrations were determined by filtering a 302 known volume of lake water under low vacuum (<200 mm Hg) onto 47 mm Whatman GF/F 303 glass fiber filters (Cytiva Life Sciences). Particulate phycocyanin sample filters were stored in 15 304 mL conical polypropylene centrifuge tubes and chlorophyll a sample filters were stored in amber 305 glass vials at -20 °C until analysis. Analysis methods for particulate phycocyanin were derived 306 from Horváth et al. (2013) where 9 mL of phosphate buffer was added to sample tubes and samples 307 were agitated using a shaker at 5 °C for 15 min at 100 rpm then vortexed for 10 s each. To 308 encourage cell lysis, samples were subjected to three freeze/thaw cycles at -20 °C followed by 309 sonication for 20 min using a Fisher FS110 H sonicator. Fluorescence of the extracted samples was 310 measured using an Aquafluor 8000-010 fluorometer (Turner Designs) with excitation from 400-600 311 nm and emission filter of >595 nm. Particulate phycocyanin was calibrated annually against C-312 Phycocyanin material from Sigma-Aldrich. Analysis methods for chlorophyll a were derived from 313 Speziale et al. (1984) where chlorophyll a was extracted from samples using dimethylformamide 314 and placed into a 65 °C water bath for 15 min. Samples were then cooled to room temperature 315 and vortexed for 15-20 s before being quantified using a 10 AU fluorometer (Turner Designs) 316 with excitation filter of 436 nm and emission at 680 nm. Phycocyanin and chlorophyll a 317 procedures were performed under low or green light to reduce pigment degradation within the cell. 318 Dissolved and particulate microcystins were quantified using a procedure adapted from 319 Wilson et al. (2008). Dissolved microcystins (dMC) were determined through duplicate samples 320 of ~ 2 mL filtrate that was passed through a 0.2 µm membrane filter and stored in glass vials at -321 20 °C until analysis. Particulate microcystins (pMC) were collected by filtering a known volume 322 of lake water onto a Whatman GF/F glass fiber filter (2012 to 2015) or a 3 µm pore size

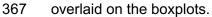
323 polycarbonate membrane filter (2016 to 2021). Particulate MC was then extracted from the 324 filters. In sampling years 2012 to 2015, glass fiber filters were submerged in a glass vial 325 containing a 75:25 methanol:water solution (MeOH/H₂O) and sonicated in an ice bath for 2 min. 326 The samples were centrifuged for 15 min and the supernatant was transferred to a clean glass 327 vial. An additional 5 mL of MeOH/H₂O was added to the filter/precipitate and the sample was 328 incubated at -20 °C for 5 h. The sample was then sonicated for 2 min, centrifuged, and the 329 supernatant was removed and added to the first extract vial. The composite supernatant was 330 then centrifuged under a vacuum until dry. The dried extract was then stored at -20 °C until 331 analysis. Particulate MC concentrations were then determined by adding 1 mL of MIIIiQ water to 332 the sample and using sonication to dissolve the dried extract. For sampling years 2016 to 2021, 333 filters were stored in 2 mL sterile microcentrifuge tubes at -20 °C until analysis. During analysis, 334 pMC were extracted from the membrane filters by adding 1 mL of MilliQ water and subjecting 335 samples to three freeze/thaw cycles at -20 °C followed by addition of Abraxis QuickLyse 336 reagents according to the manufacturer (Eurofins/Abraxis). Particulate MC samples for all 337 sampling years were analyzed immediately after extraction. For all sampling years, dMC and 338 pMC concentrations were determined using a congener-independent enzyme-linked 339 immunosorbent assay (ELISA) kit designed to detect and quantity microcystins and nodularins 340 using the ADDA moiety (Envirologix brand used from 2012 to 2015; Eurofins/Abraxis 341 microcystins/nodularins (ADDA) (EPA ETV) (EPA method 546), ELISA, 96-test kit used from 342 2016 to 2021). Analytical detection limits for the analyses were taken from the manufacturer's 343 documentation.

344 Results and Discussion

345	This dataset demonstrates the temporal and spatial variability in water quality					
346	parameters in western Lake Erie from 2012 to 2021. Overall, sites closest to the Maumee					
347	River inflow (i.e., WE06 and WE09) had the highest median concentrations of nutrients,					
348	sediments, pigments, and microcystins compared to sites further out in the basin (i.e., WE02,					
349	WE04, and WE13; Table 3). Stations WE06 and WE04 were sampled since the initiation of the					
350	monitoring program and consistently represented the high and low extremes of water quality					
351	observations during a given time point, respectively, (Table 3) and select parameters for these					
352	two sites are represented in figs. 3 and 4. Supplemental figs. 1-16 display the same parameters					
353	as figs. 3 and 4 for the remaining stations.					
354						







- 369 Table 3. Median values of each parameter at each monitoring station for all surface samples
- 370 collected between 2012 to 2021.

1	i i	r e	1	(I	n n	n n	1	r i	n n	1
(m)	0.99	0.34	2.0	1.1	2.4	0.81	0.38	09.0	0.54	0.71
PON (mg L ¹)	0.23	0.10	0.38	0.25	0.42	0.20	0.14	0.27	0.18	0.16
POC (mg L ₁)	1.4	0.63	2.4	1.5	2.5	1.2	0.78	1.7	1.1	1.0
Nitrate + Nitrite (mg L ¹)	0.44	0.27	0.83	0.45	1.4	0.31	0.25	0.17	0.27	0.30
Ammoni a (µg L¹)	12.6	12.9	11.8	13.8	43.1	8.4	10.2	2.9	23.9	10.6
SRP (µg L°)	5.7	2.2	8.7	5.8	29.5	5.4	2.7	1.5	2.0	4.0
TDP (µg L°)	12.8	4.5	18.7	12.3	44.8	10.1	5.0	4.7	5.5	7.2
TP (µg L°)	53.3	19.2	90.1	50.9	133	47.6	22.3	31.0	34.8	30.2
Chl-a (µg L°)	17.5	7.7	33.0	19.5	32.6	15.1	8.6	40.0	12.7	12.3
Phycocy anin (µg L [.])	4.8	1.2	8.0	5.7	5.2	2.9	2.6	17.0	2.7	3.4
Dissolve d MC (µg L1)	0.20	0.17	0.28	0.22	0.26	0.16	0.15	0.16	0.19	0.18
Particula te MC (µg L°)	0.78	0.46	1.5	0.88	0.95	0.67	0.56	0.80	0.86	0.91
Turbidity (NTU)	9.9	3.0	14.8	9.0	23.2	11.0	4.3	7.2	6.3	6.3
Transmi ssion (%)	28.2	58.4	20.5	34.4	4.3	25.9	52.4	40.2	43.0	40.8
Beam Attenuati on (m [.])	5.1	2.2	6.4	4.3	12.6	5.4	2.7	3.7	3.4	3.6
PAR (µE m° s ·)	264	377	173	166	127	266	456	796	391	297
DO (mg L ₁)	7.7	7.6	7.6	7.7	7.1	7.7	7.8	8.1	7.7	7.4
Cond. (µS cm ¹)	287	244	346	299	395	276	244	238	261	269
Temp. (°C)	23.1	22.9	23.0	23.3	23.9	23.1	22.9	23.2	23.0	24.1
Secchi depth (m)	0.8	2.0	0.5	1.0	0.3	0.8	1.5	1.4	1.0	1.3
	WE02	WE04	WE06	WE08	WE09	WE12	WE13	WE14	WE15	WE16

372 Physicochemical properties

373 Median surface temperatures for all samples across all years ranged from 22.9 to 24.1 374 °C and median benthic temperatures ranged from 22.8 to 23.2 °C (Table 3, Fig. 4), indicating 375 that WLE was thermally well mixed throughout the sampling period. A summary of the dataset 376 indicates that 23.8% of surface temperatures were \geq 25 °C, and these higher temperatures all 377 occurred from mid-June through the end of September. Bloom forming cyanobacteria species in 378 Lake Erie, including *Microcystis spp.*, often reach maximum growth rates at warmer 379 temperatures (\geq 25 °C) than eukaryotic phytoplankton (Steffen et al., 2014; Huisman et al., 380 2018). Despite having warmer temperatures that promote recurring HABs, there was only one 381 recorded instance of hypoxia (DO <2 mg L^{-1}) in the dataset and it occurred at WE13 on 08 July 2019. Median DO was 7.62 mg L⁻¹ in all surface samples and 7.02 mg L⁻¹ in all benthic samples 382 383 from 2012 to 2021 (Table 3), again indicating minimal stratification in WLE during sampling. 384 Median conductivity from 2012 to 2021 was highest at sites WE06 and WE09, which are closest 385 to the Maumee River input, and lowest at sites WE04 and WE13 near the middle of the basin 386 (Table 3). WE06 and WE09 were the only sites to have median conductivity values above 300 387 $\mu S \text{ cm}^{-1}$.

388 Optical properties

Biotic and abiotic particulate concentrations and movement patterns in WLE are prone to spatial and seasonal variations and are heavily influenced by loading from the Maumee River (Prater et al., 2017; Maguire et al., 2022). Secchi depth, turbidity, and PAR measurements have been correlated with distance from Maumee Bay, where light penetration was lowest near the Maumee River (Chaffin et al., 2011). Variability in optical property measurements in WLE is also dependent on Maumee River inputs, and changes in optical properties can potentially be used 395 in remote sensing algorithms to detect changes in water quality (Sayers et al., 2019). Median 396 Secchi disk depth over the entire dataset was highest at WE04 and lowest at WE06 and WE09, 397 which are closest to the Maumee River (Table 3). Other optical properties, such as PAR, beam 398 attenuation, and transmittance also followed this spatial pattern. In a summary of all samples, 399 median PAR measured at 0.5 m below surface was highest at WE13 and WE14 and lowest at 400 WE09; median transmittance was highest at WE04 and lowest at WE09; and median beam 401 attenuation and turbidity were highest at WE09 and lowest at WE04 (Table 3). Median turbidity 402 values at each site over the 2012 to 2021 period were within the range of previously reported 403 values in the WLE basin (Barbiero and Tuchman, 2004). Median CDOM absorbance and DOC, 404 TSS, and VSS concentrations were again highest at WE09 and lowest at WE04 (Table 3). 405 CDOM gradients in WLE are likewise affected by loading from the Maumee River (Cory et al., 406 2016) and DOC and CDOM values from this dataset have been used as predictor variables in 407 models estimating PAR attenuation variation in WLE (Weiskerger et al., 2018).

408 Nutrient fractions

409 The Maumee River is a major contributor of nutrients to Lake Erie (Steffen et al., 2014; 410 Kast et al., 2021). Median TP concentrations in WLE from 2012 to 2021 were lowest at WE04 411 and highest at WE09 (Table 3, Fig. 4). Median concentrations at each station from 2012 to 2021 412 were above the GLWQA Annex 4 goals for TP concentration in open waters, which is 15 µg P L⁻ 413 ¹ for WLE. This goal was met in 92 of 1275 (7.2%) samples and these target values were 414 primarily recorded from stations WE04 and WE13. Sites closer to the mouth of the Maumee 415 River had higher median TP values. While TP loading from the Maumee River tributary declined 416 between 1982 to 2018 (Rowland et al., 2020) the proportion of dissolved P has increased 417 (Joosse and Baker, 2011; Stow et al., 2015). Median TDP values in the WLE dataset were lowest at WE04 and highest at WE09 (Table 3) with a highest recorded value of 274 µg P L⁻¹ at 418

WE08 in 2015. Median SRP concentrations for each station in this dataset were lowest at WE14 419 420 and WE15 and were highest at WE09 (Table 3). The maximum recorded SRP concentration was 135.4 µg P L⁻¹ at WE06 in 2015 (Fig. 4). Using this dataset, Newell et al. (2019) found that 421 422 the Maumee River N loading has become more chemically reduced over time where ammonium 423 and PON have increased. Median ammonium concentrations in WLE from 2012 to 2019 424 were lowest at WE12 and WE14 and highest at WE09 (Table 3) with a recorded maximum concentration of 2109 µg N L⁻¹ at WE12 in 2017. Median nitrate + nitrite was lowest at WE13 425 426 and WE14 and highest at WE09 (Table 3), with a maximum recorded value of 9.5 mg N L⁻¹ at 427 WE09 in 2016. See Fig. 4 for a comparison of nitrate + nitrite concentrations between WE04 428 and WE06. Median PON concentrations were lowest at WE04 and highest at WE09 (Table 3) 429 with a recorded max of 40.93 mg N L^{-1} at WE08 in 2015.

430 Photop igments and microcystins

431 Median extracted chlorophyll a concentrations in surface waters from 2012 to 2021 were 432 lowest at WE04 and highest at WE06 (Table 3, Fig. 3). The highest recorded surface concentration of chlorophyll *a* was 6784 µg L⁻¹ on 10 August 2015 at WE08 during the most 433 434 severe bloom year in this dataset, according to the CI Index (Wynne et al., 2013; Lunetta et al., 435 2015). The highest measured levels of particulate phycocyanin, pMC, and TP were also 436 recorded at WE06 on 10 August 2015. Other notably high chlorophyll a concentrations were measured during severe bloom years in 2017 (532 µg L⁻¹ at WE09 on 04 August) and 2019 (593 437 ug L⁻¹ at WE09 on 05 August). Similarly, median surface particulate phycocyanin concentration 438 439 for 2012 to 2021 was highest at WE06 and lowest at WE04 (Table 3, Fig. 4). The highest recorded phycocyanin value was from WE08 on 10 August 2015 (8228 µg L⁻¹), followed by 3315 440 µg L⁻¹ at WE06 in 2013 during another severe bloom year. 441

442 Particulate MC concentrations had highest median concentrations at WE06 and were lowest at WE04 (Table 3, Fig. 4), similar to particulate chlorophyll a and phycocyanin 443 444 observations. The highest recorded particulate MC concentration in this dataset was from 10 445 August 2015 at WE08 during a severe bloom year (297 µg L⁻¹), followed by 289 µg L⁻¹ at WE06 446 in 2017 during another severe bloom year according to the CI Index (Wynne et al., 2013; 447 Lunetta et al., 2015). Median dMC concentrations were highest at WE06 and lowest at WE13 (Table 3). The maximum dissolved MC in the dataset was 8.19 µg L⁻¹ at WE09 on 05 August 448 449 2019, which correlates with high chlorophyll a concentrations.

450 Although the United States does not federally enforce water quality criteria or regulations for cyanotoxins in drinking water, the US EPA has a recommended health advisory of 1.6 µg L⁻¹ 451 452 microcystins in drinking water for school-age children through adults (US EPA, 2015) while the 453 WHO and the Ohio EPA use 1 μ g L⁻¹ microcystins as a guideline (WHO, 2020). From 2012 to 454 2021, 44.4% of pMC samples in this dataset exceeded the WHO guidelines and 34.1% 455 exceeded the US EPA health advisory. Monitoring MC concentrations in western Lake Erie has 456 become especially pertinent since August 2014 when the Toledo, OH drinking water treatment plant was contaminated with microcystins in excess of 1 µg L⁻¹ and customers were alerted to 457 not drink their tap water until toxin levels were decreased (Steffen et al., 2017). The pMC 458 concentrations at our WLE monitoring stations varied from 1.2-10.1 µg L⁻¹ on 04 August 2014 459 460 during this crisis.

462 Data Availability

- 463 The entire dataset detailed in this manuscript can be freely accessed through the NOAA
- 464 National Centers for Environmental Information (NCEI) data repository at
- 465 <u>https://www.ncei.noaa.gov/</u>. The data collection is titled "Physical, chemical, and biological water
- 466 quality monitoring data to support detection of Harmful Algal Blooms (HABs) in western Lake
- 467 Erie, collected by the Great Lakes Environmental Research Laboratory and the Cooperative
- 468 Institute for Great Lakes Research since 2012". The digital object identifier is
- 469 <u>https://doi.org/10.25921/11da-3x54</u>. The data presented in this manuscript are available in three
- 470 separate accession files within this collection including: 2012 to 2018 data is available under
- 471 NCEI Accession 0187718 v2.2 at https://www.ncei.noaa.gov/archive/accession/0187718; 2019
- 472 data is available under NCEI Accession 0209116 v1.1 at
- 473 <u>https://www.ncei.noaa.gov/archive/accession/0209116;</u> 2020 to 2021 data is available under
- 474 NCEI Accession 0254720 v1.1 at https://www.ncei.noaa.gov/archive/accession/0254720
- 475 (Cooperative Institute for Great Lakes Research, University of Michigan; NOAA Great Lakes
- 476 Environmental Research Laboratory, 2019). Future data will be added to this collection as it
- 477 becomes available.

478 Conclusions

The western Lake Erie data collected and compiled by NOAA GLERL and CIGLR represent ten years of routine water quality monitoring to detect, track, and predict cyanobacterial HAB events in an area of the Great Lakes that has experienced significant environmental degradation. This ongoing program provides a service to the region and contributes data for investigating the nuanced dynamics of potentially toxic HABs fueled by excess nutrient loading into the WLE basin.

485 In addition to serving the need for generating data to improve remote sensing efforts. 486 (see: Sayers et al., 2016, 2019; Stumpf et al., 2016; Avouris and Ortiz, 2019; Bosse et al., 2019; 487 Vander Woude et al., 2019; Pirasteh et al., 2020; Xu et al., 2022) this monitoring program will 488 continue to serve stakeholders and communities in the Laurentian Great Lakes. As this program 489 has grown, so too has the scope of application of its dataset. For instance, this dataset has 490 assisted in assessing progress toward binational nutrient loading reduction efforts on lake basin 491 concentrations of phosphorus. It has also been used towards determining the significance of 492 nitrogen in bloom formation and toxicity (Gobler et al., 2016; Newell et al., 2019; Hoffman et al., 493 2022). Other research groups have taken advantage of this dataset to investigate microbial and 494 algal community dynamics (Berry et al., 2017; Kharbush et al., 2019; Smith et al., 2021; Marino 495 et al., 2022; Smith et al., 2022), the genomic diversity of cyanobacteria in the WLE basin 496 (Yancey et al., 2022), and hydrogen peroxide production and dynamics within blooms (Corey et 497 al., 2016; Pandey et al., 2022). We anticipate this dataset will continue to be useful for 498 addressing the complex relationships of abiotic and biotic factors contributing to WLE HABs. 499 Long-term monitoring programs like this one provide consistent data which is useful for 500 identifying patterns and variations within the ecosystem and in determining the root cause of 501 those changes.

As the sites and parameters of this monitoring program have already changed to adapt to the needs of research, this program will continue to evolve as we consider adding parameters that encompass broader aspects of bloom dynamics. For example, lake samples can be analyzed for genomic data that will provide insights on the ability of the current phytoplankton community to produce microcystins. This decadal history has already been an invaluable resource for the research community, and it will continue to enrich our collective scientific knowledge of water quality dynamics in western Lake Erie.

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519 Author Contributions

520 Anna G Boegehold prepared the manuscript. Ashley M. Burtner performed field sampling, 521 laboratory processing, data processing, QA/QC and data management, manuscript revision. 522 data curation. Andrew Camilleri performed field sampling, laboratory processing, manuscript 523 revision. Glenn Carter performed field sampling, laboratory processing, data processing, 524 methodology. Paul DenUyl performed field sampling, laboratory processing, manuscript 525 revision. David Fanslow performed field sampling, laboratory processing. Deanna Fyffe 526 Semenyuk performed field sampling, laboratory processing, manuscript revision. Casey Godwin 527 was responsible for project administration, supervision, visualization, manuscript revision, 528 methodology, field sampling, sample processing. Duane Gossiaux performed field sampling, 529 laboratory processing, manuscript revision, methodology. Tom Johengen was responsible for 530 project administration, supervision, field sampling, methodology. Holly Kelchner performed field 531 sampling, laboratory processing, manuscript revision, Christine Kitchens performed field 532 sampling, laboratory processing, data processing, manuscript revision. Lacey A. Mason was 533 responsible for data curation, manuscript revision. Kelly McCabe performed field sampling, 534 laboratory processing, manuscript revision, methodology. Danna Palladino performed field 535 sampling, laboratory processing, data processing, manuscript revision. Dack Stuart performed 536 field sampling, data processing. Henry Vanderploeg was responsible for project administration, 537 supervision. Reagan Errera was responsible for project administration, supervision, 538 Visualization, manuscript revision, methodology.

540 Competing Interests

541 The authors declare that they have no conflict of interest

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