MODELING AND UNDERSTANDING GROUNDWATER CONTAMINATION CAUSED
BY CYANOTOXINS FROM HARMFUL ALGAL BLOOMS IN LAKE ERIE

Bidisha Faruque Abesh

A Thesis

Submitted to the Graduate College of Bowling Green
State University in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

August 2019

Committee:

Ganming Liu, Committee co-chair

Angélica Vázquez-Ortega, Committee co-chair

Enrique Gomezdelcampo

George Bullerjahn

© 2019

Bidisha Faruque Abesh

All Rights Reserved

ABSTRACT

Ganming Liu and Angélica Vázquez-Ortega, Committee co-chair

Cyanotoxins, which are produced and released into the surrounding water during harmful algal blooms (HABs), can severely deteriorate water quality and cause health-related issues and economic loss. HABs and cyanotoxin studies have been typically focused on the surface water domain (e.g., lakes, estuaries, and rivers), with few investigating or reporting on groundwater. This study aimed to explore whether groundwater can be contaminated by cyanotoxins (microcystins) from HABs in surface water due to surface water and groundwater interaction. Specifically, we created a 3-dimensional (3-D) MODFLOW/MT3DMS model to simulate pumping-induced reverse groundwater flow and solute transport from Lake Erie to the aquifer underneath South Bass Island in Ottawa County, Ohio. Simulation results show that, under the default setting, it took ~2 months, ~3 months and ~13 months for the water in pumping well to reach the EPA advisory levels of microcystins for detection (0.1 µg/l), infants and children (0.3 µg/l), and school-age children to adults (1.6 µg/l), respectively. Furthermore, scenario analyses showed that higher pumping rate and higher lakebed leakance would accelerate the microcystin transport to groundwater well. Higher hydraulic conductivity, interestingly, would increase the time to reach those EPA levels due to mixing and dilution effect. The 3-D model developed in this study was capable of simulating the complex surface-water and groundwater interaction and transport processes in the Great Lakes setting. As the first of its kind, this modeling study provides insight for managing coastal groundwater aquifer and resources while dealing with the threat of HABs in the Great Lakes.

Dedicated to my father for his irreplaceable love, dedication and hard work to make me a
successful person

ACKNOWLEDGMENTS

First of all, I would like to thank my parents, Golam Faruque and Suchitra Chakraborty. Thank you for providing me the courage, patience, and knowledge to gain the desired goal of the research work.

I convey my immense gratitude and deepest thanks to my advisors, Dr. Ganming Liu and Dr. Angélica Vázquez-Ortega. Their wise advice and consultancy made the work much easier and smoother. I am grateful to Dr. Enrique Gomezdelcampo and Dr. George Bullerjahn for their guidance throughout the research work including every single step.

I am thankful to my dear friends Mackenzie Nofziger, Md. Minhazul Islam, Anuradha Mahanama, and Kt Jannat for providing encouragement throughout the working period. I am grateful to my best friends, Arif, Ifu, Nahi for their immense support during my study at Bowling Green State University.

Last but not least, my special thanks go to the Department of Geology, Bowling Green State University for providing me with the opportunity to carry out my Master's. This experience is certainly the stepping stone to my future endeavors.

TABLE OF CONTENTS

	Page
CHAPTER 1: INTRODUCTION	1
1.1. Harmful algal blooms and microcystins in Lake Erie	1
1.2. Knowledge gap in current HABs studies	2
1.3. Surface-water and groundwater interaction	4
1.4. Modeling surface water-groundwater interaction and contaminant transport	6
1.5. Research objectives and significance.....	7
CHAPTER 2: DATA AND METHODS	8
2.1. Study area.....	8
2.1.1. Geology of South Bass Island.....	8
2.1.2. Hydrogeology of South Bass Island	8
2.2. Groundwater flow modeling.....	9
2.3. Contaminant transport modeling.....	16
2.4. Model setup for scenario simulations	18
CHAPTER 3: RESULTS	21
CHAPTER 4: DISCUSSION.....	27
4.1. Groundwater-surface water interaction and its role on contaminant transport...	27
4.2. The effect of Hydrogeologic Settings on Contaminant Transport.....	27
4.3. Limitations of current model simulation.....	36
CHAPTER 5: CONCLUSIONS AND FUTURE STUDIES	39
REFERENCES.....	41
APPENDIX A. STEADY-STATE SIMULATION	50

APPENDIX B. HEAD-CONCENTRATION PLOTS (2012-2018)	53
--	----

LIST OF FIGURES

Figure	Page
1.1 Groundwater and surface-water interactions in a lake system.....	4
1.2 Effects of pumping on lake-aquifer interaction	5
2.1 Location and extent of the 3-D simulation domain	9
2.2 Monthly average water level of Lake Erie.....	13
2.3 Monthly time series of precipitation, Put-In-Bay	15
2.4 Station used to collect contaminant concentration.....	17
2.5 Microcystin concentration in Lake Erie focused from 2011-2018.	18
2.6 Location of Put-in-Bay Village Public Water System, South Bass Island	20
2.7 Microcystin Concentration at Lake Erie Water Intake, Put-in-Bay.....	20
3.1 Simulated hydraulic head values for the month of August 2018.....	22
3.2 Simulated microcystin concentrations for the months of June-November, 2012 and 2013	23
3.3 Demonstration of simulated hydraulic head and microcystin concentration in 3-D for the month of August 2014.....	25
3.4 Simulated microcystin concentration in the pumping well from 2012-2018	26
4.1 Comparison of the simulated microcystin concentrations in the pumping well under different settings of pumping rate	31
4.2 Comparison of the simulated microcystin concentrations in the pumping well under different settings of lakebed leakance.....	32
4.3 Comparison of the simulated microcystin concentrations in the pumping well under different settings of hydraulic conductivity	33

4.4	Comparison of microcystin concentrations in the pumping well simulated by using microcystin concentration data (2016-2018) at Put in Bay as the source.....	34
4.5	Comparison of microcystin concentrations in the pumping well simulated by using concentration values (5 and 10 µg/l for July-October months) as the source.....	35

LIST OF TABLES

Table	Page
2.1 Water Well Log and Drilling Report (ODNR)	12
2.2 List of input parameter values for the default MODFLOW simulation	15
2.3 List of model parameter values for the default MT3DMS simulation.....	18
3.1 Microcystin Arrival time to the pumping well	24
4.1 List of microcystin arrival time to the pumping well for transient state simulation (default vs. Scenarios 1-3).....	30
4.2 List of microcystin arrival time to the pumping well for variable source concentration functions (default vs. Scenarios 4).....	36

LIST OF EQUATIONS

Table	Page
2.1 Partial differential equation describing the three dimensional flow of groundwater through porous and permeable earth's material.....	10
2.2 The mass transport equation of MT3DMS	16

CHAPTER 1: INTRODUCTION

1.1. Harmful algal blooms and microcystins in Lake Erie

Ranking 11th by area and 17th by volume, Lake Erie is one of the largest freshwater lakes in the world (Herndorf, 1984), providing drinking water for more than 11 million people (Watson et al., 2016). Over the past decade, however, the water quality in this Great Lake has been frequently threatened or deteriorated by harmful algal blooms (HABs). In August 2014, a weekend-long “Do Not Drink” and “Do Not Boil” order was issued by the City of Toledo (Ohio) due to elevated level of cyanotoxin/microcystin, caused by HABs detected in the water treatment plant intake. Besides threatening Lake Erie as drinking water source, HABs also affect Lake Erie’s role and contributions for tourism, shipping/transportation, and fisheries (Watson et al., 2016).

Favorable environmental factors, e.g., nutrient concentration, water temperature, light intensity, water movement, stagnation, and residence time, are the general driving forces of a dense growth of HABs (Merel et al., 2013). In Lake Erie, one of the primary reasons for extreme blooms of blue-green algae or cyanobacteria is eutrophication (Watanabe and Oishi, 1985), due to the high percentage of agricultural land use in the western basin of Lake Erie (60-80%) that input high loads of dissolved reactive phosphorus loads into Maumee River and Sandusky River basins (Force, 2010).

Release of dissolved microcystin occurs when cyanobacteria cells rupture and release intracellular toxin (Steffan et al., 2017). Hepatotoxins (e.g. microcystins, nodularins, cylindrospermopsins), neurotoxins (e.g. anatoxin-a, homoanatoxin-a, saxitoxins) and dermatotoxins (e.g. lyngbyatoxins, aplysiatoxins) are the divisions of cyanotoxin toxicology (Teneva et al., 2010). Microcystin, commonly identified as Microcystin-LR (MC-LR) in Lake Erie, is more lethal than other cyanotoxins (WHO, 2003), due to its primary impact on the human

liver (WHO, 2003) and, thus, is the interest and focus of this study. Microcystin affects humans by skin contact, inhalation, and ingestion (Codd et al., 1997). Being lethal to both human and animal health (Briand et al., 2003), microcystins are now one of the most important environmental and public health concerns (Merel et al., 2013).

1.2. Knowledge gap in current HABs studies

Most HABs studies have been focused on surface-water bodies (rivers, lakes, estuaries, etc.), through which agencies, institutions, and researchers attempted to understand the occurrence and effect of HABs and find solutions to prevent and mitigate the harmful blooms in surface waters (e.g., Chorus and Bartram, 1999; Davis et al., 2009; Ho and Michalak, 2015; Brooks et al., 2016; Bullerjahn et al., 2016). For example, the United States the Harmful Algal Blooms and Hypoxia Research and Control Amendments Act is primarily focused on the causes, consequences, monitoring, management and prevention of HABs in the Great Lakes (Congress, 2014). The Ohio NOAA-Great Lakes Environmental Research Laboratory (GLERL) perform yearly investigations to forecast the formation and movement of cyanobacterial blooms in Lake Erie. In addition, Ohio EPA Harmful Algal Toxin Monitoring provides microcystin concentration results from inland lakes, state park beaches and public water supplies from Lake Erie.

Compared to the large number of studies on surface water, few have been performed to identify and understand the process of cyanotoxin contamination in groundwater. The knowledge of groundwater cyanotoxin contamination due to microcystin infiltration from HABs polluted lake at the vicinity remains notably limited (Mohammed and Shehri, 2009; Tian et al., 2013; Yang et al., 2016). Due to lake-aquifer interaction, microcystins are likely to enter the groundwater near lakes when mass of cyanobacteria blooms occur (Yang et al., 2016). According to Yang et al. (2016), 15 groundwater wells near highly polluted Lake Chahou in China had substantial

microcystin concentrations. Their results confirm that microcystins in groundwater originate from infiltration of nearby lake water.

Microcystin's presence in groundwater was also reported in the Asir region at southwest of Saudi Arabia (Mohamed and Shehri, 2009). According to their study, rainwater carrying cyanobacterial cells can enter into the open groundwater wells and microcystin can be released due to eutrophic well water and favorable temperature (Mohamed and Shehri, 2009). Additional pathways of contamination in groundwater wells containing no living cyanobacterial cells is microcystin leaching from surrounding contaminated ponds due to surface water-groundwater interaction. The significant correlation ($r = 0.9$) between microcystin in groundwater wells and surrounding rainwater ponds prove the linkage between groundwater and surrounding ponds (Mohamed and Shehri, 2009).

Another contamination case of groundwater getting polluted by surface-water HABs was found in the Huai River Basin, China (Tian et al., 2013). There, Tian et al. (2013) collected water samples from upstream, midstream, and a tributary of the Shaying River, ponds, and groundwater wells. Their multilinear regression analysis yielded a best-fit model relating microcystin in groundwater to that of the midstream of Shaying River. Such a result clearly suggested that microcystin contamination in groundwater originated from surface water, e.g., rivers.

The limited amount of groundwater studies shows that most were designed to identify the existence of microcystin in groundwater and its connectivity to surface water, qualitatively. There is still much unknown with respect to microcystin contamination in groundwater, such as the source, fate and transport. To fill these important knowledge gaps, especially the timing and concentration changes of microcystin along the pathway from surface water to groundwater, one of the first as well as essential steps is to apply modern quantitative approaches, i.e., hydrologic

models, to characterize, simulate and understand those key flow and transport processes theoretically in the context of groundwater and surface-water interaction.

1.3. Surface-water and groundwater interaction

In most landscapes, surface-water and groundwater systems are connected and inter-related (e.g., Freeze and Cherry, 1979; Winter et al., 1998; Liu et al., 2016). Lakes, for example, may interact with groundwater underneath and nearby in three possible ways: groundwater inflow, seepage loss, or partial combination of both the processes (Winter et al., 1998) (Figure 1.1). Groundwater inflow occurs when groundwater recharges the lake by high gradient groundwater moving to low gradient lake water. If the lake stage is higher than groundwater then according to Darcy's law higher elevated lake water would move towards lower elevated groundwater domain (Freeze and Cherry, 1979). In addition, due to the cone of depression created by excessive pumping, lake water can move towards groundwater due to pumping-induced gradient change (Figure 1.2).

Figure 1.1: Groundwater and surface-water interactions in a lake system: (A) groundwater discharges to lake – “gaining” lake; (B) lake water seepages to groundwater – “losing” lake; and (C) combination of both A and B, which makes a flow-through lake system. (source: Winter et al., 1998).

Figure 1.2: Effects of pumping on lake-aquifer interaction: (A) groundwater flows or discharges to lake in a natural hydraulic gradient; and (B) lake water migrates to groundwater because of the gradient change induced by excessive pumping (source: Alley et al., 1999).

Such physical interaction between surface water and groundwater has great implication for contaminant migration or mass transport across the domains (Kong et al., 2018). One widely recognized example of mass transport due to surface-water and groundwater interaction is saltwater intrusion in coastal regions. Saltwater intrusion is a process by which saline sea water moves into fresh aquifers due to density differences as well as gradient change due to excessive groundwater pumping (Figure 1.2) (Huyakorn et al., 1987; Cheng et al., 2000; Mantoglou, 2003). As a consequence, fresh groundwater resources would be contaminated or even depleted as its salinity becomes higher.

Contaminants produced both from point (landfill leachate, pharmaceuticals) and non-point sources (nutrients, pesticide) are found in groundwater due to surface water-groundwater interaction (Lapworth et al., 2012). The hydraulic connectivity of the river-aquifer system controls the spread of contaminants from the river into the aquifer, or from the aquifer into the river (Batlle-Aguilar., 2008). Likewise, microcystin can contaminate groundwater due to surface water-groundwater interaction (Mohamed and Shehri, 2009; Tian et al., 2013; Yang et al., 2016). However, less attention has been paid to the presence of cyanotoxin in groundwater. If groundwater quality deteriorates due to cyanotoxin presence, degradation of the quality of groundwater would be similar to saltwater intrusion.

1.4. Modeling surface water-groundwater interaction and contaminant transport

At present, one of the most commonly used hydrologic model in simulating surface water–groundwater interaction is MODFLOW, a 3-D modular hydrologic model developed by scientists of the U.S. Geological Survey (Barlow and Harbaugh, 2006). Considered as an international standard for simulating and predicting groundwater conditions, MODFLOW has been successfully used to understand and solve various water resources problems. For examples, Sheets et al. (2005) used MODFLOW to simulate and understand the pumping effects near regional ground-water divides and river/aquifer systems in the Great Lakes Basin and Mississippi River Basin. Krohelski et al. (2002) applied MODFLOW to understand the hydrologic connection of Fish, Mud and Crystal Lakes with regional groundwater flow and how pumping water out from the lakes would reduce the lake stage. Sherif et al., (2012) presented a MODFLOW based study of how groundwater pumping in the coastal aquifer of Wadi Ham would cause salt water migration to inland aquifer. More recently, MODFLOW was also utilized to characterize the dynamic relationship between groundwater and an artificial lake, Lake Turawa, in Poland (El-Zehairy et al., 2018).

To simulate groundwater solute or contaminant transport, MODFLOW relies on its package, MT3DMS, which communicates with MODFLOW through data files (Ghoraba et al., 2012). MODFLOW/MT3DMS was successfully used to determine the rate and number of pumping wells needed to dewater ammonium contaminated groundwater as a remediation technique to purify the Berma region (Ghoraba et al., 2012). Lautz and Siegel (2006) used the MODFLOW/MT3DMS paired approach to simulate both advective transport and sink/source mixing of solutes in the hyporheic zone around debris dams and meanders along a semi-arid stream. In addition, MODFLOW/MT3DMS was also used to understand the river-aquifer interaction and how benzene

could disperse from contaminated river water to groundwater due to the interaction (Batlle-Aguilar et al., 2008). Capabilities and success demonstrated in the related studies discussed above, plus free of charge, all make MODFLOW/MT3DMS an ideal tool for this study.

1.5. Research objectives and significance

This study aimed 1) to develop a 3-D MODFLOW/MT3DMS model to simulate the surface-water and groundwater interaction in a typical Great Lake hydrogeological setting, i.e., a coastal area in the South Bass Island, Ottawa County, Ohio; and 2) to quantitatively understand how this interaction would trigger and control the transport of microcystin from Lake Erie to the aquifers underneath and in the vicinity. Specifically, the study would answer three research questions: 1) Can coastal aquifers be contaminated by HABs in the lake? 2) How long does it take for microcystin to move from lake to groundwater? And, 3) what hydrogeological conditions/settings would facilitate the transport?

This is one of the first studies aiming to model the transport of microcystin from the Great Lakes to groundwater. Therefore, this study is exploratory and theoretical in nature, focusing on modeling the migration of microcystin via dominant transport processes such as advection and mechanical dispersion, rather than diffusion, adsorption and reaction, whose characteristics and rate in porous media of deep aquifer remained unknown or uncertain (Schmidt et al., 2014). Despite the theoretical nature, the study results and findings might provide practical implication for the management of groundwater resources along the coast of Lake Erie.

CHAPTER 2: DATA AND METHODS

2.1. Study area

South Bass Island is located in the western basin of Lake Erie. The Island is a part of Ottawa County, Ohio. South Bass Island which has the nickname of “Key West of the Midwest” is one of the main tourist destinations in the Midwest (Fong et al., 2007).

Island and coastal regions adjacent to the western basin of Lake Erie were reported to suffer from HABs due to extreme turbidity in western basin compared to the eastern and central basins (Herdendorf, 1970). To reduce the robustness of our simulation, the southern corner of the South Bass Island was considered as the model domain (Figure 2.1). The model boundary was determined based on groundwater divides and dominant groundwater flow directions in the region.

2.1.1. Geology of South Bass Island

The bedrock in the island region of western Lake Erie is sedimentary in origin (Herndorf, 1984). From the generalized stratigraphic section, it is noted that the western basin of Lake Erie consists of upper Silurian and lower Devonian dolomites, limestones and shales (Holcombe et al., 1997). Bass Islands is formed of resistant upper Silurian dolomites of the Put-in-Bay Formation (Holcombe et al., 1997). Mud (clay and silt sized particles), mixed sand, gravel and glacio-lacustrine clay are the primary composition of lake sediments (Holcombe et al., 1997). Many Breccia filled sinkholes are present in South Bass Island (Holcombe et al., 1997).

2.1.2. Hydrogeology of South Bass Island

The western part of Ohio is composed of carbonate bedrock aquifer system (Ohio EPA, 2014). High total dissolved solids and high aquifer yields are the main characteristics of the carbonate aquifer system (Ohio EPA, 2014). In South Bass Island the principal aquifer is limestone which has a direct connection with overlying glacial till (localized deposits of sand and gravel)

(Smith, 1994). Depth to water table ranges from 15ft - 30ft (4m - 9m) (Smith, 1994).

Figure 2.1: Location and extent of the 3-D simulation domain. (a) MODFLOW grid in planar view and (b) vertical grid along cross-section A-A'.

2.2. Groundwater flow modeling

The groundwater model was developed with MODFLOW-2000 in the platform of Groundwater Modeling Software (GMS). GMS is a graphically based software tool (Owen et al., 1996). GMS conveniences the simulation of all aspects of the groundwater flow and transport modeling processes (Owen et al., 1996). MODFLOW is the USGS's modular hydrologic model

(USGS, 2017) and it was first published in 1984. MODFLOW simulates 3-D groundwater flow using finite-difference method (Harbaugh et al., 2005). Although the initial purpose of the model was to identify groundwater flow in all three dimensions, now MODFLOW-related programs can simulate coupled groundwater/surface-water systems, solute transport, variable-density flow, salt water intrusion and vice-versa (USGS, 2017).

According to McDonald and Harbaugh (1984), the partial differential equation describing the three dimensional flow of groundwater through porous and permeable earth's material is:

$$\frac{\partial}{\partial x} \left(K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial h}{\partial z} \right) - W = S_s \frac{\partial h}{\partial t} \quad (\text{Equation 2.1})$$

where K_{xx} , K_{yy} , and K_{zz} represent hydraulic conductivities along x, y, and z axes, respectively; h represents the hydraulic head; W quantifies the volumetric flux per unit volume through the sources and/or sinks of water; S_s represents specific storage of the porous material; and t is time. However, except for very simple systems, analytical solutions of the given equation are impracticable (McDonald and Harbaugh, 1984). Therefore, employing numerical methods assist to obtain approximate solutions (McDonald and Harbaugh, 1984). One such numerical method is the finite difference method where finite spatial and temporal points are used to replace the continuous system (McDonald and Harbaugh, 1984).

3-D Grid construction: The objective of 3-D grid construction was to get adequate resolution and discretization of the area of interest. The hydrogeologic setting of South Bass Island illustrates limestone/dolomite overlain by glacial till or clay (Smith, 1994). The well log obtained from Ohio water wells (water well log and drilling report) of Ohio Department of Natural Resources (ODNR) verifies the presence of two layers; upper clay layer and the lower limestone layer (Table 2.1). Therefore, the primary two layers for our simulation were clay/glacial till and dolomite/limestone. However, to increase the resolution of the model simulation, the upper clay layer was divided into

two layers with each layer having 1.5m thickness. The limestone layer was divided into 7 layers with 1m (layer 3), 2m (layers 4 and 5) 5m (layers 6, 7 and 8) vertical discretization (Figure 2.1). The thickness of the layers were chosen based on trial-error process to reduce the simulation convergence error. To get high resolution along the groundwater well, the cells were refined with a base size of 10m and a bias of 1.1. As a result, the 3-D grid consists of 80 rows, 70 columns and 9 layers.

Elevation of the layers: Elevation of the layers were specified by providing the top and bottom elevation of each layer. The elevation of the first layer was assigned by interpolating the Digital Elevation Model (DEM) of the study area. From the Statewide Aquifer Mapping Program of ODNR, it was observed that the thickness of the glacially related sediments and limestones/dolomites are <25ft (<7.62m) and >100ft (>30.5m) respectively. Put-in-Bay Dolomite has a thickness of 35ft- 60ft (10m-18m) (Forsyth, 1988). From the well log of ODNR, 0ft-10ft (0m -3m) is Clay and 10ft-65ft (3m-20m) is limestone (Table 2.3). Therefore, the thickness of the clay layer and limestone layer for our model were specified as 3m and 20m~40m respectively. The elevation of the bottom layer (layer 9) is given as 145m.

Stress Period: Stress period is the time interval with constant input parameters and external stresses (i.e. recharge, pumping rate) (XMS Wiki). The stress period input starts from a reference time or $t=0$, which indicates the beginning of the simulation (XMS Wiki). In our simulation the reference time was set at December, 1990. After that, the model was simulated monthly from 1991 to 2018. Within this timeline 1991-2011 was the spin up time; and 2012-2018 was the period of interest. The spin up time was considered so that the model stabilizes before introducing microcystin in lake in 2012.

Starting heads: The starting head was assigned the same as the top layer elevation. MODFLOW

does not allow starting head input below any layer's top elevation. Therefore, our solution from MODFLOW steady head output (Appendix A.1) could not be considered as starting head or initial condition. An alternative of such a condition is assigning the reference time of transient simulation as steady state (Aquaveo GMS 10.4 tutorial). In this way, our transient simulation started from a stabilized steady state.

Table 2.1: Water Well Log and Drilling Report (Ohio Department of Natural Resources, ODNR)

	Parameter (unit)	Values
Location	Well log number	502248
	Latitude, longitude	41.636159, -82.82568
Construction Details	Borehole depth (ft)	65
	Casing length (ft)	26
Well Hydrogeology	Yellow clay thickness (ft)	10
	Limestone thickness (ft)	55
	Static water level (ft)	12
	Pumping rate (m ³ /d)	160

Boundary Condition (Ibound):

No-flow boundaries. An impermeable fault zone, a groundwater divide or streamline may be represented by no-flow boundary (flux=0) (Anderson et al., 2015). Except for the specified head boundary on the south-eastern side (Figure 2.1a), other 3 sides were considered as no-flow boundaries.

Specified Head boundary: In our simulation, it was assumed that the lake acts as constant source of water despite of groundwater level change. In other words, lake water levels were predefined and would not be calculated or simulated. Therefore, the lake cells were assigned as a time variant

specified head boundary (CHD) to input constant lake stages for each stress period. The monthly water level collected from NOAA Great Lakes Environmental Research Laboratory (GLERL) was used as input for Specified Head (CHD) package (Figure 2.2).

Figure 2.2: Monthly average water level of Lake Erie (data source: NOAA-Great Lakes Environmental Research Laboratory, GLERL)

Horizontal Hydraulic Conductivity (K_h): The K_h range of the clay layer is 10^{-7} m/d to 10^{-3} m/d (Heath, 1983). In our study area, the clay layer is mixed with glacial till. K_h range of glacial till is 10^{-7} m/d to 10^{-1} m/d (Heath, 1983). In the default or reference model, therefore, the K_h of the top two layers were assigned as 0.05 m/d, as listed in Table 2.2. K_h of carbonate rocks range from 10^{-4} m/d (fractured) to 10^4 m/d (cavernous) (Heath, 1983). The K_h of the limestone layers were assigned as 1 m/d for the model simulation. K_h values of limestone and clay layers were decided by trial-error process. The lake cells were considered as specified head, because high-K method doesn't calculate lake stage based on mass balance calculation as MODFLOW LAK3 package (Anderson et al., 2002). Instead, hydraulic conductivity and storage values assigned to the lake

nodes are used to calculate the lake stage (Anderson et al., 2002). For our model the hydraulic conductivity of the lake cells were set as a very high value (10^6 m/d). The lakebed was considered as a thin layer of 1m. The lakebed was set as a layer of very low K_h (0.1m/d).

Specific Yield (S_y): The S_y of clay and limestone are 6% and 14% respectively (Morris and Johnson, 1967). The S_y of lake cells were assigned as 1 because of using high-K method.

Specific Storage (S_s): The S_s of sound rock is less than 3.3×10^{-6} m⁻¹ (Domenico, 1972). In the model, the S_s is assigned as 1×10^{-6} for all the layers.

Recharge: Because of the high elevation and the overlying clay layer, the recharge of South Bass Island is assumed to be moderate (Smith, 1994). Therefore, for our MODFLOW simulation 10% of the total precipitation was considered as the rate of recharge to groundwater. Monthly precipitation data for 1991-2018 was collected from NOAA-National Centers for Environmental Information (NCEI) global summary of the month.

Well: Information of the groundwater well was collected from Ohio water wells (water well log and drilling report) of ODNR (Table 2.1). Construction of the well was completed on 28 July, 1976. The borehole depth was 65 ft. (20m). The casing having a diameter of 5.63 inches (0.14 m) was extended until 26 ft. (7.92 m). The aquifer media was limestone (Table 2.2). The bedrock depth was 65 feet (19.8 m). From the well log it was observed that yellow clay (0 ft.-10 ft.) or (1m-3m) is overlain by limestone (10 ft. to 65 ft.) or (3m to 19.8m). The static water level of the well was at 12 ft (3.7m). Therefore in our model, the pumping well was extended from 175m to 155m. The pumping rate from one time monitoring was ~ 160 m³/d. Drawdown Limited, Multi-Node Well (MNW1) is used to simulate the pumping well. If a well screen extends through multiple layers, MNW wells are used for the simulation (Halford and Hanson, 2002).

Table 2.2: List of input parameter values for the default MODFLOW simulation

	Parameter (unit)	Values
Grid Construction	Number of rows, columns, layers	89, 79, 9
Layer Hydrological Properties	Hydraulic conductivity, K_h of clay with glacial till (m/d)	0.05
	K_h of limestone (m/d)	1
	K_h of lake cells (m/d)	10^6
	Lake leakance (1/d)	0.1
	Specific Yield, S_y of clay with glacial till	0.06
	S_y of limestone	0.14
	Specific storage, S_s (1/m)	10^{-6}
	Vertical anisotropy (K_h/K_v)	10
	Recharge rate (m/d)	0.1*Precipitation
Pumping well	From (m)	175
	To (m)	155
	Pumping rate (m^3/d)	160

Figure 2.3: Monthly time series of precipitation, Put-In-Bay (NOAA-National Centers for Environmental Information, NCEI).

2.3. Contaminant transport modeling

The primary process of contaminant transport is advection, by which contaminants are transported by water movement (Zheng and Wang, 1999). Contaminants or solutes can additionally be transported by dispersion (spreading of contaminants due to interaction with GW) and chemical reactions (Zheng and Wang, 1999). Model Transport Three Dimensional Model Simulator (MT3DMS) is implemented with an optional, dual-domain formulation for modeling mass transport (Zheng et al., 1999). MT3DMS is able to combine the head simulation of MODFLOW as groundwater flow input and perform contaminant transport. The mass transport equation of MT3DMS is formulated as below:

$$\frac{\partial(\theta C^k)}{\partial t} = \frac{\partial}{\partial x} \left(\theta D_{ij} \frac{\partial C^k}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i C^k) + q_s C_s^k + \sum R_n \quad (\text{Equation 2.2})$$

where C^k represents the dissolved concentration of species k , θ represents the porosity of the subsurface medium, t represents time, x_i represents the distance along the respective Cartesian coordinate axis, D_{ij} represents hydrodynamic dispersion coefficient tensor, v_i represents seepage or linear pore water velocity; it is related to the specific discharge or Darcy flux through the relationship, q_s represents the volumetric flow rate per unit volume of aquifer representing fluid sources (positive) and sinks (negative), C_s^k represents the concentration of the source or sink flux for species k and $\sum R_n$ represents the chemical reaction term.

Advection and Dispersion: In case of advection, the third order TVD (Total Variation Diminishing) scheme, implemented with universal flux limiter or the ULTIMATE (Universal Limiter for Transient Interpolation Modeling of the Advective Transport Equations) algorithm was used. TVD minimizes both numerical dispersion (smearing of concentration fronts) and artificial oscillation (overshoot or undershoot of contaminant transport) (Zheng and Wang, 1999). Dispersion is caused both by mechanical dispersion (microscale velocity gradient) and molecular

diffusion (concentration gradient) (Zheng and Wang, 1999). In this study, both advection and mechanical dispersion were included in our model. TRPT (ratio of horizontal transverse dispersivity to longitudinal dispersivity) and TRVT (ratio of vertical transverse dispersivity to longitudinal dispersivity) are assigned as 0.1 and 0.01 respectively. Values of the transport parameters are summarized into Table 2.3.

Porosity: The porosity range of clay is 40% -70% and limestone, dolomite is 0%-10% (Freeze and Cherry, 1979). Therefore, the porosity of clay layers and limestone layers were assigned as 0.4 and 0.1 respectively (Table 2.3).

Source/Sink Mixing: A transient concentration input was assigned to the lake cells. The microcystin sampling data was collected from NOAA Great Lakes Environmental Research Laboratory (GLERL) (Figure. 2.4). For the default simulation, data from the Lake Erie Master station WE6 (Figure 2.4) was used, mainly because this station has one of the longest records (2012-2018) with relatively high detected microcystin concentrations, an ideal representative of coastal conditions where HABs could be the worst. Figure 2.5 plots the concentration data input to the default model, with zero values assigned to no-data or not-detected months.

Figure 2.4: Station used to collect contaminant concentration. WE6: NOAA-GLERL Master Monitoring Station.

Figure 2.5: Microcystin concentration in Lake Erie (NOAA-GLERL) focused from 2011-2018. Inset: microcystin concentration input for default transient MT3DMS simulation from 1991-2018.

Table 2.3: List of model parameter values for the default MT3DMS simulation.

	Parameter (unit)	Values
Advection	Simulation type	Third Order TVD scheme (ULTIMATE)
Dispersion	Longitudinal dispersivity (m)	5
	Horizontal transverse dispersivity (m)	0.5
	Vertical transverse dispersivity (m)	0.05
Porosity	Clay	0.4
	Limestone	0.1

2.4. Model setup for scenario simulations

To address the question of “what and how hydrogeological conditions/settings would facilitate the transport”, four different scenarios were set up and simulated to understand and quantify the timing (i.e., arrival time) of microcystin from Western Lake Erie to the groundwater

well as a function of various settings. Specifically, Scenarios 1, 2, 3 and 4 were designed to explore the effects of pumping rate, lakebed leakance, hydraulic conductivity, and the microcystin concentration, respectively, with other model parameters/variables remained the same as those of the default case (Tables 2.2 and 2.3). In all default and scenario simulations, arrival time for the microcystin to reach the three EPA advisory levels (detectable level: 0.1 µg/l; infant-children: 0.3 µg/l; school going children-adults: 1.6 µg/l) (EPA, 2016) in the pumping well were estimated. The time calculated the days after the microcystin was detected in Lake.

Scenario 1: Changes in pumping rates: 170m³/d, 125m³/d, 100 m³/d

Scenario 2: Changes of Lakebed Leakance (C): 0.1C, 5C

Scenario 3: Change of Hydraulic Conductivity: 2 m/d, 5 m/d

Scenario 4: Change of Microcystin concentration in the lake

Scenario 4.1 Low microcystin concentration

Scenario 4.2 Extremely high microcystin concentration

Scenario 4.1: Microcystin data at Put-in-Bay Village Public Water System on South Bass Island (Figure. 2.6), collected from Ohio EPA Harmful Algal Bloom toxin monitoring, was used in this scenario to explore how low initial concentration in lake water would affect the quality of groundwater. The data provided weekly microcystin concentration from 2016-2018 (Figure. 2.7). For our model simulation, July, 2016-October, 2018 average monthly concentrations were considered as input. For other years the concentration was assumed as ~0 mg/l.

Scenario 4.2: In this scenarios, two sets of uniform but relatively upper range of microcystin concentration values in a typical bloom year, e.g., 5 µg/l and 10 µg/l, were separately inputted to the model for the months of July to October each year from 1991-2018. In terms of lasting period, the scenario provided an extreme situation. Such a hypothetical setting would help

to address our curiosity on how groundwater would be contaminated by a long-lasting, severe HABs event.

Figure 2.6: Location of Put-in-Bay Village Public Water System, South Bass Island (Harmful Algal Bloom Toxin Monitoring, Ohio EPA)

Figure 2.7: Microcystin Concentration at Lake Erie Water Intake, Put-in-Bay (Harmful Algal Bloom Toxin Monitoring, Ohio EPA) focused from 2013-2018. Inset: Microcystin Concentration at Lake Erie Water Intake, Put-in-Bay (1991-2018).

CHAPTER 3: RESULTS

Both steady state and transient state of the 3-D lake-groundwater system were simulated by MODFLOW. The steady-state simulation was conducted as a learning process for me to get familiar with the software as well as a verification process to check the validity of model being set up in a quick manner. Therefore, further effort was not devoted to explaining and discussing the steady-state results, which are included in Appendix A. The remainder of this section describes results from the transient-state simulation, at a month time step spanning a period of time from January 1, 2012 to December 31, 2018. As mentioned in Section 2, a preceding time period from 1991 to 2011 was also simulated in order to warm up the model and to obtain a quasi steady-state head distribution, which later would be used as the initial condition for the period of our interest, i.e., 2012-2018. To facilitate temporal comparison and visualization, results along the 2-D vertical profile, i.e., cross-section A-A' (Figures 3.1 and 3.2), which includes the pumping well and the topography gradient from highland to the lake (see Figure 2.1), was of our primary interest. For demonstration purpose only, 3-D simulation results of hydraulic head and microcystin concentration for a selected month, i.e., August 2014, are also provided in Figure 3.3a and Figure 3.3b, respectively.

Figure 3.1 illustrates simulated values of hydraulic head along the A-A' profile for the month of August, 2018, with head distributions of other months plotted in Appendix B. When comparing the head values and the water-table position in Figure 3.1 to those shown in the left column of Appendix B, there is not much difference or change from month to month since January 2012. Such results indicate head distribution and groundwater flow pattern were relatively stable, with little fluctuation. It is clear that pumping in the well generated a steep gradient between the lake and aquifer near the well, along which groundwater would flow reversely from the lake towards

the well.

Figure 3.1: Simulated hydraulic head values (in meter) along the A-A' cross-section for the month of August 2018. Dashed line shows the position of water table (aquifer) and the water level/surface of the lake. Note that simulated head distribution for all other months are included in Appendix B.

Similarly, simulated microcystin concentration of A-A' cross-section for the months of June to November for two selected years, 2012 and 2013, are plotted into Figure 3.2, with the results for all other months shown in Appendix B. Note that, during the simulation period of 2012-2018, microcystins were first detected and introduced to the model in July 2012 (Figure 2.5) and extremely high concentration of microcystin was detected in the lake in the summer of 2013 (35+ $\mu\text{g/l}$). Results from these two years would enable us to visualize the dynamics of concentration right after the transport began in the system (2012) and the process to reach a peak (2013) as well as to quantify the arrival time for the groundwater in the well to reach certain concentration levels of health related concerns (Table 3.1).

Based on the results shown in the left column (Figure 3.2), the model was able to represent the concentration dynamics within the lake from low concentration (July 2012) to relatively high concentration (September 2012), and back to low later (November 2012). More importantly, the evolution of contaminant plumes, representing the transport process of microcystins from the lake to the well, was also well captured and simulated by the 3-D model. Taking 2013 (right column) for example, the plot shown in July indicates the microcystins were mainly contained in the lake, with a front of plume slightly developed and moving towards the well (the lower-left corner of the

lake, July 2013 panel). Just one month later, the plume extended to the well, suggesting microcystins originating from the lake were able to migrate and contaminate the well in a short amount of time.

Figure 3.2: Simulated microcystin concentrations (in mg/l) along the A-A' cross-section for the months of June-November, 2012 (left) and 2013 (right). Note that simulated concentration distribution for all other months can be found in Appendix B.

The transport simulation results also made it possible to quantify the arrival time of our interest (Table 3.1). Figure 3.4 plots the changes of microcystin concentration in the pumping well versus time over the simulation period. After first detecting or introducing microcystin in the lake in July 2012, according to Figure 3.4 it took about 2 months for the well to reach the detectable level (i.e., 0.1 $\mu\text{g/l}$). Moreover, about ~ 3 months and ~ 13 months later, the concentration in the

well reached the EPA advisory levels for infant-children (0.3 $\mu\text{g/l}$) and school age children-adults (1.6 $\mu\text{g/l}$), respectively (Table 3.1), above which the contaminant would cause serious health issues to the population groups.

Table 3.1: Microcystin Arrival time to the pumping well after microcystin was detected on Lake. Time: the time duration for the groundwater in pumping well to reach certain EPA advisory concentration levels after microcystin was detected on the lake cells.

EPA advisory levels	Concentration ($\mu\text{g/l}$)	Time
Detectable level	0.1	~2 months
Infant-children	0.3	~3 months
School-age children-Adults	1.6	~ 13 months

It is worth noting that the simulation results also show some interesting inter-annual pattern of the groundwater contamination (right column, Appendix B). In general, higher microcystin concentrations in the well as well as larger migration plumes were found from 2012 to 2014 (Figure 3.2) as responses to the severe HABs and high microcystins occurred in the lake shown in Figure 2.5. After 2014, low microcystin values were detected in the lake (Figure 2.5) and, thus, lower concentrations in the well (Figure 3.4) and smaller plumes near the lake were generated by our simulation. To be more specific, the years of 2013 and 2014 had a very high concentration of microcystin in Lake Erie compared to 2016-2018 (Figure 2.5). For example, August 2013 and July 2014 had concentrations of 35 $\mu\text{g/l}$ and 13 $\mu\text{g/l}$, respectively in the monitoring site of the lake (NOAA-GLERL), whereas August 2018 had a concentration of 0.1 $\mu\text{g/l}$ of microcystin on Lake Erie. Due to such a decline of the contaminant mass in the source (i.e., the lake), plume size of the microcystin transport towards the pumping well decreased after 2014.

Figure 3.3: Demonstration of simulated hydraulic head (Panel a) and microcystin concentration (mg/l, Panel b) in 3-D for the month of August 2014.

Figure 3.4: Simulated microcystin concentration in the pumping well from 2012-2018.

CHAPTER 4: DISCUSSION

4.1. Groundwater-surface water interaction and its role on contaminant transport

Previous studies (e.g., Mohamed and Shehri, 2009; Tian et al., 2013; Yang et al., 2016) suggest that microcystins released from HABs in surface water could be able to contaminate groundwater and aquifers due to the interaction between surface water and groundwater. In this study, we developed the first 3-D, MODFLOW-based flow and transport model in the Western Lake Erie Basin, one of the most contaminated HABs study areas, and provided theoretical support to the existence of such contamination in real hydrologic systems.

In our case, the interaction between the lake and the underlying and coastal aquifers occurred due to the groundwater pumping in the well near the shore. The drawdown lowered the water table and formed a sharp gradient between the water table (lower) and the lake level (higher). Consequently, the groundwater did not flow from the land to the lake anymore; instead, it flowed reversely from the lake to the well inland. Such an interaction between the lake and groundwater shifted the role of the lake from a “gaining” lake to a recharge lake, losing water to aquifer (Winter et al., 1998; Alley et al., 1999). And once the lake is experiencing HABs and being contaminated by the cyanotoxins, the lake would behave like “leaking storage” or contaminant source-releasing microcystins to the aquifer. And the reverse flow would drive and transport the microcystins released from the lake towards the well, via dominant advection and dispersion processes (Schwartz and Zhang, 2003).

4.2. The effect of Hydrogeologic Settings on Contaminant Transport

An advantage of hydrologic models is that, once built, they can be used conveniently to test and answer “what if” questions, especially for systems with uncertainties. In this study, the 3-D model that we developed was used to explore various uncertain or undecided settings of the

interacting lake-groundwater system and to test how different settings would affect the transport of microcystins. To accomplish this objective, four scenario simulations were carried out. Note that, in any scenario simulation, we only changed the model parameters or variables related to the scenario being tested and kept all others the same as those of the default model. Since arrival time or the time it takes for the well to reach the EPA advisory levels is of our particular interest, we mainly compared the arrival time among the scenarios and the default simulation case.

However, the timing needed for microcystin to reach the EPA advisory levels in the pumping well would increase if the reactivity of microcystin is taken into consideration in the model. Because, microcystin can be degraded or transformed in shallow water bodies (e.g. lakes) due to photodegradation (Schmidt et al., 2014). While transporting from lake to aquifer microcystin can get adsorbed or biodegraded in lake and aquifer sediments depending on sediment structure and the presence of microbial population (e.g algae, bacteria) (Grützmacher et al., 2009; Schmidt et al., 2014). The effect of chemical reactions on concentration peaks could be explained by Mao et al. (2006) who simulated a seawater intrusion tank experiment. In the study, he carried out two scenarios with and without accompanying the cation exchange reaction to quantify the effect of ignoring chemical reactions in seawater transport. The study reported that the concentration of Na, K, and Mg lowered when cation exchange was taken into consideration, because, the exchanger site adsorbed a portion of cations after the seawater intruded the tank. To that end, it can be said that microcystin arrival time might increase in case of advective, dispersive and reactive transport than in a scenario including advective, dispersive and non-reactive transport.

Scenario 1: Change of Pumping Rate

Figure 4.1 summarizes and compares the microcystin concentrations in the well among different pumping rates. Table 4.1 lists the arrival time of each scenario setting. It is evident that

as pumping rate increased, the concentration of microcystin in the well also increased (Figure 4.1). Such effect of the pumping rate on the concentration is even more significant if looking at the peaks. Meanwhile, the lower the pumping rate, the longer it took for the contaminant to reach the detectable levels in the pumping well (Table 4.1). The plausible explanation could be that, due to low pumping rate, groundwater removal rate from the aquifer reduced. Therefore, low amount of contaminated lake water moved to the groundwater domain due to low hydraulic gradient change and vice-versa. Sherif et al. (2012) similarly concluded that switching off pumping wells in Kalbha well field reduced the amount of saltwater intrusion in the observation wells of Wadi ham than the intrusion in normal pumping condition. On the other hand, double pumping rates on the well field showed gradual increase on landward migration of seawater (Sherif et al., 2012).

In section 2, it was stated that the pumping rate from one time monitoring was $160 \text{ m}^3/\text{d}$. Therefore, the pumping rates considered for the scenarios ($170 \text{ m}^3/\text{d}$, $125 \text{ m}^3/\text{d}$, $100 \text{ m}^3/\text{d}$) were within the range of typical pumping rates of South Bass Island site. In case of higher pumping rate ($170 \text{ m}^3/\text{d}$), it took ~ 1 month to reach the detectable level. For lower pumping rates, $125 \text{ m}^3/\text{d}$ and $100 \text{ m}^3/\text{d}$, it took ~ 3 months and ~ 4 months respectively to reach the detectable level. In case of $170 \text{ m}^3/\text{d}$, it took ~ 3 months and ~ 13 months to reach the level of $0.3 \text{ }\mu\text{g/l}$ and $1.6 \text{ }\mu\text{g/l}$ (Table 4.1). To reach the level of $1.6 \text{ }\mu\text{g/l}$, it took ~ 14 months and ~ 16 months for the pumping rates of $125 \text{ m}^3/\text{d}$ and $100 \text{ m}^3/\text{d}$ respectively (Table 4.1). Therefore, the lower the pumping rate, the less the risk of the groundwater to get contaminated by microcystin from HABs of Lake Erie.

Table 4.1: List of microcystin arrival time to the pumping well for transient state simulation (default vs. Scenarios 1-3). Time: the time duration for the groundwater in pumping well to reach certain EPA advisory concentration levels after microcystin was detected in the lake cells.

EPA advisory levels	Concentration ($\mu\text{g/l}$)	Time for microcystin migration to pumping well							
		Default		Scenario 1		Scenario 2		Scenario 3	
		170 m3/d	125 m3/d	100 m3/d	0.1C	5C	2m/d	5m/d	
Detectable	0.1	~2	~1 month	~3	~4 months	~13	~1	~3	~13
level		months		months		months	month	months	months
Infant-	0.3	~3	~3 months	~12	~13	~14	~2	~12	~14
children		months		months	months	months	months	months	months
School-age	1.6	~13	~13	~14	~16	~28	~12	~14	~28
children-		months	months	months	months	months	months	months	months
Adults									

Scenario 2: Change of Lakebed Leakance (C)

Scenario analysis on leakance or C was conducted by changing the value of leakance to 10 times lower of the default value (i.e., 0.1C) and 5 times higher of the default value (i.e., 5C). Under the lower leakance, it took ~13 months to reach the detectable level in the pumping well. It took ~14 months to reach the level for infants and school-age children (Table 4.1). The highest microcystin concentration in the pumping well was 1.3 $\mu\text{g/l}$ in case of 0.1C (Figure 4.2). Therefore, it could be assumed it would take a very long time (~28 months) for the groundwater in the pumping well to reach the level of 1.6 $\mu\text{g/l}$ (Table 4.1). With higher lakebed leakance, it takes ~1 month, ~2 months, and ~12 months to reach the level of 0.1 $\mu\text{g/l}$, 0.3 $\mu\text{g/l}$ and 1.6 $\mu\text{g/l}$ respectively (Table 4.1).

Figure 4.1: Comparison of the simulated microcystin concentrations in the pumping well under different settings of pumping rate, 2011-2018.

Lakebed leakance, as a function of lakebed hydraulic conductivity and thickness, controls the amount of lakewater seepage to groundwater. While calibrating the simulation model of Turwa lake and groundwater interaction, El- Zehairy et al. (2018) considered lakebed leakance as a key parameter for lake-groundwater interaction. By checking the sensitivity of lakebed leakance with 10 times higher and lower value, El- Zehairy et al. (2018) concluded that lower lakebed-seepage results into lower lakebed seepage flux. Likewise, in our model with lower lakebed leakance, the movement of contaminated lakewater to the pumping well was less compared to the high lakebed leakance. It was found that lakebed leakance was a sensitive parameter based on our simulation as well, that is, changes in lakebed leakance resulting significant changes in contaminant transport or concentration.

Figure 4.2: Comparison of the simulated microcystin concentrations in the pumping well under different settings of lakebed leakance, 2011-2018.

Scenario 3: Change of Hydraulic Conductivity

The K_h of layer 3 to 9 (limestone/ dolomite) have been increased to 2m/d and 5m/d to understand how the contaminant transport would be affected by K_h . With high K_h , discharge of water per unit area is higher (Freeze and Cherry, 1979). Therefore, one would quickly think that with higher K_h the contaminant should move faster from lake to groundwater than the lower K_h . Our results, however, show that it took longer time for the contaminant to reach the well under higher K_h (Figure 4.3). With higher K_h (2m/d and 5m/d), it took longer time to reach the EPA advisory concentration levels in the pumping wells (Figure 4.3). With 2 m/d it took ~3 months, ~12 months and ~14 months to reach the levels of 0.1 µg/l, 0.3 µg/l and 1.6 µg/l respectively (Table 4.1). In case of 5m/d, it took more time, for instance, ~13 months to reach 0.1 µg/l in groundwater abstraction well (Table 4.1). A reasonable explanation of such an interesting finding is that, with

higher K_h , larger amount of groundwater would be sucked into the well from the other or higher elevated side of the aquifer (Figure 2.1b). There, the water contains no microcystin and mixing it with contaminated water from lake would dilute or reduce the concentration of microcystin in the well. Obviously, this finding is new and worths future invesitgation to quantify the portions of the mixed fluid and how portions would be affected by other settings as well (e.g., pumping rate, topography, groundwater recharge rate, etc.).

Figure 4.3: Comparison of the simulated microcystin concentrations in the pumping well under different settings of hydraulic conductivity, 2011-2018.

Scenario 4: Change of microcystin concentration in the lake

To explore how low and high microcystin concentration in lake or the source zone could affect the time and intensity of microcystin migration to the pumping well, two different scenarios were assumed.

Scenario 4.1 Low microcystin concentration in lake:

In case of scenario 4.1, it is assumed that the microcystin was released into the lake starting from 7/1/2016. For the other years, the concentration was assumed ~ 0 mg/l. As the concentration input was very low (highest input is $1.4 \mu\text{g/l}$ for 9/1/2017), it took longer to reach the EPA advisory levels in the pumping well than default state. It took ~ 12 months to reach the level of $0.1 \mu\text{g/l}$. The highest concentration of microcystin in the pumping well was $0.2 \mu\text{g/l}$ which migrated on 10/1/2017 (Figure 4.4). And it took ~ 14 months and >24 months to reach the level of $0.3 \mu\text{g/l}$ and $1.6 \mu\text{g/l}$ respectively (Table 4.2).

Therefore, it can be said with low concentrations of microcystin in the lake, it would take more time for the contaminants to migrate to the groundwater abstraction well.

Figure 4.4: Comparison of microcystin concentrations in the pumping well simulated by using microcystin concentration data (2016-2018) at Put in Bay as the source.

Figure 4.5: Comparison of microcystin concentrations in the pumping well simulated by using hypothetical, uniform concentration values (5 and 10 $\mu\text{g/l}$ for July-October months) as the source.

Scenario 4.2 Using extreme microcystin concentration in Lake

In case of scenario 4.2, it was assumed that the lake was contaminated with microcystin concentration of 5 $\mu\text{g/l}$ and 10 $\mu\text{g/l}$ for the months of July to October from 1991-2018. For both of the scenarios, microcystin migrated to the well faster than the default case (Table 4.2). The reason was the concentration input was significantly higher than the default case and the high concentration persisted for four months (July-October) each year. For 5 $\mu\text{g/l}$ input it took ~ 1 month, ~ 2 months, ~ 14 months to reach the levels of 0.1 $\mu\text{g/l}$, 0.3 $\mu\text{g/l}$ and 1.6 $\mu\text{g/l}$ respectively. On the other hand, for 10 $\mu\text{g/l}$ input it took < 1 month, ~ 1 month and ~ 3 months to reach the levels of 0.1 $\mu\text{g/l}$, 0.3 $\mu\text{g/l}$ and 1.6 $\mu\text{g/l}$ respectively. This scenario setting provided a conception about how fast the contaminant migrates in case of extreme microcystin concentration in lake.

Table 4.2: List of microcystin arrival time to the pumping well for variable source concentration functions (default vs. Scenarios 4). Time: the time duration for the groundwater in pumping well to reach certain EPA advisory concentration levels after microcystin was detected in the lake cells.

EPA advisory		Time for microcystin migration to pumping well			
levels	Concentration	Default	Scenario 4		
	(µg/l)		5 µg/l seasonal	10 µg/l seasonal input	Low concentration
			input		input on Lake
Detectable level	0.1	~2 months	~1 month	<1 month	~ 1 year
Infant-children	0.3	~3 months	~2 months	~1 month	~14 months
School-age children-Adults	1.6	~ 13 months	~ 14 months	~3 months	>24 months

4.3. Limitations of current model simulation:

There are a few limitations or assumptions in this study which worth noting and would potentially motivate future studies. Using high-K technique, the lake domain was treated and modeled with specified head, high-K nodes, instead of employing LAK3 package for MODFLOW. LAK3 is a head-dependent flow boundary. The specified head represents an inexhaustible supply of water despite groundwater recharging from or discharging to the system (Anderson et al., 2015). The flux across a head-dependent flux boundary is dependent on the groundwater exchange to and from the lake (Anderson et al., 2015). For our model simulation, we did not want the lake stage to change as part of simulation. Instead we intended the stage to be constant as our input. Therefore, we assumed the lake as a hydraulic boundary providing a constant water level for each stress period by using time variant specified head (CHD) package.

Lack of continuous microcystin monitoring data from 1991-2018 prompted us to assume a

close to 0 mg/l concentration for years 1991- 2012. Lack of actual lakebed leakance, hydraulic conductivity, and aquifer depth data directed us to assume multiple variables. However, the variables were assumed based on trial-error process. Additionally, the scenarios provided an idea of how much the contaminant transport might change in case of change of the variables. The aquifer depth data was assumed based on ODNR well log and statewide aquifer maps of ODNR.

As mentioned in previous sections, this study, based on our knowledge, might be the first to model both the surface-water/groundwater interaction and the microcystin transport from the Lake Erie to an aquifer in a 3-D framework. Although efforts have been devoted to “mirror” and understand the real hydrogeological settings of our study area, we would rather consider our 3-D simulation a theoretical exploration than an exercise trying to reproduce the reality, mainly because we do not have sufficient field data (groundwater level and concentration data) for model calibration/validation. Still, as discussed earlier in section 4.1, our modeling results were able to provide theoretical support to the findings from the field, i.e., the existence of microcystin contamination in groundwater due to surface-water and groundwater interaction.

For the current model which we developed has a focus on the dominant mechanism of the contaminant transport, i.e. advection and dispersion. However, microcystin is a reactive organic molecule. Microcystin is a cyclic peptide hepatotoxin with seven amino acids and two carboxyl functional groups (de Maggd et al., 1999). Due to two free ionizable carboxyl groups and one free ionizable amino group in microcystin, partitioning is correlated with the pH of water (de Maggd et al., 1999). The strengths of organic acids and bases are expressed using the P_{Ka} values (Perrin et al., 1981). The lower the P_{Ka} ($P_{Ka} < 4$), the stronger the acid (Perrin et al., 1981). P_{Ka} of microcystin is (~ 3.5) (Zhao et al., 2006). The average water pH in Western Lake Erie Basin is 8.4 (Herdendorf, 1970). Therefore, the carboxyl group will be deprotonated in the basic Lake Erie

water. The aquifer material is primarily limestone/dolomites overlain by clay and glacial till (Smith, 1994). Due to deprotonation, the carboxyl groups in microcystin will bond with the clay mineral by cation bridging and ligand exchange (Pochodylo et al., 2016). This way, microcystin can get adsorbed into aquifer and lake sediments. The possibility of sorption of the toxin into sediments increases with the increase of the organic material due to cation bridging, ligand exchange and hydrophobic reactions between toxin and organic material (Wu et al., 2011; Pochodylo et al., 2016). Clay material can remove 81% of microcystin-LR from water (Morris et al., 2000). Due to the sorption of microcystin to lake and aquifer sediments, the microcystin concentration and migration to groundwater pumping well can be reduced as well.

A substantial amount of microcystin can get sorbed and degraded before reaching the pumping well by abiotic (adsorption, photodegradation) and biotic processes (metabolism, bacterial degradation) (Schmidt et al., 2014). Degradation can reduce the toxicity of microcystin (Schmidt et al., 2014). Per meter of water depth, the half-life of microcystin-LR is about 90 to 120 days (Munusamy et al., 2012). After degradation, some microcystin degradation products are less reactive than the parent microcystin (Harada et al., 2004). Linearized microcystin-LR ($\text{NH}_2\text{-Adda-Glu-Mdha-Ala-LeuMeAsp-Arg-OH}$), tetrapeptide ($\text{NH}_2\text{-AddaGlu-Mdha-Ala-OH}$) and Adda are the intermediate products of microcystin degradation (Harada et al., 2004). It is plausible that the toxicity of microcystin might be reduced before migrating to the pumping well, which was not taken into consideration for the model simulation. To model a more realistic system in the future, the model should be modified by incorporating retardation and degradation parameters and potential calibration/validation with real data would be helpful.

CHAPTER 5: CONCLUSION AND FUTURE STUDIES

Our 3-D simulation results indicated that HABs in the Great Lakes could contaminate groundwater in the aquifer of the island and coastal regions by contaminant transport driven by advection and dispersion. Due to the pumping induced reverse groundwater flow, microcystin-contaminated lake water would migrate towards the groundwater along the hydraulic gradient. For our default transient simulation, we considered the average monthly lake level and precipitation from 1991-2018. We used the microcystin concentration from the coast side from 2012-2018 as input transient concentration. Under the default setting (K_h : 1m/d, lakebed leakance 0.1/d and pumping rate 160 m³/d), it took ~2 months to reach the detectable concentration level of microcystin after it was released or detected in the lake. It takes ~3 months and ~13 months to reach EPA's advisory levels for infants and children (0.3 µg/l) and school-age children to adults (1.6 µg/l), respectively.

The 3-D model was further employed to explore different hydrogeological settings and their effects on the microcystin transport. Pumping rate, hydraulic conductivity, and lakebed leakance were tested with higher and lower values. Based on the scenario analyses, we concluded that a higher pumping rate and a higher lakebed leakance facilitated the migration of contaminant from the lake to groundwater. Under higher hydraulic conductivity settings, however, it took longer for the well to reach the same detectable levels. Such a finding is very interesting and surprising, which certainly warrants further investigation. Not surprisingly, it could also be concluded that with higher and longer existence of microcystin concentration in the lake, groundwater would be endangered more compared to lower microcystin concentration in the lake.

The 3-D model developed in this study, despite of some of its limitations at this stage, was able to simulate the complex flow and transport processes in the Great Lakes. Results and findings

from this study provided valuable insights and implications on how coastal groundwater aquifer and water supply could be threatened and degraded by the HABs occurred in the lake. For future research, studies should narrow the model uncertainties by collecting more data from field and lab work and to integrate chemical reactions package (sorption, degradation) into the existing model.

REFERENCES

- Alley, W. M., Reilly, T. E., & Franke, O. L. (1999). Effects of ground-water development on ground-water flow to and from surface-water bodies. US Geological Survey Circular, 1186. Retrieved from https://pubs.usgs.gov/circ/circ1186/html/gw_effect.html
- Anderson, M. P., Hunt, R. J., Krohelski, J. T., & Chung, K. (2002). Using high hydraulic conductivity nodes to simulate seepage lakes. *Groundwater*, 40(2), 117-122.
- Anderson, M. P., Woessner, W. W., & Hunt, R. J. (2015). *Applied groundwater modeling: Simulation of flow and advective transport* (Second ed.). London: Academic Press.
- Aquaveo GMS 10.4 Tutorials. Managing transient data. Retrieved from <http://gmstutorials10.4.aquaveo.com/MODFLOW-ManagingTransientData.pdf>
- Barlow, P.M., and A. Harbaugh. 2006. USGS directions in MODFLOW development. *Ground Water* 44, no. 6: 771–774.
- Battle-Aguilar, J. (2008). Groundwater flow and contaminant transport in an alluvial aquifer: in-situ investigation and modelling of a brownfield with strong groundwater-surface water interaction (No. THESIS_LIB). University of Liège (Belgium).
- Briand, J. F., Jacquet, S., Bernard, C., & Humbert, J. F. (2003). Health hazards for terrestrial vertebrates from toxic cyanobacteria in surface water ecosystems. *Veterinary research*, 34(4), 361-377.
- Brooks, B. W., Lazorchak, J. M., Howard, M. D., Johnson, M. V. V., Morton, S. L., Perkins, D. A. & Steevens, J. A. (2016). Are harmful algal blooms becoming the greatest inland water quality threat to public health and aquatic ecosystems? *Environmental toxicology and chemistry*, 35(1), 6-13.
- Bullerjahn, G. S., McKay, R. M., Davis, T. W., Baker, D. B., Boyer, G. L., D'Anglada, L. V., &

- Kudela, R. M. (2016). Global solutions to regional problems: Collecting global expertise to address the problem of harmful cyanobacterial blooms. A Lake Erie case study. *Harmful Algae*, 54, 223-238.
- Cheng, A. D., Halhal, D., Naji, A., & Ouazar, D. (2000). Pumping optimization in saltwater-intruded coastal aquifers. *Water Resources Research*, 36(8), 2155-2165.
- Chorus, I., & Bartram, J. (1999). Toxic cyanobacteria in water: a guide to their public health consequences, monitoring and management.
- Codd, G. A., Ward, C. J., & Bell, S. G. (1997). Cyanobacterial toxins: occurrence, modes of action, health effects and exposure routes. In *Applied Toxicology: Approaches Through Basic Science* (pp. 399-410). Springer, Berlin, Heidelberg.
- Congress, U. S. (2014). Harmful algal bloom and hypoxia research and control amendments act of 2014. Pub. S, 1254. Retrieved from <https://www.congress.gov/bill/113th-congress/senate-bill/1254>
- de Maagd, P. G. J., Hendriks, A. J., Seinen, W., & Sijm, D. T. (1999). pH-dependent hydrophobicity of the cyanobacteria toxin microcystin-LR. *Water Research*, 33(3), 677-680.
- Davis, T. W., Berry, D. L., Boyer, G. L., & Gobler, C. J. (2009). The effects of temperature and nutrients on the growth and dynamics of toxic and non-toxic strains of *Microcystis* during cyanobacteria blooms. *Harmful algae*, 8(5), 715-725.
- Domenico, P. A. (1972). Concepts and models in groundwater hydrology.
- El-Zehairy, A. A., Lubczynski, M. W., & Gurwin, J. (2018). Interactions of artificial lakes with groundwater applying an integrated MODFLOW solution. *Hydrogeology journal*, 26(1), 109-132.

- Environmental Protection Agency (EPA). Harmful Algal Bloom and Drinking Water Factsheet. Retrieved from https://www.epa.gov/sites/production/files/2016-11/documents/harmful_algal_blooms_and_drinking_water_factsheet.pdf
- Fong, T. T., Mansfield, L. S., Wilson, D. L., Schwab, D. J., Molloy, S. L., & Rose, J. B. (2007). Massive microbiological groundwater contamination associated with a waterborne outbreak in Lake Erie, South Bass Island, Ohio. *Environmental health perspectives*, 115(6), 856-864.
- Force, O. L. E. P. T. (2010). Ohio Lake Erie Phosphorus Task Force Final Report. Ohio Environmental Protection Agency, Division of Surface Water. Retrieved from https://www.epa.ohio.gov/portals/35/lakeerie/ptaskforce/Task_Force_Final_Executive_Summary_April_2010.pdf
- Forsyth, J. L. (1988). The geologic setting of the Erie Islands. *The Biogeography of the Island Region of Western Lake Erie*. Ohio State Univ. Press, Columbus, 13-23.
- Freeze, R. A., & Cherry, J. A. (1979). *Groundwater*. Englewood Cliffs, N.J: Prentice-Hall.
- Ghoraba, S. M., Zyedan, B. A., & Rashwan, I. M. H. (2013). Solute transport modeling of the groundwater for quaternary aquifer quality management in Middle Delta, Egypt. *Alexandria Engineering Journal*, 52(2), 197-207.
- Grützmacher, G., Wessel, G., Klitzke, S., & Chorus, I. (2009). Microcystin elimination during sediment contact. *Environmental science & technology*, 44(2), 657-662.
- Halford, K. J., & Hanson, R. T. (2002). User guide for the drawdown-limited, multi-node well (MNW) package for the US Geological Survey's modular three-dimensional finite-difference ground-water flow model, versions MODFLOW-96 and MODFLOW-2000 (Vol. 2, No. 293). US Department of the Interior, US Geological Survey.

- Harada, K. I., Imanishi, S., Kato, H., Mizuno, M., Ito, E., & Tsuji, K. (2004). Isolation of Adda from microcystin-LR by microbial degradation. *Toxicon*, 44(1), 107-109.
- Harbaugh, A.W., E.R. Banta, M.C. Hill, and M.G. McDonald. 2000. MODFLOW-2000, the U.S. Geological Survey modular ground-water model—User guide to modularization concepts and the Ground-Water Flow Process. USGS Open-File Report 00-92. Reston, Virginia: U.S. Geological Survey. Retrieved from <https://pubs.usgs.gov/of/2000/0092/report.pdf>.
- Heath, R. C. (1983). Basic Groundwater Hydrology: US Geological Survey Water Supply Paper 2220; prepared in cooperation with the North Carolina Department of Natural Resources and Community Development.
- Herdendorf, C. E. (1970). Lake Erie physical limnology cruise, midsummer 1967. Ohio. Division of Geological Survey.
- Herndorf, C. E. (1984). Inventory of the morphometric and limnological characteristics of the large lakes of the world. *Ohio State Univ. Tech. Bull*, 17, 70.
- Ho, J. C., & Michalak, A. M. (2015). Challenges in tracking harmful algal blooms: A synthesis of evidence from Lake Erie. *Journal of Great Lakes Research*, 41(2), 317-325.
- Holcombe, T. L., Warren, J. S., Taylor, L. A., Reid, D. F., & Herdendorf, C. E. (1997). Lakefloor geomorphology of western Lake Erie. *Journal of Great Lakes Research*, 23(2), 190-201.
- Huyakorn, P. S., Andersen, P. F., Mercer, J. W., & White, H. O. (1987). Saltwater intrusion in aquifers: Development and testing of a three-dimensional finite element model. *Water Resources Research*, 23(2), 293-312.
- Kong, F., Song, J., Zhang, Y., Fu, G., Cheng, D., Zhang, G., & Xue, Y. (2018). Surface Water-Groundwater Interaction in the Guanzhong Section of the Weihe River Basin, China.

Groundwater.

- Krohelski, J. T., Lin, Y. F., Rose, W. J., & Hunt, R. J. (2002). Simulation of Fish, Mud, and Crystal Lakes and the shallow ground-water system, Dane County, Wisconsin (No. 2002-4014). U.S. Geological Survey.
- Lapworth, D. J., Baran, N., Stuart, M. E., & Ward, R. S. (2012). Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. *Environmental pollution*, 163, 287-303.
- Lautz, L. K., & Siegel, D. I. (2006). Modeling surface and ground water mixing in the hyporheic zone using MODFLOW and MT3D. *Advances in Water Resources*, 29(11), 1618-1633.
- Liu, G., Schwartz, F. W., Wright, C. K., & McIntyre, N. E. (2016). Characterizing the climate-driven collapses and expansions of wetland habitats with a fully integrated surface–subsurface hydrologic model. *Wetlands*, doi: 10.1007/s13157-016-0817-9.
- Mao, X., Prommer, H., Barry, D. A., Langevin, C. D., Panteleit, B., & Li, L. (2006). Three-dimensional model for multi-component reactive transport with variable density groundwater flow. *Environmental Modelling & Software*, 21(5), 615-628.
- Mantoglou, A. (2003). Pumping management of coastal aquifers using analytical models of saltwater intrusion. *Water resources research*, 39(12).
- McDonald, M. G., & Harbaugh, A. W. (1984). A Modular Three-dimensional Finite-difference Ground-water Flow Model. US Geological Survey.
- Merel, S., Walker, D., Chicana, R., Snyder, S., Baurès, E., & Thomas, O. (2013). State of knowledge and concerns on cyanobacterial blooms and cyanotoxins. *Environment international*, 59, 303-327.
- Mohamed, Z. A., & Al Shehri, A. M. (2009). Microcystins in groundwater wells and their

- accumulation in vegetable plants irrigated with contaminated waters in Saudi Arabia. *Journal of hazardous materials*, 172(1), 310-315.
- Morris, D.A. and A.I. Johnson, 1967. Summary of hydrologic and physical properties of rock and soil materials as analyzed by the Hydrologic Laboratory of the U.S. Geological Survey, U.S. Geological Survey Water-Supply Paper 1839-D, 42p.
- Morris, R. J., Williams, D. E., Luu, H. A., Holmes, C. F., Andersen, R. J., & Calvert, S. E. (2000). The adsorption of microcystin-LR by natural clay particles. *Toxicon*, 38(2), 303-308.
- Munusamy, T., Hu, Y. L., & Lee, J. F. (2012). Adsorption and photodegradation of microcystin-LR onto sediments collected from reservoirs and rivers in Taiwan: a laboratory study to investigate the fate, transfer, and degradation of microcystin-LR. *Environmental Science and Pollution Research*, 19(6), 2390-2399.
- NOAA-Great Lakes Environmental Research Laboratory (GLERL). Great lakes water Levels. Retrieved from <https://www.glerl.noaa.gov/data>
- NOAA-Great Lakes Environmental Research Laboratory (GLERL). Lake Erie Microcystin Sampling Data. Retrieved from https://www.glerl.noaa.gov/res/HABs_and_Hypoxia/WLEMicrocystin.html
- NOAA-National Centers for Environmental Information (NCEI). Retrieved from <https://www.ngdc.noaa.gov>
- ODNR Division of Water Resources-Statewide Aquifer Mapping Program. Retrieved from <http://water.ohiodnr.gov/maps/statewide-aquifer-maps>
- Ohio Water Wells, ODNR Division of Water Resources. Retrieved from <https://gis.ohiodnr.gov/MapView/?config=waterwells>

- Ohio EPA (2014). Major aquifers in Ohio and associated water quality. Retrieved from https://epa.ohio.gov/Portals/28/documents/gwqcp/Aquifer&Geochem_ts.pdf
- Ohio, E. P. A. (2012). Public water system harmful algal bloom response strategy.
- Owen, S. J., Jones, N. L., & Holland, J. P. (1996). A comprehensive modeling environment for the simulation of groundwater flow and transport. *Engineering with computers*, 12(3-4), 235-242.
- Perrin, D. D., Dempsey, B., & Serjeant, E. P. (1981). pKa prediction for organic acids and bases (Vol. 1). London; New York: Chapman and Hall.
- Pochodylo, A. L., Aoki, T. G., & Aristilde, L. (2016). Adsorption mechanisms of microcystin variant conformations at water–mineral interfaces: a molecular modeling investigation. *Journal of colloid and interface science*, 480, 166-174.
- Schmidt, J., Wilhelm, S., & Boyer, G. (2014). The fate of microcystins in the environment and challenges for monitoring. *Toxins*, 6(12), 3354-3387.
- Schwartz, F. W. and Zhang, H. (2003). *Fundamentals of groundwater*. John Wiley & Sons, Inc., p. 583.
- Sheets, R. A., Dumouchelle, D. H., & Feinstein, D. T. (2005). Ground-water modeling of pumping effects near regional ground-water divides and river/aquifer systems- Results and implications of numerical experiments. U. S. Geological Survey. Retrieved from https://pubs.usgs.gov/sir/2005/5141/pdf/sir2005_5141.pdf
- Sherif, M., Kacimov, A., Javadi, A., & Ebraheem, A. A. (2012). Modeling groundwater flow and seawater intrusion in the coastal aquifer of Wadi Ham, UAE. *Water resources management*, 26(3), 751-774.
- Smith, C. (1994). Groundwater pollution potential of Ottawa County, Ohio. Ohio Department of

- Natural resources, Division of Water, Water Resources Section. Retrieved from https://water.ohiodnr.gov/portals/soilwater/pdf/maps/groundwater%20pollution/Preprintd/Ottawa_GWPP_wMap.pdf
- Steffen, M. M., Davis, T. W., McKay, R. M. L., Bullerjahn, G. S., Krausfeldt, L. E., Stough, J. M., & Gossiaux, D. C. (2017). Ecophysiological examination of the Lake Erie Microcystis bloom in 2014: linkages between biology and the water supply shutdown of Toledo, OH. *Environmental science & technology*, 51(12), 6745-6755.
- Teneva, I., Mladenov, R., Belkinova, D., Dimitrova-Dyulgerova, I., & Dzhambazov, B. (2010). Phytoplankton community of the drinking water supply reservoir Borovitsa (South Bulgaria) with an emphasis on cyanotoxins and water quality. *Open Life Sciences*, 5(2), 231-239.
- Tian, D., Zheng, W., Wei, X., Sun, X., Liu, L., Chen, X., & Wang, X. (2013). Dissolved microcystins in surface and ground waters in regions with high cancer incidence in the Huai River Basin of China. *Chemosphere*, 91(7), 1064-1071.
- United States Geological survey (USGS), 2017. Retrieved from <https://water.usgs.gov/edu>
- Watanabe, M. F., & Oishi, S. (1985). Effects of environmental factors on toxicity of a cyanobacterium (*Microcystis aeruginosa*) under culture conditions. *Appl. Environ. Microbiol.*, 49(5), 1342-1344.
- Watson, S. B., Miller, C., Arhonditsis, G., Boyer, G. L., Carmichael, W., Charlton, M. N., ... & Matisoff, G. (2016). The re-eutrophication of Lake Erie: Harmful algal blooms and hypoxia. *Harmful algae*, 56, 44-66.
- Winter, T. C., Harvey, J. W., Franke, O. L., Alley, W. M., & Geological Survey (U.S.). (1998). Ground water and surface water: A single resource. Denver, Colo: U.S. Geological Survey.

- World Health Organization (WHO). (2003) Cyanobacterial Toxins: Microcystin-LR in Drinking Water; WHO/SDE/WSH/03.04/57. World Health Organization, Geneva, Switzerland.
- Wu, X., Xiao, B., Li, R., Wang, C., Huang, J., & Wang, Z. (2011). Mechanisms and factors affecting sorption of microcystins onto natural sediments. *Environmental science & technology*, 45(7), 2641-2647.
- XMS Wiki. Online help for GMS, SMS, WMS. GMS stress periods. Retrieved from https://www.xmswiki.com/wiki/GMS:Stress_Periods
- Yang, Z., Kong, F., & Zhang, M. (2016). Groundwater contamination by microcystin from toxic cyanobacteria blooms in Lake Chaohu, China. *Environmental monitoring and assessment*, 188(5), 280.
- Zhao, Y. Y., Hrudehy, S., & Li, X. F. (2006). Determination of Microcystins in Water Using Integrated Solid-Phase Microextraction with Microbore High-Performance Liquid Chromatography—Electrospray Quadruple Time-of-Flight Mass Spectrometry. *Journal of chromatographic science*, 44(6), 359-365.
- Zheng, C., & Wang, P. P. (1999). MT3DMS: a modular three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems; documentation and user's guide. Alabama University.
- Zheng, C., & Wang, P. P. (1999). MT3DMS: Documentation and user's guide. Contract Report SERDP-99-1, US Army Engineer Research and Development Center, Vicksburg, MS.

APPENDIX A: STEADY-STATE SIMULATION

2D Simulation results with steady state default model set-up are illustrated in Figure A.1. Figure A.2 represents the head simulation and contaminant transportation plots in 3D. Transportation or migration of microcystin from the lake to groundwater was simulated based on the steady-state groundwater flow in MODFLOW. For the steady state simulation, 10% of 27-year (1991-2018) average precipitation (0.00229 m/d) and 27 year average lake level (173.25 m) was considered as input. The contaminant transport in MT3DMS was simulated based on an assumption of a constant concentration level (2 mg/l) of microcystins in lake since Day 0. The microcystins concentration of 2 mg/l was assumed based on the high concentration of ~3mg/l that occurred on Lake Erie at Gibraltar Island Docks on 7/24/2015. The data was collected from Ohio EPA Harmful Algal Toxin Monitoring. From the plots, it was observed that contaminants gradually migrates towards the groundwater abstraction well from day 1 to day 1000.

Figure A.1: 2D head distribution contour (m) and microcystin concentration (mg/l) for MODFLOW steady state simulation. (a) Head distribution contour for MODFLOW steady state simulation. (b) Microcystin migration after 1 day. (c) Microcystin migration after 100 days. (d) Microcystin migration after 1,000 days.

Based on EPA advisory levels (detectable level, advisory level for infant-children and the advisory level for school age children- adults); the days needed for contaminant transport days have been tested (Table A.1).

Figure A.2: 3D head distribution contour (m) and microcystin concentration (mg/l) for MODFLOW steady state simulation. (a) Head distribution contour for MODFLOW steady state simulation. (b) Microcystin migration after 1,000 days.

Table A.1 represents the time it took for the groundwater in the pumping well to reach certain EPA advisory concentration levels after microcystin is detected on the lake. In case of default simulation, it took 5 days to reach the detectable level ($0.1 \mu\text{g/l}$) after releasing a constant concentration (2 mg/l) into the lake. To reach EPA's advisory levels for infants and children ($0.3 \mu\text{g/l}$) and school-age children to adults ($1.6 \mu\text{g/l}$) for microcystins, it took about 6 and 9 days, respectively.

Figure A.3: Microcystin concentration in pumping well (Default Steady State). Time: the time duration for the groundwater in pumping well to reach certain EPA advisory concentration levels after microcystin was detected on the lake cells.

Table A.1 Microcystin arrival time to the pumping well after microcystin is detected on Lake for MODFLOW Steady State Simulation.

EPA advisory levels	Concentration (µg/l)	Days
Detectable level	0.1	5
Infant-children	0.3	6
School-age children-Adults	1.6	9

APPENDIX B: HEAD-CONCENTRATION PLOTS (2012-2018)

Table B.1 represents the 2D head concentration plots from January, 2012 to December, 2018. The lake cells were assumed to get contaminated from July, 2012 due to lack of data from earlier years. Therefore the plots are included from 2012

Table B.1 2D head-concentration plot for the simulation of transient system (January, 2012-December, 2018)

Time (mm/yy)	Head 177.7 175.75 173.8 171.85 169.9 167.95 166.0 2D Head contour (m)	Microcystin 0.02 0.015 0.008 0.003 0.0 2D Contaminant concentration contour (mg/l)
January, 2012		
February, 2012

December,
2018