A Thesis

entitled

Spatial and Temporal Trends in Thermal Structure and Oxygen Depletion in Western Lake Erie

By

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Master of Science Degree in Biology

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An Abstract of

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Periods of hot, calm weather can cause temporary thermal stratification and benthic hypoxia in the western basin of Lake Erie. The degree of hypoxia may be related to how quickly surface water temperature increases during periods of hot, calm weather and the resulting temperature difference between the surface and bottom waters. The effect of these periods of hot, calm weather may also vary depending on the temperature of the sediments, timing of the hot, calm weather, and the depth at which the temporary thermocline occurs. I explored patterns in thermal structure and oxygen depletion rates using in situ data collected in 2013 and 2014 by HOBO temperature and dissolved oxygen loggers. Oxygen depletion rates were calculated and piece-wise linear regression models and step function models were used to determine monthly oxygen depletion thresholds (TDcrit) based on surface to bottom temperature differences from May-September. In early summer, low TDcrit values paired with high depletion rates suggest that thermal stratification is not the contributing factor to low oxygen concentrations. However, in mid-summer, higher TDcrit values paired with high depletion rates suggested that oxygen depletion in mid-summer is due to thermal stratification.
Acknowledgements

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List of Abbreviations

BOD ....................... Biochemical Oxygen Demand

Chl a ...................... Chlorophyll a

NCWQR .................... National Center for Water Quality Research
NOAA ....................... National Oceanic and Atmospheric Administration

ODNR ........................ Ohio Department of Natural Resources
OEPA ........................ Ohio Environmental Protection Agency
OSU-AEL .................... Ohio State University Aquatic Ecology Laboratory
OSU-SL ...................... Ohio State University Stone Laboratory

SOD ........................ Sediment Oxygen Demand

TP .......................... Total Phosphorus
TDcrit ........................ Critical Temperature Difference

USGS ....................... United States Geological Survey
Chapter 1

Review of Hypoxia in Western Lake Erie and Overview of Thesis

Since the 1920s, the western basin of Lake Erie has been experiencing periods of temporary thermal stratification. Generally, it was thought that the western basin never ran out of oxygen due to its shallow depth and constant turnover. However periods of hot, calm weather can cause the water column to stratify, resulting in short periods of thermal stratification and hypoxia. Given that climate change has the potential to change air and water temperatures, and wind patterns, and that the re-eutrophication of Lake Erie has the potential to increase oxygen depletion rates, it is possible that the frequency of severe hypoxic events in western Lake Erie will increase. The relationship between these physical factors and the development of stratification and hypoxia have not been extensively investigated and other factors should be explored.

1.1. Goals of Thesis

My thesis project contains two separate parts, both focusing on aspects of eutrophication in western Lake Erie. In chapter two, my goal was to better understand the factors that influence hypoxia and oxygen depletion rates in the western basin. To accomplish this goal, I examined how temporal and spatial differences in the thermal structure of the western basin during summer impacts oxygen depletion rates.
Chapter 3 is a methods comparison study done in collaboration with Dr. Justin Chaffin of Ohio State Stone Laboratory to compare western Lake Erie water quality data collected using different sampling and analytical methods. My goal for this chapter was to determine whether common sampling and analytical methods used by western Lake Erie research agencies were comparable. To do this, Dr. Chaffin collected water using different methods then analyzed them using a single method, then I collected water using a single and sent the samples to the agencies for analysis. The two parameters that we focused on were total phosphorus and chlorophyll $a$. Both are important when measuring productivity and eutrophication. High levels of phosphorus loading leads to higher levels of chlorophyll, which in turn, can cause hypoxia and oxygen depletion by way of decomposition.

1.2. Overview of Subsequent Chapters

1.2.1 Spatial and Temporal Trends in Thermal Structure and Oxygen Depletion Rates in Western Lake Erie.

Temporal and spatial trends in the thermal structure and oxygen dynamics in the western basin of Lake Erie have not been extensively studied. Because western Lake Erie is highly affected by wind, waves, and ambient temperatures, episodic weather conditions and overall climate change could have a major impact on hypolimnetic oxygen concentrations. Declines in oxygen concentrations could have adverse effects on benthic organisms that support important western Lake Erie fisheries. By examining spatial patterns and temporal trends, we determined how the physical factors that affect oxygen depletion rates change throughout the season. Knowing how weather conditions affect
these factors is important when determining impacts and management strategies of global climate on western Lake Erie.

1.2.2. A Statistical Comparison of Sampling and Analytical Methods Used by Western Lake Erie Research Institutions

This portion of my thesis was co-authored with Dr. Justin Chaffin from Ohio State’s Stone Laboratory. Dr. Chaffin contributed the data for the sampling method comparison section and I contributed the data for the analytical method comparisons.

Tracking eutrophication in Lake Erie requires thorough monitoring of chlorophyll $a$ and total phosphorus concentrations involving many agencies and organizations. However, these institutions often use different sampling and/or analytical methods, thus measured chlorophyll $a$ and total phosphorus concentrations may not be comparable. The differing methods can make data set integration difficult. In this chapter, we determined which institutions were potential outliers and attempted to assign multipliers to aid in data set integration.

1.3. General Background

1.3.1. History of Hypoxia in Lake Erie

Since as early as the 1950s, Lake Erie has been experiencing periods of thermal stratification and seasonal low oxygen, or hypoxia (Bartish 1984). Studies done during the 1960s suggest that the lake was going through a period of accelerated eutrophication caused by excessive phosphorus loading (Beeton 1961). Excessive phosphorus loading caused massive cyanobacteria blooms that would eventually cause large areas of hypolimnetic hypoxia by way of decomposition and increased sediment oxygen demand.
(Lashaway and Carrick 2010, International Joint Commission 2013). Some of the indirect consequences of this accelerated eutrophication was the development of hypoxia, loss of benthic fauna and the collapse of important fisheries in Lake Erie (Beeton 1961, Hartman 1972).

1.3.2. Morphology and Thermal Stratification

Lake Erie is the smallest of the five Great Lakes but has the largest watershed to surface area ratio. The Lake Erie watershed supports the highest population, the highest percentage of agriculture, and the highest number of urban areas (Great Lakes Environmental Research Laboratory). It is divided into three basins that vary both physically and ecologically. All three basins can experience thermal stratification into the epilimnion (top layer), the metalimnion (middle layer that includes the thermocline) and the hypolimnion (bottom layer). The thicker the hypolimnion, the more oxygen that can hold (Charlton 1980). The eastern basin is the deepest (average depth~ 24 meters) and the coldest. Due to its depth and cold temperatures, the hypolimnion is very thick, oxygen-rich and does not experience hypoxia. The central basin makes up the largest portion of the lake (about 60% of the surface area) and is shallower and warmer than the eastern basin (average depth~18 meters) (Great Lakes Environmental Research Laboratory). The high amount nutrient loading from agricultural and urban areas, along with a unique morphology and thin hypolimnion, makes central Lake Erie highly susceptible to seasonal hypoxia. During the summer, the central basin develops typical seasonal temperate-zone lake stratification that lasts from spring until fall. Oxygen in the hypolimnion is gradually depleted, reaching hypoxic levels in July and anoxic levels in August. Finally, the western basin, which is the shallowest (average depth~ 7 meters),
and the warmest and most productive basin (Beeton 1961). Both the western and central basins of the lake are capable of experiencing hypolimnetic hypoxia, however the well-known Lake Erie “dead zone” occurs in the central basin.

1.3.3. Hypoxia in the Western Basin

In contrast to the central basin, the shallow western basin is usually well mixed during the summer, but weak stratification events (~1°C between top and bottom), and consequently hypoxic episodes, may occur during periods of low wind speed (<6 m/s) and high air temperatures (Britt et al. 1968, Bartish 1984, 1987, Boegman et al. 2008). In western Lake Erie, hypoxia is heavily influenced by weather factors such as radiative heating and wind conditions, making it very unpredictable (Andrews 1948, Schertzer and Sawchuk 1990). Eutrophication of the western basin caused by the external loading of phosphorus exacerbates hypoxia by increasing phytoplankton biomass and decomposition rates, thus accelerating biogeochemical processes, such as sediment oxygen demand (Hansen and Blackburn 1992, Loewen et al. 2007, Bouffard et al. 2013, International Joint Commission 2013). Although central basin hypoxia is more predictable and covers a larger area, hypoxia in the western basin can have more serious effects on the biotic community. Oxygen depletion rates in the central basin hypolimnion tend to be about 0.1 mg/L/day (Bertram 1993) where the depletion rates in the western basin can be as high as 4 mg/L/day (Bridgeman et al. 2006) under stratified conditions. The extreme depletion rates found in the western basin can have detrimental effects on the benthic macroinvertebrate communities (Britt 1955b). The unpredictable nature of hypoxia in the western basin doesn’t allow benthic organisms to adapt to the rapidly changing and harsh environment. Since the severity of hypoxia in the western basin is ultimately dependent
upon weather conditions, it is important to understand how changes and timing of weather events might impact oxygen levels in western Lake Erie.

1.3.4. Effects of Weather and Climate Change on Hypoxia

Long-term climate change threatens to increase oxygen depletion Lake Erie. In 1983, the lower Great Lakes experienced an unusually warm year. Warmer surface water temperatures and reduction in duration of ice cover resulted in earlier stratification in the central basin of Lake Erie (Schertzer and Sawchuk 1990). Since then, increased global temperatures have warmed not only the surface waters of Lake Erie, but the entire water column. Consequences of this warming include increases in duration of stratification and deepening of the thermocline in early summer while decreasing the depth in late summer and fall (Foley et al. 2012). Earlier onset, along with increased duration of stratification, increases the risk for hypoxia in Lake Erie (Blumberg and Di Toro 1990).

Contrary to monomictic systems, like the central basin that stratify for the duration of the summer, polymictic systems, like the western basin, mix throughout the year. Negative effects that are frequent in eutrophic polymictic lakes all over the world include increases in internal and external phosphorus loading, increases in frequency and duration of stratification events, and higher thermal stability (Wilhelm and Adrian 2008, Jeppesen et al. 2009). Climate models indicate that as ambient temperatures rise, future springs and winters will become warmer and wetter. Increased precipitation will result in increases in external loading of phosphorus and warmer water temperatures will result in earlier onset of decomposition and decreases in dissolved oxygen with subsequent nutrient fluxes (Jankowski et al. 2006).
1.3.5. Effects Hypoxia on Aquatic Organisms

Hypoxia has negative effects on biotic communities. According to studies done as a part of ECOFORE, hypoxia in the central basin alters food-web interactions and predator-prey relationships in fish communities by diminishing prey abundance and increasing competition (Kidwell et al. 2009, Pothoven et al. 2012). Fish which are forced to forage in hypoxic areas are also smaller due reduced physiological capabilities (Arend et al. 2011). In the western basin and other temperate polymictic lakes, it is the pollution intolerant macroinvertebrates that are most affected by low oxygen conditions. In Lake Simcoe Ontario, declines in other macrobenthos, such as chironomids and oligochaetes, have been observed after just a few days of low oxygen conditions (Nürnberg et al. 2013).

The mayfly (*Hexagenia* spp.) populations are indicators of the quality of western Lake Erie and are sensitive to both dissolved oxygen concentrations and water temperature, which is why they are not present in the central basin (Krieger et al. 2007). Even periods of light hypoxia can have negative effects on mayfly growth rates and fecundity (Edwards et al. 2009). The absence of *Hexagenia* between the 1960s and the 1990s has been attributed to low dissolved oxygen levels (Britt 1955a). In the last decade, *Hexagenia* recruitment failures have been linked to warm summers with a number of stratification events (Bridgeman et al. 2006). A study done in 2010 found that the mayfly populations that were present at the time were found within 1 km from the shore, suggesting that they either recolonized in areas that do not experience hypoxia or that hypoxia continues to affect their abundance in the deeper regions of the lake (Krieger et al. 1996, Corkum 2010). A shift in the species of mayfly in Lake Erie was also found. It
was believed that the shift from \( H. \text{rigida} \) to \( H. \text{limbata} \) was due to \( H. \text{limbata}'s \) higher tolerance to low oxygen conditions (Green et al. 2013).

The major hypoxic event observed in 1953 that decimated the mayfly population is also thought to have caused declines in the silver chub (\( \text{Macrhybopsis storriana} \)) population in the western basin of the lake (Bartish 1984, 1987). Declines in species like the silver chub can affect the populations of top predators that feed on them, like the Northern Pike (\( \text{Esox lucius} \)) and the Walleye (\( \text{Sander vitreus} \)) (Bartish 1984, 1987). These recruitment failures periods of hypoxia have also had significant effects on the Yellow Perch (\( \text{Perca flavescens} \)) population in western Lake Erie (Roberts et al. 2009). During periods of low recruitment, perch growth rates and abundance were significantly lower than during periods of high Hexagenia recruitment (Tyson and Knight 2001). This could have significant repercussions for the Lake Erie sport fishery (Madenjian et al. 1998).

1.3.6. Nutrients, Algal Blooms, and Dissolved Oxygen

In 1972, the implementation of phosphorus abatement programs greatly reduced the amount of total phosphorus loading into Lake Erie. These programs controlled the input of phosphorus from point sources such as commercial detergents and sewage treatment plants (Scavia et al. 2014). Over the following decades, increases and decreases in hypoxia matched up with increases and decreases in non-point source pollution from agricultural and urban run-off (Bertram 1993, International Joint Commission 2013). It was proposed in 1987 that oxygen depletion depends on the average trophic conditions and primary production prior to the stratification event and that a reduction in nutrient loading would improve oxygen concentrations (Charlton 1987). After changes in
agricultural practices in the mid-1990s, hypolimnetic oxygen levels began to increase and total phosphorus concentrations began to decrease (Ohio Lake Erie Phosphorus Task Force 2013). Even though total phosphorus loading into the lake had decreased and is now fairly consistent, the fraction of dissolved reactive phosphorus (DRP) has been increasing (Johnson et al. 2014, Scavia et al. 2014). Increases in DRP led to the re-eutrophication of Lake Erie and the development of cyanobacteria blooms and hypoxia once again (Zhou et al. 2012, Kane et al. 2014, Scavia et al. 2014).
1.4. References


Bartish, T. M. 1984. Thermal stratification in the western basin of Lake Erie: its characteristics, mechanisms of formation, and chemical and biological consequences. The Ohio State University.


Chapter 2

Spatial and Temporal Trends in Thermal Structure and Oxygen Depletion in Western Lake Erie

2.1. Introduction

Since the 1920s, the western basin of Lake Erie has been experiencing periods of temporary thermal stratification (Chandler 1940, 1942, Wright et al. 1955, Carr et al. 1965). It was originally believed that even during brief stratified conditions, oxygen concentrations in the western basin were never depleted and the water column was always well-oxygenated (Chandler 1944). The first detection of significant oxygen depletion was found in 1953 after a month-long period of hot, calm weather (Britt 1955). This particular oxygen depletion event was significant because it killed off the mayfly (Hexagenia spp.) larvae that were living in the bottom sediments. The mayflies did not return until 40 years later. It was determined that low wind speed (<6-7 m/s) and high ambient air temperatures were two major factors that contributed to the temporary thermal stratification and the development of the low oxygen conditions, which led to the disappearance of mayflies in 1953 (Carr et al. 1965, Britt et al. 1968, Bartish 1984, 1987, Loewen et al. 2007, Boegman et al. 2008).

Given that climate change has the potential to change air and water temperatures, and wind patterns, and that the re-eutrophication of Lake Erie has the potential to
increase oxygen depletion rates (Kane et al. 2014, Scavia et al. 2014), it is possible that the frequency of severe hypoxic events in western Lake Erie will increase (Kane et al. 2014). In order to understand how stratification and hypoxia may change, it is important to develop a better understanding of how factors such as thermocline depth, seasonality, and oxygen depletion rates. The relationship between these factors and the development of stratification and hypoxia has been investigated in only a semi-quantitative manner and needs to be explored further.

Temporary stratification and oxygen depletion in western Lake Erie may occur when the surface and bottom waters differ by only a few degrees Celsius (Bridgeman et al. 2006). In the present study, I determined the “critical temperature difference” between surface and bottom waters needed to initiate oxygen depletion of bottom waters. I examined how this metric varied throughout the summer season (May-September) at different lake depths (6 meters and 9 meters), and how it was affected by other physical factors such as thermocline depth, average water temperature, and oxygen depletion rates. My objectives were to 1) determine if there were any lake depth patterns or temporal trends among these factors and 2) learn what factors were driving these patterns and trends. My first hypothesis was that the deeper regions would have higher oxygen depletion rates and spend more time at low oxygen concentrations. The deeper regions of the basin are more likely to stay stratified longer and are less likely to be mixed by wind and waves than the shallow nearshore regions. When these areas are stratified for a long period of time, the oxygen concentrations deplete to low levels. Oxygen demand is the driving factors that determines how fast the oxygen depletes. Organic matter will settle out in the deeper regions of the basin which increases the oxygen demand. My second
hypothesis was that oxygen depletion rates would peak in mid-summer due to the higher probability of hot, calm weather events, and therefore a greater chance of thermal stratification.

2.2 Methods

In order to investigate changes in oxygen depletion, I first determined temporal patterns in stratification at two sites using data collected in the summers of 2013 and 2014. Next, I examined how stratification event duration and hypolimnion thickness impacted the epibenthic oxygen concentrations in the western basin. Finally, I determined temperature difference thresholds for oxygen depletion for each month sampled.

2.2.1. Data Collection

Temperature and epibenthic oxygen data were collected using arrays of Onset HOBO Temperature Pro v2 Data Loggers (Onset # U22-001) and Onset HOBO Dissolved Oxygen Loggers (Onset # U26-001) attached at specific depths to polypropylene rope which were anchored in the lake sediment at one end and suspended by a floating buoy at the other. In 2013, a temperature/oxygen array was deployed from June 28 to August 27 at a deep water station (Station 4P, 41°45’00” N, 83°06’14”W) (Figure 2-1) where hypoxia had been measured in the past (Bridgeman et al. 2006). At this station, temperature loggers were placed at depths of 1, 3, 5, 7, and 8 meters and a dissolved oxygen logger that also measured temperature was placed at a depth of 9 meters. Measurements were logged at 15-minute intervals that were later used to compute hourly averages. In 2014, two arrays of loggers were deployed using the same equipment from May 17 until September 25 at Station 4P and a second, shallower station (Station 7M: 41°44’05” N, 83°17’43”W) to determine if and how a thermocline develops at
different depths relative to the lake bottom. At this station, temperature loggers were placed at depths of 1, 3, 4, and 5 meters and a dissolved oxygen logger that also measured temperature was deployed at a depth of 6 meters. The loggers were set to record measurements at 15 minute intervals as before.

2.2.2. Hypolimnion Thickness and Oxygen Depletion Rates

A time series of temperature and oxygen profiles was created for 2013 and 2014 to determine timing and duration of major stratification events (defined as >48 hours duration) (Figure 2-10). A time period of at least two days was chosen because previous research suggests that it takes about that long for thermal stratification to set up (Bridgeman et al. 2006). The time series were then separated into monthly periods (May through September) to determine temporal changes throughout the summer season at each station. Thermocline depth was defined as the depth halfway between two adjacent temperature sensors that recorded greatly differing temperatures relative to the temperatures recorded by loggers either farther above or below this point. The rates at which dissolved oxygen concentrations decreased that corresponded with these major stratification events were then calculated by measuring the slope of the decreasing oxygen concentrations.

2.2.3. Temperature Difference Threshold (TDcrit) Determination

In western Lake Erie, which is usually well mixed, it is assumed that the water column is isothermal and that oxygen depletion of benthic waters does not occur. During summer months, however, water near the surface may warm faster than water near the bottom. At some point, the difference in density between the surface waters and bottom water leads to thermal stratification and begins to impede vertical mixing and the
movement of dissolved oxygen from the lake surface to the bottom. Once this temperature difference between the surface and the bottom of the water column reaches a certain point, rapid oxygen depletion starts to occur. The temperature difference at which this occurs may be considered to be the “Critical Temperature Difference” or TDcrit. I determined TDcrit values and how they changed over the summer at locations with different depths. To determine TDcrit, the natural log of the difference between surface and bottom water temperatures was plotted against the epibenthic dissolved oxygen concentrations. Two different types of change point models were used to determine TDcrit (Qian 2010). Change point models were used because this data indicated that there was a natural threshold between temperature difference and oxygen depletion that occurred. At this threshold is where the slope of oxygen concentrations suddenly decreased or dropped. The first model was a piecewise linear regression (also known as the Hockey Stick model) is shown below:

\[ \text{DO} = \alpha + [\beta + \delta \cdot I(\text{TempR} - \varphi)](\text{TempR} - \varphi) + e \]

Where \( I(\Theta) = 0 \) if \( \Theta \leq 0 \) and 1 otherwise.

The fit of the model was determined by how gradual or strong the threshold response was. When the threshold response was gradual, the piecewise linear regression model fit the data the best. When the threshold response was very strong, the Hockey Stick model did not properly fit the data, so a step function was used (Qian 2014). The step function was very similar to the Hockey Stick model. The only difference was that the two linear models broke apart at \( \varphi \) instead of meeting at \( \varphi \). The equation for the step function is shown below:

\[ \text{DO} = \alpha + [\beta + \delta \cdot I(\text{TempR} - \varphi)] \]
This change point, or $\phi$, was named TDcrit because it describes a critical difference in temperature from the surface to the bottom in which oxygen depletion begins to increase. To get TDcrit, the inverse natural log of $\phi$ must be calculated. A small TDcrit meant that a small temperature difference from top to bottom was sufficient to result in rapid oxygen depletion while a large TDcrit meant that a larger difference in temperature from top to bottom was needed for the onset of rapid oxygen depletion to occur. Separate analyses were done for each month to determine if there were any temporal changes in TDcrit throughout the summer season. TDcrit values from all months (May-September), years (2013 and 2014), and stations (4P and 7M) were compared to determine temporal trends and spatial patterns in the relationship between stratification and oxygen depletion.

2.3. Results

2.3.1. Stratification Event Duration and Hypolimnion Thickness

2.3.1.1. Station 4P: 9 meter site

In 2013, the average duration of stratification events varied from 2 days (June) to 10 days (August) (Figure 2-2). The average hypolimnion thickness gradually increased from 1.5 meters in June to 2.5 meters in August (Figure 2-3). In 2014, the average duration of stratification events peaked in May with 14 days and varied between 4 and 10 days from June through August (Figure 2-2). Average hypolimnion thickness ranged from 1.8 meters (June) to 4 meters (July) (Figure 2-3). No stratification events were observed in September of 2014.

2.3.1.2. Station 7M: 6 meter site
The thermistor string and oxygen sensor were only deployed at station 7M in 2014. The average duration of stratification events varied from 2 to 5 days (Figure 2-4). The hypolimnion thickness fluctuated from 1 meter to 3 meters (Figure 2-5). This station experienced frequent internal wave action. Average hypolimnion thickness for this site includes multiple measurements per event. No stratification events were observed in September of 2014.

When hypolimnion thicknesses were compared between Stations 7M and 4P, it was determined that in June, both stations had a hypolimnion thickness of about 2 meters. In July and August, the average hypolimnion thickness for Station 7M remained 2 meters while it increased to about 4 meters at Station 4P (Figure 2-11).

2.3.2. Oxygen Depletion Rates

Oxygen depletion rates were only calculated for major depletion events, which I defined as events that were a result of major stratification events (48+ hours of stratification). There weren’t enough data points to perform a test of significance between the rates for different months.

2.3.2.1. Station 4P: 9 meter site

Average oxygen depletion rates were calculated for July and August in 2013. I did observe part of a major stratification event in June but I was unable to determine the initial oxygen concentrations due to the sensors being deployed mid-depletion event. Average depletion rate for July was 2.64 mg/L/day and increased to 4.23 mg/L/day in August (Figure 2-6). The array detected a total of 34 hours below 4 mg/L. Four of those hours were in July and remaining 30 were in August (Figure 2-7).
In 2014, I was able to calculate depletion rates for all major stratification events. From May to July, the depletion rate increased from 0.87 to 5.23 mg/L/day. The rate then decreased in August to 2.75 mg/L/day (Figure 2-6). No major stratification events and therefore no major depletion events were recorded for September 2014. Overall, less time was spent at low oxygen levels in 2014. There was a total of 27 hours spent below 4 mg/L, 11 in June and 16 in July (Figure 2-7).

2.3.2.2. Station 7M: 6 meter site

Average depletion rates fluctuated between 3.53- 4.37 mg/L/day from May to July then peaked in August at 5.84 mg/L/day (Figure 2-8). The array detected 14 hours of low dissolved oxygen concentrations in August (Figure 2-9). No major stratification events or major depletion events were recorded for September 2014.

2.3.3. Temperature Difference Thresholds (TDcrit)

2.3.3.1. Station 4P: 9 meter site

In 2013, TDcrit values were calculated for June through August. These values peaked in July at 1.8 degrees Celsius. In 2014, TDcrit values were also calculated for May through September. TDcrit peaked in May at 2.46 degrees Celsius. I did observe a similar pattern in TDcrit values over the three month period of June through August where the TDcrit value in July was higher than the values in both June and August. All change points for both 2013 and 2014 were significant at $\alpha = 0.05$ (Table 1).

2.3.3.2. Station 7M: 6 meter site

In 2014, the highest TDcrit value of 1.26 degrees Celsius occurred in May. TDcrit values for June through September varied between 0.12-0.64 degrees Celsius. All values are significant $\alpha = 0.05$ (Table 2).
2.4. Discussion

2.4.1. Spatial Patterns

My first hypothesis was that the deeper station would have higher oxygen depletion rates and spend more time at low oxygen concentrations. I compared the shape of the thermocline from the shallow site to the deep site. If the thermocline only developed at a specific depth, then that would result in a thick, bowl-shaped hypolimnion. If the thermocline followed the contour of the bottom of the lake across the basin, there would be a greater chance for the basin to go hypoxic due to this creating a thin, widespread hypolimnion (Beletsky et al. 2012). I found that the thermocline generally follows the contour of the bottom of the basin. Organic matter content in the sediment is another factor that would determine spatial patterns. Organic matter and suspended sediments settle out in the deeper profundal zone which could potentially lead to a higher potential oxygen demand in those deeper regions (Schloesser et al., 2005). My data, along with a probable high potential oxygen demand, support my hypothesis that the deep water station will have higher depletion rates and lower oxygen concentrations during stratification events.

2.4.2. Temporal Trends

Many of the factors that would affect temporal trends in hypoxia and the development of a thermocline are weather dependent. For example, changes in the amount of precipitation will change water depth. Water depth, along with wind speed, will determine when and how often the water column will mix. Air temperatures and timing of hot, calm weather will determine when and how long the water column stratifies. My second hypothesis was that oxygen depletion rates would peak in mid-
summer due to the higher probability of hot, calm weather events, and therefore a greater chance of thermal stratification. Based on the results, my hypothesis was supported by the data. The relationships between the physical factors that I examined and my conclusions from the data can be seen in Table 2.3. In May, the sediment and water temperatures were still cold and depletion rates were low. By June, warmer air temperatures started to warm the surface of the water. Once this began, sediment temperatures significantly influence the water temperature by cooling the bottom of the water column while air temperatures heated the surface causing a high thermocline to form. Low \( \text{TD}_{\text{crit}} \) values and high depletion rates in June suggest that distinct stratification is unnecessary in early summer; even small differences in temperature between surface and bottom waters are sufficient to cause oxygen depletion. When a low \( \text{TD}_{\text{crit}} \) is paired with a high oxygen depletion rate, as seen in early summer of both 2013 and 2014, this means that stratification was probably \textit{not} the main contributing factor to the high depletion rates. By August, the temperature of the sediment caught up with the temperature of the overlying water column and this cooling effect no longer occurred. The thermocline was able to develop lower in the water column producing a thin hypolimnion and higher oxygen depletion rates. A high \( \text{TD}_{\text{crit}} \) paired with high oxygen depletion rates suggest that thermal stratification \textit{is} a contributing physical factor during late summer.

Hypolimnion thickness, water temperature, and sediment temperature (or the difference between the two, \( \text{TD}_{\text{crit}} \)) were the physical factors that appeared to have the greatest influence on temporal trends in oxygen depletion and thermal structure. Biological factors were not measured in this study, but these results suggest that
biochemical oxygen demand could have a significant impact on oxygen concentrations in the early summer months.

Even though a thermocline developed at the shallow water station, no significant trends were observed. This could be due to the high variability in the weather and the fact that is it nearshore instead of offshore. This station is in an area where currents from the Maumee River frequently go through so the water is constantly moving. This station is also more easily mixed by wind and waves because it is shallow. When going through the data, it was also obvious that there were frequent internal wave episodes at this site that were not present at the deep water site.

To get a better understanding of what affects oxygen depletion in the western basin, long term data sets need to be acquired. I would suggest deploying more arrays in other areas of the western basin. The data that I collected was limited in both location and time. Arrays deployed for a longer amount of time and at more than 2 locations would allow for large scale and long term studies.
2.5. References


2.6. Tables

2.1. TDcrit values, measured in degrees Celsius, calculated using the Hockey Stick Model (italicized) and step functions for Station 4P in 2013 and 2014. Column two shows the level of significance for the values calculated using the Hockey Stick Model and column three shows the 95 percent confidence interval for the values calculated using the step function.

<table>
<thead>
<tr>
<th>4P</th>
<th>TDcrit (C)</th>
<th>Significance</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>May-14</td>
<td>2.44</td>
<td></td>
<td>(2.36, 2.77)</td>
</tr>
<tr>
<td>June-13</td>
<td>0.36</td>
<td>**</td>
<td></td>
</tr>
<tr>
<td>June-14</td>
<td>0.34</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>July-13</td>
<td>1.80</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>July-14</td>
<td>0.87</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>August-13</td>
<td>0.80</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>August-14</td>
<td>0.40</td>
<td></td>
<td>(0.28, 0.58)</td>
</tr>
<tr>
<td>September-14</td>
<td>0.13</td>
<td></td>
<td>(0.03, 0.19)</td>
</tr>
</tbody>
</table>

** p ≤ 0.01     ***p ≤ 0.001
2.2. TDcrit values, measured in degrees Celsius, calculated using the Hockey Stick Model (italicized) and step functions for Station 7M in 2014. Column two shows the level of significance for the values calculated using the Hockey Stick Model and column three shows the 95 percent confidence interval for the values calculated using the step function.

<table>
<thead>
<tr>
<th>7M</th>
<th>TDcrit (C)</th>
<th>Significance</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>May-14</td>
<td>1.26</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>June-14</td>
<td>0.46</td>
<td></td>
<td>(0.30, 0.53)</td>
</tr>
<tr>
<td>July-14</td>
<td>0.29</td>
<td></td>
<td>(0.11, 0.30)</td>
</tr>
<tr>
<td>August-14</td>
<td>0.64</td>
<td></td>
<td>(0.60, 1.33)</td>
</tr>
<tr>
<td>September-14</td>
<td>0.12</td>
<td></td>
<td>(0.07, 0.17)</td>
</tr>
</tbody>
</table>

***p ≤ 0.001
2.3. Summary of conclusions and trends for the deep water station (Station 4P).

<table>
<thead>
<tr>
<th>Month</th>
<th>TDcrit</th>
<th>Hypolimnion Thickness</th>
<th>Water Temp.</th>
<th>Sediment Temp.</th>
<th>OD Rate</th>
<th>Conclusions</th>
</tr>
</thead>
</table>
| May      | High   | Large (3 meters)       | Low         | Low            | Low (1 mg/L)          | High temperature difference  
Large hypolimnion thickness  
Cold water/sediment temps  
*No depletion due cold water holding more oxygen and cool air temperatures.* |
| June     | Low    | Moderate (2 meters)    | Moderate    | Low            | High (5 mg/L)          | Low temperature difference  
Moderate hypolimnion thickness  
*High depletion rates were not due to temperature differences or stratification* |
| July     | High   | Large (4 meters)       | High        | Moderate       | High (5 mg/L)          | High temperature difference  
Sediments still cooler than surface water  
Frequent periods of hot, calm weather  
*High depletion rate due to stratification* |
| August   | Moderate | Moderate (2 meters)  | High        | High            | Moderate (3 mg/L)     | Moderate temperature difference  
Moderate hypolimnion thickness  
Warm water/sediments  
Frequent periods of hot, calm weather  
*Moderate depletion rate due to stratification* |
| September| Low    | ---                    | Moderate    | Moderate        | ---                   | Low temperature difference- isothermal  
Frequent weather changes and cooler temperatures  
*No depletion due to frequent mixing* |
2.7. Figures

2-1. Sensor array locations. Station 4P was deployed at a depth of 9 meters and station 7M was deployed at a depth of 6 meters.
2-2. Average duration of stratification events measured by the array at our deep water station (Station 4P). Arrays were deployed June-August in 2013 and May-September 2014. Average event durations are depicted with error bars. June and August 2013 and May 2014 only had one major event detected. No major stratification events were detected in September of 2014.
2-3. Average hypolimnion thickness measured by the array at our deep water station (Station 4P). Arrays were deployed June-August in 2013 and May-September 2014. No major stratification events, therefore no hypolimnion, were detected in September of 2014.
2-4. Average duration of stratification events measured by the array at our shallow water station (Station 7M). The array was deployed May-September. Average event durations are depicted with error bars. Only one major event was detected in May-July and no events were detected in September.
2-5. Average hypolimnion thickness measured by the array at our shallow water station (Station 7M). Arrays were deployed May-September 2014. Only one major event was detected May-July. There were fluctuations in the thermocline in May due to internal waves. No major stratification events, therefore no hypolimnion, were detected in September of 2014.
2-6. Average oxygen depletion rates measured by the array at our deep water station (Station 4P). Arrays were deployed June-August in 2013 and May-September 2014. No major oxygen depletion events, were detected in September of 2014.
2-7. Hours that the deep water station (Station 4P) spent at low dissolved oxygen concentrations. Arrays were deployed June-August in 2013 and May-September 2014. Not every depletion event resulted in low dissolved oxygen concentrations.
2-8. Oxygen depletion rates measured by the array at our shallow water station (Station 7M). Arrays were deployed May-September 2014. No major oxygen depletion events, were detected in May, July, and September.
2-9. Hours that the shallow water station (Station 7M) spent at low dissolved oxygen concentrations. Array was May-September 2014. The oxygen depletion event that occurred in June did not result in low dissolved oxygen concentrations.
2-10. Temperature and oxygen profiles from 4P in 2013(A) and 2014(B) and station 7M in 2014 (C). Periods of stratification are depicted by the uncoupling of the surface and bottom water temperature.
Hypolimnion thickness comparison between Station 7M (shallow water site) and Station 4P (deep water site). In early summer, the thermocline follows the contour of the bottom of the lake producing a thin hypolimnion. The thermocline rises in the water column in mid and late summer.
Chapter 3

A Statistical Comparison of Sampling and Analytical Methods Used by Western Lake Erie Research Institutions

3.1. Abstract

Monitoring the trend towards increasing eutrophication in Lake Erie involves many agencies and organizations collecting frequent water quality measurements, including chlorophyll a (chl a) and total phosphorus (TP) concentrations. However, monitoring institutions often use different sampling and/or analytical methods and therefore measured chl a and TP concentrations may not be comparable across data sets.

We compared sampling and analytical methods used by major laboratories in the western Lake Erie region: University of Toledo (UT), Ohio State University’s Aquatic Ecology Lab (AEL), Ohio EPA (OEPA), NOAA Great Lakes Environmental Research Laboratory (NOAA-GLERL), USGS Great Lakes Science Center (USGS), National Center for Water Quality Research (NCWQR), and Ohio State University’s Stone Laboratory (SL). Linear regressions were used to compare the reported concentrations. Four different sampling methods that were employed produced very similar chl a and TP concentrations when regressed against each other (slopes=0.96-1.04, r-squared >0.98). Differences were found
in analytical methods. The USGS reported chlorophyll $a$ concentrations at least two times lower (slope= 1.91-3.22, r-squared= 0.81) than all other institutions and UT reported highly variable data (r-squared <0.58). There were no significant differences in the reported TP values (slopes=0.88-1.09, r-squared >0.91). The results suggest that sampling methods used by different monitoring groups are interchangeable and with a few exceptions for chlorophyll $a$, analytical methods were in agreement.

3.2. Introduction

In the previous chapter, I speculated that organic matter is an important factor in determining how fast oxygen will deplete in the western basin of Lake Erie. Decomposing algal biomass is a significant portion of that decaying organic matter and the further eutrophication of Lake Erie is resulting in larger algal blooms and total biomass. Monitoring of eutrophication requires thorough testing of chlorophyll (chl) $a$ and total phosphorus (TP) concentrations over time. These parameters are especially important because total phosphorus concentrations indicate the lakes productivity potential and chl $a$ concentrations are a surrogate for algal biomass. Because of its large size (25,700 km$^2$), monitoring the western basin of Lake Erie involves many agencies and organizations (Chapra and Dobson, 1981) that have been independently building long-term data sets since the early 1980s. These data sets cover different areas of the basin, with differing sampling methods, and at differing frequencies and dates. Although a combined data set would provide great benefit for the analysis of large-scale spatial patterns and temporal trends, integration of the individual data sets has never been attempted.
One challenge that may arise when comparing data from several agencies is their use of different water sampling protocols. For both chl $a$ and TP, sampling depth and time of day could play a large part in determining precise concentrations between agencies (Martin et al., 1992). Some algae and cyanobacteria, Microcystis in particular, can regulate their buoyancy depending on light levels and will sink during periods of high light conditions to avoid photoinhibition (Thomas and Walsby 1984). For example, if a surface grab was taken during high light conditions, this could result in an underestimation of the chl $a$ concentrations. Higher concentrations of TP could also be found near the bottom as opposed to the surface if there are low oxygen conditions. Under low oxygen conditions, phosphorus is released from the sediments and if a sample were to be taken from the surface, the TP concentration would also be underestimated and not representative of the whole water column (Martin et al 1992). Another challenge could be comparing data from agencies that use different analytical procedures. Differences in instrumentation and solvents used in chl $a$ analysis can cause concentrations to be significantly under or overestimated while the methodology for TP determination is fairly uniform (Jacobsen and Rai, 1990; Schagerl and Künzl, 2007).

The objectives of this study were 1) to determine if the different depth sampling protocols used by the various organizations had an effect on TP and chl $a$ estimates at a given location in the lake, and 2) whether there were inherent differences in the TP and chl $a$ data produced by each lab due to different analytical procedures. Knowing if differences in methodologies can cause differences in these particular parameters will allow the agencies to either statistically standardize their data or change their methods to reduce the differences when studying trends in Lake Erie. For many years, agencies have
been collecting data in western Lake Erie and have never been able to combine their data to compare and analyze the basin as a whole. This will also allow researchers to combine their data and look for trends in the entire basin over time, which can lead to better understanding of the dynamics of the western basin.

3.3. Methods

3.3.1. Sampling Method Comparison

Several institutions routinely collect water samples in western Lake Erie, but do so using differing methods. We compared four of these water collections methods in side-by-side fashion (Figure A-1). (1) The full water column method utilizes a tube sampler constructed of clear, flexible polycarbonate tubing (1 inch internal diameter) with a 5 pound weight attached at one end in order to collect a vertically integrated water column sample from the surface to near-bottom (or up to 8 m maximum depth). The sampler is lowered slowly into the water to the desired depth and the surface end is plugged with a rubber cork. The sampler is then quickly lifted, and water drains from the weighted-end into a rinsed bucket as the cork is removed. This method is used routinely by UT and SL. Because the water column method has the greatest chance to capture a stratified algal bloom (i.e. surface scum or deep chlorophyll maximum), all other sample methods were collectively termed “comparison methods” for our study. 2) The 2-meter integrated method utilizes a 2-meter long tube sampler constructed of ridged polyvinylchloride, and the sampler is deployed to collect an integrated surface to 2 meter water sample. This method is used by a volunteer sampling network on Lake Erie. 3) The
Twice-the-Secchi disk-depth (2xSD) method is used to collect water representing the photic zone and utilizes an integrated tube sampler lowered to a depth twice that of the Secchi disk. Depending on the Secchi disk depth, either the long, flexible or short, ridged sampler can be used to collect the 2xSD sample. This method is used by the Ohio Department of Natural Resources. 4) The Discrete Depth sampling method utilizes a Van Dorn sampler to collect and pool water from three discrete depths (1 meter below the surface, 1 meter above the lake bottom or thermocline, mid-depth between the first two samples). This method is used by OEPA.

During summer and fall of 2013 and 2014 (15 July 2013 and 1 October 2014) we sampled 23 sample locations in Lake Erie with a range of eutrophic conditions in nearshore zones (Maumee Bay and Sandusky Bay) to offshore oligotrophic conditions (center of the central basin) (Figure A-2- sampling method map), and most sites were sampled on multiple dates. A total of 82 water column samples with comparison method samples were collected.

At every sample location GPS coordinates, site depth, Secchi disk depth, and a profile of water temperature were recorded. Water temperature profile was recorded at 0.5-meter intervals with a water quality sonde (YSI 6600v2) to determine if a thermocline was present. All sample bottles were rinsed with surface water and all water sampling equipment was deployed to the appropriate depth. The water column sample was collected first (to a depth of 1 meter above the lake bottom, or thermocline if present, or down to 8 meters if water column was deeper than 9 meters) and water deposited into a 18.9-L rinsed bucket, and then water intended for chl a analysis was poured into a 2-L
dark polyethylene bottle and water for TP was poured into a 250-mL polyethylene bottle. Next, the comparison method samples collected to the appropriate depths were handled in the same manner as the water column sample. In a few cases, two sampling methods were duplicated. For example, if the Secchi depth was 1 m, then the 2xSD and the 2-m sample methods were identical. In these cases, only one sample was collected and analyzed representing both methods. All bottles were stored on ice during transportation back to the laboratory for processing. Between 1 hour and 6 hours passed between sample collection and processing.

Upon returning to the laboratory the 250-mL bottles for TP analysis were placed in a -20°C freezer until analysis. Water from the 2-L bottle was filtered onto GFF filters (47 mm diameter) for chl a analysis. Between 50 and 1000 mL of lake water was filtered and then stored at -80°C until analysis. All TP and chl a samples collected during the side-by-side were analyzed at Stone Laboratory using methods described below.

Total P concentration was quantified following an acid-persulfate digestion and quantification via the molybdate-ascorbic acid method (EPA method 365.4) on a SEAL Analytical QuAAtro nutrient analyzer. Chlorophyll a concentration was determined by placing the filtered sample into 10 mL of dimethyl sulfoxide (DMSO), heating to 70°C for 45 minutes, centrifuging at 21,000 g, and absorbance measured at 665.1nm and 649.1nm on a Shimadzu-1240 spectrophotometer and chl a concentration calculated as:

\[ \text{Chl} \ a = \frac{[12.47 \times \text{ABS}_{665.1} - 3.62 \times \text{ABS}_{649.1}]}{\text{Vol}_{\text{DMSO}} \times \text{Vol}_{\text{Lake Water}}} \]
Where chl \(a\) is the chlorophyll \(a\) concentration in \(\mu\)g/L, ABS is absorbance measured at 665.1 nm and 649.1 nm, Vol\(_{DMSO}\) is the volume of DMSO used in mL and Vol\(_{Lake\ Water}\) is the volume of lake water filtered in L (Chaffin et al., 2012; Wellburn, 1994). During 2013 one bottle replicate was used, whereas in 2014 two bottle replicates (i.e. 2 separate filters for chl and 2 separate digestions for TP) were analyzed and averaged.

During 2014, a subset of water column samples (\(n = 30\)) were analyzed using the DMSO method and the more traditional acetone method (EPA method 446.0). Four filters from the 2-L bottle were collected, frozen, and then two filters analyzed by DMSO and the other two by acetone. Briefly, filters were placed in 10 mL of 90% acetone and sonicated for 20 seconds, incubated for 3 hours at 4°C, centrifuged at 4000 rpm, and absorbance measured at 750nm, 664nm, 647 nm, and 630nm. Chlorophyll \(a\) concentration calculated as:

\[
\text{Chl } a = \frac{(11.85\times \text{ABS}_{750-664} - 1.54\times \text{ABS}_{750-647} - 0.08\times \text{ABS}_{750-630})}{\text{Vol}_{Acetone} \times \text{Vol}_{Lake\ Water}}
\]

Where chl \(a\) is the chlorophyll \(a\) concentration in \(\mu\)g/L, ABS is absorbance measured at at 750nm, 664nm, 647 nm, and 630nm, Vol\(_{Acetone}\) is the volume of acetone used in mL and Vol\(_{Lake\ Water}\) is the volume of lake water filtered in L.

### 3.3.2. Analytical Method Comparison

To determine if different analytical methods could result in differences in the data, we performed a round-robin study in which identical samples were sent to each of the participating laboratories for analysis. In order to include a wide range of chlorophyll \(a\) and TP concentrations we sampled 15 locations between the Maumee River mouth
(typically high in chl a and TP concentration) and the center of the western basin (Fig. 2). Sampling was conducted twice, once before the annual Microcystis spp. bloom (25 July 2014) and once during the bloom (7 August 2014). At each site, GPS coordinates, Secchi depth, and enough raw lake water (~20 liters) were collected using a 2-meter integrated tube sampler to provide institutions with an adequate sample. Lake water from the sampler was dispensed into a 20-L bucket and then poured into 21 250-mL bottles for TP analysis and 15 1-L bottles for chlorophyll a analysis. Triplicate samples were collected for TP analysis at three sites. All samples were held on ice during transportation back to the laboratory. In the laboratory, sample water was filtered (50 to 100 mL per filter; 25mm GF/F) in duplicate for chlorophyll a analysis. Total phosphorus samples were stored at -20ºC and filtered chlorophyll a samples were stored at -80ºC on silica gel until they could be shipped and processed.

For TP, all laboratories utilized a variation of the same method, which involved a digestion step with persulfate followed by quantification by colorimetry (Table A.1). For chl a, several different organic solvents, extraction methods, and quantification methods were used (Table A.2).

3.3.3. Data Analysis

Once all samples were analyzed, linear regressions were used to compare the data from the four sampling methods as well as compare all chlorophyll a and TP concentrations reported by the participating laboratories. Each institution was compared against the other institutions. The slope of each comparison was used to determine the overall difference between the reported concentrations and the r-squared values were
used to determine the variability in the reported concentrations. The two sampling dates were compared separately due to higher variability at higher TP and chl \(a\) concentrations.

3.4. Results

3.4.1. Sampling Method Comparison

In the sampling method comparison, concentrations of TP ranged from 3.47 to 182.96 µg P/L, whereas chl \(a\) concentration ranged from 1.5 to 127.8 µg/L, indicating that a wide range of trophic conditions were sampled. The linear regressions between the sampling methods were highly correlated and resulted in \(R^2\) values exceeding 0.90 and slopes of nearly 1.00 (Figures A-3 & A-4).

3.4.2. Analytical Method Comparison

For chlorophyll \(a\), the slopes from each comparison were between 0.98 and 1.23 except for the comparisons to concentrations reported by the USGS (Tables A.3 & A.4). The USGS consistently reported chlorophyll \(a\) values about 2x lower (1.91-2.04) than all other agencies for both sampling dates (Figure A-4). The r-squared values for these institutions were 0.81-0.99 for the samples taken prior to the bloom but the University of Toledo was the outlier on the second sampling date. The r-squared values for the Toledo comparisons on August 7 were between 0.46 and 0.58. All the other r-squared values ranged from 0.88 to 0.99 (Table A.5 and A.6). This suggests that Toledo’s analytical procedure is not accurate at high concentrations (Figure A-4).

For TP, there were no significant differences in the concentrations reported by the National Center for Water Quality Research, Stone Lab, or NOAA (Tables A-7 through A-10). Water samples for TP analysis were sent to the Ohio EPA, however the OEPA processed the samples as if the samples were acidified upon collection as called for in
OEPA protocols. The differing pH between their standards and our samples resulted in invalid results, and the Ohio EPA TP data was not considered in our data analysis.

We also calculated the standard error of reported concentrations between the duplicate filter measurements for chl $a$ and between and within the triplicate bottles for TP. Most agencies had a small standard error at low chl $a$ concentrations and as the concentration increased, so did the standard error (Figure A-5). Higher concentrations were reported the closer the site was to the mouth of the Maumee River. The standard error between the triplicate samples followed the same pattern. As the TP concentrations increased, so did the standard error (Figure A-6). The NCWQR and OSU SL also tested each triplicate three times. We calculated the standard error for each bottle and found that OSU SL consistently had a relatively high SE compared to the NCWQR, which had a very small SE (Figure A-7).

3.5. Discussion

The results suggest that collecting sample water at different depths, as is customary by the different monitoring organizations, had no discernable effect on TP and chl $a$ measurements from Lake Erie. It should be noted that the summer of the study was characterized by windy conditions and a well-mixed water column. Even during the HAB sampling period, dense surface scums of *Microcystis* spp. which would have been expected to cause a low chl $a$ bias, were rare. Therefore, although in most cases we would expect collection method to have little effect, additional studies should be conducted during dense surface bloom conditions. Likewise, windy and well-mixed conditions also likely caused an even distribution of suspended sediment as well as algae in the water column, resulting in a homogeneous vertical distribution of TP.
Researchers or agencies monitoring water quality may consider many factors when deciding on which method to use to collect water samples. Sampling methods may be chosen based on historical continuity within the organization, familiarity, or with the goal of generating data that is compatible with another data set. Financial resources, time and equipment limitations may also factor into the choice of sampling method. Because western Lake Erie is usually well-mixed, our results suggest that monitoring organizations need not be overly concerned about their different sampling protocols resulting in disparate measurements.

The results of our round-robin study suggest that, with a few exceptions, TP and chl \(a\) analyses performed by the various monitoring organizations are highly compatible. For chl \(a\) the various combinations of solvents and extraction technique produced similar results except for the combination of acetone and no filter grinding. Although DMF and DMSO are very similar in extraction efficiency (Chaffin, 2009), acetone is not as effective at extracting chl \(a\) when chl \(a\) concentrations are high. The lower extraction efficiency of acetone may be compensated by grinding the filter, as was performed by OSU AEL. The use of acetone without grinding however, is likely to result in under-extraction of chl \(a\) and is probably the reason for the consistently low chl \(a\) values reported by USGS. It is difficult to explain the high variability of the UT chl \(a\) results from the sampling date. One possibility was UT’s use of a fluorometer equipped with optical filters that had exceeded the recommended replacement date.

TP concentrations reported by the participating laboratories were in close agreement across both sampling dates and a range of concentrations from highly productive Maumee Bay to the open waters of the western basin. TP results returned by
by OEPA were consistently lower than the other labs, but we attributed this to a variance in OEPA’s standard procedure. OEPA alone acidifies samples in the field as a method of sample preservation and then adjusts analytical standards accordingly. The samples that were delivered to OEPA were not acidified, which may have affected their results.

The smaller differences in the data might not have necessarily been due to differences in methodologies. Average reported concentrations were often close between institutions, but a few of institutions had higher variation in their reported data. In future studies, factoring in the standard error between the concentrations reported by the agencies would be helpful in determining how to minimize these differences. Preservation methods should also be compared. Differences in preservation methods between the participating laboratories caused us to lose data because we did not account for that. Important factors that need to be studied are the duration of time that the samples are stored before they are analyzed, how the samples are stored and if there are any solvents or acids added to the sample. Once we know how different sampling, preservation, and analytical methods can affect TP and chl a concentrations, we can come up with a way to bring all of the data sets together without making any major changes to the way institutions collect their data. It would also be beneficial to look at historical data and see if the same differences can be seen in long-term data sets. If we were able to combine data sets without altering methodologies, agency specific long-term data sets could be combined into one large, long-term data set, which could make studying historical trends easier.

Another future study that we suggest is using these same ideals and comparing the different sampling and analytical methodologies that are used to monitor microcystin
concentrations. We did not address microcystin in this study because of the high cost of 
testing for the toxin. We chose TP and chl $a$ for this study because most agencies already 
have monitoring programs that use TP and chl $a$ data to monitor algal biomass and algal 
growth potential which, along with microcystin toxin testing, is very important for 
monitoring the health of Lake Erie.

In conclusion, we found that TP and chla data are generally comparable among 
methods if performed correctly and functioning equipment is used. We suggest that 
monitoring agencies either all decide on one method going forward (unlikely) or all 
participate in a similar method comparison study to insure comparable data. We also 
suggest those using other analytical methods not tested here, test their methods against a 
method used here.
3.6. References


3.7. Tables

3.1. Total Phosphorus analytical procedures by research institution. Each institution was given 1 sample per site except for the triplicates collected at 3 sites. The NCWQR tested each bottle 3 times and OSU-SL tested each bottle twice.

<table>
<thead>
<tr>
<th>Institutions</th>
<th>Equipment used</th>
<th>Preservation</th>
<th>Methods</th>
<th>Replicates Per Bottle</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCWQR</td>
<td>Autoanalyzer</td>
<td>Frozen Not Acidified (for this study)</td>
<td>Variation of Lachat Method 10-115-01-1-F</td>
<td>3</td>
</tr>
<tr>
<td>OEPA</td>
<td>Autoanalyzer</td>
<td>Refrigerated Acidified</td>
<td>Lachat Method 10-115-01-1-F</td>
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<tr>
<td>NOAA</td>
<td>Autoanalyzer</td>
<td>Analyzed Immediately</td>
<td>Variation of Lachat Method 10-115-01-1-F</td>
<td>1</td>
</tr>
<tr>
<td>OSU-SL</td>
<td>Autoanalyzer</td>
<td>Frozen Not Acidified</td>
<td>Variation of Lachat Method 10-115-01-1-F</td>
<td>2</td>
</tr>
</tbody>
</table>
3.2. Chlorophyll $a$ analytical procedures by research institution. Two filters per site were given to each institution. The OEPA chose to only analyze one of the filters.

<table>
<thead>
<tr>
<th>Institutions</th>
<th>Equipment used</th>
<th>Solvent</th>
<th>Methods</th>
<th>Number of Filters Analyzed</th>
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<td>Fluorometer</td>
<td>DMF No Acidification</td>
<td>Whole Filters</td>
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</tr>
<tr>
<td>Toledo</td>
<td>Fluorometer</td>
<td>DMF Acidification</td>
<td>Whole Filters</td>
<td>2</td>
</tr>
<tr>
<td>OEPA</td>
<td>Fluorometer</td>
<td>Acetone Acidification</td>
<td>Grind Filters</td>
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<tr>
<td>USGS</td>
<td>Fluorometer</td>
<td>Acetone No Acidification</td>
<td>Whole Filters</td>
<td>2</td>
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<tr>
<td>OSU- AL</td>
<td>Spectrophotometer</td>
<td>Acetone Acidification</td>
<td>Grind Filters</td>
<td>2</td>
</tr>
<tr>
<td>OSU- SL</td>
<td>Spectrophotometer</td>
<td>DMSO No Acidification</td>
<td>Whole Filters</td>
<td>2</td>
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</tbody>
</table>
3.3. Slope Correlation Matrix for pre-bloom (July 25) Chlorophyll $a$ analyses. **Bold** numbers represent significant differences in slopes between research institutions.

<table>
<thead>
<tr>
<th></th>
<th>Toledo</th>
<th>USGS</th>
<th>NOAA</th>
<th>OEPA</th>
<th>OSU-AEL</th>
<th>OSU-SL</th>
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3.4. Slope Correlation Matrix for mid-bloom (August 7) Chlorophyll $a$ analyses. **Bold** numbers represent significant differences in slopes between research institutions.

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3.5. R-squared Correlation Matrix for pre-bloom (July 25) Chlorophyll $a$ analyses.

<table>
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<th>OEPA</th>
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<th>OSU-SL</th>
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3.6. R-squared Correlation Matrix for mid-bloom (August 7) Chlorophyll $a$ analyses.

**Bold** numbers represent significant differences in slopes between research institutions.

<table>
<thead>
<tr>
<th></th>
<th>Toledo</th>
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</table>
3.7. Slope Correlation Matrix for pre-bloom (July 25) Total Phosphorus analyses. No significant differences between laboratories were found. OEPA data was not included in these analyses due to unusable data.

<table>
<thead>
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<th>NCWQR</th>
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3.8. Slope Correlation Matrix for mid-bloom (August 7) Total Phosphorus analyses. No significant differences between laboratories were found. OEPA data was not included in these analyses due to unusable data.

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3.9. R-squared Correlation Matrix for pre-bloom (July 25) Total Phosphorus analyses. No significant differences between laboratories were found. OEPA data was not included in these analyses due to unusable data.

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3.10. R-squared Correlation Matrix for mid-bloom (August 7) Total Phosphorus analyses.

No significant differences between laboratories were found. OEPA data was not included in these analyses due to unusable data.

<table>
<thead>
<tr>
<th></th>
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</tr>
</tbody>
</table>
3.8. Figures

3-1. Sampling methods commonly used in Western Lake Erie that were used in the side-by-side method comparison study. The red areas indicate water sampled.
3-2. Sample site locations for the side-by-side methods comparison and the round robin study. Side-by-side method comparison sites are shown as a filled circle and analytical method comparison is shown as a circle with an X. Four sites were sampled for both studies.
3-3. Total Phosphorus (A) and Chlorophyll $a$ (B) concentrations measured in the side-by-side method comparison. The x-axis data are from the whole water column and the y-axis data are the three comparison methods. The black line is the 1-to-1 line. R-squared > 0.97.
3-4. Average reported chlorophyll $a$ concentrations from each agency. Outliers were USGS (open circle) on both dates and Toledo (filled circle) on 8/7/2014.
3-5. Reported chl a concentrations with standard error bars. Higher concentrations and higher SE were calculated for sites closer to the mouth of the Maumee River.
3-6. Reported TP concentrations between triplicate samples with standard error bars. Higher concentrations and higher SE were calculated for sites closer to the mouth of the Maumee River. OSU SL consistently had a relatively high SE compared to the other agencies. OEPA results were omitted from this study due to preservation and analytical method discrepancies.
3-7. Reported TP concentrations within triplicate samples standard error bars. Higher concentrations and higher SE were calculated for sites closer to the mouth of the Maumee River. OSU SL consistently had a relatively high SE compared to the NCWQR.
References


Bartish, T. M. 1984. Thermal stratification in the western basin of Lake Erie: its characteristics, mechanisms of formation, and chemical and biological consequences. The Ohio State University.


