A Thesis

entitled

Effect of Temperature on Phosphorus Release from Anoxic Western Lake Erie Sediments

by

Kenneth J. Gibbons

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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The Laurentian Great Lakes contain approximately 2% of the world's freshwater and provide drinking water for more than 30 million people. Lake Erie is the shallowest and smallest of the Great Lakes. The western basin is the shallowest portion of Lake Erie and receives a majority of its water from the Maumee River and Detroit River. The Maumee River Watershed is the largest watershed in the Great Lakes and land use in the watershed dominated by urban and agricultural areas. Farm field run-off and combined sewer overflows from urban and agricultural areas contribute high concentrations of nutrients to the Maumee River. The high nutrient water flowing out of the Maumee River into the Western Basin of Lake Erie creates a good environment for Harmful Algal Blooms (HABs), which are primarily composed of *Microcystis,* to rapidly grow. HABs are a serious issue for Lake Erie because *Microcystis* produces a toxin that is harmful to humans. Research focused on decreasing HABs has identified phosphorus as the limiting nutrient.

Phosphorus enters the lake through either external (phosphorus entering from outside the lake i.e. farm field run-off or inputs from tributaries) or internal loading (release of phosphorus from lake sediments). For Western Lake Erie, there are numerous studies on external loading of phosphorus, however there is considerably less research on internal phosphorus loading. Estimating internal loading of phosphorus is important because phosphorus concentrations in lake sediments can be orders of magnitude higher than phosphorus concentrations in lake water and can be a significant source of phosphorus. Phosphorus release rates from lake sediments can be affected by a variety of environmental factors such as pH, temperature, and dissolved oxygen concentration. If lake sediments become warmer and more hypoxic in response to climate change, the contribution of phosphorus from lake sediments may increase.

The research conducted in this thesis investigates the effect of temperature on the release of phosphorus from anoxic lake sediments. This study aims to estimate phosphorus release rates for a range of temperatures under anoxic conditions for Western Lake Erie and to improve estimates of internal phosphorus loading. Sediment cores collected during the summer of 2014 and 2015 were incubated at 10°C, 20°C, 22°C, 27°C, and 30°C under anoxic conditions. Results from the sediment core incubations indicate that temperature, location, and duration of anoxia are significant influences on phosphorus release. Extrapolating the phosphorus release rates for the entire western basin, four days of anoxia at 30°C for the entire basin could result in the release of ~240 metric tons of phosphorus.

This thesis is dedicated to my parents, James and Esther Gibbons, who have encouraged me to follow my interests in the environment.

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Table of Contents

List of Figures

Chapter 1

Overview of Thesis and Review of Internal Loading

1.1 Goal of Thesis

Lake Erie is experiencing an increase in harmful algal blooms, which are thought to be the result of phosphorus loading into the lake. Internal loading of phosphorus from lake sediments may be a substantial contribution of phosphorus and may be influenced by temperature and dissolved oxygen concentration. The goal of this thesis is to improve our understanding of the estimated contribution of phosphorus from internal loading by determining the effects of anoxia and temperature on internal loading in the Western Basin of Lake Erie. Previous research suggests that lake sediments release phosphorus under anoxic conditions, which are known to occur intermittently in the Western Basin of Lake Erie (Bridgeman et al. 2006). Phosphorus release rates from sediments are dictated by chemical reaction rates and biological activity, which are both affected by temperature. Water temperature in the western basin can vary throughout a year depending on the season and potentially over the course of decades due to climate change. Research on climate change suggests that the Great Lakes region could experience longer summers and as much as a 5 °C temperature increase by the end of the century (Hayhoe et al. 2010). Increased temperatures may cause increased rates of internal phosphorus loading under anoxic conditions. Understanding the potential contribution of phosphorous from the sediments is important for predicting HAB size. Currently, springtime loading of phosphorus from the Maumee River is used to predict HABs. Adding the estimated contribution from internal loading could increase accuracy of the predictions, and help to determine a target reduction of external loading needed to decrease HAB size.

1.2 History of Lake Erie

The Great Lakes are the world's largest source of freshwater and contain one-fifth of the world's freshwater. Lake Erie, the smallest of the Great Lakes, contains about 2% of the water in the Great Lakes and provides drinking water for over 11 million people. As population has increased and land has been converted from forest and wetlands to urban areas and agricultural fields, nutrient loading and pollution into the lake has also increased (Burns 1985). As a result of the increased nutrient loading, Harmful Algal Blooms (HABs) and reduced hypolimnetic oxygen levels became an annual occurrence during the 1950s-60s. In response to the declining health of Lake Erie, the Great Lakes Water Quality Agreement (GLWQA) was introduced in 1972, which focused efforts to clean up the Great Lakes. During the 1980s and 1990s, water quality in Lake Erie started to rebound, however beginning in the mid-1990s dissolved reactive phosphorus (DRP) loading increased resulting in significant harmful algal blooms (HABs) starting to occur annually in the early 2000s. In this section, I will discuss the pertinent history of Lake Erie as it relates to changes in water quality.

In the 1820s, when European settlers began populating the Lake Erie watershed the Great Black Swamp covered nearly 1,500 square miles of the Maumee River watershed and the southern shoreline of the lake was bordered by vast marshes (Verduin 1969). As human populations increased, the landscape was developed and modified. Clearing swamps resulted in lost ecosystem services such as filtering surface runoff, which led to increased amounts of sediment and pollutants entering the lake (Verduin 1969). Swamps were replaced with agricultural fields, which increased soil loss and nutrient input into the lakes. During the 1960s, Lake Erie started experiencing excessive algal growth and massive fish kills that fouled the shorelines of Lake Erie with dead fish (Matisoff and Ciborowski 2005). In the late 1960s and early 1970s, public concern and outcry regarding the poor conditions of Lake Erie was at an all time high. In response in 1972, the United States and Canada signed the Great Lakes Water Quality Agreement, which set a bi-national phosphorus-loading limit for Lake Erie of 11,000 metric tons annually (MTA).

Limiting phosphorus loading into the lake was thought to be the best means of controlling eutrophication (Schelske and Stoermer 1971, Schindler et al. 1973, Vollenweider 1976, Charlton 1980, Di Toro and Connolly 1980). External loading of total phosphorus into Lake Erie declined from 25,000 MTA in the 1960s to the current levels between 8,000 and 12,000 MTA phosphorus, which was accomplished in part by placing limits on point sources such as municipal sewage treatment plants (Dolan and McGuangle 2005). Decreased total phosphorus loading coincided with a decrease in phytoplankton biomass and frequency of HABs (Makarewicz 1993). However, since the mid-1990s Lake Erie has experienced a decrease in water quality (Matisoff and Ciborowski 2005, Kane et al. 2014). Although total phosphorus loadings have remained at or below the target loading of 11,000 MTA, the extent and frequency of harmful algal blooms has increased (Michalak et al. 2013).

1.3 Harmful Algal Bloom (HABS)

As a result of total phosphorus reductions to the lake total phytoplankton biomass declined from 1970 to 1987 (Makarewicz 1993). However, beginning in the mid-1990s phytoplankton biomass started to increase in the Western Basin of Lake Erie despite relatively consistent total phosphorus loading (Conroy et al. 2005, Kane et al. 2014). In 2003, the western basin began experiencing large summer time algal blooms that consisted mostly of the cyanobacteria *Microcystis spp*, which are of concern largely because of their production of hepatotoxic microcystins. Concentrations of microcystin in the western basin have been found to exceed the USEPA guidelines for safe drinking water 1.6-µg/L for adults and 0.3-µg/L for children for a 10-day exposure (Rinta-Kanto et al. 2005, Wilson et al. 2008). Microcystin concentrations in the water increase treatment costs for municipalities who depend on the lake as their primary source of drinking water (Lewitus et al. 2012, Raymond 2012). Since the reoccurrence of large harmful algal blooms (HABs) in the Western Basin of Lake Erie started, more research has focused on determining the drivers of the HABs.

Increases in incidence and intensity of HABs, abundance of benthic algae, extent of central basin hypoxic zone, and an increased number of beach closings suggest that Lake Erie has been entering a period of re-eutrophication starting in the mid-1990s (Burns et al. 2005, Conroy et al. 2005, Higgins et al. 2005, Bridgeman and Penamon 2010, Michalak et al. 2013). The increasing eutrophic status of the lake despite relatively stable total phosphorus loading has challenged our understanding of nutrient loading and algal growth in Lake Erie. Original management strategies that lead to a reduction in phytoplankton biomass focused on reducing total phosphorus, however in-lake concentrations of dissolved reactive phosphorus and overall phytoplankton biomass has increased while total phosphorus loading has stayed relatively constant (Conroy et al. 2005). Increased DRP concentrations in the lake may be the result of increased contribution of DRP from the Maumee River (Joosse and Baker 2011). Updating the understanding of phosphorus cycling in Western Lake Erie by creating a phosphorus budget is important in order to create new management strategies and set expectations for recovery.

1.4 Sources of Phosphorus Loading into Lake Erie

1.4.1 Forms of Phosphorus

Phosphorus is of interest in freshwater systems because of its major role in biological metabolism. In comparison to other naturally supplied nutritional and structural components (carbon, nitrogen, and sulfur), phosphorus is least abundant and most commonly limits biological productivity in freshwater systems (Wetzel 2001). Phosphorus is found in varying states and depending on the state and environmental conditions, it can be bio-available P (BAP) or unavailable. Bioavailability refers to phosphorus in a form that plants and algae can readily uptake (Reynolds et al. 2006).

In freshwater, there are three main categories of phosphorus: dissolved phosphorus, particulate phosphorus, and total phosphorus. Dissolved phosphorus is defined as the fraction of phosphorus that can pass through a 0.45-micron filter, while particulate phosphorus is the fraction of phosphorus attached to particles or in organisms (Jarvie et al. 2002). Total phosphorus is the sum of particulate and dissolved phosphorus. In practice, concentrations for total phosphorus and dissolved phosphorus are measured and particulate phosphorus is calculated. Typically, dissolved phosphorus is considered to be the most bio-available form (Reynolds et al. 2006) and total phosphorus is used to measure phosphorus loading.

In lake sediments, there are multiple forms of phosphorus and typically the different fractions of phosphorus are operationally defined. Different fractions of phosphorus can become detached and released into the overlying water. Understanding phosphorus cycling in sediments is important because the phosphorus concentration in the sediments is typically orders of magnitude higher than in surface waters (Wetzel 2001, Sondergaard et al. 2001). The majority of the phosphorus in the sediment is bound to alkali metals, alkaline earth, and transition elements (Reynolds and Davies 2001). Redox sensitive elements, most notably iron and manganese, are of most importance because of their ability to both sequester and release phosphorus depending on the oxygen concentration in the overlying water. Organic phosphorus is another important form readily found in the sediments, and although it constitutes a smaller fraction of total phosphorus than in-organic phosphorus, however organic phosphorus is considered to be more labile than in-organic phosphorus (Tessnow 1972, Prairie et al. 2002).

1.4.2 External Loading of Phosphorus

External loading of phosphorus comes from sources outside the lake, such as tributaries, farm field run-off, and sewage treatment plants (Wetzel 2001). Phosphorus abatement programs implemented in the 1970s by the GLWQA targeted point sources (i.e. sewage treatment plants, industrial waste), but did not place any regulations on non-point sources (i.e. agricultural fields) (De Pinto et al. 1986). In the Western Basin of Lake Erie, the largest source of external loading is the Maumee River (Baker and Richards 2002). Agriculture is the main form of land use in the Maumee River watershed, covering 85% of the watershed (Nelson and Weschler 1998). Phosphorus loss from land increases as the amount of agricultural land in a watershed increases (Hobbie and Likens 1973, Omernik 1977, Harper 1992).

Previous research suggests that the HAB biomass and springtime total phosphorus loading from the Maumee River are highly correlated (Stumpf et al. 2012, Michalak et al. 2013, Wynne et al. 2013, Lunetta et al. 2014). However, there is considerable uncertainty in estimating bloom size due to other factors that influence bloom size, such as internal loading of phosphorus, underestimation of some phosphorus inputs, ecosystem changes that have led to altered nutrient balances in the lake, and climate induced changes that affect water temperatures (Ohio EPA 2010). In order to more accurately predict future bloom sizes, it is important to create a phosphorus budget for Western Lake Erie that accounts for sources of phosphorus outside the lake (external loading) and phosphorus released from lake sediments (internal loading). Understanding the magnitude of internal loading of phosphorus could help increase the accuracy of bloom estimations.

1.4.3 Internal Loading of Phosphorus

Internal loading of phosphorus is defined as phosphorus that is released from lake sediments into the overlying water (Dodson 2004). In lake sediments, phosphorus is bound in variety of forms and depending on the lake conditions (e.g. pH, dissolved oxygen concentration) some phosphorus may be liberated from the sediments into the water column (Holdren and Armstrong 1980, Brady and Weil 1996). Typically, phosphorus concentrations in sediments are substantially higher than concentrations in the lake water, and in some cases lake sediments are a substantial source of phosphorus when compared to external sources. For lakes Tabor, Charlie, Nulki, and Tachick, located in British Columbia, summertime chlorophyll a concentrations were predicted using external loading of phosphorus. The addition of estimated internal phosphorus loading and temperature data increased the accuracy of chlorophyll a predictions (French and Petticrew 2006). Internal loading of phosphorus can also delay improvements in water quality by contributing phosphorus after external loads of phosphorus have been reduced (Søndergaard et al. 2003).

Early research on internal loading by Mortimer linked phosphorus release to low oxygen conditions. Mortimer suggested that when the dissolved oxygen concentration in overlying water is above 2 mg/L, ferric iron in the sediment is bound to phosphorus. However, during periods when dissolved oxygen drops below 2 mg/L dissolved oxygen, ferric iron is reduced to ferrous iron and the attached phosphorus is released (Mortimer 1942). In lake sediments, oxic conditions are usually only found in the first few millimeters of the sediments (Bostrom et al. 1988). The oxic conditions at the sediment water interface (SWI) create a barrier where phosphorus is bound to iron (Jensen and Andersen 1992, Katsev et al. 2006). The oxic barrier can be deteriorated through a variety of mechanisms (e.g. re-suspension and decomposition), and the dominant mechanism is dependent on lake properties and conditions (Gachter 1987, Søndergaard et al. 2003).

Phosphorus bound to iron only constitutes one fraction of P in the sediment (Moore et al. 1992, Brunberg 1995). Another pool of phosphorus is organic bound P found in bacteria and detritus (Nedwell 1984). In eutrophic lakes, organic P can settle to the bottom as algal detritus (Pettersson 1998, Kleeburg 2002, Eckert et al. 2003, Hupfer and Lewandowski 2005). Tessnow (1972) simulated sedimentation of diatoms and found that 70% of the P incorporated into diatoms was released within the following three weeks. Microbes can decompose organic matter accumulating on the bottom, which liberates some organic phosphorus into the overlying water (Hupfer et al. 2007). During decomposition, microbes are also consuming oxygen, which can cause the oxic barrier to deteriorate (Reitzel et al. 2007). When oxygen at the sediment water interface is depleted, anaerobic bacteria can continue to decompose organic matter. Instead of reducing oxygen like aerobic bacteria, anaerobic bacteria reduce other ions, such as iron, during decomposition. After iron is reduced, it releases any bound phosphorous into the overlying water (Frevert 1980, Jensen and Andersen 1992).

Temperature is an important factor that can affect microbial activity, which results in changes in phosphorus release rates. As temperature increases, microbial activity in lake sediments increases resulting in higher sediment oxygen demand, lowering of redox potential, and reduction of oxic barrier (Lovley and Phillips 1986, Hunting and Kampfraath 2013, Small et al. 2013). Increased temperature can also cause an increase in diffusion rates and chemical reaction rates and thereby increase the flux of phosphorus from the sediments to the water column (Jiang et al. 2008, Anthony and Lewis 2012).

Temperature has been shown to increase phosphorus release rates during sediment core incubations (James and Barko 2004), however Jensen and Andersen (1992) found that the effect of temperature on phosphorus release from lake sediments is not consistent between lakes and therefore it is important to investigate temperature effects on the lake of interest.

1.5 Overview of Subsequent Chapters

Chapter 2: Effect of Temperature on Phosphorus Release from Anoixc Western Lake Erie Sediments

Research suggests that climate change may extend growing seasons and increase summertime temperatures in the Great Lakes region. Increased lake temperatures may led to increased internal loading rates of phosphorus and therefore exacerbate harmful algal blooms (HABs). This chapter presents evidence suggesting that increased lake temperatures may increase internal loading rates of phosphorus under anoxic conditions.

In this chapter, sediment core incubations were used to measure phosphorus release rates from anoxic sediments collected from four locations in the Western Basin of Lake Erie. Sediment core incubations have been used in numerous experiments to estimate phosphorus release. Sediment cores are advantageous over bottom flux chambers or mass balance experiments because of their ease of collection and ability to manipulate environmental conditions. In this experiment, sediment cores collected from the Western Basin of Lake Erie were incubated under anoxic conditions at 5 different temperatures.

Chapter 3: Use of Micro-electrodes to Determine Phosphorus Flux from Sediments.

After the onset of anoxic conditions, phosphorus release rates from sediment cores can be affected by the oxidation-reduction potential (ORP) at the sediment water interface. ORP has been used to determine potential reactions occurring in sediments and suggest mechanisms for phosphorus release under anoxic conditions. In this chapter, we employ the use of platinum microelectrodes to measure ORP profiles in sediment cores collected from Western Lake Erie and investigate the relationship between ORP and phosphorus release from anoxic sediment cores.

Chapter 2

Effect of Temperature on Phosphorus Release from Anoxic Western Lake Erie Sediments

2.1 Abstract

The Western Basin of Lake Erie experiences annual Harmful Algal Blooms (HABs), which degrade water quality and deter recreation. The size of annual HABs in Lake Erie is highly correlated with the external loading of phosphorus from a major tributary, the Maumee River, to the lake during the spring and summer months. Because HAB size is largely explained by external loading, the recycling of phosphorus from lake sediments (internal loading) is often ignored. However, if lake sediments become warmer and more hypoxic in response to climate change, the relative contribution of internal P loading from sediments may become greater. In this study, I examined the potential effect of temperature on internal loading of phosphorus under anoxic conditions. Sediment cores were collected during Summer 2014 and 2015 from 4 locations in the Western Basin of Lake Erie ranging from highly productive areas near Maumee Bay to less productive offshore areas. Cores were incubated for 4 days under anoxic conditions under different temperatures (2014: 10°C, 20°C, and 30°C. 2015: 22°C and 27°C) chosen to represent spring, summer, and potentially elevated summer temperatures. Phosphorus release rates varied greatly between temperature treatments and sites. Average

phosphorus release rates for cores incubated at 20°C and 30°C were 2 and 14 times higher respectively, than for cores incubated at 10°C. The site closest to the mouth of the Maumee River had the highest phosphorus release rate, 10 times higher than the furthest site, and highest total phosphorus concentration in the surface sediment, 2 times higher than the furthest site, suggesting a gradient of sediment P characteristics associated with the river plume in Lake Erie. Extrapolating these fluxes across the entire western basin suggests that during four days of anoxic conditions at 30°C, lake sediments could potentially contribute ~240 metric tons of dissolved phosphorus, which is equivalent to all of the springtime dissolved phosphorus loading from the Maumee River in 2013.

2.2 Introduction

Lake Erie is currently in a state of re-eutrophication as evident by the increase in frequency and size of HABs (Kane et al. 2014). Phosphorus concentrations in Lake Erie are a primary driver of HABs (Schindler et al. 1973). Research on phosphorus loading into Western Lake Erie primarily focuses on external sources (i.e. tributary loading, farm field run-off, and point sources) which are correlated with algal biomass (Stumpf et al. 2012, Lunetta et al. 2014). However, to predict the success of new management strategies and set expectations for lake recovery, phosphorus input by both external and internal loadings must be considered.

Internal loading of phosphorus is defined as phosphorus released from lake sediments. Typically, phosphorus bound to lake sediments is unavailable for use by phytoplankton. However, under certain conditions, such as increased temperature or low dissolved oxygen concentrations, phosphorus can be released from lake sediments into the water column and become available for phytoplankton (Sondergaard et al. 2003). According to a 1969 International Lake Erie Water Pollution Board report, 80% of phosphorus entering Lake Erie is retained in the sediment, therefore the sediment constitutes a substantial pool of phosphorus (International Lake Erie Water Pollution Board 1969). Mobilization of phosphorus from lake sediments into the water column happens through a variety of mechanisms. Different mechanisms of phosphorus release can be dominant depending on physical and chemical conditions in the lake.

For the Western Basin of Lake Erie, dissolved oxygen concentrations and temperature are two potentially important environmental conditions that can affect phosphorus release from sediments. The Western Basin of Lake Erie is relatively shallow compared to the rest of the Laurentian Great Lakes, which makes the western portion of the lake warmer and susceptible to mixing due to wind. Consistent mixing prevents the western basin from developing a season long thermocline, however, previous studies have shown evidence of intermittent stratification events that can result in anoxia (Carr et al. 1965, Bartish 1984, Bridgeman et al. 2006).

Anoxia is known to cause increased rates of phosphorus release from lake sediments (Mortimer 1942). Anoxic events cause changes in sedimentary chemistry, which can lead to increased phosphorus release from lake sediments. When the overlying water contains dissolved oxygen, the sediment water interface (SWI) is oxidized and creates a layer where phosphorus is bound to ions, such as iron or manganese. The oxidized boundary at the SWI only extends a few millimeters below the sediment surface. Below the oxidized SWI, oxygen is depleted causing iron and manganese bound phosphorus to be released into the pore water (Katsev et al. 2006). However, the phosphorus contained in the pore water cannot diffuse past the oxidized boundary. When oxygen at the SWI is depleted during an anoxic event, iron and manganese bound phosphorus is released and pore water containing high concentrations of phosphorus can diffuse into the overlying water (Mortimer 1971, Bostrom et al. 1988). Phosphorus release from iron and manganese can be facilitated by microbial decomposition of organic matter (Frevert 1980, Jensen and Andersen 1992).

Temperature has been shown to affect anoxic phosphorus release rates from lake sediments (James and Barko 2004). Elevated temperature is thought to increase phosphorus release rates by stimulating mineralization and thereby liberating organic-bound phosphorus into the pore water (Jensen and Andersen 1992). In addition, increased microbial activity lowers the redox potential at the surface sediment, which may induce the release of iron-bound phosphorus (Lovley and Phillips 1986, Hunting and Kampfraath 2013, Small et al. 2013). Increased temperature can also cause an increase in diffusion rates, which increases the flux of phosphorus from the sediments to the water column (Jiang et al. 2008, Anthony and Lewis 2012). Because temperature affects a multitude of factors that influence anoxic phosphorus release, the effect of temperature is not consistent between lakes (Jensen and Andersen 1992, Wu et al. 2013). Within a lake, differences in sediment composition may cause differences in phosphorus release (Jones and Simon 1981). Therefore, in order to estimate anoxic release of phosphorus for the Western Basin of Lake Erie it is important to consider a range of temperatures from a representative set of locations.

The research conducted in this paper is part of a collaborative study to estimate internal loading of phosphorus in the Western Basin of Lake Erie. The goal of this study is to estimate the internal loading of phosphorus under anoxic conditions and to investigate the potential effect of temperature on phosphorus release rates. The release rates calculated in this study will be combined with release rates calculated by different institutions and extrapolated to estimate internal phosphorus loading for the Western Basin of Lake Erie.

2.3 Methods

Study Site and Collection

Sediment cores were collected from four sites (7M, 4P, 91M, and C5) in the Western Basin of Lake Erie during the Summer of 2014 and two sites (7M and 4P) during the Summer of 2015 (Figure 1). The four sites spanned the Western Basin from North to South and represented varying depths and sediment types. Sediment cores from 91M (41° 50' 27.6"N, 82° 54' 58"W, water depth 11 meters) and C5 (41° 58' 1.2"N, 82° 46' 1"W, water depth 11.5 meters) were collected on July 22, 2014 aboard the R/V Lake Guardian by subsampling an Ekman 30 x 30 cm box corer. Sediment cores from 7M (41°44’05” N, 83°17’43”W, water depth 5 meters) collected on August 21, 2014 and August 10, 2015 and 4P (41°45’00” N, 83°06’14”W, water depth 9 meters) collected on September 6, 2014 and August 24, 2015 were collected aboard the University of Toledo’s Mayflier using a gravity corer (Aquatic Research Instruments). After collection, cores were stored in the dark at 4 °C. Prior to incubation, the overlying water was siphoned off the sediment and replaced with 500ml of Lake Erie water, which was collected from the same location as the sediment core, filtered through a 0.45 μm filter (Millipore GWSC 045).

Effect of Temperature

In order to pick incubation temperatures that would simulate bottom water temperatures in Lake Erie, I used water quality monitoring data collected from 2002-2012 by the Bridgeman Lab. Water temperature data from the Bridgeman Lab spanned the entire water column, however I was only interested in the water temperatures just above the sediment. I isolated the water temperature data collected just above the sediment surface from location 7M, one of the locations used for sampling sediment cores, using the PLYR package in R (R project software, version 3.1.1, 2014) and plotted all recorded bottom water temperatures (n=139) by month (Figure 2). Water temperatures directly above the sediment at location 7M from May-October ranged from 9-27°C with a mean temperature of 21°C. Therefore, I decided to set the incubations to 10°C, to represent an anoxic event in the spring, 20°C, to represent an anoxic event occurring during an average summer temperature, and 30°C, which would represent an anoxic event during an extremely warm summer event.

In 2014, three cores from each location were incubated for four days at either 10 °C, 20 °C, or 30 °C, for a total of nine cores incubated for each location. Temperature was maintained by incubation chambers (Percival E36HO) or warm water bath for the 30°C treatment. Nitrogen gas was slowly bubbled into each core throughout the duration of the incubation period to achieve anoxic conditions (dissolved oxygen= 0 mg/L). Water samples (15mL) were collected at 24 hour intervals from each sediment core and frozen for future analysis. After incubation, organic content of the top 1 cm of sediment was determined using Loss on Ignition (Schumacher et al. 2002). Water samples were analyzed for total reactive phosphorus using the Ascobic Acid Method (Eaton et al 2005). Total phosphorus of the top 1 cm of different sediment cores collected at the same locations were analyzed at the National Center for Water Quality Research (NCWQR).

In 2015, sediment cores collected from sites 4P and 7M were incubated in the same manner only under 22°C or 27°C temperature treatments. The initial phosphorus concentration for sediment cores incubated in 2014 was different for cores incubated in 2015, therefore to compare the phosphorus release we calculated the change in phosphorus concentration from the initial day, ΔP. Plotting ΔP allows for comparison between cores collected in different years and with different initial phosphorus concentrations (Figure 5).

Data Analysis

An analysis of variance model (ANOVA) was used to determine differences in phosphorus release between locations and temperature treatments. For this study, a two-way ANOVA was run on a combined data set of all locations for temperature and location on each day of incubation. To compare the results from my sediment core incubations to the results published in a 2014 Army Corps of Engineers report on internal loading of phosphorus, I calculated phosphorus release rates (mg P/m^2 d) as the linear change in phosphorus concentration in the overlying water divided by length of incubation and area of sediment core (Army Corps of Engineers 2014).

Estimation of Lake Wide Phosphorus Flux During an Anoxic Event

Instead of using a linear regression to calculate phosphorus release rates, I calculated multiple release rates based on duration of anoxia. Release rates for a 1, 2, 3, and 4 day anoxic event were calculated separately using the average change in phosphorus concentration from the initial phosphorus concentration. I chose to do this method for two reasons. First, the phosphorus concentrations in the overlying water did not appear to follow a strictly linear relationship with time. Second, the Western Basin of Lake Erie is shallow and well mixed, and therefore does not experience a season long thermocline. Due to the consistent mixing, stratification events in the western basin are thought to last only a few days (Bridgeman et al. 2006). Calculating rates for individual days of anoxia is a better representation of conditions present in the lake.

The estimated amount of phosphorus entering Western Lake Erie is the result of the phosphorus release rate multiplied by anoxic area. Since my four sampling locations represented different depths, sediment types, and influenced by different rivers, determining a single rate for anoxic phosphorus release for the western basin is difficult. The most conservative approach is to simply average the 4 sites release rates to obtain a single anoxic phosphorus release rate for the Western Basin of Lake Erie. However, each location sampled may not represent an equal area of Western Lake Erie due to differences in sedimentation and river influence. Therefore, I calculated a weighted average, which weighted each site based on what percentage of the Western Basin the sites depth represented.

An area of the Western Basin of Lake Erie was calculated by importing a bathymetry map from the Great Lakes Information Network (GLIN) into Arc GIS

(ArcGIS Desktop: Release 10.2. Redlands, CA: Environmental Systems Research Institute.). First, I calculated the area of Western Lake Erie deeper than 4 m. I chose a 4 m cutoff because Bridgeman (2006) indicated that stratification in the Western Basin of Lake rarely occurs in waters less than 4 m deep. Then, the bottom area of the lake was split up into three depth categories, 4-7 m, 7-10 m, and 10+ m, to represent areas similar to my sampling sites. Locations 91M and C5 were combined for the weighted average because the difference in depth at these two locations was 0.5 meters. Using the depth categories, sites were weighted based on how much area their depth represents. Then the weights of each site were applied to the release rates calculated from each site, which resulted in a single phosphorus release rate for an anoxic event in the Western Basin of Lake Erie.

2.4 Results

Sediment Core Incubations

Phosphorus concentrations from cores collected from the same site and incubated under the same temperature treatment were averaged and plotted against day of incubation (Figure 3). The resulting plot indicates that sediment cores incubated at 30°C had higher phosphorus concentrations than cores incubated at 10°C and 20°C for all sites. On average, phosphorus concentrations in the overlying water for cores incubated at 20°C and 30°C were 2 and 14 times higher respectively, than cores incubated at 10°C. Comparing sites in Figure 3, there are large changes in phosphorus concentrations in the overlying water between locations. For example, the highest phosphorus concentration in the overlying water for 7M is an order of magnitude larger than the highest phosphorus concentration for C5. In Figure 4, cores collected from different sites, but incubated at 30°C are plotted together. The southern most location (7M) had the highest phosphorus concentrations in the overlying water, while the northern most location (C5) had the lowest phosphorus concentrations. The trend between sites was most evident under the 30°C temperature treatment, but was also apparent in the 20°C and 10°C incubations.

An ANOVA was used to test for significant differences between temperature treatments and locations. A separate two-way ANOVA was run on the combined data for each day of incubation, which resulted in a total of 4 ANOVAs. Results from the ANOVA produced a significant result for location ($p<0.01$) and temperature ($p<0.01$) for each day of the incubation. A multiple comparisons test was used to compare specific temperatures and locations. For every day of the incubation, phosphorus concentrations from the 10 and 20°C treatments were not significantly different, but phosphorus concentrations from the 30°C treatment were significantly different than phosphorus concentrations from both 10 and 20°C treatments. Comparing locations, the first day of the incubation yielded no significant differences in phosphorus concentrations in the sediment cores from the two southern most sites (7M and 4P) and the two northern most sites (91M and C5). On the second and third day of the incubation, phosphorus concentrations in the overlying water from sediment cores collected from 4P and 91M were not significantly different and phosphorus concentrations in the overlying water from sediment cores collected from 91M and C5 was also not significantly different. On the final day of incubation, phosphorus concentrations from sediments cores collected from 4P and 91M were not significantly different.

Since there was a significant difference in phosphorus concentrations for sediment cores incubated at 30°C compared to sediment cores incubated at 10°C and 20°C, more sediment cores were collected the summer of 2015 from 7M and 4P and incubated at 22°C and 27°C. The purpose of these incubations was to further investigate the effect of temperature and to determine if there was a temperature threshold between 20°C and 30°C where phosphorus release rates dramatically increased. Data from the 2015 sediment core incubations conducted at 22°C and 27°C were difficult to compare to the 2014 incubations because the initial concentration of phosphorus in the overlying water for the sediment cores incubated in 2015 was higher than in 2014. For example, the initial phosphorus concentration for sediment cores collected at 4P in 2015, 0.615 mg/L P, was sixty times higher than the initial phosphorus concentration for sediment cores collected at 4P in 2014. The higher initial phosphorus concentration for sediment cores incubated in 2015 may have interfered with anoxic phosphorus release by creating a different diffusion gradient for 2015 cores than the diffusion gradient in 2014 cores. However, data from the 2015 sediment core incubations is still valuable and helps explain the relationship between temperature and anoxic phosphorus release for Western Lake Erie sediments. Therefore, to compare locations we plotted ΔP for both 2014 and 2015 sediment cores in Figure 5. For location 7M, there appears to be no difference between 10°C, 20°C, 22°C, and 27°C. The 7M core collected in 2015 incubated at 27°C has no significant change in phosphorus, while the core incubated at 22°C aligns closely with the 20°C core from 2014. However for location 4P, 10°C, 20°C, and 22°C did not appear to be different, but the 27°C sediment core incubation produced a ΔP that was between the ΔP calculated for sediment cores incubated at 20°C and 30°C from 2014.

Sediment Characteristics

Total phosphorus in the top 1cm of the sediment was plotted against distance from the mouth of the Maumee River (Figure 6). Total phosphorus concentrations range from 0.56-0.98 mg TP/g sediment. The graph displays a negative trend between distance from the mouth of the Maumee River and total phosphorus concentration in the top 1cm of the sediment.

The organic content between sites was compared using an ANOVA. Site 7M (3.85% ± 0.23%) had significantly less ($p<0.01$) organic content than 4P (4.92% ± 1.64%), 91M (5.51% ± 0.28%), and C5 (4.88% ± 0.06%). Sites 4P, 91M, and C5 did not have statistically significant differences in organic content.

Estimation of Lake Wide Phosphorus Flux During an Anoxic Event

Using Arc GIS, the area of the Western Basin of Lake Erie deeper than 4 m was calculated to be 1,371 km^2. Then the areas of the set depth intervals were calculated to be 522 km^2 (4-7 m), 605 km^2 (7-10 m), and 244 km^2 (10+ m). Therefore, I weighted the release rate for location 7M at 38.1%, 4P at 44.1%, and the average of 91M and C5 at 17.8%. The weights were applied to the release rate calculated for each day of incubation and the weighted release rate was multiplied by the area of Western Lake Erie deeper than 4 m to estimate a phosphorus load during a basin wide anoxic event. The estimated load of phosphorus resulting from an anoxic event (Figure 7) does not appear to follow a linear trend. On average, the phosphorus released from a 2-day anoxic event is 4 times higher than from a 1-day anoxic event. The estimated phosphorus release from a 4-day anoxic event at 30°C, calculated using the weighted phosphorus release rate was ~300 MT P.

2.5 Discussion

Effect of Temperature

Temperature had a significant effect on phosphorus release rates for sediment cores collected in 2014. The 10°C and 20°C treatments had similar release rates, while the 30°C temperature treatment resulted in significantly higher phosphorus release rates for all locations. Lower phosphorus release rates at 10°C and 20°C, and increased release rates at 30°C suggest that anoxic events in the spring and fall, when the water is cooler, may have a substantially lower contribution to lake phosphorus concentrations than an anoxic event during the warmer parts of the summer.

If the relationship between temperature and phosphorus release was linear from 20°C to 30°C, then final ΔP for cores incubated at 27°C should have been close to the ΔP for cores incubated at 30°C. However, the final ΔP for 27°C was approximately halfway between the final ΔP 20°C and 30°C, which suggests the relationship between temperature and phosphorus release under anoxic conditions is not linear. The idea that temperature and anoxic phosphorus release do not adhere to a linear relationship is somewhat strengthened by the ΔP graph for location 7M. The sediment cores incubated at 22°C from location 7M produce a ΔP very similar to the sediment cores incubated at 20°C. If temperature and phosphorus release did strictly adhere to a linear relationship then I would have expected to see the ΔP for the sediment core incubated at 22°C to be approximately one fifth of the way between the ΔP for sediment cores incubated at 20°C and 30°C.

Previous studies suggest that the relationship between temperature and phosphorus release from anoxic sediments does not follow a linear relationship (James and Barko 2004, Jiang et al. 2008). Temperature can influence a variety of factors, such as biological activity and diffusion rates, which can change phosphorus release rates. Depending on the lake, the effect of temperature on phosphorus release may be different due to differences in sediment characteristics (Jensen and Andersen 1992). Therefore, phosphorus release rates from this study will be useful in estimating phosphorus release from anoxic events in Western Lake Erie, which may occur in different seasons and under different temperatures.

Differences in Phosphorus Release Between Locations

The effect of temperature on phosphorus release from anoxic sediment cores had a consistent trend between locations. For each location sampled, the 30°C temperature treatment released significantly more phosphorus than the 10 and 20°C treatment. However, the phosphorus release rates between locations varied. The sediment core with the highest phosphorus release was collected from the southern most site, 7M, and the lowest rate was collected from the northern most site, C5. There was a general trend across the sites of increasing phosphorus concentrations from the northeast to the southwest. In the southwest corner of the Western Basin of Lake Erie is the Maumee River, which inputs high concentrations of phosphorus and high quantities of sediment. Agricultural fields and urban areas dominate land use in the Maumee River watershed.

Run-off from the agricultural fields can be high in nutrients, specifically phosphorus. The potentially high amounts of nutrient rich sediment being deposited at the southern portion of the lake may be the reason that phosphorus release rates were higher for the southern sites.

Total phosphorus concentrations in the top 1 cm of sediment cores collected from the same sites suggest that the southern most site, 7M, had the highest total phosphorus concentration in the top 1 cm of the sediment, while the other three sites had similar total phosphorus concentrations in the top 1 cm of the sediment. Data from my sediment core incubations indicate a similar trend where the southern most site exhibits the highest phosphorus release and the other three sites exhibit a significantly lower phosphorus release.

Although this is the first study in Western Lake Erie to increase temperatures of anoxic sediment core incubations to 30°C, other studies conducted in the western basin have used 20°C. A study in 2013 sought to determine if open lake dumping of dredge material contributed to internal phosphorus loading (Army Corps of Engineers 2014). A portion of this study was to perform anaerobic sediment core incubations with sediment from the placement site, location where dredge material was dumped, and an undisturbed reference site located near the mouth of the Maumee River. The sediment core incubations were conducted in the same manner as the sediment core incubations in this study with the major difference being the length of incubation (7 days versus the 4 day incubation in this study). The results of the 2013 sediment core incubations yielded an average phosphorus release rate of 9.5 mg P/m^2 d for cores collected from the reference site and incubated at 20°C (Army Corps of Engineers 2014). Comparing my closest sampling site, 7M which is 7 km from the 2014 sampling location, I obtained an average phosphorus release rate of 11.5 mg P/m^2 d for cores incubated at 20°C.

Estimation of Lake Wide Phosphorus Flux During an Anoxic Event

The results of anoxic sediment core incubations were used to estimate phosphorus release during 4 days of anoxia at 20°C spanning the Western Basin of Lake Erie. Under these conditions, 35 MT P would be released into the water column. According to the National Center for Water Quality Research, the annual load of phosphorus from the Maumee River is 2,508 MT P. Dividing the annual load of the Maumee River into an average daily load, I estimate the Maumee River contributes ~ 7 MT P per day. Therefore, the phosphorus loading from two days of anoxia in the Western Basin of Lake Erie would equal 5 days of Maumee River flow.

Climate change predictions expect warmer summer temperatures for the Western Basin of Lake Erie and the climate for the Great Lakes area to resemble the current climate of Northern Texas by the end of the century (Hayhoe et al. 2010). Warmer summer temperatures may result in an increased frequency of stratification events resulting in anoxia. Not only does climate change have the potential to increase the frequency of anoxic events in Western Lake Erie, but also increased bottom water temperatures due to climate change would result in higher rates of phosphorus release from anoxic lake sediments. Lake Texoma, a reservoir in Northern Texas, regularly experiences water temperatures of 30°C at a depth of 8 meters (Churchill 2013). If bottom water temperatures in Lake Erie resembled Lake Texoma by the end of the century, then rates for internal loading of phosphorus during an anoxic event would increase 7 times.

2.6 Figures

Figure 2-1: Sampling locations for 2014 and 2015 sediment core collections. Sediment cores were collected from C5 and 91M on 7-22-14, 7M on 8-21-14 and 8-10-15, and 4P on 9-6-14 and 8-24-15.

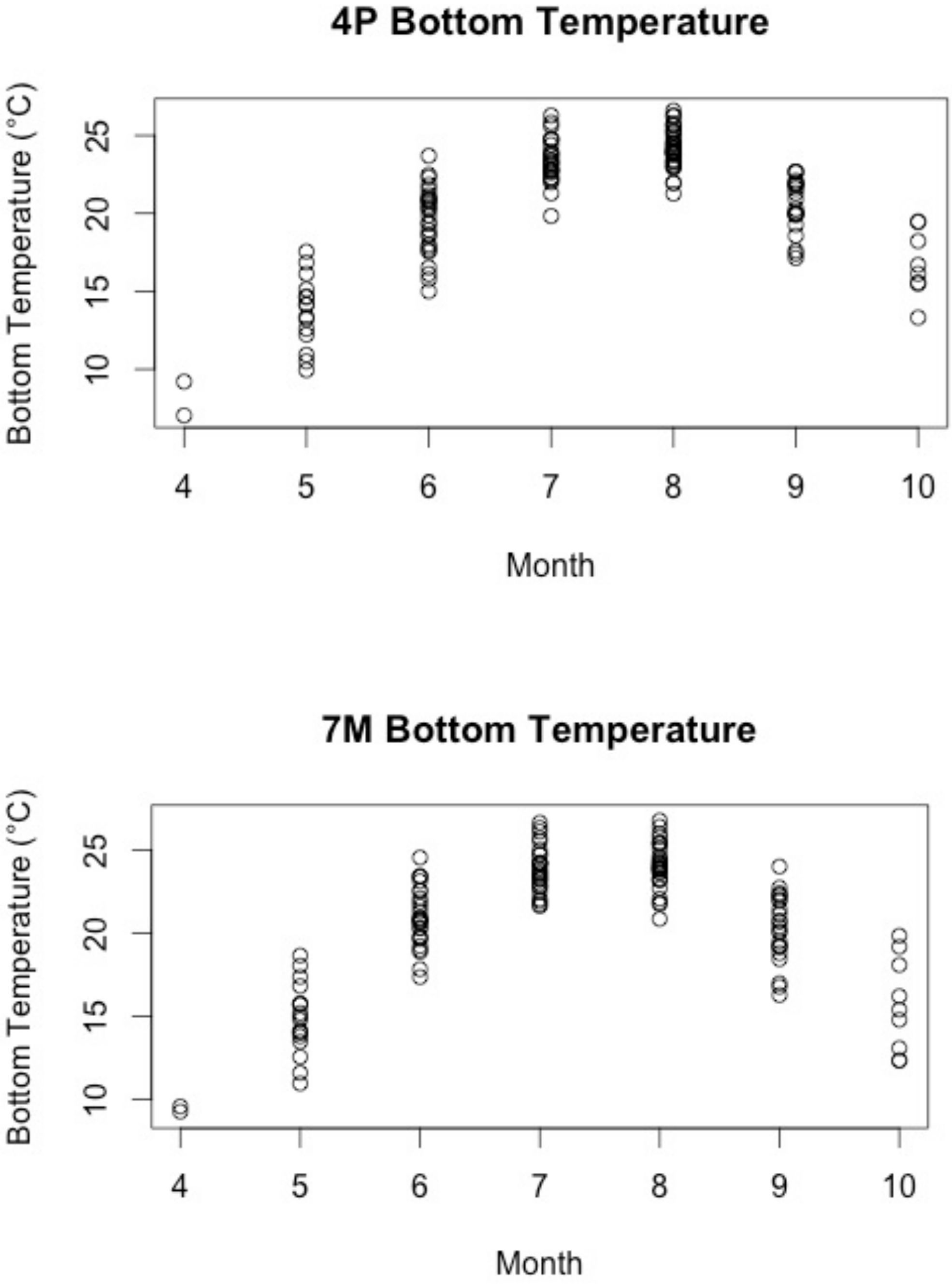

Figure 2-2: Bottom water temperature data collected by the Bridgeman Lab from 2001-2013 for two of the sampling locations used in this study 4P and 7M (n=139).

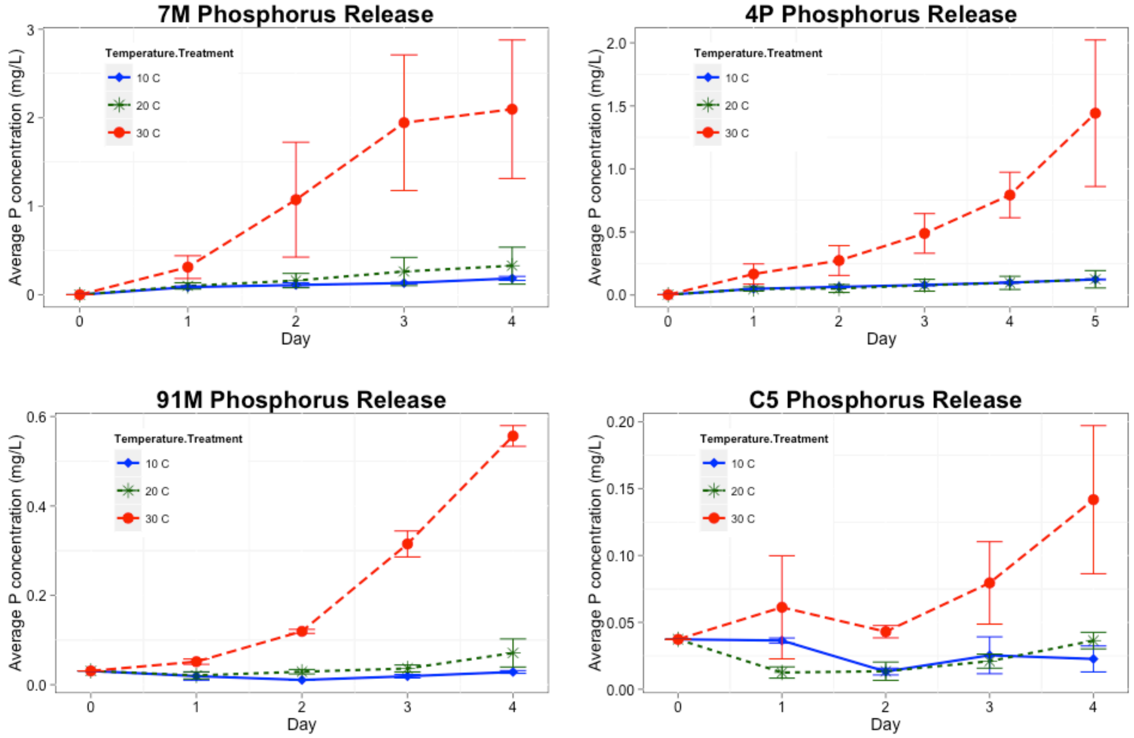

Figure 2-3: Sediment core incubations conducted in summer of 2014 for sites 7M, 4P, 91M, and C5 at spring (10 °C), summer (20 °C) and elevated (30 °C) temperatures. Symbols indicate P concentration in lake water overlying sediments and bars represent standard error for three replicate cores. Note different P concentration scales for the sites. At all sites, phosphorus concentrations in the overlying water were significantly greater ($p < 0.05$) under 30°C temperature treatments.

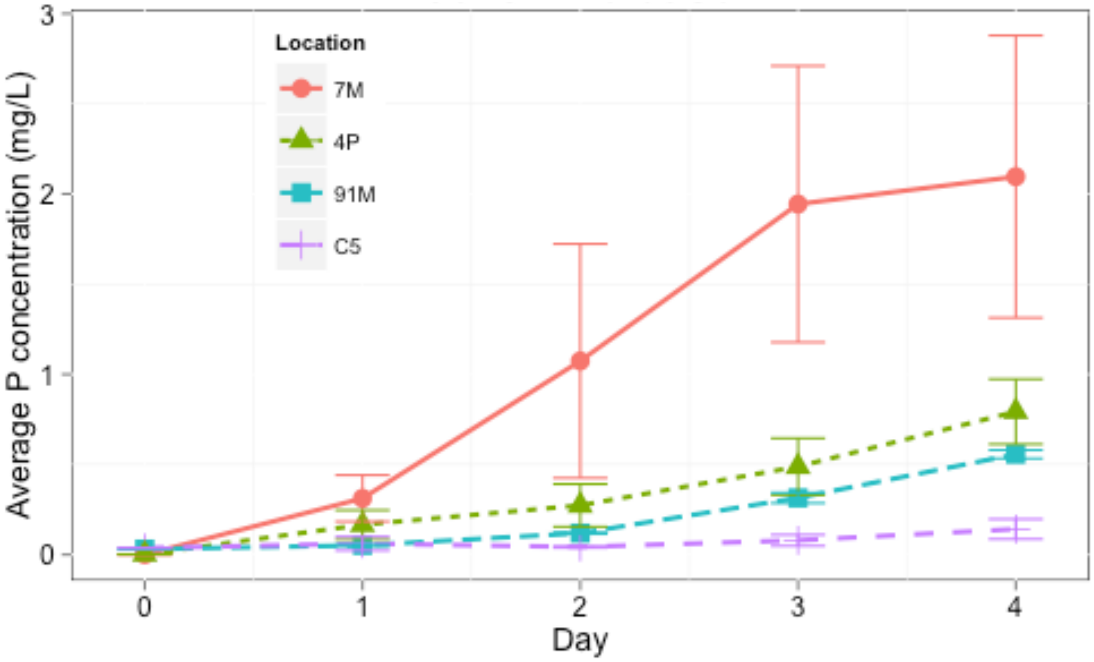

Figure 2-4: Phosphorus release from sediment cores over a 4-day anoxic incubation at 30 °C. Phosphorus release increased with proximity to the mouth of the Maumee River. Site 7M is closest to the mouth of the Maumee River (13 km) followed by 4P (35 km), 91M (60 km) and C5 (80 km).

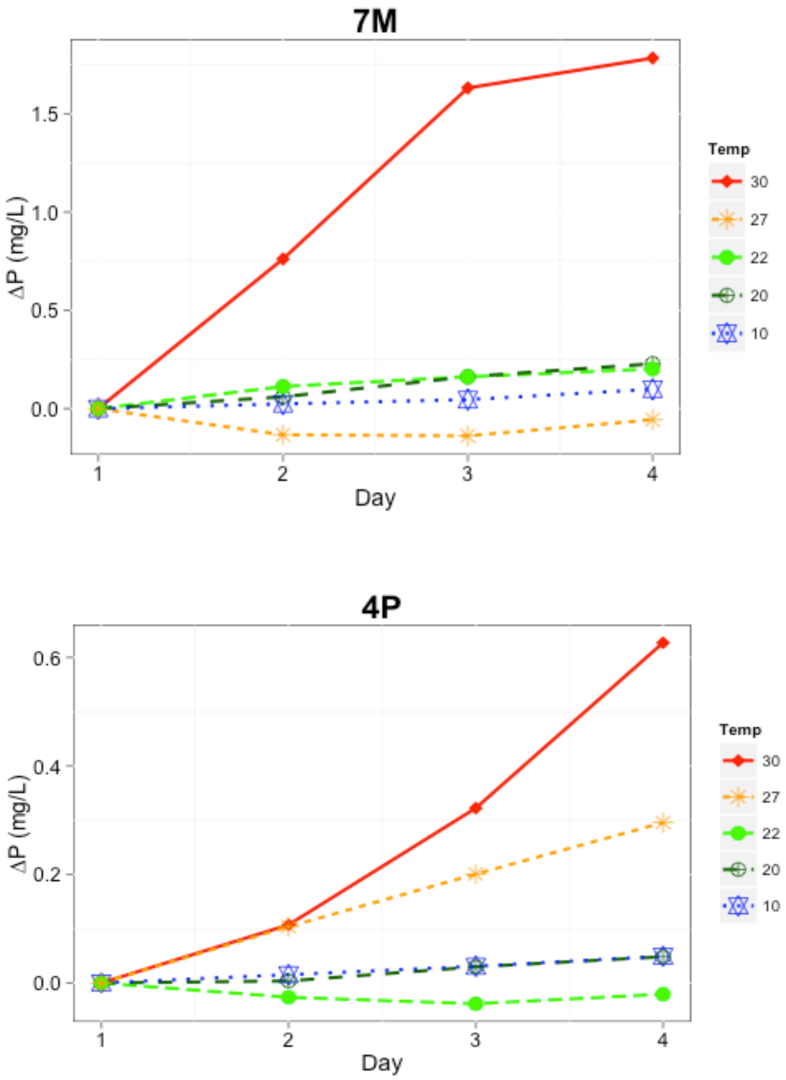

Figure 2-5: Change in phosphorus from initial concentration, ΔP, plotted against day of incubation for sediment cores incubated in 2014 (10, 20, and 30 °C) and 2015 (22 and 27 °C). There is little difference between 10°C, 20°C, 22°C, and 27°C for location 7M. However for location 4P, 10°C, 20°C, and 22°C did not appear to be different, but 27°C produced phosphorus concentrations that were approximately half of the 30°C treatment.

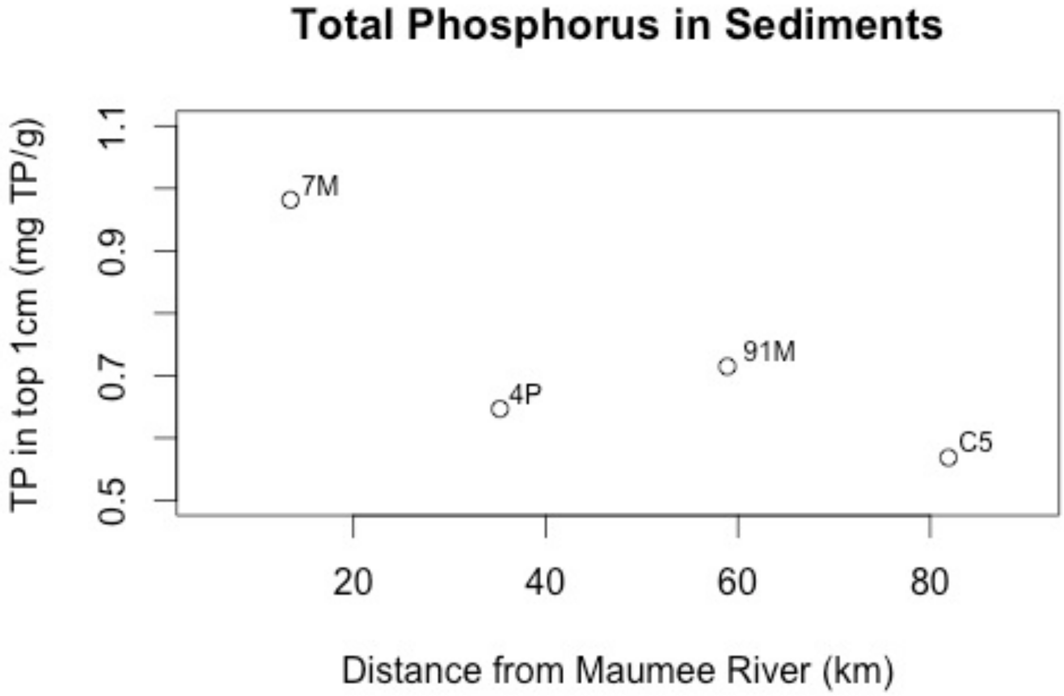

Figure 2-6: Sediment TP decreases as distance from Maumee River increases suggesting significant phosphorus input from the Maumee River Watershed. (Data from NCWQR).

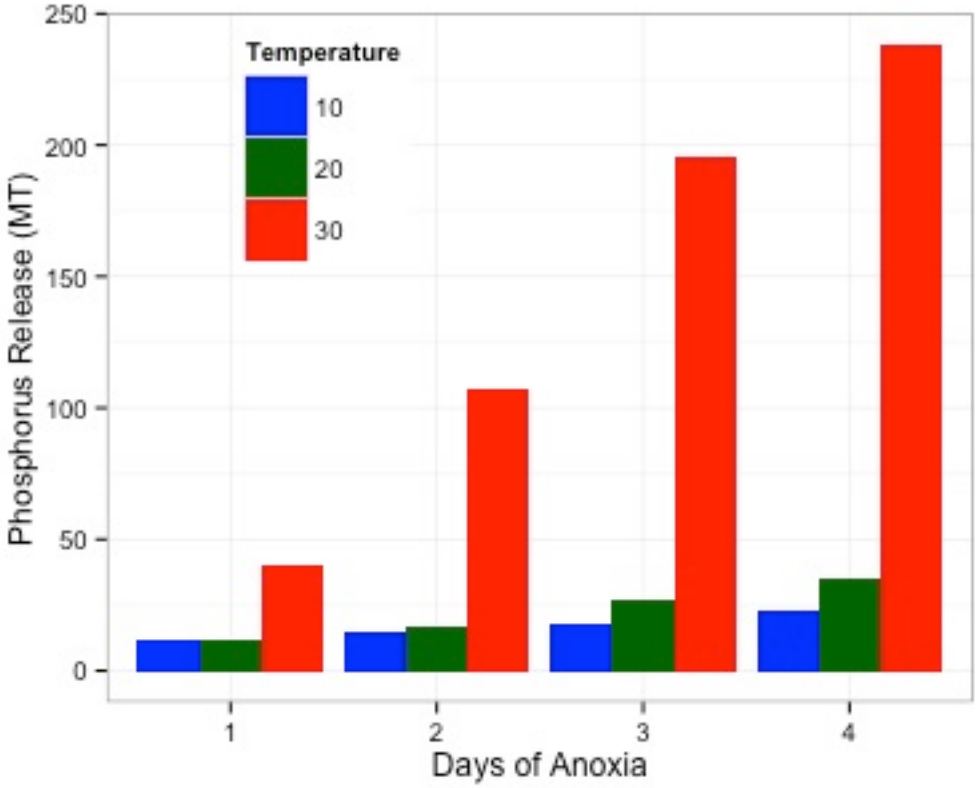

Figure 2-7: Estimates of phosphorus release for an anoxic event that covers the entire western basin. Since location had a significant effect on phosphorus release, the release rate for the entire western basin was a weighted average calculated from the release rates estimated at the 4 sampling locations. The weight of the release rate for each sampling location was determined by depth at the sampling location and the percentage of that depth that covered the Western Basin of Lake Erie. Site 4P (depth= 9m) was weighted at 44.1%, 7M (depth= 5m) was weighted at 38.1%, and C5 and 91M, which were combined because of similar depths, (C5= 11.5m and 91M= 11m) were weighted at 17.8%.

Chapter 3

Application of Microelectrodes on Western Lake Erie Sediments

3.1 Abstract

The Western Basin of Lake Erie has experienced an increase in algal biomass. Current management strategies focus on phosphorus reduction from external sources to reduce algal biomass. In order to predict success of management strategies, it is important to understand the contribution of phosphorus from both external sources (tributaries) and internal sources (lake sediments). Lake sediments can contain orders of magnitude higher concentrations of phosphorus than the overlying lake water and in some cases can be significant sources to lake phosphorus concentrations. Lake conditions, such as temperature, pH, and dissolved oxygen concentration control whether sediments are a source or sink of phosphorus. Oxidation-reduction potential (redox) is a measure of the potential for ions to donate or accept electrons which dictates phosphorus release from sediments and indicates whether sediments will be a source or sink of phosphorus (Mortimer 1942). The application of microelectrodes is useful to obtain fine scale *in-situ* measurements of redox potential at the sediment water interface. Redox potential at the sediment water interface is a primary factor that dictates the flux of nutrients from the sediment (Anthony and Lewis 2012). In this study, I used fabricated platinum electrodes

to measure redox profiles in sediment cores collected from Lake Erie and correlated the results of the redox profile to the phosphorus release rate of the core. Results from redox profiles indicate a negative correlation between redox potential (Eh) and phosphorus concentration in the overlying water.

3.2 Introduction

Excessive nutrient loadings into lakes cause eutrophication, which is an increasing problem worldwide (Conley et al. 2009). Eutrophication events can lead to the occurrence of harmful algal blooms (HABs). HABs reduce water quality and in some cases have shutdown municipal water supplies, such as the case for the City of Toledo during August 2014 (Kane et al. 2014). Understanding nutrient inputs, specifically phosphorus, is important to predict HABs and create management strategies to diminish HABs. In Western Lake Erie, there is extensive knowledge about external loading of phosphorus, but there have been few studies investigating internal loading of phosphorus. Stumpf found that springtime loading of total phosphorus in the Maumee River is highly correlated with HAB biomass and can be used to predict size of bloom (Stumpf et al. 2012). Since Maumee River springtime phosphorus load is highly correlated with HAB size, it can be inferred that external loading of phosphorus is a more important source of phosphorus than internal loading. However, internal loading can still be an important factor when trying to predict success of reducing external loading of phosphorus. Quantifying internal loading can help set expectations for lake recovery and tailor management strategies for reduced external loading that result in decreased HAB biomass.

Redox potential is the tendency for an ion to become oxidized (donate electron) or reduced (accept electron). The redox potential in lake sediments can be influenced by a variety of factors, such as pH, dissolved oxygen concentration, and microbial activity. In natural waters, the redox potential at pH 7 ranges from +800 mV to -400 mV, which is divided into the positive range, defined as oxidizing conditions, and the negative range, defined as reducing conditions (Sigg et al. 2000). In the presence of dissolved oxygen, the redox potential typically stays in the oxidized range (positive values), however under anoxic conditions the redox potential drops to around +100 mV and can go even lower depending on microbial activity, pH, and available ions (Hargrave 1972).

In lake sediments, iron is an important ion that can either bind to or release phosphorus depending on the redox conditions (Mortimer 1971). When the redox potential drops below 100 mV, ferric iron can be reduced to ferrous iron and release any bound phosphorus (Burley et al. 2001). Above 100 mV, iron binds to phosphorus and therefore trapping phosphorus into the sediment (Ann et al. 1999). Redox potential in sediments has been previously measured using millivolt potentials produced from a platinum electrode placed in the sediment and a Ag/AgCl reference electrode in the water (Mortimer 1971). Platinum is utilized in the working electrode because platinum is an inert metal and therefore will not interfere with the reactions, but platinum still provides a surface for oxidation/reduction reactions and the conduction of electrodes (Bohn 1971). Measuring redox potential in lake sediments is important to understand the potential reactions going on in the sediment and their influence on phosphorus concentrations.

The purpose of this research is to investigate differences in sediment redox potentials for anoxic core incubations. Sediment redox conditions may help explain differences in phosphorus concentrations in the overlying water from cores incubated under anoxic conditions at the same temperature.

3.3 Methods

Sediment Core Collection

Sediment cores were collected from 4 sites in the western basin of Lake Erie during the summer of 2014 (Figure 1). The 4 sites spanned the Western Basin from North to South and represented varying depths and sediment types. Sediment cores from 91M (41° 50' 27.6"N, 82° 54' 58"W, water depth 11 meters) and C5 (41° 58' 1.2"N, 82° 46' 1"W, water depth 11.5 meters) were collected on July 22, 2014 aboard the R/V Lake Guardian by subsampling an Ekman 30 x 30 cm box corer. After collection, cores were stored in the dark at 4 °C with the top cap off until needed for incubation. Prior to incubation, the overlying water was drained off and replaced with 500ml of lake water filtered through 0.45 µm filter (Millipore GWSC 045).

Core Incubation

Three cores from each location were incubated for 5 days under either a 10 °C, 20 °C, or 30 °C treatment, for a total of nine cores incubated for each location. In order to hold temperature constant, sediment cores were placed in incubation chambers (Percival E36HO), or warm water bath for the 30°C treatment. Dissolved oxygen was maintained at 0 mg/L by gently bubbling nitrogen and cores were kept in the dark throughout incubation. Every 24 hours, 15 ml samples were collected and frozen for future phosphorus analysis.

Fabrication of microelectrodes

Fabrication of ORP electrodes began by heating the middle of a borosilicate pipette (O.D. 1.2mm, I.D. 0.69mm, 15cm length, Sutter Instruments Co.) and then elongating the pipette by pulling both ends to create a thin section in the middle of the pipette. Then a section of platinum wire (diameter 0.5 mm, Sigma Aldrich) was then inserted into one end of the pipette. A platinum trough heating filament was used to melt the glass directly adjacent to the platinum wire, which encapsulated the wire in glass. Next, the platinum wire was exposed by sanding away the glass using a diamond abrasive plate (BV10-1684, Sutter Instruments Co.). Finally, a copper wire is connected to the platinum wire using a bismuth alloy (44.7% bismuth, 22.6% lead, 19.1% indium, 8.3% tin and 5.3% cadmium).

Characterization

After fabrication, performance of ORP electrodes was tested using a two-point ORP Quinhydrone Kit (Pulse Instruments). First, the fabricated ORP electrode and Ag/AgCl reference electrode (MI-402, Microelectrodes Inc.) was placed in a pH 4 quinhydrone solution, which has an expected value of +96 ±15mV at 20°C. If the reading fell within the expected range for pH 4, then both the fabricated electrode and reference electrode were placed in a pH 7 solution where we expected to see a minimum increase of +170mV and a maximum increase of +185mV for a good working electrode.

ORP profiles

ORP profiles were conducted in a faraday cage to minimize interference. Measurements were taken by reading the millivolt potential (Fisher AB15) produced between a fabricated platinum electrode in the sediment and Ag/AgCl reference electrode placed in the overlying water. The position of the platinum electrode was controlled by a World Precision Instruments XYZ manual micromanipulator. Profiles started at the sediment surface and progressed down at 5mm increments to a final depth of 30mm.

3.4 Results

In total, 26 ORP electrodes were fabricated and the performance of the electrode was tested using a two point quinhydrone calibration in which 8 electrodes passed the quinhydrone calibration. Those 8 electrodes were used to conduct ORP profiles on 17 different sediment cores collected from locations 91M and C5 with some cores being profiled over the course of multiple days. In total, 39 profiles were conducted on cores collected from locations 91M and C5 during the summer of 2014.

Redox potentials in the sediments ranged from -187 mV to +181 mV with a mean redox potential of +77.5 mV. Phosphorus concentrations in the overlying water ranged from 0.005 mg P/L to 0.36 mg P/L with a mean phosphorus concentration of 0.03 mg P/L. Sediment surface redox potential and phosphorus concentration in the overlying water were plotted together and a linear regression was used to check for relationship between sediment redox potential and phosphorus concentration in the overlying water (Figure 2). The linear model was not a good fit (R squared = 0.07) for the data, however the graph does show the highest phosphorus concentrations occurred when the sediment surface redox potential is at the lowest.

Comparing individual redox potential profiles to phosphorus concentrations in the overlying water, I found some cases where redox potential could be used to explain differences in phosphorus concentrations in the overlying water for cores incubated under the same conditions. Figure 3 depicts phosphorus concentrations in the overlying water plotted against day of incubation (left panel) and redox potential profiles taken on day 3 of the incubation. On day 3 of the incubation, the phosphorus concentration in the overlying water for replicate 2 was 0.14 mg P/L and for replicate 1 was 0.03 mg P/L. The redox potential at the sediment surface for replicate 2 was -71 mV and for replicate 1 was 69 mV.

3.5 Discussion

Fabricated platinum electrodes performed well in standard redox solutions and therefore can be used to accurately measure redox potential. The results of this study also suggest that microelectrodes can be used in sediment cores to measure redox potential, which allows for fine scale measurements of the sediment to be taken with minimal disturbance. Accurate ORP measurements can be useful to determine the tendency for ions to be oxidized and reduced.

Although fabrication and characterization of electrodes was relatively easy, there were some drawbacks to ORP microelectrodes. Due to the small tip diameter, microelectrodes are fragile and prone to breaking when probing into sediments. Therefore, multiple electrodes needed to be fabricated as backups. Also, lab fabricated

ORP electrodes showed good performance in standard solutions, however fabricated ORP electrodes took much longer to stabilize in the sediments. A faraday cage was used to minimize external interference. Even with the faraday cage, fabricated ORP electrodes took much longer to stabilize in the sediments. Potential interferences in the sediment or clogging of the electrode may have slowed the response time.

The scatter plot of redox potential at the sediment surface and phosphorus concentration in the overlying water had no observable trend. I expected to see a negative correlation between surface redox value and phosphorus concentration in the overlying water. A potential reason we did not see a trend between sediment surface redox potential and phosphorus concentration in the overlying water is that the sediment is heterogeneous. Unlike the standard solutions, the sediment composition varies in organic content, which may cause differences in microbial activity resulting in different redox potentials. Also, the sediment structure is not uniform due to zebra mussel shells and invertebrates, such as mayflies.

Although the results from redox profiles were inconclusive, the results in Figure 3 suggest a link between sediment surface redox conditions and phosphorus concentration in the overlying water. Even though both sediment cores in Figure 3 were anoxic, differences in redox potential resulted in replicate 2 releasing more phosphorus into the overlying water than replicate 1. Differences in microbial activity or organic matter could have affected the phosphorus release rate, which suggests that anoxia is only one part of the mechanism for phosphorus release from lake sediments. Once the bottom of the lake goes anoxic, the redox potential in the sediment surface will dictate the rate of phosphorus release rate, which could explain why phosphorus release from anoxic sediment cores is not a linear relationship.

In chapter 2, I found that a 2-day anoxic event released 4 times more phosphorus than a 1-day anoxic event. During the first day of anoxia, the redox potential is hovering around +100 mV and only some iron bound phosphorus is being released (Burley et al. 2001). Then on the second day, the redox potential continues to drop due to microbial activity and as the redox potential declines, more iron is being reduced which releases more phosphorus. Once the redox potential approaches -100 mV then iron and manganese bound phosphorus start to rapidly release into the water column (Miao et al. 2006). Therefore, changes in redox potential could be a contributing factor as to why phosphorus release from anoxic sediments does not follow a linear relationship.

3.6 Figures

Figure 3-1: Map of sampling locations.

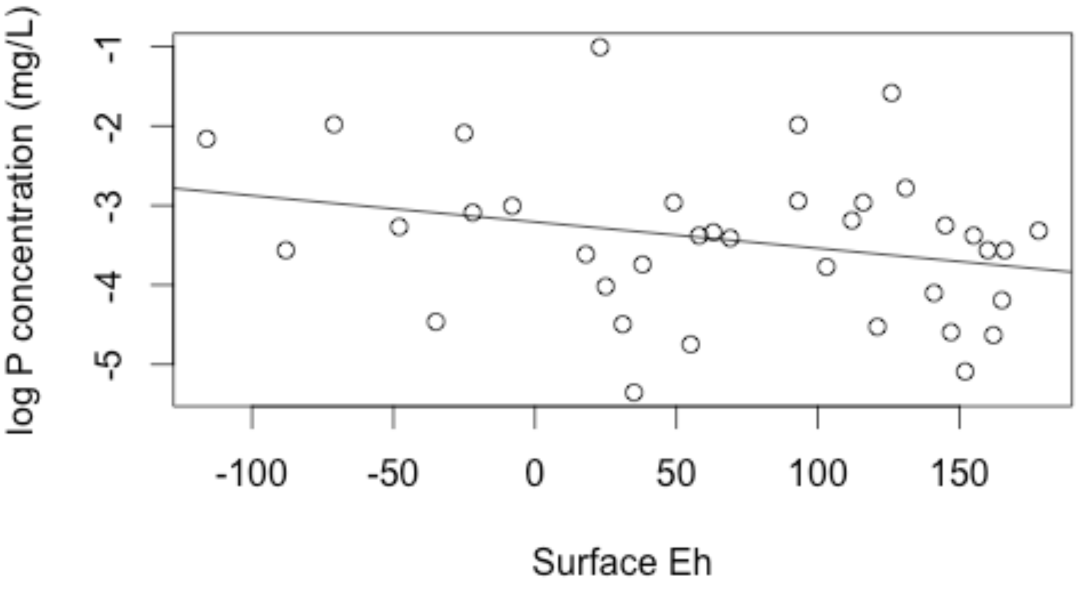

Figure 3-2: Negative correlation between surface redox potential (Eh) and phosphorus concentration in the overlying water.

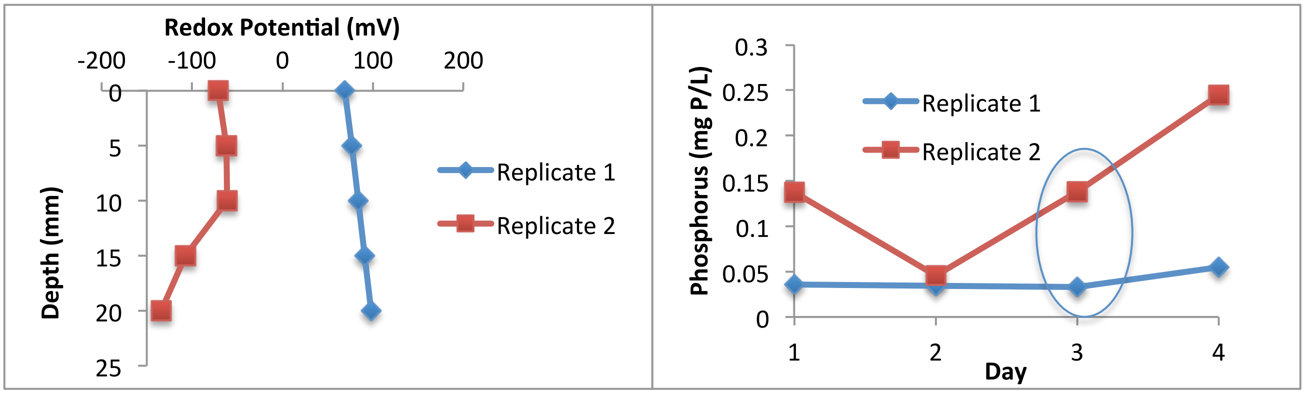

Figure 3-3: Phosphorus release data from individual sediment cores collected at location C5 and incubated at 30°C (right panel) coupled with ORP profiles taken on day 3 of the incubation (left panel). Replicate 2 has a surface redox potential of -71 mV and a phosphorus concentration of 0.14 mg P/L, while replicate 1 has a surface redox potential of 69 mV and a phosphorus concentration of 0.03 mg P/L.

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Appendix A

Application of Phosphorus Microelectrodes To Western Lake Erie Sediments

Monitoring phosphate concentration is very important to properly control eutrophication in Great Lakes. In this study, cobalt-based microelectrodes with small tip size (<100 μm) were fabricated, calibrated and tested to assess their performances for soluble reactive phosphorous (SRP) monitoring. First, the performance of phosphate microelectrodes was fully examined for different characteristics such as detection limit, response time, selectivity, reproducibility, and ion interference. Then, phosphate microelectrodes were applied to sediment samples collected from different locations in Lake Erie and SRP loading was monitored under both oxic and anoxic conditions with 1 mm measurement increment. Phosphate sensors possessed detection limits up to 10-7 M concentration of phosphate ion with stable signal responses. However, signal interferences (especially with oxygen) needed to be considered and properly addressed for sample analysis with phosphate microsensors. For in-situ SRP profiling in Lake Erie sediment samples, the phosphate sensor could monitor phosphate concentration changes with high resolution and sensitivity. Overall, obtained results showed that the phosphate microelectrode can be an effective tool for the measurement of phosphate in both bulk water and sediment samples for SRP monitoring.