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MODELING THE PHYSICAL AND BIOGEOCHEMICAL PROCESSES IN LAKE SUPERIOR USING LAKE2K

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MODELING THE PHYSICAL AND BIOGEOCHEMICAL PROCESSES
IN LAKE SUPERIOR USING LAKE2K

By
Sheelagh M. McCarthy

A THESIS
Submitted in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
In Geology

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This thesis has been approved in partial fulfillment of the requirements for the Degree of
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Abstract

Modeling lake processes and dynamics improves understanding of the system and supports predictions of the response of the lake to perturbations, such as climate change. LAKE2K, a 3-layer surface water quality model, uses a mass balance approach to simulate the physical and biogeochemical cycles in Lake Superior. The model is successfully calibrated with data from offshore Lake Superior in 2011, a year with average meteorological conditions. The thermal regime, phytoplankton populations, and phosphorus cycle of Lake Superior are modeled, resulting in a representation of seasonal trends in this dimictic system. The calibrated model is confirmed with an application for Lake Superior during 2012, a climatic anomaly. Recommendations for improvement include expanding the model to a more finely segmented multi-layered version and partitioning the particulate phosphorus variable. The model serves as a test bed to simulate temporal variations in Lake Superior and predict its response to perturbations.

1.0 Introduction

1.1 Background

The Great Lakes are an invaluable resource not only for their provision of ecosystem services, but culturally and aesthetically as well. Among the Great Lakes, Lake Superior has the largest volume and the smallest population density in its basin, resulting in limited impacts to its watershed (Matheson and Munawar, 1978). The expansive surface area of Lake Superior provides heightened opportunity for atmospheric input, and human influence to the system is primarily due to this source of pollutants (Eisenreich et al., 1998). Understanding the processes driving Lake Superior is critical when working to predict responses to perturbations that the lake could encounter.

Increasing temperatures in lakes is a common, growing change observed around the world (Adrian et al., 2009; Vincent, 2009). Lakes are particularly vulnerable to the effects of climate change, displaying a greater sensitivity to changes in air temperatures than the surrounding land (Williamson et al., 2009). The Great Lakes are all displaying the effects of climate change in their water temperatures, with an increase in average water temperature of 2.5°C in Lake Superior since 1976 (Magnuson et al., 1997; Austin and Colman, 2007). By identifying and characterizing ecosystem dynamics and processes in Lake Superior, the response to potential changes due to increased human activity induced climate change may be better understood.

Changes in temperature influence both the physical and biogeochemical nature of the system, including nutrient cycling, primary production, and the thermal regime (Magnuson et al., 1997; Mortsh and Quinn, 1996). Biogeochemical cycling is dependent

on the annual thermal regime of the system, and increases in lake temperatures could have strong ecosystem impacts (Zepp et al., 2007). In particular, as phosphorus is the limiting nutrient for Lake Superior, temperature-driven changes to phosphorus cycling can have significant impact on rates of primary production, the foundation of ecosystem function (Auer et al., 1986; Baehr and McManus, 2003; Sterner 2010).

Mathematical modeling provides a framework for simulating physical and biogeochemical processes in a lake, as well as the response to perturbations. Mathematical models represent an idealized system, e.g., a lake, and simulate the response of that system to perturbations (Chapra, 2008). Mechanistic mathematical models utilize a mass balance approach to model and understand a system (Chapra, 2008). The ability to simulate the response to perturbations of physical and biogeochemical processes in Lake Superior results in a greater understanding of the factors that not only drive the system, but also in predicting how the lake will change in response to climate change or other anthropogenic influences.

1.2 Study Site Description

Lake Superior provides a unique opportunity for research due to its large volume and depth, with an average depth of 147 meters and maximum of 400 meters. Lake Superior is a temperate, dimictic system that displays thermal stratification during summer and inverse stratification in winter (Bennet, 1978). The system undergoes two periods of mixing throughout the spring and fall (Hutchinson, 1957). The period of thermal stratification in Lake Superior lasts an average of 170 days (Austin and Coleman, 2008). Biannually, turnover occurs during the spring and fall in Lake Superior (Croley et al.,

1998). At the point of turnover, the lake has reached uniform temperature and density, and the system cycles nutrients and heat within the lake profile. Recognizing the influence of the thermal regime of Lake Superior on its nutrient cycling and algal growth processes is necessary to understand climate-driven changes.

Vertical turbulent diffusion coefficients¹ represent the magnitude of mixing within the layers of the lake (Chapra, 2008). The mixing strength is dependent on the exposed, unobstructed lake surface, or fetch, water temperature, and wind speed (Bennington et al., 2010). Increased lake surface area allows for stronger vertical mixing, and thus the expansiveness of Lake Superior allows for high mixing rates, particularly during fall and spring mixing (Bennington, 2010). In the early summer months, as the lake begins to thermally stratify, there are progressively lower rates of mixing between the layer boundaries. However, as the season progresses, these diffusion coefficients reach a minimum during the period of strongest stratification, occurring in late August in Lake Superior (Dijkstra, 2015).

Rates of biogeochemical cycling influence ecosystem processes and can be influenced by climate change (Schlesinger, 2013). In Lake Superior, the interaction between phosphorus cycling and algal growth is particularly important (Auer et al., 1986; Baehr and McManus, 2003). Modeling of algal populations utilizes a mass balance approach, where growth (a function of light, temperature, phosphorus) is the source term and zooplankton grazing, death, and settling are sinks (Chapra, 2008).

¹ “Vertical diffusion” is used to represent solute mass moved by large-scale eddies in water within a lake profile. Vertical diffusion coefficients representative vertical mixing caused by water density changes resulting from changes in heat at the surface (Chapra, 2008)

The phosphorus cycle is critical in biogeochemical processes within Lake Superior due to the role of phosphorus as the limiting nutrient (Auer et al., 1986; Baehr and McManus, 2003; Sterner, 2010). In oligotrophic systems, such as Lake Superior, inputs of phosphorus are relatively small compared to the lake volume (Reynolds and Davies, 2001; Sterner, 2010). The offshore waters of Lake Superior are largely isolated from the direct and immediate impacts of tributary and point-source inputs, and phosphorus dynamics typically depend on the cycling of the nutrient (Sterner, 2010). Phosphorus levels are low in Lake Superior, due not only to the small load:volume ratio, but also because the nutrient is rapidly taken up by phytoplankton and removed from the water column by settling. Therefore, the presence of phosphorus in Lake Superior plays a significant role for algal growth (Auer et al., 1986; Sterner et al., 2004; Urban, 2009).

The phosphorus cycle within Lake Superior includes three pools (soluble reactive-P, dissolved organic-P, and particulate-P), each with a differing degree of bioavailability in sustaining algal growth and ecosystem stability (Baehr and McManus, 2003; Sterner, 2010). Soluble reactive phosphorus (SRP) is fully and freely bioavailable for phytoplankton uptake and is then converted into particulate phosphorus (PP), where it is either captured by zooplankton, settles or is solubilized into dissolved organic phosphorus (DOP). Dissolved organic phosphorus is then mineralized into SRP form. The rates of phosphorus uptake, mineralization, and dissolution determine SRP bioavailability necessary for phytoplankton growth. Additionally, a hindrance in transfer among pools of phosphorus may have significant repercussions for the rest of the system (Scavia, 1976).

Recent studies demonstrate the relationship between phosphorus availability and temperature in Lake Superior (Dijkstra, 2015). The phenomenon of the “summer desert” is apparent in average and warm summers in Lake Superior (Dijkstra, 2015). The “summer desert” refers to phosphorus depletion in offshore waters caused by temperature enhancement of phytoplankton growth in a phosphorus-limited system (Dijkstra, 2015). The phytoplankton populations consume phosphorus throughout the growing season during early summer, and in late summer, the phosphorus quantities are exhausted. The lack of phosphorus within the lake creates a “summer [phosphorus] desert”, resulting in extreme nutrient limitation. The occurrence of the “summer desert” is noted in average and warm summers and is nonexistent during the cold years, which are historically characteristic for Lake Superior (Dijkstra, 2015). The duration of the summer desert in warm years and its absence in cold years is due to the timing and duration of temperature conditions favorable for phytoplankton growth.

2.0 Objectives & Approach

The interconnectedness between physical and biogeochemical cycles within Lake Superior are described above; modeling provides a framework for developing a better understanding of these dynamics. Thus, this study seeks to answer:

- Can the physical and biogeochemical dynamics observed in Lake Superior, particularly algal growth and phosphorus cycling, be represented satisfactorily through the use of a model? How do these dynamics change between years, e.g. average vs. anomalous climate conditions?

The research questions are addressed within this study to model and better understand the kinetic processes within Lake Superior by utilizing LAKE2K, a 3-layer surface water quality model. The model results are calibrated and confirmed with data collected from offshore Lake Superior in 2011 and 2012, respectively.

LAKE2K is calibrated for Lake Superior to:

- illustrate annual heat flux, vertical mixing, and the thermal regime
- simulate phytoplankton populations and growth
- model the biogeochemical trends of phosphorus cycling

Following the calibration of the model for temperature, phytoplankton growth, and phosphorus cycling, the foundation for the use of LAKE2K is set. The calibrated model is then used for simulating the same physical and biogeochemical trends for a different year with extreme weather conditions, 2012, to assess the validity of the model.

LAKE2K calibration facilitates a more intimate understanding of the processes within Lake Superior, and it provides a basis for examining changes to its thermal regime,

biogeochemistry, and plankton dynamics. The calibrated surface water quality for Lake Superior can be used as a test bed for future applications. LAKE2K will serve as a useful tool for those interested in the response of Lake Superior to changes to physical and biogeochemical cycles, particularly in regards to climate change.

3.0 Methods

3.1 Modeling Methods

LAKE2K, a model created by Chapra and Martin (2004) is used to simulate the thermal regime and nutrient-phytoplankton-zooplankton dynamics. The model can be adapted to various lakes by employing site-specific inputs defining geographic, physical, and biogeochemical conditions. The model was written and executed in Microsoft Visual Basic, and it utilizes Microsoft Excel as its graphical user interface (GUI). The LAKE2K GUI includes worksheets for model inputs (e.g., system volume, inflow/outflow, mass transport/kinetic coefficients and initial conditions) and output (field measurements and results for all state variables trends), in both tabular and graphical form.

The year 2011 is chosen for model simulations as it displays average seasonal conditions for Lake Superior. Data obtained from field sampling is used to calibrate the model results. Offshore sampling of Lake Superior occurred aboard the *R/V Agassiz* from May through November of 2011 (Dijkstra, 2015). Data was collected monthly or bimonthly at station, HN260, located 26 km offshore the western coast of the Keweenaw Peninsula with a depth of ~190 meters. Field data is used to establish initial conditions within LAKE2K and is used as a comparison with the model output in the calibration process.

3.2 Conceptual Model

LAKE2K models lakes by creating a water balance, heat balance, and mass balance related to various physical and biogeochemical constituents for the epilimnion, metalimnion, and hypolimnion of a system (Chapra and Martin, 2004). The water balance is determined by specifying boundaries for the epilimnion, metalimnion, and hypolimnion.

The extent to which those layers are mixed seasonally is controlled by the magnitude of the vertical turbulent diffusion coefficients specified as a user-defined time series. The water balance accommodates inflows, precipitation, evaporation, and outflows, with inflows set equal to outflows for the lake (as opposed to reservoirs).

LAKE2K models the heat balance of the system through analyzing the surface heat exchange at the air-water interface of the lake. Daily and seasonal variability in the meteorological conditions driving the heat balance are inputted by the user. The sources and sinks for surface heat exchange include solar shortwave radiation, atmospheric longwave radiation, water longwave radiation, conduction and convection, and evaporation and condensation (Chapra, 2008). Solar shortwave, atmospheric longwave, and water longwave radiation all contribute to net absorbed radiation, whereas the other processes are water dependent² terms (Figure 3.1; Chapra, 2008). Heat is transferred within the system based on the turbulent diffusion coefficients used for vertical mixing. Model output from the heat balance includes layer specific temperature trends for the study duration. The goodness of fit compared to temperature data confirms the utility of the model for the thermal regime and simulating the mixing of other constituents for mass balance processes.

² Water dependent terms refer to surface heat exchange components that are dependent on water temperature variability, whereas the other non-water dependent terms are independent forcing functions (Chapra, 2008)

Figure 3.1 Conceptual physical model of Lake Superior in LAKE2K segmented into 3 vertical layers (epilimnion, metalimnion, and hypolimnion). Top arrows (shaded) represent surface heat exchange sources and sinks that determine the heat balance of the system. White arrows represent turbulent diffusion, or mixing, between layers.

LAKE2K includes as state variables: carbon, nitrogen, oxygen, phosphorus, silica, and phytoplankton and zooplankton biomass. This current application of LAKE2K focuses on phosphorus and plankton with the latter represented as organic carbon. A mass balance for each constituent is performed for the epilimnion, metalimnion, and hypolimnion. The mass balances account for the sources and sinks of dissolved and particulate carbon and phosphorus concentrations and phytoplankton and zooplankton populations. The mass balance equations include algorithms describing kinetic and mass transfer processes and their related coefficients.

Carbon in LAKE2K is represented by phytoplankton-C, zooplankton-C, and detrital C (Figure 3.2a). The total phosphorus analysis is represented in three forms (DOP, detrital-PP, and SRP) in LAKE2K (Figure 3.2b). Algal growth and phosphorus cycling are interdependent processes, and perturbations of one state variable (e.g., through a kinetic coefficient) may have a strong reaction on the entire system. For example, SRP can be taken up by phytoplankton and thus transferred to the PP constituent. That PP can be transferred up the food chain through grazing, transferred to the detrital particulate phosphorus through death and settling (Chapra and Martin, 2004). Therefore, it is necessary to determine and use the correct kinetic or coefficient in this model, otherwise a process or pool within the cycle could be accelerated or limited, resulting in an inability of model output to fit well to observations.

Figure 3.2a Carbon cycle

Figure 3.2b Phosphorus cycle

Figure 3.2a and 3.2b Box and arrow diagram for carbon cycle (top) and phosphorus cycle (bottom) in LAKE2K indicating sources, sinks, and reactions

3.3 Model Inputs

LAKE2K requires user-inputs regarding the physical, chemical, and biological components of the lake. The model includes worksheets for numerical inputs of the system: volume, inflow/outflow, meteorological forcing conditions, vertical mixing, kinetic coefficients, initial conditions, and model execution specifications. Other data worksheets accept field data (Lake Superior station HN260) for the epilimnion, metalimnion, and hypolimnion for use in model calibration and confirmation.

3.3.1 Meteorological Forcing Conditions

Meteorological data input to LAKE2K includes daily measurements of air temperature, dew-point temperature, wind speed, cloud cover, atmospheric turbulence factor, precipitation rate, and average daily solar radiation. Photosynthetically active radiation, available to phytoplankton, represents 47% of solar radiation (Chapra and Martin, 2004). Meteorological data is used from a previous study that acquired and analyzed from sources including multiple NOAA offshore buoys and EPA open lake stations (Gawde, 2015). Hydrodynamic simulations using this data set proved an accurate representation of the impact of meteorological forcing conditions on vertical mixing in offshore waters in Lake Superior (Gawde, 2015). LAKE2K utilizes the meteorological data inputs to create a heat balance for the thermal layers based on surface heat exchange processes.

3.3.2 Vertical Mixing

LAKE2K accepts user-defined time series of vertical turbulent diffusion coefficients to simulate mixing across the epilimnion-metalimnion and metalimnion-

hypolimnion boundaries (Chapra and Martin, 2004). The magnitude of the diffusion coefficients reflects meteorological conditions and results in seasonal periods of mixing and stratification. Values for the diffusion coefficients are found by calibration to measure layer temperatures throughout the model duration. LAKE2K uses linear interpolation to calculate mixing between the user-inputted dates.

3.3.3 Kinetic Coefficients

Kinetic algorithms and coefficients are used to quantify energy and mass transfer processes for state variables. LAKE2K simulates net phytoplankton growth ($\text{gC}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$) as the difference between the gross maximum specific growth rate (a function of temperature, light and phosphorus availability) and losses to algal populations (respiration, death, settling, and zooplankton grazing) times the phytoplankton standing crop. Death is combined with the grazing term, as both deliver phytoplankton biomass to the detrital-phosphorus pool and the processes are not separable experimentally. This yields,

$$\frac{dC_{phyto}}{dt} = [\mu_{max,gross} \cdot f(T) \cdot f(I) \cdot f(P) - (R + S + G)] \cdot C_{phyto}$$

where dC_{phyto}/dt is the net rate of change in phytoplankton carbon concentration ($\text{gC}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$), $\mu_{max,gross}$ (1.30 d^{-1}) is the gross specific growth rate coefficient. $f(T, I, P)$ are dimensionless and normalized functions describing relative growth limitations by temperature, light and phosphorus. R , S , and G are the rate constants for respiration (0.02 d^{-1}), settling (0.03 m d^{-1}) and grazing (0.20 d^{-1} for herbivorous zooplankton; Chapra, 2008; Viera et al., 2013).

The temperature dependence of the gross specific growth rate coefficient is calculated using an optimum temperature sub-model. This algorithm, developed

specifically for the warm water phytoplankton assemblage within Lake Superior, has an optimum temperature of 13.3°C with fitting parameters (κ_1 , κ_2) of 0.02, describing the slope of the growth response above and below the optimal temperature (Dijkstra, 2015). Light limitation for phytoplankton growth is found through a sub-model using the Beer-Lambert law, which utilizes photosynthetically active radiation (47%) and light extinction coefficients (Chapra and Martin, 2004; Di Toro, 1978). These values are used within the Michaelis-Menten half-saturation light model to determine the phytoplankton growth attenuation and light parameter (Baly, 1935). Nutrient growth limitation also uses a sub-model that includes a Michaelis-Menten equation for SRP, which depends on both the concentration of the limiting nutrient, SRP, and the phosphorus half-saturation constant (Chapra and Martin, 2004). The half-saturation constant represents the nutrient concentration of SRP when growth is half the maximum rate (Chapra, 2008). The phosphorus half-saturation constant used in this study is 2.0 $\mu\text{gP}\cdot\text{L}^{-1}$ and is consistent with previous modeling studies in the Great Lakes (Table 3.1).

Phosphorus kinetics support the tracking of the dynamics of the SRP, DOP and PP pools. The phosphorus cycle in offshore Lake Superior is essentially a closed loop with phosphorus lost to the sediments and replaced by phosphorus transported offshore from nearshore waters that are impacted by river discharge. In a closed loop system of the phosphorus cycle, phosphorus enters the SRP pool through mineralization of DOP (0.03day^{-1} ; Imboden, 1974; Lung et al., 1976) and phytoplankton respiration (0.02 d^{-1}) and is lost through the SRP pool through phytoplankton uptake (Figure 3.2). Uptake of SRP occurs in proportion to the net specific growth rate,

$$\frac{dSRP}{dt} = -\frac{\frac{dC}{dt}}{C:P} \quad [2]$$

where C:P is the stoichiometric ratio of carbon to phosphorus in phytoplankton, used as a constant throughout modeling as 260:1 (molar basis). C:P ratios vary from 101:1 to 474:1 throughout the algal growing season in Lake Superior as phosphorus rich spring phytoplankton grow and distribute their stored phosphorus among new biomass in the phosphorus deficient lake (Dijkstra, 2015). However, the model does not accommodate seasonal C:P ratios, so an average is used. Limitations to this modeling method and its influence on algal- PP, measurements are discussed within the recommendations section.

Table 3.1: Comparison of LAKE2K plankton kinetics for Lake Superior with previous studies. **Settling velocity for Lake Superior (Chapra and Dolan, 2012)

<u>Phytoplankton Kinetics</u>	<u>LAKE2K L.Superior</u>	<u>Chapra L. Ontario</u>	<u>Fillingham L. Michigan</u>	<u>Units</u>
Max. Growth Rate	1.3	2.0	1.4	d ⁻¹
Respiration rate	0.015	0.025	0.05	d ⁻¹
Settling Velocity	0.027	0.04**	0.5	m·d ⁻¹
Death Rate	0	0	0.01	d ⁻¹
Phosphorus Half Saturation	2	2	3.1	µgP·L ⁻¹

Table 3.2: Comparison of LAKE2K plankton kinetics with Dijkstra (2015)

	<u>Dijkstra</u>	<u>LAKE2K</u>	<u>Units</u>
Growth	0.21 (net)	1.3 (max)	d ⁻¹
Topt	13.3	13.3	°C
Kappa 1	0.02	0.02	°C ⁻²
Kappa 2	0.02	0.02	°C ⁻²

3.3.4 Initial Conditions and Model Execution Specification

Selected system characteristics, e.g., latitude (47.7° N) and maximum depth at the sampling station (190 m) are set as a primary step in performing model runs. Inflows and outflows are zeroed for this 1D, offshore application to the essentially homogenous open

lake conditions of Lake Superior (Russ et al., 2004). Inflows and outflows may be included for future applications involving the nearshore influence, i.e. with riverine inputs. Initial conditions, including temperature, phosphorus and plankton concentrations are set to be consistent with data from the first day of sampling (HN260 on May 5, 2011). The epilimnion, metalimnion, and hypolimnion thicknesses are set at annual averages for the study period of 20.0 m, 15.0 m and 155.0 m, respectively, and remain at these positions for the entire simulation. An ability to accommodate time variable layer thickness may be desirable in some applications (see subsequent discussion). The model is run for the ice free season on Lake Superior with a time step of 0.1 day, for model run-time and calculating efficiency. Model results are generated on LAKE2K worksheets with model output (lines) compared to field measurements (points) for each layer.

4.0 Model Calibration

The adoption of a conceptual model and input of model coefficients and parameters sets the foundation for calibrating LAKE2K for Lake Superior in 2011. The calibration examines both physical (heat balance and thermal regime) and biogeochemical (phosphorus cycling and algal growth) features of ecosystem function in Lake Superior. Calibration is performed by adjusting model coefficients between previous research accepted bounds, seeking an appropriate fit of model output to field data over the May through November period of 2011.

4.1 Modeling Heat Flux

LAKE2K utilizes the meteorological data provided for 2011 to account for the various sources and sinks of heat within the lake and create a heat balance (Gawde, 2015). The model results, depicted in Figure 4.1, illustrate the losses and gains of heat throughout the system from May through November 2011. Heat gains during the spring and summer are due to a combination of atmospheric longwave radiation, solar shortwave radiation, and conduction. Heat is typically transferred to the lake through evaporation, although a small quantity of heat is also lost through evaporation during May, due to the cooler lake temperature that is only beginning to warm. The lake is consistently heated throughout the summer months through August. Heat is lost from the lake during late summer and continues throughout the fall season. Heat is primarily lost through evaporation, and to a lesser extent, conduction. The lake experiences its maximum heat loss through evaporation during September and October.

The LAKE2K results are consistent with the anticipated response of heat flux in the spring, summer, and fall in Lake Superior. The lake is experiencing a net gain of heat during spring and early summer. However, as summer progresses and the amount of solar radiation decreases, the lake experiences a net loss of heat and consequentially cools. The loss of heat is also evident in conduction and evaporation, both water dependent terms. Evaporation is a particularly significant heat loss term for a lake during fall and winter months (Blanken et al., 2011). The heat flux modeled by LAKE2K for 2011 represents a base for predicting the heat losses and gains within Lake Superior in response to changes, for example, climate anomalies (e.g., the Big Heat and Big Chill years of 2012 and 2014; Dijkstra, 2015).

Figure 4.1 LAKE2K modeled heat flux of Lake Superior 2011. Positive values indicate net gain of heat, negative values indicate net loss of heat in the system.

4.2 Modeling the Thermal Regime

LAKE2K output successfully tracks historical patterns of the thermal regime in Lake Superior as well as those for 2011 with little difference between the data and model predicted results (Bennett, 1978; Dijkstra, 2015). Additionally, the duration of thermal stratification for Lake Superior (typically four months) is well simulated (Austin and Coleman, 2008). This feature of the thermal regime plays an important role in evaluating climate change scenarios.

While the thermal regime of Lake Superior is well represented, conditions in the metalimnion are least accurately represented by LAKE2K. This is due to a limitation of the 3-layer model where LAKE2K uses set thicknesses for the epilimnion, metalimnion and hypolimnion for the entire study duration, i.e., it does not account for variability in the metalimnion thickness over the stratified period. It is well known and evident in data for Lake Superior in 2011 that the epilimnion undergoes thickening (migrates downward) over the stratified period as shear at the epilimnion-metalimnion boundary entrains metalimnetic waters (Barbiero and McNair, 1996; Dijkstra, 2015). With the position of the epilimnion-metalimnion boundary held constant (deepening not simulated), averaging of field data does not accurately represent conditions in the metalimnion for the entire modeled duration, i.e., epilimnetic water is included in the metalimnion average. Addition of layers to the model (e.g., $n = 100$) would better represent gradients in temperature within the metalimnion throughout the stratified period and yield a better fit to the data.

Figure 4.2 LAKE2K modeled thermal regime with data for Lake Superior 2011

Figure 4.3 Vertical diffusion coefficients at epi-meta and meta-hypo boundaries 2011

4.3 Modeling Algal Growth

Following the establishment of the well-simulated thermal regime and vertical mixing rates of Lake Superior within LAKE2K, modeling phytoplankton is addressed. LAKE2K can either model distinct classes of phytoplankton (e.g., diatoms, green algae) or can represent the whole natural plankton assemblage of Lake Superior, which is used in this simulation. Phytoplankton biomass is represented as particulate organic carbon (POC) due to the absence of other sources of POC found in Lake Superior offshore (Sterner, 2010; Urban et al., 2005). The use of measuring POC, rather than chlorophyll, avoids complications related to shade adaptation where POC remains constant, but algal-chlorophyll increases in low light environments (Munawar and Munawar, 1978; Nalewajko et al., 1981). Algal growth in LAKE2K is modeled as a function of temperature, light, and phosphorus availability (see LAKE2K Conceptual Model above). For temperature, kinetic coefficients are representative of the Lake Superior warm water plankton assemblage (Dijkstra, 2015). Light availability is quantified based on measurements of incident light (meteorological forcing conditions) and light parameters in the water column (user-specified extinction coefficients). Phosphorus availability at the start of the simulation is specified as an initial condition.

LAKE2K model output for phytoplankton-carbon is consistent with observations, particularly for the epilimnion and hypolimnion (Figure 4.4). The less satisfactory fit in the metalimnion (under prediction) likely reflects the accumulation of phytoplankton in that layer from depth-variable settling velocities. The layers initially have uniform

concentrations of phytoplankton-carbon due to the high mixed state of the system during the pre-stratified period (May through the end of June). Phytoplankton growth is limited during this time due to lack of available sunlight (extensive mixing depth) and low lake temperatures (Nalwajko et al., 1981, Nalwajko and Voltino, 1986). Algal populations have sufficient levels of phosphorus at this time, because light and temperature conditions are limiting growth. With the onset of thermal stratification in July, epilimnetic temperatures warm (Figure 4.2) and the mixing depth is significantly reduced. Phytoplankton retained in the metalimnion and hypolimnion at the onset of stratification settle to the lake bottom where light conditions are unfavorable for growth.

Phytoplankton in the epilimnion increase steadily following the onset of stratification, reaching a maximum in August (Figure 4.4). While light availability remains favorable throughout the stratified period, temperatures eventually exceed the optimum (13.3 °C) and phosphorus resources are depleted through uptake and settling during the growth season. Model output predicts a gentle decline in phytoplankton biomass with the approach to turnover. Throughout October, phytoplankton population reach similarity, signaling the beginning of mixing and reach uniform concentrations in November, following turnover. LAKE2K accurately models phytoplankton-carbon in the stratified period, as populations increase following stratification and as growth slows in mid and late summer (the “summer desert”). The model performs less well at turnover, represented at the outlier epilimnion data point in October, failing to capture elevated observed POC level, likely evolving from resuspension of plankton trapped in the deep chlorophyll maximum (layer with phytoplankton communities containing heightened concentrations of

chlorophyll; Barbiero and Tuchman, 2004) and benthic nepheloid layer (found directly above bottom sediments containing large concentrations of suspended solids, composed heavily of organic carbon; Urban et al., 2004); two features not accommodated in this 3-layer version of LAKE2K.

Figure 4.4 LAKE2K modeled phytoplankton growth and Lake Superior data 2011

4.4 Modeling Phosphorus Cycling

Phosphorus cycling in LAKE2K is modeled for each of the three layers over the May through November interval of 2011 as total phosphorus and its components (SRP, DOP, and PP). SRP is the targeted phosphorus form, due to its role as the limiting nutrient in Lake Superior and its strong connection with algal populations. Because it is the bioavailable form of phosphorus that is necessary for growth, SRP trends are representative of phytoplankton growth.

SRP levels are similarly low (near the limit of detection) in the three layers during the mixed pre-stratification period (Figure 4.5). SRP levels increase in all three layers as the system approaches stratification in early July, maintaining comparable concentrations, but less similar than during pre-stratification. Summer SRP depletion is a striking feature of the phosphorus cycle in Lake Superior (Figure 4.5). SRP depletion coincides with phytoplankton growth as uptake of SRP increases in the relatively warm, well-lit waters of the epilimnion. Subsequent settling of the resulting PP (phytoplankton) removes phosphorus from the surface layer, and limited vertical mixing (thermal stratification) and distance from nearshore (allochthonous sources; Sterner, 2010) inhibits recirculation of phosphorus. Juxtaposition of model results for phytoplankton carbon with those for SRP (Figure 4.6) confirms the ability of this application of LAKE2K to simulate the phenomenon. Increases in SRP in the metalimnion and hypolimnion may be due to solubilization of PP and hydrolysis of DOP during phytoplankton settling (Baines et al., 1994).

Figure 4.5 LAKE2K modeled SRP and data from Lake Superior 2011

Figure 4.6 Model comparison of epilimnion SRP and phytoplankton

In the open waters of Lake Superior, PP represents phosphorus found stored in plankton. The model illustrates PP at uniform concentration during the mixed period (Figure 4.7). With a limited amount of phosphorus in the water column, data exhibit a parabolic shape reflecting a decrease throughout the summer season from settling and, in the epilimnion, an increase during late summer and early fall due to resuspension and mixing of phosphorus from the deep chlorophyll and benthic nepheloid layers. LAKE2K model results for PP are low, compared with data from Lake Superior throughout 2011. The low concentration of PP is due to a modeling parameter that LAKE2K employs and is addressed within the model limitations and further studies sections.

Figure 4.7 LAKE2K modeled PP and data from Lake Superior 2011

TDOP represents the non-reactive form of phosphorus within Lake Superior (Baehr and McManus, 2003). The data illustrates similar concentrations of TDOP within the epilimnion and hypolimnion (Figure 4.8). The modeled results for TDOP display uniform concentrations throughout the lake profile, with a slight increase in concentration within the epilimnion and a small decrease within the hypolimnion during the height of stratification. Increases in TDOP are a result of increased solubilization from the PP pool. Although the model results do not implicitly follow the increasing and decreasing periods of TDOP, the overall trend of DOP in offshore Lake Superior is consistent with previous studies from Baehr and McManus (2003), showing little variation both over the summer and within the vertical lake profile.

The final phosphorus cycle component modeled with LAKE2K for Lake Superior is TP and includes the phosphorus components of the previously modeled SRP, PP, and TDOP (Figure 4.9). LAKE2K models the average concentrations of TP within the epilimnion, metalimnion, and hypolimnion with little spatial or temporal variation throughout the study duration. The only distinction between the model results layers is during August through September, representing the maximum period of thermal stratification in Lake Superior. Variation within the TP modeled results and data is due to the underestimation of PP that is addressed within the model limitations section.

Figure 4.8 LAKE2K modeled TDOP and data from Lake Superior 2011

Figure 4.9 LAKE2K modeled TP and data from Lake Superior 2011

5.0 Model Confirmation

Following modeling Lake Superior within LAKE2K for 2011, the model can be adapted and applied for another year to confirm the modeled results. Here, LAKE2K is used for modeling phosphorus cycling and phytoplankton carbon in Lake Superior in 2012, considered an extremely warm year (Dijkstra, 2015). Adapting LAKE2K for 2012 begins with adding field data from the same station, HN260, for the new study period. In 2012, field sampling occurred from April 4, 2012 through October 13, 2012; the model is set to run for this study period, and uses the data for initial conditions. The meteorological data used for LAKE2K in the 2011 application is a portion of a larger dataset that includes information for 2012 (Gawde, 2015). Vertical diffusion coefficients are adjusted to fit the 2012 thermal regime for model confirmation (Figure 5.1 and Figure 5.2). LAKE2K then models Lake Superior for 2012, using the same volume, inflows/outflows, light and heat parameters, and kinetics as 2011. In doing so, the modeled results can be confirmed for a year with different forcing conditions than the one used for calibration, but with no change in kinetics. Confirmation focuses on algal-growth (carbon) and SRP, two features well simulated for Lake Superior in 2011.

LAKE2K modeled results regarding the thermal regime for 2012 display an earlier onset of thermal stratification during the summer season than in the average seasonal conditions year (2011), with stratification beginning in June as opposed to July (Figure 4.2 and Figure 5.1). The influence of an earlier stratification period, as expected in a year with warmer temperatures, on phytoplankton and phosphorus can then be modeled.

Figure 5.1 LAKE2K modeled thermal regime and data for Lake Superior confirmation 2012

Figure 5.2 Vertical diffusion coefficients at epi-meta and meta-hypo boundaries for 2012

LAKE2K model results for both phytoplankton-carbon and SRP are depicted in Figures 5.3 and 5.4. Figure 5.3 displays model results for phytoplankton-carbon measurements, compared with data collected from the epilimnion of Lake Superior during 2012. The model results illustrates the lake as mixed, with uniform concentrations of phytoplankton throughout the mixing period. The lake begins to display disassociation of phytoplankton concentrations in June, indicating the onset of thermal stratification. The model then over predicts the concentration of phytoplankton throughout July and August, before trending to a mixed period at the end of the modeled duration. Although the model results are not entirely similar with field data from 2012, the initial concentration of modeled phytoplankton is consistent with data, during the beginning of thermal stratification, on June 26, 2012.

LAKE2K model results for SRP in Lake Superior during 2012 are illustrated in Figure 5.4. Similar to phytoplankton populations, the model indicates a mixed period within the system from the beginning of the model duration through May. In June, the lake begins to thermally stratify, signaling phytoplankton populations to uptake SRP for growth. The decreasing concentrations of SRP correlates with increasing phytoplankton populations in Figures 5.3 and 5.4, indicating the relationship between phosphorus and algal growth. The SRP pool is depleted throughout thermal stratification, with a sharp decrease from June 26 – July 19, 2012. SRP concentrations begin to reach similar concentrations at the end of the model duration, indicating the system approaching a mixed period and fall turnover.

2012 in Lake Superior is referred to as the “big heat” (Dijkstra, 2015). Comparing LAKE2K model results for 2011, a year with average temperature conditions, with 2012,

a year with above average temperatures, gives insight to the model application for further studies, particularly in regards to climate change scenarios. The model results displays an earlier thermal stratification period in Lake Superior, which is consistent with expected results with warm weather conditions. The earlier onset of thermal stratification influences both the phytoplankton population and phosphorus pools, particularly SRP. Because phytoplankton populations grow earlier in the summer season compared to a typical Lake Superior year, the phosphorus pool is depleted earlier in the growing season. The depletion of SRP creates a “summer desert” effect, consistent with the modeled and expected results in 2011 (Dijkstra, 2015).

Figure 5.3 LAKE2K model confirmation phytoplankton 2012

Figure 5.4 LAKE2K model confirmation results for SRP 2012

6.0 Modeling Limitations

LAKE2K provides a user friendly modeling system suitable for application to lakes that thermally stratify. The model is successfully adopted here to represent trends in temperature, phosphorus, and algal carbon in Lake Superior. In its present form the model is designed to simulate a 3-layer system. This approach fails to accommodate certain phenomena important in reproducing water column dynamics, e.g.:

- thermocline migration and deepening of the epilimnion throughout the beginning of the stratification period; this feature, which leads to misrepresentation of metalimnetic constituent concentrations, could be improved through adoption of temporal variable layer thicknesses
- accumulation of particles in the deep chlorophyll and benthic nepheloid layers; the additional layers in the metalimnion and hypolimnion would support development of a pool of particles (carbon and phosphorus) supplying material for fall resuspension, as observed in the data.

Accommodation of these recommendations could be accomplished through development of a more finely segmented multi-layered version of LAKE2K that would provide greater insight regarding phosphorus and plankton variability in the water column. The expansion of LAKE2K into an increased number of layers, e.g. $n=100$, may include variations of layer thicknesses to more accurately represent surface layer processes. Additionally, layer-specific kinetics could be accommodated to account for the influences of temperature on depth-variable rates, such as DOP mineralization.

Presently, LAKE2K underestimates PP concentrations, and consequentially TP, due to not accounting for seasonal variation in stored algal-phosphorus within Lake Superior. Separating the PP state variable into two parts, one including terrigenous and detrital PP and the other algal-PP would permit better simulation of particulate phosphorus by,

- accommodating allochthonous sourced phosphorus, an important consideration in the nearshore of lakes where riverine inputs are received, and detrital phosphorus, a form important in P-cycling but not available for driving growth
- permitting simulation of growth driven by internal stores using the Droop function (1974), i.e. C:P ratios; a feature known to be of significance in Lake Superior (Dijkstra, 2015).

By using the Droop function to simulate stored algal-phosphorus, observed variations in seasonal C:P ratios better reflect algal-PP and potential for algal growth. Significant differences in C:P ratios reflect elevated stored-PP abundance in spring and early summer, and lower quantities in late summer leading to the summer desert phenomenon in Lake Superior (Dijkstra, 2015). Although all models contain some error, improving LAKE2K with the aforementioned suggestions would increase model accuracy and consistency for future applications and would reduce modeling limitations discovered during this study.

7.0 Conclusion

Among the global climate change impacts currently facing the world and its many ecosystems, Lake Superior is an excellent example of a system especially vulnerable to changes in atmospheric and lake temperatures (Austin and Colman, 2007; Williamson et al., 2009). Therefore, having a calibrated and confirmed model to simulate perturbations to the system will allow for a greater understanding for scientists, policy makers, and the public regarding the response of Lake Superior to these changes.

This study represents multiple efforts related to modeling temporal variations in Lake Superior utilizing LAKE2K, a 3-layer surface water quality model. The foundation for modeling Lake Superior is set through the simulation of the annual thermal regime. LAKE2K is then used to model the biogeochemical processes related to phosphorus cycling (SRP, DOP, PP) and algal growth (carbon) seeking consistency with observations. The use of model inputs, forcing conditions, and kinetic coefficients, results in output that represents the magnitude and timing of dynamics in the thermal regime and biogeochemical cycles.

The research questions are addressed and answered through the successful calibration of LAKE2K during 2011, a year with average climatic conditions, and is confirmed for 2012, a year representing a warm climatic anomaly. Additionally, the calibrated model, to model trends in algal growth and phosphorus cycling. Calibration and confirmation were performed for the thermal regime, phytoplankton growth and SRP in offshore Lake Superior. Although the target phosphorus component (SRP) was modeled successfully for 2011 and 2012, limitations when simulating other forms of phosphorus

(PP, DOP). Improvements to modeling these forms of phosphorus are discussed with the recommendations and include expanding LAKE2K into a more finely segmented multi-layered model, along with adopting the Droop function to accommodate changes in stored algal-phosphorus and their impact on growth. These suggestions for LAKE2K will improve accuracy and consistency of modeled results. The calibrated model can then be used efficiently as a test bed in further studies regarding the response of Lake Superior to perturbations in the lake due to climate change.

References

- Auer, M.T., Kieser, M.S., and Canale R.P. 1986. Identification of critical nutrient levels through field verification of models for phosphorus and phytoplankton growth. *Canadian Journal of Fisheries and Aquatic Sciences* 43.2, 379-388.
- Austin, J.A. and., and Colman, S.M., 2007. Lake Superior summer water temperatures are increasing more rapidly than regional air temperatures: A positive ice-albedo feedback. *Geophysical Research Letters* 34.6
- Austin, J.A. and., and Colman, S.M., 2008. A century of temperature variability in Lake Superior. *Limnology and Oceanography* 53.6, 2724-2730.
- Baehr, M.M., McManus, J. 2003. The Measurement of Phosphorus and Its Spatial and Temporal Variability in the Western Arm of Lake Superior. *Journal of Great Lakes Research* 29, 479-487.
- Baines, S. B., Pace, M.L., and Karl, D.M., 1994. Why does the relationship between sinking flux and planktonic primary production differ between lakes and oceans? *Oceanography* 39.2
- Barbiero, R.P., and McNair, C.M., 1996. The dynamics of vertical chlorophyll distribution in an oligomesotrophic lake. *Journal of plankton research* 18.2, 225-237.
- Barbiero, R.P., and Tuchman, M.L., 2004. The deep chlorophyll maximum in Lake Superior. *Journal of Great Lakes Research* 30, 256-268.
- Bennett, E.B., 1978. Characteristics of the thermal regime of Lake Superior. *Journal of Great Lakes Research* 4.3, 310-319.
- Bennington, V., McKinley, G.A., Kimura, N. and Wu, C.H., 2010. General circulation of Lake Superior: Mean, variability, and trends from 1979 to 2006. *Journal of Geophysical Research: Oceans* 115(C12)
- Blanken, P.D., Spence, C., Hedstrom, N. and Lenters, J.D., 2011. Evaporation from Lake Superior: 1. Physical controls and processes. *Journal of Great Lakes Research* 37.4, 707-716.
- Brady, D.K., Graves, W.L. and Geyer, J.C., 1969. Surface heat exchange at power plant cooling lakes.
- Chapra, S.C., 1977. Total phosphorus model for the Great Lakes. *Journal of the Environmental Engineering Division* 103.2, 147-161.
- Chapra, S.C., 2008. Surface water-quality modeling. Waveland press.

- Chapra, S. C. and Dolan, D.M., 2012. Great Lakes total phosphorus revisited: 2. Mass balance modeling. *Journal of Great Lakes Research* 38.4, 741-754.
- Chapra, S. C., and Martin, J.L., 2004. LAKE2K: A Modeling Framework for Simulating Lake Water Quality (Version 1.2): Documentation and Users Manual. Civil and Environmental Engineering Dept., Tufts University, Medford, MA
- Chapra, S.C. and Sonzogni, W.C., 1979. Great Lakes total phosphorus budget for the mid 1970s. *Journal (Water Pollution Control Federation)* 2524-2533.
- Di Toro, D.M., 1978. Optics of turbid estuarine waters: approximations and applications. *Water research* 12.12, 1059-1068.
- Dijkstra, Marcel L. Climate anomalies and primary production in Lake Superior. Dissertation, 2015.
- Droop, M.R., 1974. The nutrient status of algal cells in continuous culture. *Journal of the Marine Biological Association of the United Kingdom* 54: 825–855.
- Eisenreich, S.J., Looney, B.B., Thornton, J.D., 1981. Airborne organic contaminants in the Great Lakes ecosystem 15.1, 30-38.
- Fillingham, J.H., 2015. Modeling Lake Michigan Nearshore Carbon and Phosphorus Dynamics Paper 871.
- Gawde, R.K., 2015. Application of hydrodynamic models in simulating the thermal regime of Lake Superior.
- Hutchinson, G. E., 1957. A Treatise on Limnology, Vol. 1, Geography, Physics. Chemistry. New York: John Wiley & Sons, Inc
- Imboden, D.M., 1974. Phosphorus model of lake eutrophication. Swiss Federal Institute for Water Resources and Water Pollution Control
- Lenters, J.D., 2004. Trends in the Lake Superior water budget since 1948: A weakening seasonal cycle. *Journal of Great Lakes Research* 30, 20-40.
- Lung, W.S., Canale, R.P., Freedman, P.L., 1976. Phosphorus models for eutrophic lakes. *Water Research* 10.12, 1101-1114.
- Magnuson, J.J., Webster, K.E., Assel, R.A., Bowser, C.J., Dillon, P.J., Eaton, J.G., Evans, H.E., Fee, E.J., Hall, R.I., Mortsch, L.R. and Schindler, D.W., 1997. Potential effects of climate changes on aquatic systems: Laurentian Great Lakes and Precambrian Shield Region. *Hydrological processes* 11(8), 825-871.
- Matheson, D.H., and Munawar, M., 1978. Lake Superior basin and its development. *Journal of Great Lakes Research* 4.3, 249-263

- Munawar, M., Munawar, I.F., 1978. Phytoplankton of Lake Superior 1973. *Journal of Great Lakes Research* 4, 415–442.
- Nalewajko, C., Lee, K., and Shear, H., 1981. Phosphorus kinetics in Lake Superior: light intensity and phosphate uptake in algae. *Canadian Journal of Fisheries and Aquatic Sciences* 38.2, 224-232.
- Nalewajko, C., and D. Voltolina, D., 1986. Effects of environmental variables on growth rates and physiological characteristics of Lake Superior phytoplankton. *Canadian Journal of Fisheries and Aquatic Sciences* 43.6, 1163-1170.
- Reynolds, C. S., and Davies, P.S., 2001. Sources and bioavailability of phosphorus fractions in freshwaters: a British perspective. *Biological reviews* 76.1, 27-64.
- Russ, M.E., Ostrom, N.E., Gandhi, H., Ostrom, P.H. and Urban, N.R., 2004. Temporal and spatial variations in R: P ratios in Lake Superior, an oligotrophic freshwater environment. *Journal of Geophysical Research: Oceans* 109(C10)
- Scavia, D., 1979. Examination of phosphorus cycling and control of phytoplankton dynamics in Lake Ontario with an ecological model. *Journal of the Fisheries Board of Canada* 36.11, 1336-1346.
- Schlesinger, W. H. and Bernhardt, E.S., 2013. *Biogeochemistry: An Analysis of Global Change*. Third Edition. Academic press
- Sterner, R.W., 2010. In situ-measured primary production in Lake Superior. *Journal of Great Lakes Research* 36.1, 139-149.
- Sterner, R.W., Smutka, T.M., McKay, R.M.L., Xiaoming, Q., Brown, E.T. and Sherrell, R.M., 2004. Phosphorus and trace metal limitation of algae and bacteria in Lake Superior. *Limnology and Oceanography* 49.2, 495-507.
- Thomann, R.V., 1975. *Mathematical modeling of phytoplankton in Lake Ontario (Vol. 1)*. National Environmental Research Center
- Urban, N.R., 2009. *Nutrient cycling in Lake Superior: a retrospective and update*. State of Lake Superior. New Delhi: Goodword Books, 83-115.
- Urban, N.R., Auer, M.T., Green, S.A., Lu, X., Apul, D.S., Powell, K.D. and Bub, L., 2005. Carbon cycling in Lake Superior. *Journal of Geophysical Research: Oceans* 110(C6).
- Urban, N.R., Jeong, J. and Chai, Y., 2004. The benthic nepheloid layer (BNL) north of the Keweenaw Peninsula in Lake Superior: composition, dynamics, and role in sediment transport. *Journal of Great Lakes Research*. 30, 133-146.

Vieira, J.M.P., Pinho, J.L.S., Dias, N., Schwanenberg, D. and van den Boogaard, H.F.P., 2013. Parameter estimation for eutrophication models in reservoirs. *Water Science & Technology* 68.2.

Vincent, W.F., 2009. Effects of climate change on lakes. *Encyclopedia of inland waters*. Elsevier, 55-60.

Williamson, C.E., Saros, J.E., Vincent, W.F. and Smold, J.P., 2009. Lakes and reservoirs as sentinels, integrators, and regulators of climate change. *Limnology and Oceanography* 54.6.2, 2273-2282.

Zepp, R.G., Erickson III, D.J., Paul, N.D. and Sulzberger, B., 2007. Interactive effects of solar UV radiation and climate change on biogeochemical cycling. *Photochemical & Photobiological Sciences* 6.3, 286-300.