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Dissolved Oxygen Dynamics and Modeling - A Case Study in A Subtropical Shallow Lake

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DISSOLVED OXYGEN DYNAMICS AND MODELING - A CASE STUDY IN A SUBTROPICAL SHALLOW LAKE

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ABSTRACT

As one of the most valued and treasured natural resources, today many lakes in the world face degradation of their water quality due to nutrient enrichment, toxic contamination, and hydrological modification from their drainage areas. Among various water quality impairments, dissolved oxygen (DO) depletion is often a leading stressor in lake systems. Despite numerous studies on DO in deep water lakes in temperate regions, the knowledge of DO dynamics in eutrophic shallow lakes in subtropical regions is still limited. This thesis research conducted intensive DO monitoring in an eutrophic shallow lake in south Louisiana to characterize diel cycles of DO to determine trophic state changes, develop a deterministic model that can predict hourly change in DO of a water body with high-time resolution weather parameters, and develop a rapid field method of predicting biochemical oxygen demand (BOD) using chlorophyll-*a* fluorescence. DO concentrations in the studied lake were recorded at 15-minute intervals during 2012-2014, along with other water quality parameters. Field trips were made to measure lake water fluorescence and collect water samples for BOD and nutrient analysis. Additionally, a comparative study was done to discern trophic state changes over the past 5 years. The research yielded a substantial set of findings and conclusions to the research questions initially proposed. A comparison of diel DO cycles between 2008-2009 and 2013-2014 successfully revealed a clear intensification of eutrophication in the studied lake, indicating that analyzing the change in diel DO ranges can improve the current methods for classifying trophic states and assessing the change of eutrophication status of water bodies. A one-dimensional, deterministic DO model was developed for estimating the hourly change of source and sink components of DO, such as photosynthesis, re-aeration, respiration, BOD and sediment oxygen demand. The modeling yielded successful results of simulating high-time fluctuation of DO in the studied lake overall

and showed good predictability for extreme algal bloom events. There was a linear, positive relationship between chlorophyll *a* fluorescence and BOD, and the relationship appeared to be stronger with the 10-day BOD ($r^2 = 0.83$) than with the 5-day BOD ($r^2 = 0.76$).

CHAPTER 1: INTRODUCTION

Lakes are highly valued for their recreational, aesthetic, and scenic qualities, and the water they contain is one of the most treasured of our natural resources (Garn et al., 2003). At the same time, many lakes are important habitats and food resources for a variety of aquatic species, hence for human and wildlife as well. Lakes are often a fragile system whose ecosystems can undergo rapid environmental changes when exposed to external stressors from the atmosphere, their watersheds, groundwater, and, most importantly, anthropogenic effects (Garn et al., 2003). Today, in the United States, about 44% of all lakes and 59% of man-made lakes are classified to be in fair or poor biological conditions (USEPA, 2009) resulting from oxygen depletions in water columns.

Oxygen is needed for aquatic life and the amount of oxygen dissolved in a water body is, therefore, an important water quality parameter. Low dissolved oxygen (DO) has been identified as a serious water quality problem (Caraco and Cole, 2002). When DO declines below 5 mg L^{-1}, sensitive species of fish and invertebrates can be negatively impacted, and at DO levels below 2 mg L^{-1}, an oxygen depletion stage known as hypoxia, most fish species could be negatively impacted (Frodge et al., 1990). Hypoxia in water bodies is a growing problem worldwide that is associated with negative impacts on not only sensitive species of fish and invertebrates, but also on metal, nitrogen, and phosphorus transformations (Kemp et al., 1990; Breitburg, 1992; Hamilton et al., 1997; Gray et al., 2002; Harrison et al., 2005; Stevens et al., 2006). Therefore, DO levels are commonly used as a key indicator of the health of a water body.

Due to its significance in aquatic community, dissolved oxygen has been monitored by many agencies and groups for causes of and solutions to dissolved oxygen depletion for lake

systems. In the past several decades, studies have applied real time monitoring (Markogianni et al., 2014), phytoplankton activities (Oliva Martinez et al., 2008; Alves-da-Silva et al., 2013), nutrients transformations (Guo et al., 2012), aquatic vegetation management (Morris et al., 2003; Morris et al., 2004), and so on. However, many DO studies have only limited point-by-time measurements whereas field data are usually collected at insufficient time interval. Some studies have found that strongly eutrophicated lakes often have DO saturation and/or DO super-saturation during the daytime, resulting in an overall higher average DO when compared to healthier lakes (Matthews et al., 2006; O'Boyle et al., 2013). This indicates that comparison of point-by-time measurements of DO may not be a good approach for determining water quality changes.

Over the last two decades modeling studies have been intensified to predict DO changes. Specifically, DO modeling for lake systems is becoming more and more significant because many lakes are strongly affected by anthropogenic stressors including modified inflow due to land use change, inputs of various pollutants and contaminants, overexploitation, invasive species, and climate change (Mooij et al., 2010). However, modeling efforts on DO dynamics in subtropical lakes is very limited, especially for those that are shallow, eutrophic suffering periodic and/or episodic hypoxia. Beyond that, most DO models are not able to predict DO dynamics in a high-time resolution (i.e. hourly), which further limits their application for eutrophic/hyper-eutrophic shallow water bodies that often suffer from sporadic algal blooms. Eutrophic water bodies are phytoplankton-rich, and a sudden algal bloom leads to severe oxygen depletion killing fish and other sensitive organisms. This is especially the case for shallow lakes in tropical and subtropical regions, where the climatic and anthropogenic environments can accelerate eutrophication of waters. DO levels in eutrophic lakes in warm regions have been

found to fluctuate rapidly during the day, declining from oversaturation to hypoxia within a few hours (Yin et al., 2004). Prediction of DO dynamics in a high time resolution can be a useful tool for both scientific research and practical management of lakes and reservoirs. For instance, a good hourly model could provide important information to managers about the probable effectiveness of various remedial actions at affordable costs (Pena et al., 2010).

The main reason for lake water quality degradation and related oxygen depletion has been attributed to excess nutrients and organic inputs and production to the lake water bodies, leading to eutrophication and organic pollution. On the one hand, as one of the world's most serious environmental problems, eutrophication is especially widespread in lake systems. It causes oxygen depletion in water columns, affecting aquatic communities, food web, and biodiversity (Moustaka-Gouni et al., 2006; Markogianni et al., 2014). On the other hand, organic pollution could also adversely affect the health of the aquatic system by consuming a large amount of dissolved oxygen in water, resulting in hypoxic conditions. Therefore, except for direct measurements and simulations for dissolved oxygen dynamics, issues leading to oxygen depletion, like eutrophication and organic pollution, have also attracted a lot of attention.

To assess eutrophication, health conditions of lakes are often evaluated by their trophic states that generally indicate the biological production, both aquatic plant and animal life, that occurs in them. Various indicators have been used in the past to describe trophic state. As one of the most popular methods, Carlson (1977) developed a Trophic State Index (TSI) using algal biomass as the basis for trophic state classification, in which three attributes (the concentrations of chlorophyll *a*, total phosphorus, and water clarity normally given as Secchi disk transparency) are used to estimate algal biomass. Although being widely used, existing evaluating criteria for trophic states, like Carlson's TSI, have been reported with limitations in many studies (An and

Park, 2003; Santhanam et al., 2011), especially in shallow water bodies (Joniak et al., 2009; Santhanam and Amal Raj, 2011). Considering that most concerns regarding the change of trophic state and eutrophication are on DO (Rabalais et al., 2002; Kemp et al., 2005; Diaz and Rosenberg, 2008), however, DO is rarely considered in trophic state determination.

Organic consumption of dissolved oxygen in an aquatic system is normally presented as biochemical oxygen demand (BOD). BOD measures the amount of oxygen consumed within a certain period of time by bio-degradable organic matter in a water column. Therefore, BOD is an important parameter frequently used in assessment of water quality, as well as for developing management strategies for water quality protection (Basant et al., 2010). BOD measurements are commonly given as a 5- to 20-day test, with a 5-day test at a standard temperature of 20 °C being the most common period, also known as BOD_5. As a laboratory based biodegradation test, it delays analysis of potential pollution events. If BOD can be estimated rapidly using a real time monitoring technique, it would be of great usefulness to environmental regulators and resource managers in predicting the degree of organic pollution and taking prompt actions.

Many urban water bodies are monitored by local communities and volunteers. A rapid BOD testing method can be not only time- and cost-saving, but it offers a tool for predicting potential oxygen depletion. Several recent studies have used fluorescence techniques as a portable tool for rapid determination of the presence of biodegradable organic matter. It is a rapid testing technique that does not use chemical reagents and requires little sample preparation (Hudson et al., 2008). In the recent decade, studies have been conducted on the relationship between BOD_5 and tryptophan-like fluorescence ($\lambda_{excitation}$ = 280 nm, $\lambda_{emission}$ 350 nm) for waters collected from rivers (Comber et al., 1996; Baker and Inverarity, 2004; Hudson et al., 2008), sewage (Comber et al., 1996; Reynolds and Ahmad, 1997; Ahmad and Reynolds, 1999;

Reynolds, 2002; Baker and Curry, 2004; Hudson et al., 2008) and industrial effluents (Comber et al., 1996; Hudson et al., 2008). However, to our knowledge, no report exists on a numeric relation between BOD and field chlorophyll *a* fluorescence ($\lambda_{excitation}$ = 460 nm, $\lambda_{emission}$ 685 nm) measurements.

This thesis research was conducted at University Lake on the campus of Louisiana State University (Latitude 30°24’50”N; Longitude 91°10’00”W) in Baton Rouge, Louisiana, USA (Figure 1.1). The lake is a 76-ha shallow lake in a highly developed urban area. It receives runoff from a 187.4-ha watershed with a small drainage ditch in the north, a dozen of storm drains around the lake shore, and direct surface runoff from the surrounding area. The lake has an outlet weir located at the south edge (Figure 1.1). The gate was raised 20 cm during 2010-2012 (Figure 1.2).

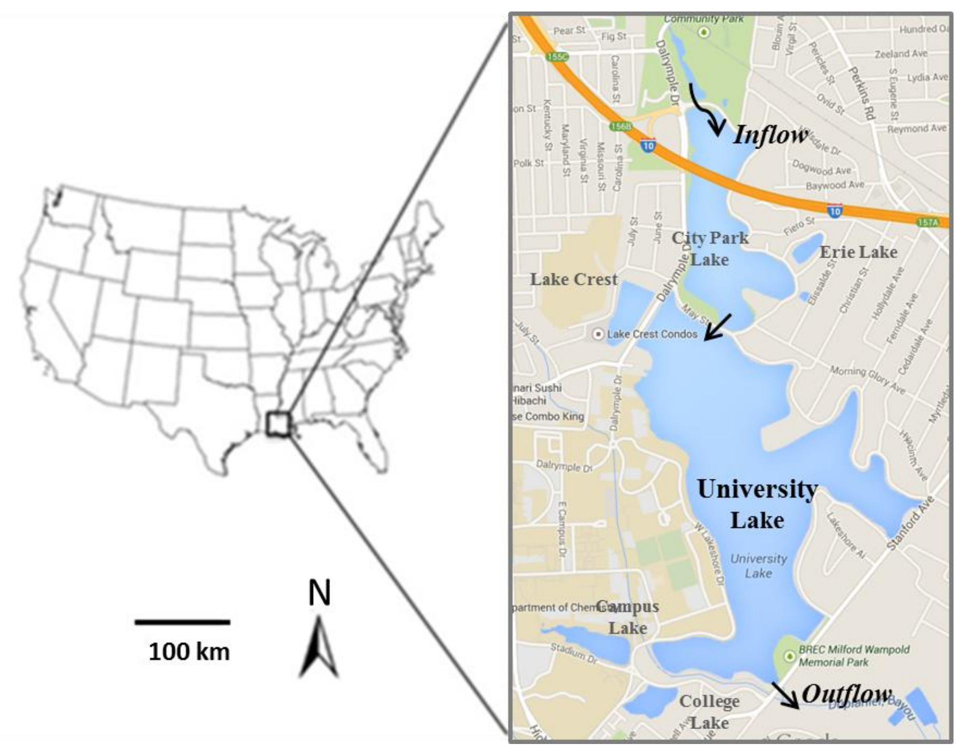

Figure 1.1 Geographical location of University Lake in Baton Rouge, Louisiana, USA and its inflow and outflow.

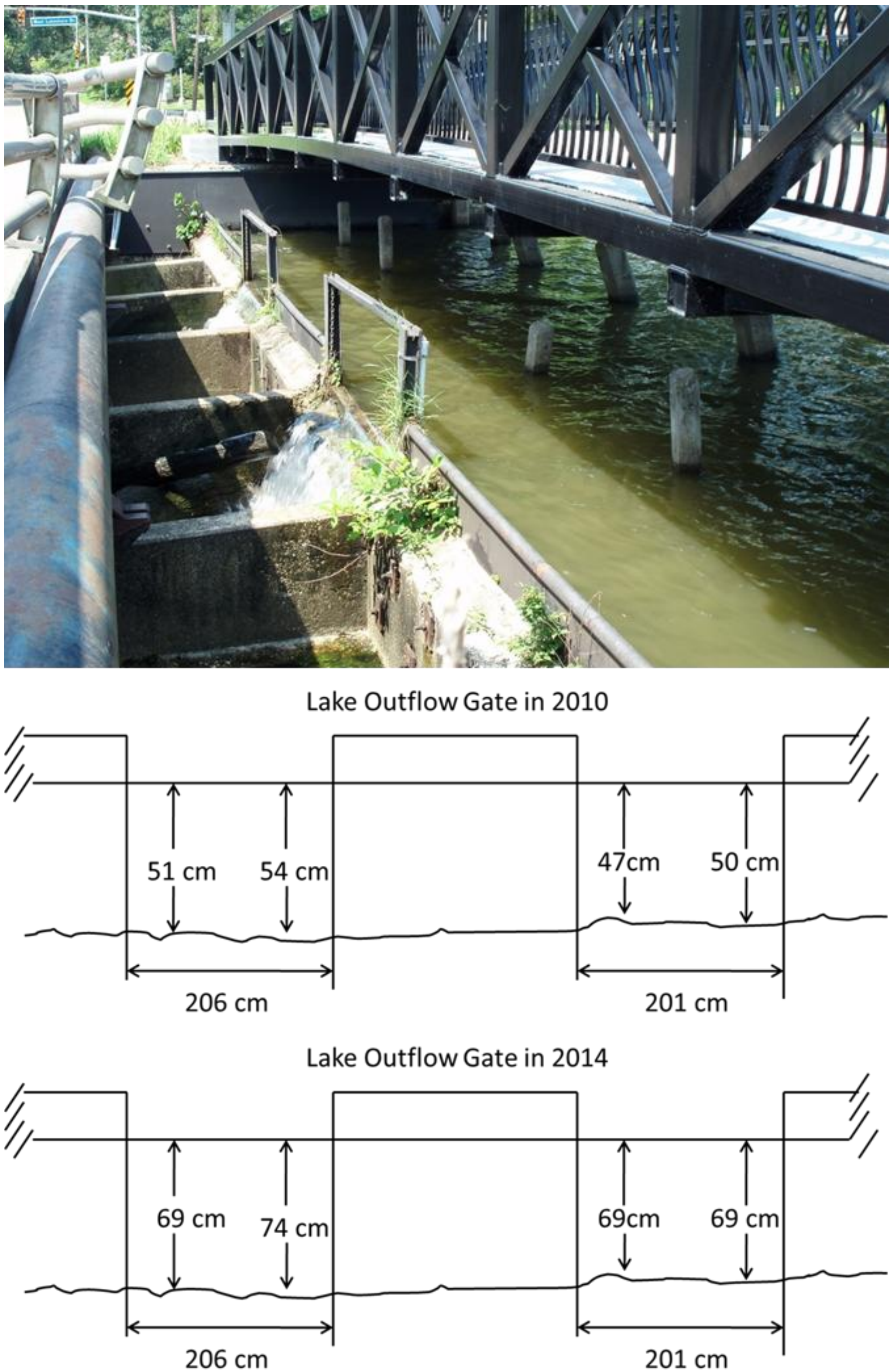

Figure 1.2 The gate at outflow of University Lake (above) and its height measured in 2010 and 2014. Photo courtesy of Y. Jun Xu.

The objectives of the research were to 1) characterize diel cycles of DO and utilize it to determine the change in trophic state and water quality; 2) develop a deterministic model that can predict hourly change in DO of a water body with high-time resolution weather parameters; and 3) develop a rapid field method of predicting BOD using chlorophyll *a* fluorescence. An environmental monitoring buoy (Figure 1.3b) and pressure transducer (Figure 1.3c) were deployed in the studied lake recording DO and water levels at 15-minute intervals. Biweekly water samples were collected to analyze BOD and nutrient concentrations (Figure 1.3d), while field measurements on fluororescene were done. Research findings and discussions towards the

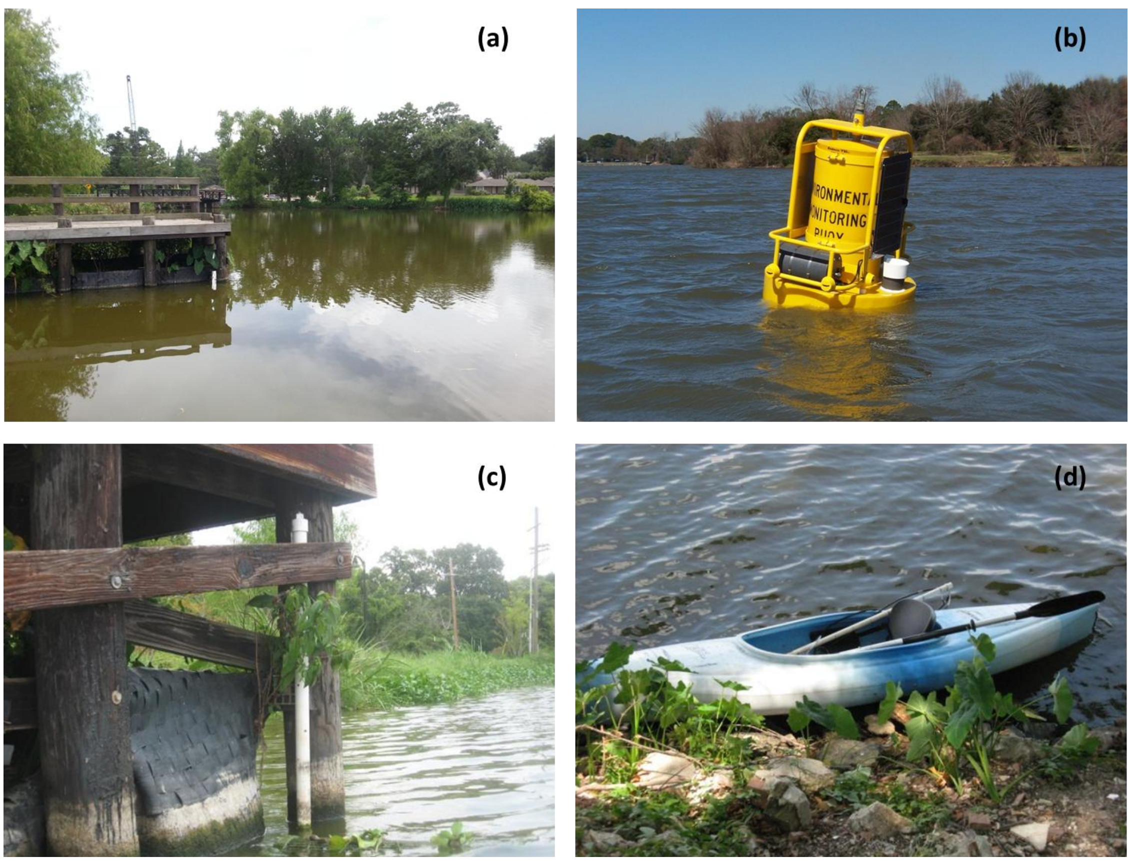

Figure 1.3 (a) Summer eutrophication in University Lake on LSU campus; (b) The environmental monitoring buoy with multi-probe sensors deployed in University Lake; (c) Pressure transducers installed on University Lake to measure water depth; (d) Water samples for nutrient analysis were collected using a kayak throughout the study period. Photo courtesy of Y. Jun Xu.

objectives are broken down into three chapters. The second chapter presents a study to discern a method using DO to determine trophic state change and water quality degradation in shallow waters. The third chapter focuses on developing a one-dimensional, deterministic DO model that can predict hourly change in DO of a water body with high-time resolution weather parameters. Chapter four concentrates on a numeric relationship between chlorophyll *a* fluorescence and BOD for a rapid BOD testing method. Chapter two, three and four are written as stand-alone manuscripts for peer-reviewed journals. For that reason there will be some repetitions among these chapters.

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CHAPTER 2: DETERMINATION OF TROPHIC STATE CHANGE WITH DIEL DISSOLVED OXYGEN RANGES: A CASE STUDY IN A SHALLOW EUTROPHIC LAKE

2.1 INTRODUCTION

Eutrophication of water bodies has become one of the world's most concerned environmental problems. Eutrophication can stimulate excessive growth of algae, causing sudden oxygen depletion in water columns (Rabalais et al., 2009) and affecting aquatic communities, food web, and biodiversity (Moustaka-Gouni et al., 2006; Markogianni et al. 2014). Studies have shown that when the dissolved oxygen (DO) level of a water body is below 5 mg L^{-1}, sensitive species of fish and invertebrates can be negatively affected (e.g., Frodge et al. 1990; Diaz and Rosenberg, 2008). Severe oxygen depletion (i.e., DO is less than 2.0 mg L^{-1}) can have significantly negative impacts on most fish species, as well as impede nitrogen and phosphorus transformations (Kemp et al., 1990; Breitburg, 1992; Hamilton et al., 1997; Gray et al., 2002; Harrison et al., 2005; Stevens et al., 2006). Due to its significance, understanding DO dynamics is important for water quality management to maintain aquatic ecosystem health.

Eutrophication is especially widespread in lake systems because of easy accumulation of nutrients and toxic elements from agricultural, industrial, and urban stormwater runoff. In the United States, about 44% of all lakes and 59% of man-made lakes have been classified for poor biological conditions (USEPA, 2009). This is especially prevalent for urban lakes, since water bodies in urban areas are often negatively affected by a range of anthropogenic activities such as water withdrawal, discharge of sewage water, urban stormwater runoff, and industrial effluent (Walsh, 2000; Juutinen et al., 2009; Whitehead et al., 2009; Zhang et al., 2014).

In the past several decades, there have been many studies looking into the causes of and solutions to dissolved oxygen depletion for lake systems, including application of real time monitoring (Markogianni et al., 2014), phytoplankton activities (Oliva Martinez et al., 2008; Alves-da-Silva et al., 2013), nutrients transformations (Guo et al., 2012), and aquatic vegetation management (Morris et al., 2003; Morris et al., 2004). However, many DO studies have only limited point-by-time measurements whereas field data are usually collected at insufficient time intervals. Some studies have found that strongly eutrophicated lakes often have DO saturation and/or DO super-saturation during the daytime, resulting in an overall higher average DO when compared to healthier lakes (Matthews et al., 2006; O'Boyle et al., 2013). This indicates that comparison of point-by-time measurements of DO may not be a good approach for determining water quality changes.

Health conditions of water bodies, especially lakes, are also often evaluated by their trophic states that generally indicate the biological production, both aquatic plant and animal life, that occurs in them. Various indicators have been used in the past to describe trophic state. As one of the most popular methods, Carlson (1977) constructed a Trophic State Index (TSI) using algal biomass as the basis for trophic state classification, in which three attributes, the concentrations of chlorophyll *a*, total phosphorus, and water clarity normally given as Secchi disk transparency, are used to estimate algal biomass. Although being widely used, existing evaluating criteria for trophic states, like Carlson’s TSI, have been reported with limitations in many studies (An and Park, 2003; Santhanam et al., 2011), especially in shallow water bodies (Joniak et al., 2009; Santhanam and Amal Raj, 2010). Presently most concerns in the change of trophic state and eutrophication are on DO (Rabalais et al., 2002; Kemp et al., 2005; Diaz and Rosenberg, 2008). However, up to now DO is rarely considered in trophic state determination.

This study was conducted in a shallow eutrophic urban lake over two 1-year periods: from August 2008 to July 2009 and from August 2013 to July 2014. During the periods an intensive DO monitoring was employed with a 15-minute interval of recording, together with collection and analysis of other water quality and climatic parameters. The study analyzed diel DO dynamics during different seasons and identified changes in ambient conditions from 2008-2009 to 2013-2014. The ultimate goal of the study was to discern an effective approach using DO for determination of trophic state change in shallow waters.

2.2 METHODS

2.2.1 Site description

This study was conducted at University Lake in Baton Rouge, Louisiana, USA (Latitude 30°24’50”N; Longitude 91°10’00”W) (Figure 2.1). The lake is 74.6 ha with a perimeter of about 6.7 km and an average depth of 0.9 meter. The drainage area of the entire lake watershed is about 187.4 ha (Reich Assoc, 1991; Xu and Mesmer, 2013) and land use of the watershed consists of residential, recreational, and university campus areas. The lake was developed from dredging a swamp in the 1930s as a public works project to create an open water environment. The most recent dredging was conducted in 1983 when large amounts of sediments and excess nutrients from surface runoff were removed (Reich Assoc., 1991). The lake was classified as eutrophic based on the high concentrations of phosphorus and chlorophyll *a* (Mesmer, 2010).

Climate in the region is humid-subtropical, with long hot summers and short mild winters. Long-term annual temperature in the area is about 20 °C, with monthly averages ranging from 11 °C in January to 28 °C in July (Xu and Mesmer, 2013). Long-term annual precipitation in the area is about 1477 mm, ranging from 159 mm in July to 81 mm in October (Xu and Mesmer, 2013).

2.2.2 Field DO measurements and water sample collection

An environment monitoring buoy (EMB) (YSI Inc., Yellow Springs, OH, USA) was deployed in the center of University Lake in the spring of 2008 (Figure 2.1). The EMB was equipped with multi-probe data sondes (YSI 6920) that measured a series of water quality parameters at 15-minute intervals at about 0.6 m below the water surface. The parameters included dissolved oxygen, water temperature, pH, conductivity, turbidity, and chlorophyll-*a* concentration. During the study periods from August 2008 to July 2009 and from August 2013 to July 2014, the probes were calibrated monthly. The sensor of YSI 6920 for chlorophyll-*a* concentration was broken from August 2013 to July 2014. As compensation, biweekly field trips were made from August to October in 2013 to conduct *in-situ* measurements on fluorescence at various locations in the studied lake by an AquaFluor® Handheld Fluorometer (Turner Designs, CA, USA). A relationship developed between fluorometer reading and chlorophyll *a* concentration by another study for University Lake was used to calculate chlorophyll *a* concentrations (Xu and Xu, in review).

In the Septembers of 2008 and 2013 and Aprils of 2009 and 2014, composited water samples from the lake were collected (S1, Figure 2.1). Water samples were taken by a sampler at about 10 cm below water surface and were stored in 2000-ml sample bottles. The samples were kept in a cooler with wet ice during the transportation for later laboratory analysis.

2.2.3 Laboratory nutrients measurements

Nitrate, nitrite, total Kjeldahl nitrogen (TKN) and total phosphorus (TP) were measured in the studied lake. Water samples in 2008-2009 were analyzed by the Department of Agricultural Chemistry, Louisiana State University. TP was determined with EPA method 365.3 with a detection limit of 0.008 mg L^{-1}. Nitrate and nitrite were filtered through a 47μm glass fiber

filter (GF/F Whatman International Ltd, Maidstone, England) and determined EPA method 353.3 with a detection limit of 0.05 and 0.003 mg L^{-1}, respectively. TKN was determined with EPA method 351.2 with a detection limit of 3.0 mg L^{-1}. In 2013-2014, TP and TKN were analyzed at The W.A. Callegari Environmental Center, Louisiana State University. Nitrate and nitrite were analyzed at Wetland Biogeochemistry Analytical Services, LSU School of the Coast and Environment. TP was analyzed using EPA method 365.3, Nitrate and nitrite were analyzed using EPA method 300.0, and TKN was analyzed using EPA method 351.1.

2.2.4 Ambient data collection

Two HOBO pressure sensors (U20-001-01, Onset Computer Corp., Bourne, MA) were installed in the lake to record water level changes at 15-minute intervals, one at the outflow gate of the lake and another close to the outflow gate (S1, Figure 2.1). Hourly climatic records were gathered for the study period from a near-by weather station (Ben Hur Station, the Louisiana Agriclimatic Information System, http://weather.lsuagcenter.com/) located approximately 5 km east of the study site for a variety of weather parameters including air temperature, precipitation, maximum wind speed, average wind speed, average wind direction, humidity, solar radiation and soil temperature.

2.2.5 Data analysis

To further investigate the effectiveness of simple comparison of point-by-time measurements, the original 15-minute interval data were subsampled. DO records of concentration and saturation at 10:00 every day during the two 1-year periods were used to simulate a sampling strategy of once a day at 10:00. Comparison based on those subsampling data was reported as simple statistics. Student t-test was employed to determine the significance of annual and seasonal DO concentration and saturation, water level, and subsampled data

between the two 1-year periods. The criteria for significance were set at $P < 0.05$. Records of DO concentration and saturation were also used to get seasonal and annual averages for each hour in a day between the two 1-year periods. Averaged hourly data were used for diel DO dynamics.

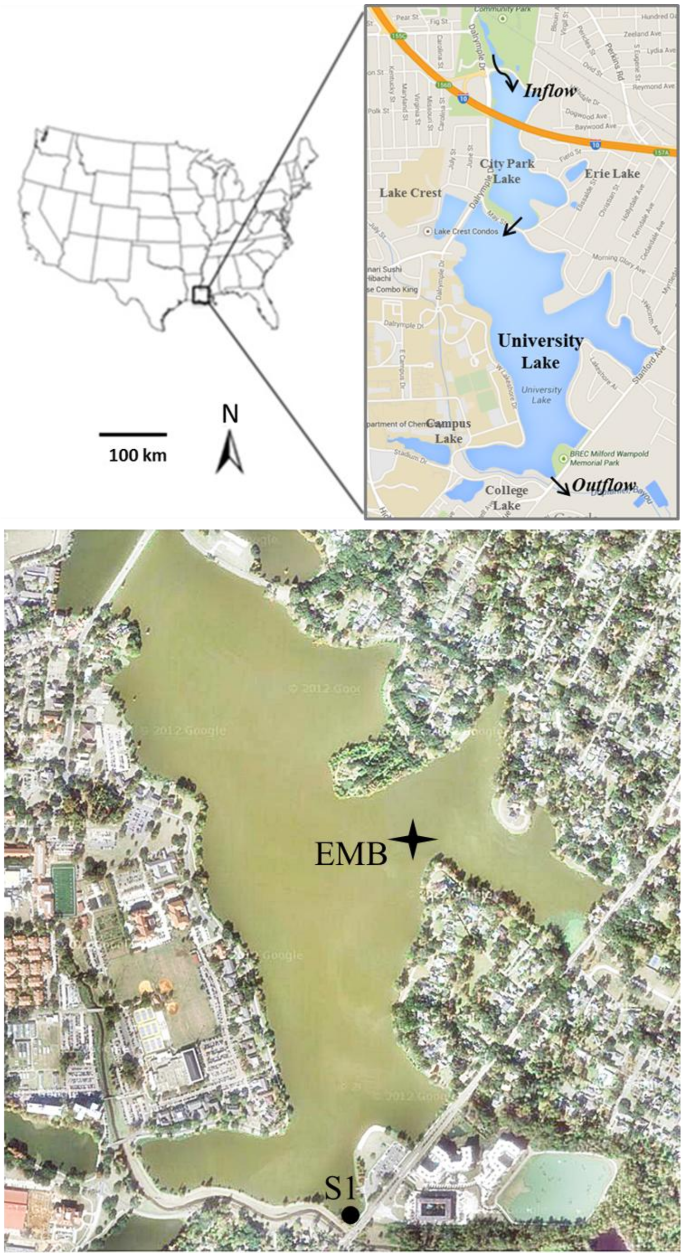

Figure 2.1 Geographical location of University Lake in Baton Rouge, Louisiana, USA (above) and the locations of the environment monitoring buoy (EMB) and water level logger (S1) (below).

In this study, total nitrogen (TN) was determined from the sum of nitrite, nitrate and TKN.

Water levels were calculated by the following equation:

$$Water\ level = [(P_{water} - P_{atm}) / (\rho * g)] + D_s \quad (1)$$

where P_{water} is the pressure recorded by the pressure sensor in kPa, P_{atm} is the atmospheric pressure in kPa, ρ is the density of water in g m^{-3}, g is the gravitational constant, and D_s is the distance of sensor to the lake bottom in meter. Water depth at S1 was used to represent water level of the studied lake during the studied periods. Due to an equipment failure at S1, pressure data for the site were missing for August 2013 - March 2014. The missing data were estimated with pressure records from the sensor at the outflow gate since a strong linear relationship of pressure records exists between the two close locations (Figure 2.2).

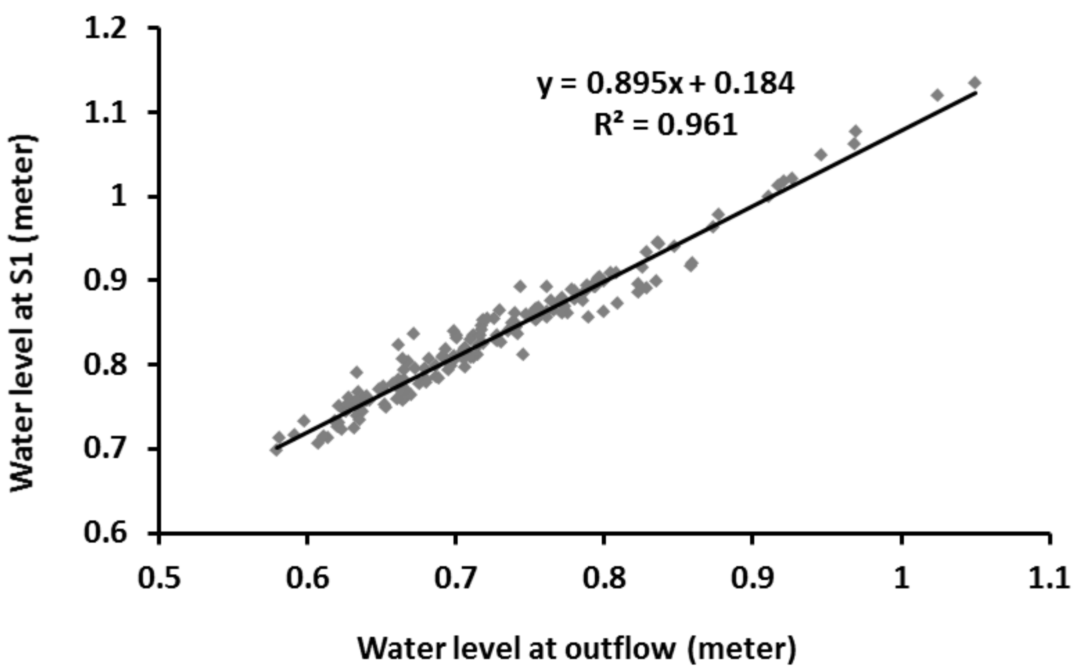

Figure 2.2 A strong linear relationship between water level at the outflow gate and the site close to outflow based on data from September 2012 to March 2013.

For frequency analysis, independent and homogeneous data are required for frequency analysis (Greb and Graczyk, 1995). In the test for independence (Kleiner, 1977), a weekly time step was found to be optimal in preserving independence of the values while keeping the number of observations as large as possible. In addition, to avoid seasonality effects and assure that the weekly time step was homogeneous, only warm months records (twenty-one-week period from May to September) was used for calculation.

To calculate cumulative hours of DO less than 5 mg L^{-1} and DO less than 2 mg L^{-1} in a week, the data were firstly grouped into weekly units. A week was defined as a 168-hour period beginning and ending at midnight. For each week, total hours of DO less than 5 mg L^{-1} and DO less than 2 mg L^{-1} were added up separately (one single record represent a time duration of 15 minutes). Then all observations (cumulative hours) were ranked from highest to lowest value for both DO less than 5 mg L^{-1} and DO less than 2 mg L^{-1} separately. A probability was assigned:

$$P_{hour} = m / (n+1) \tag{2}$$

where P_{hour} is the probability of cumulative hours in a week for DO less than 5 mg L^{-1} or DO less than 2 mg L^{-1}; m is the rank of total hours; n is the total number of observations. In the last step, the return periods, which are the reciprocal of probabilities, were calculated for P_{Hour}.

All the calculations were performed by SAS Statistical Software package (SAS Institute, Cary, NC).

2.3 RESULTS

2.3.1 Comparison of daily average DO between 2008-2009 and 2013-2014

Daily DO concentration of University Lake averaged 7.3 mg L^{-1} (standard deviation = 3.18) during 2008-2009 and 7.7 mg L^{-1} (standard deviation = 3.21) during 2013-2014 (Table 2.1). Daily average DO saturation was 81.7 % during 2008-2009 and 87.2% during 2013-2014. Although the ranges of daily DO concentration and saturation during 2008-2009 (0.6 – 11.7 mg L^{-1}; 7.0 -141.1 %) were similar to those during 2013-2014 (1.5 - 12.0 mg L^{-1}; 20.5 -153.0 %), the year 2013-2014 showed statistically higher DO concentration ($p = 0.02$) and DO saturation ($p = 0.003$).

Seasonally, daily DO concentration and saturation were highest in the winter months and lowest in the summer months for both of the two 1-year periods (Table 2.1). In the summer, average daily DO concentration and saturation were higher during 2013-2014 (6.4 mg L^{-1}; 87.3 %) than during 2008-2009 (4.5 mg L^{-1}; 60.4 %), while no significant difference in average daily DO concentration and saturation was found for the other three seasons between the two 1-year periods (Table 2.1). Notably, daily DO concentration ranges were much wider in the spring of 2008-2009 (4.2 – 11.2 mg L^{-1}) than in the spring of 2013-2014 (6.6 – 9.7 mg L^{-1}), but were close to each other during the summers, falls and winters between the two periods (Table 2.1). The same trends of DO saturation were seen for the two periods. In summary, significant differences were found only in the summer ($P \ll 0.05$) for DO concentration, and in the summer ($P \ll 0.05$), fall ($P = 0.03$) and winter ($P \ll 0.05$) for DO saturation between the periods.

2.3.2 Comparison of diel DO between 2008-2009 and 2013-2014

Diel DO concentration and saturation began rising in the early morning (7:00 – 8:00), reaching their peaks in the late afternoon (16:00 - 17:00), and declining in the evening until

reaching the troughs shortly before sunrise (Figure 2.3).Wider diel ranges of DO concentration and saturation were observed in 2013-2014 (5.3 – 10.7 mg L^{-1}; 55.2 – 126.2 %), compared with 2008-2009 (6.0 – 8.7 mg L^{-1}; 64.0 – 98.7 %). In 2013-2014, the dynamics of DO concentration and saturation were similar to those in 2008-2009 with their peaks at 17:00 and their lowest values at 7:00 (Figure 2.3). The difference between the daily DO maximum and minimum during 2013-2014 (5.4 mg L^{-1}) was twice as large as the difference during 2008-2009 (2.7 mg L^{-1}). Also, no supersaturation was found in the diel DO trends during 2008-2009, while eight hours of DO saturation within a day were observed during 2013-2014 (from 13:00 to 20:00).

The differences between diel DO concentration maxima and minima were significantly wider in the spring, summer and fall in 2013-2014 (4.6 mg L^{-1}, 8.6 mg L^{-1}, and 6.5 mg L^{-1}, respectively) when compared with those in 2008-2009 (3.5 mg L^{-1}, 3.4 mg L^{-1}, and 2.2 mg L^{-1}, respectively). During the winter, the difference was marginal: 2.0 mg L^{-1} in 2013-2014 and 2.3 mg L^{-1} in 2008-2009. The large difference in the summer diel ranges between the two periods was mainly caused by peaks being much larger in 2013-2014 then in 2008-2009 (Figure 2.4). In the fall of 2013-2014 diel range was nearly three times as large as the range in 2008-2009, which was caused by a larger fluctuation throughout the day (Figure 2.4).

For DO saturation, diel trends showed similar characteristics compared to DO concentration for all seasons. The diel range from spring to winter in 2008-2009 were 44.9 %, 47.1 %, 28.8 % and 26.1 %, respectively, and in 2013-2014 were 60.6 %, 120.2 %, 82.6 %, and 21.4 %, respectively. Similar to DO concentration, larger differences in diel variations were found in summer and fall, which were mainly caused by greater peaks. For instance, in summer 9 hours in a day were supersaturated in 2013-2014 while none was found in 2008-2009 (Figure 2.5).

Table 2.1 Daily mean, minimum and maximum of dissolved oxygen concentration (mg L^{-1}) and saturation (%, in *italic*) in University Lake in four seasons

Season	2008-2009	2013-2014
Spring (Mar., Apr. and May)	8.2 (4.2 – 11.2)	8.4 (6.6 – 9.7)
	95.0 (53.7 – 133.0)	*98.9 (74.7 -127.5)*
Summer (Jun., Jul. and Aug.)	4.5 (1.1 – 10.0)	6.4 (2.3 – 10.8)
	60.4 (14.2 – 141.1)	*87.3 (31.0 – 153.0)*
Fall (Sep., Oct. and Nov.)	6.3 (0.6 – 10.2)	6.9 (1.5 – 10.5)
	71.1 (7.0 – 121.7)	*79.7 (20.5 -123.4)*
Winter (Dec., Jan. and Feb.)	9.7 (4.5 – 11.7)	9.3 (5.9 – 12.0)
	95.9 (48.2 – 119.5)	*85.1 (62.6 – 108.7)*
Average	7.3 (0.6 – 11.7)	7.7 (1.5 - 12.0)
	81.7 (7.0 -141.1)	*87.7 (20.5 -153.0)*

2.3.3 Comparison of oxygen depletion and super-saturation between 2008-2009 and 2013-2014

Most oxygen depletion occurred in summer and fall for the two 1-year periods. In the summer months of 2008-2009, the percentage for DO less than 5 mg L^{-1} and 2 mg L^{-1} among all observations were 60.8 % and 20.5 %, respectively (Table 2.2). DO concentration was less than 5 mg L^{-1} for nearly 42 % of the summer in 2013-2014, and hypoxia occurred for more than 15 % of the total observations (Table 2.2). For fall, percentage of DO less than 5 mg L^{-1} and less than 2 mg L^{-1} among all observation were 35.7 % and 14.2 %, respectively, in 2008-2009 and were 29.2 % and 9.4 %, respectively, in 2013-2014 (Table 2.2).

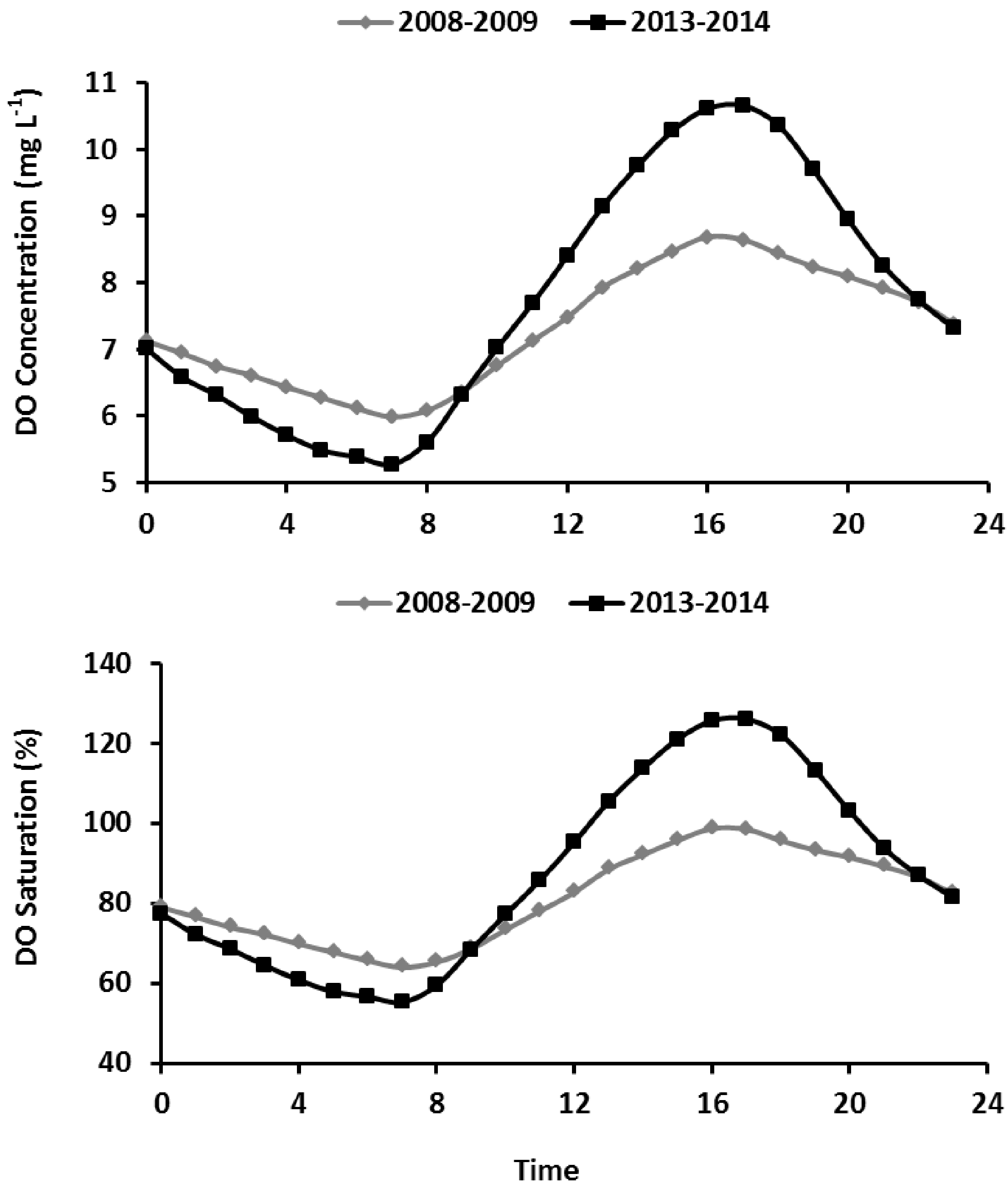

Figure 2.3 Diel dynamics for dissolved oxygen concentration (above) and saturation (below) in 2008-2009 and 2013-2014. Data for each hour are the mean of annual observations.

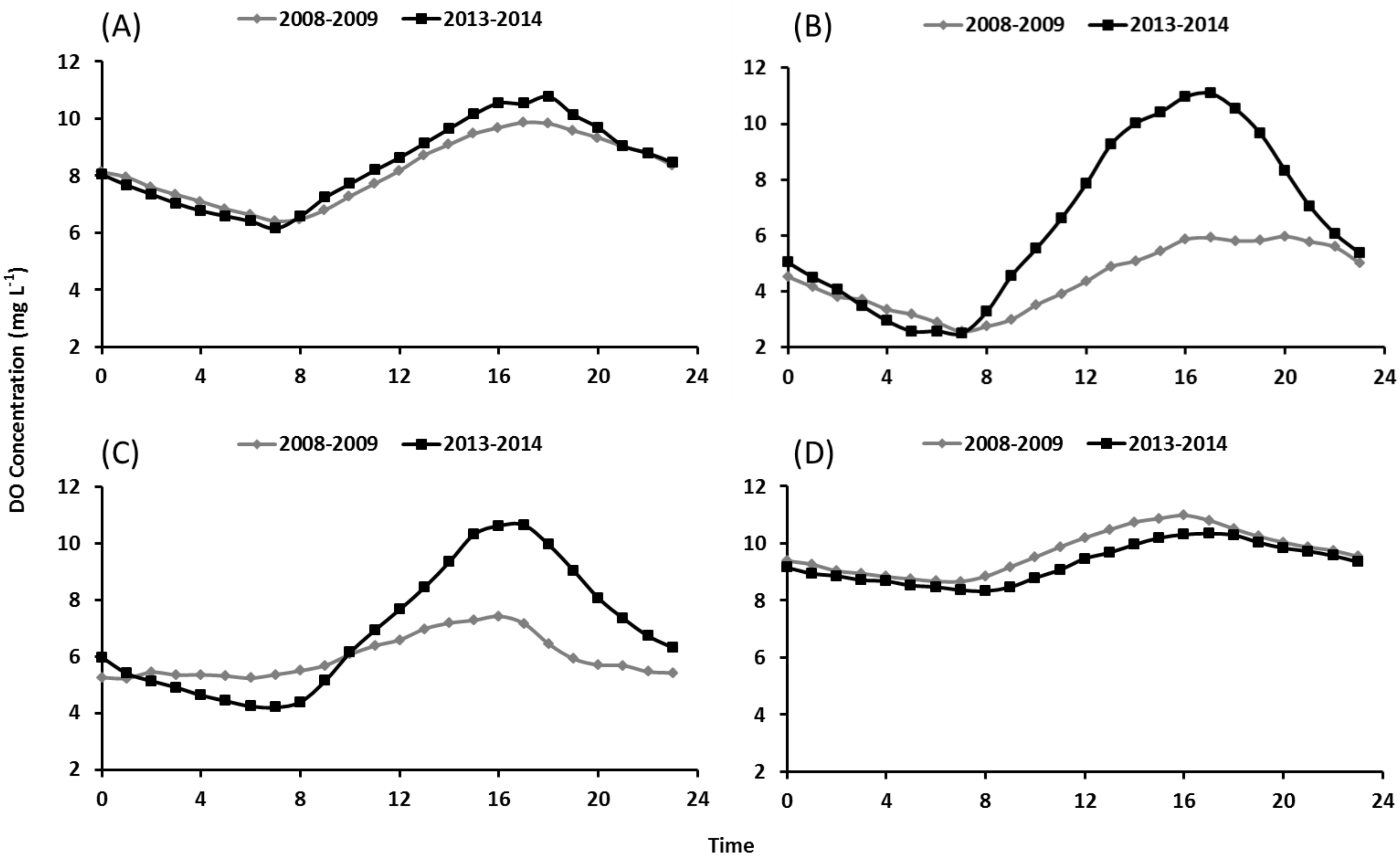

Figure 2.4 Diel dynamics for dissolved oxygen concentration in (A) spring, (B) summer, (C) fall and (D) winter during 2008-2009 and 2013-2014. Data for each hour are the mean of seasonal observations.

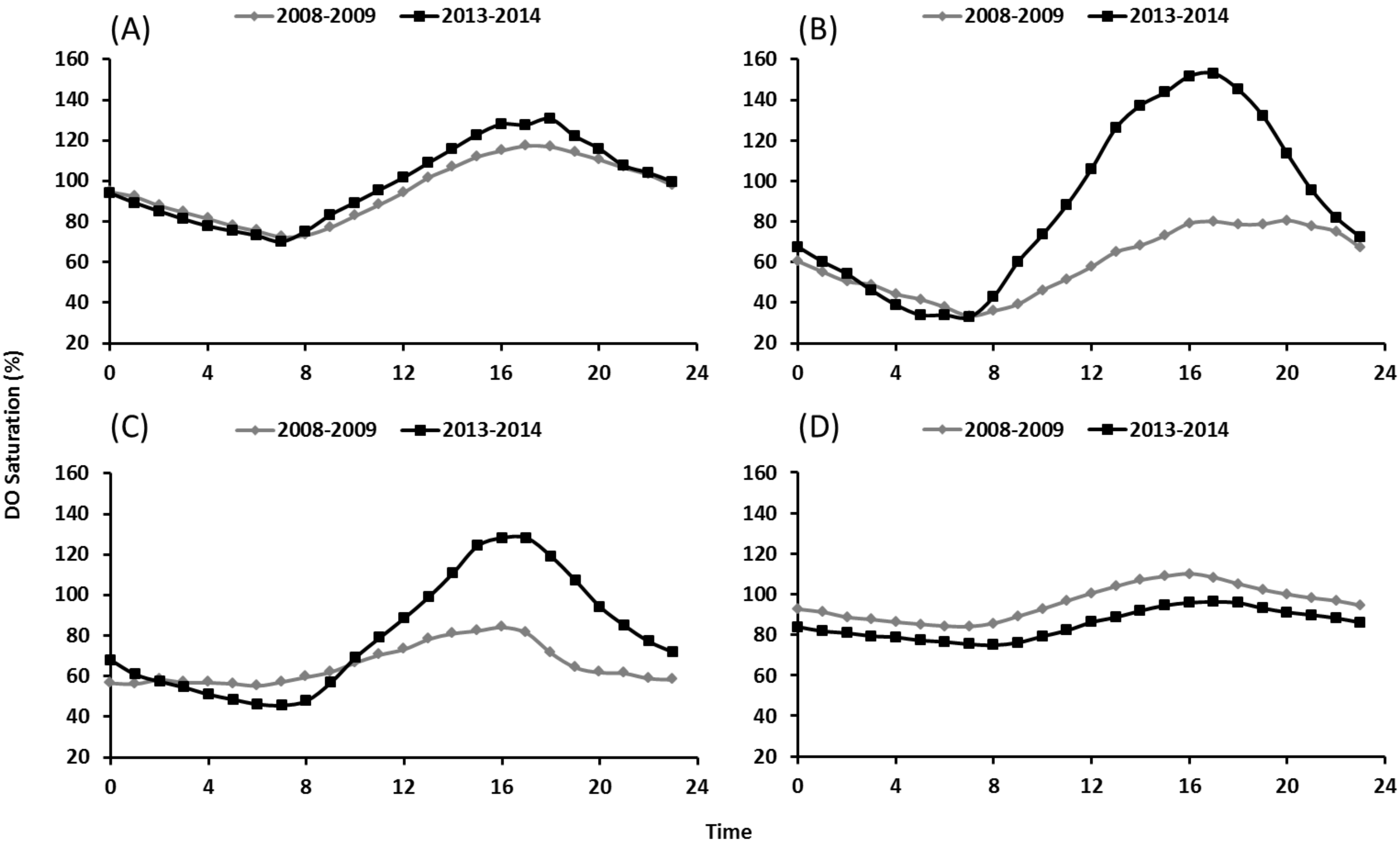

Figure 2.5 Diel dynamics for dissolved oxygen saturation in (A) spring, (B) summer, (C) fall and (D) winter during 2008-2009 and 2013-2014. Data for each hour are the mean of seasonal observatio

In the fall of 2008, 15.7 % of total observations were supersaturated while in the fall of 2013 26.5 % of all records were supersaturated (Table 2.2). Percentages of super-saturation for summer during 2008-2009 and during 2013-2014 were 14.4 % and 37.7 %, respectively (Table 2.2).

Table 2.2 Number of observations for dissolved oxygen depletion and oversaturation in summer and fall months in University Lake for 2008-2009 and 2013-2014

	Summer		Fall	
	2008-2009	2013-2014	2008-2009	2013-2014
Total	6638	8662	5930	8237
DO < 5 mg L^{-1}	4035	3632	2119	2406
DO < 2 mg L^{-1}	1362	1343	843	778
DO% > 100 %	957	3266	931	2179

The frequencies that DO was less than 5 mg L^{-1} for equal or less than nighty hours a week were nearly the same for 2008-2009 and 2013-2014 (Figure 2.6A). However, for DO deficiency persisting more than one hundred hours, it was very obvious that the curve representing 2008-2009 was above the line for 2013-2014, indicating that long time DO deficiency was more frequent in 2008-2009 (Figure 2.6A).

Hypoxia occurred more frequently in 2013-2014 when cumulative hours for oxygen depletion was under 55 hours (Figure 2.6B). However, beyond that hypoxia was much more frequent in 2008-2009 (Figure 2.6B). For instance, a week with 40 hours' hypoxia occurred every 4.8 weeks in 2008-2009 but almost twice as frequently (every 2.5 weeks) in 2013-2014.

Conversely, a week with 60 hours' hypoxia happened every 6.2 weeks in 2008-2009 but nearly half as frequently (every 12.8 weeks) in 2013-2014.

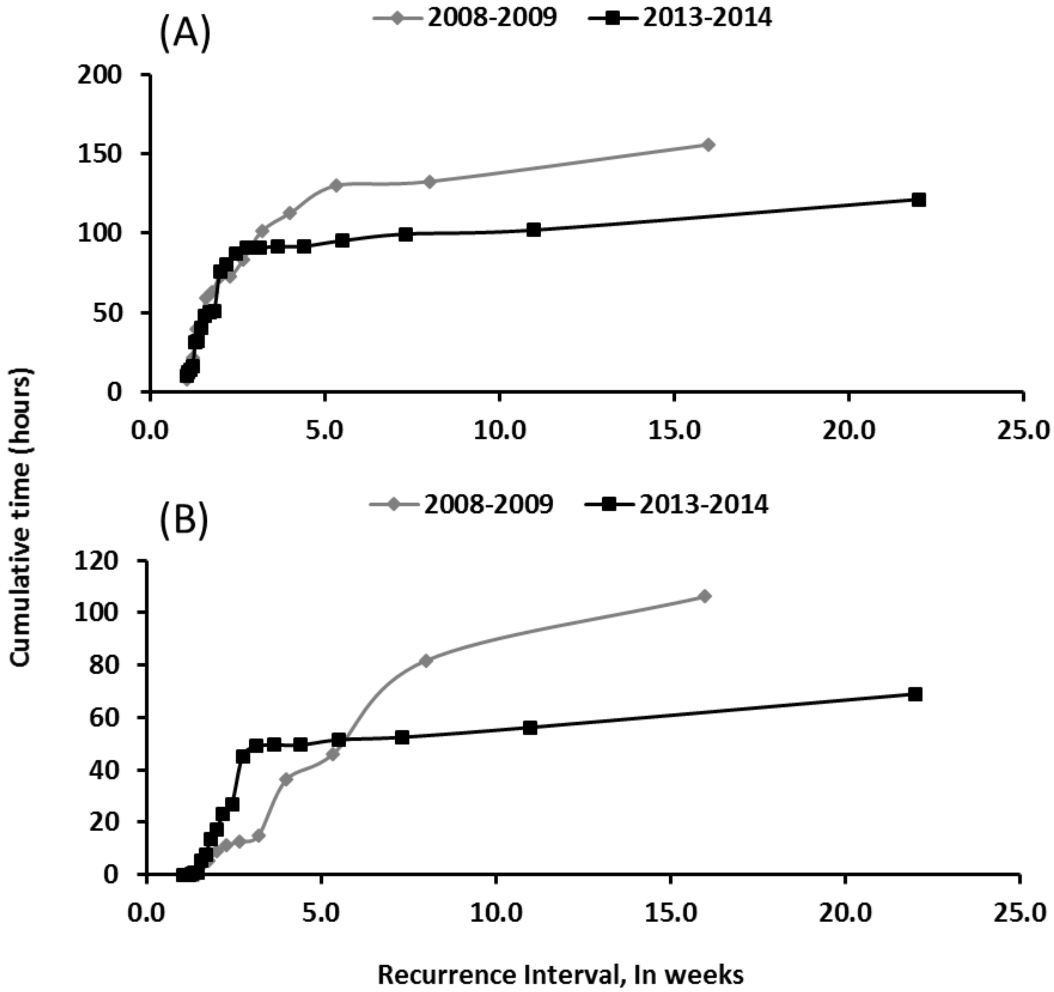

Figure 2.6 Frequency of different cumulative hours for (A) DO less than 5 mg L^{-1} and (B) DO less than 2 mg L^{-1} (hypoxia) in a week for 2008-2009 and 2013-2014.

2.3.4 Comparison of subsampling DO data between 2008-2009 and 2013-2014

For subsampling data at 10:00, annual mean DO concentration and saturation were similar during 2008-2009 (6.6 mg L^{-1}; 71.3 %) and 2013-2014 (6.7 mg L^{-1}; 73.8 %). More total observations were reported as less than 5 mg L^{-1} in 2008-2009 while fewer were observed in

2013-2014 (Table 2.3). Variations for DO concentration between 2008-2009 and 2013-2014 were 9 and 5.8 respectively (Table 2.3). No significant difference was found for concentration ($P = 0.4$) and saturation ($P = 0.2$) between the two 1-year period.

Table 2.3 Comparison of average DO measured at 10 am in University Lake during 2008-2009 and 2013-2014

	2008-2009 (n=318)	2013-2014 (n=335)
Mean concentration (mg L^{-1})	6.6	6.7
Mean saturation (%)	71.3	73.8
% of samples withDO < 5 mg L^{-1}	29.2 %	20.3 %
Variation for DO concentration	9	5.8

2.3.5 Changes in ambient conditions, water level and nutrients

Water level averaged 0.56 m during 2008-2009 with a range of 0.27 to 1.1 m, while averaging 1.0 m during 2013-2014 with a range of 0.77 to 1.2 m (Figure 2.7). Although total annual precipitation in 2012-2013 (1560 mm) was higher than that in 2008-2009 (1217 mm), the significant increase ($P \ll 0.05$) of water level was mainly due to the lift of the lake's outflow gate. From May to September (frequency analysis), average water temperature in 2013-2014 (29.8 °C) was similar to that in 2008-2009 (29.2 °C), and precipitation was much less in 2008-2009 (616 mm) than in 2013-2014 (859 mm).

Total phosphorus (TP) concentrations in University Lake averaged 0.152 mg L^{-1} in September 2008, 0.194 mg L^{-1} in April 2009, 0.306 mg L^{-1} in September 2013, and 0.322 mg L^{-1} in April 2014 (Figure 2.8). Total nitrogen (TN) concentrations were 1.543 mg L^{-1} in September 2008, 1.527 mg L^{-1} in April 2009, 2.231 mg L^{-1} in September 2013, and 1.807 mg L^{-1} in April

2014. Between the two study periods, the TN:TP ratio decreased from 10.2:1 to 7.3:1 in September, and decreased from 7.9:1 to 5.6:1 in April. According to Carlson's TSI (1977), the studied lake was hyper-eutrophic during the two 1-year periods in terms of TP.

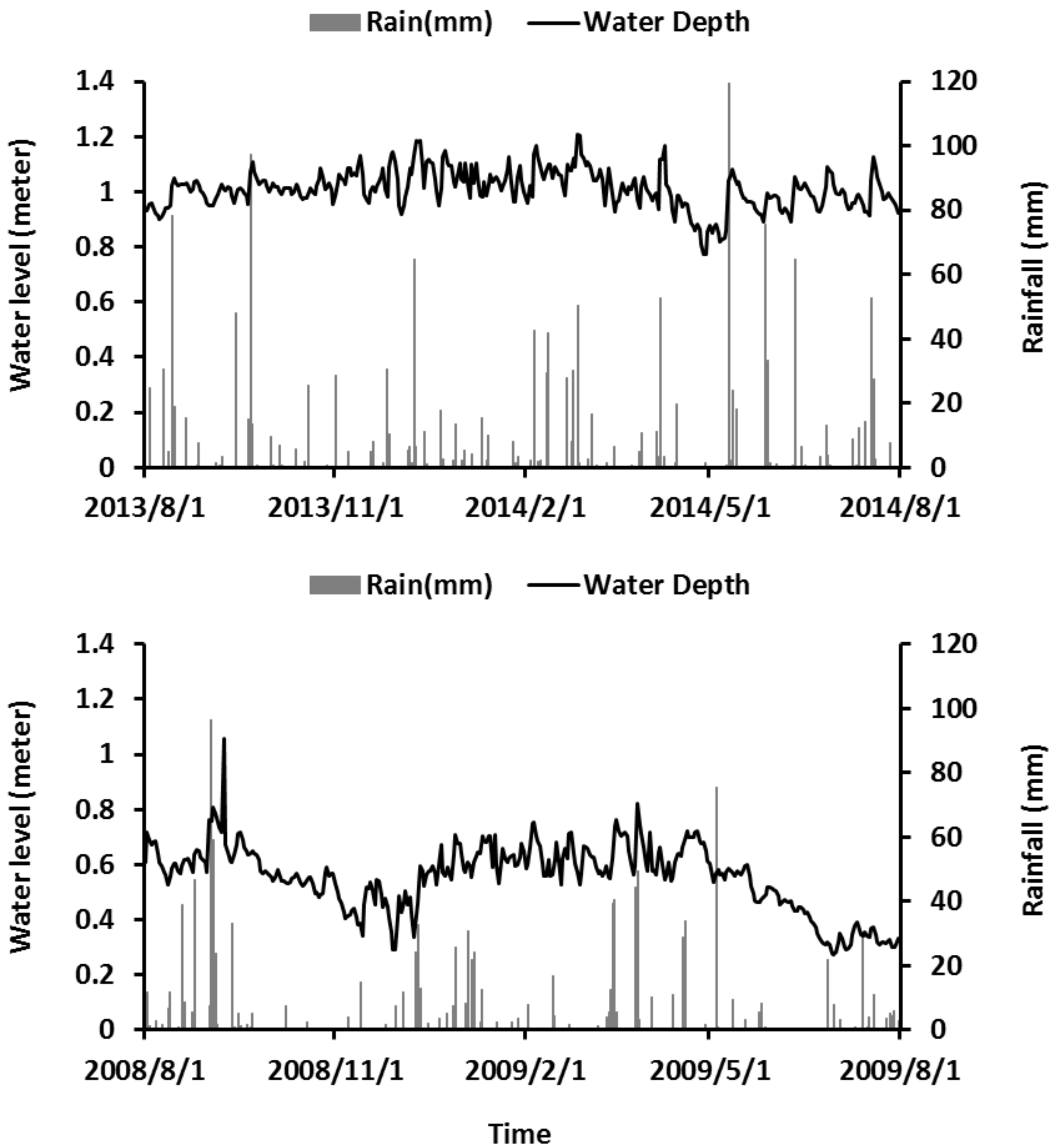

Figure 2.7 Comparison of water level for University Lake during 2008-2009 and 2013-2014

Chlorophyll *a* concentration averaged 30.1 μg L^{-1} in August, 15.8 μg L^{-1} in September, 47.6 μg L^{-1} in October in 2008, and 111.2 μg L^{-1} in August, 129.6 μg L^{-1} in September, 136.7 μg L^{-1} in October in 2013 (Figure 2.9). It indicates that University Lake was eutrophic in 2008 and hyper-eutrophic in 2013 (Carlson, 1977).

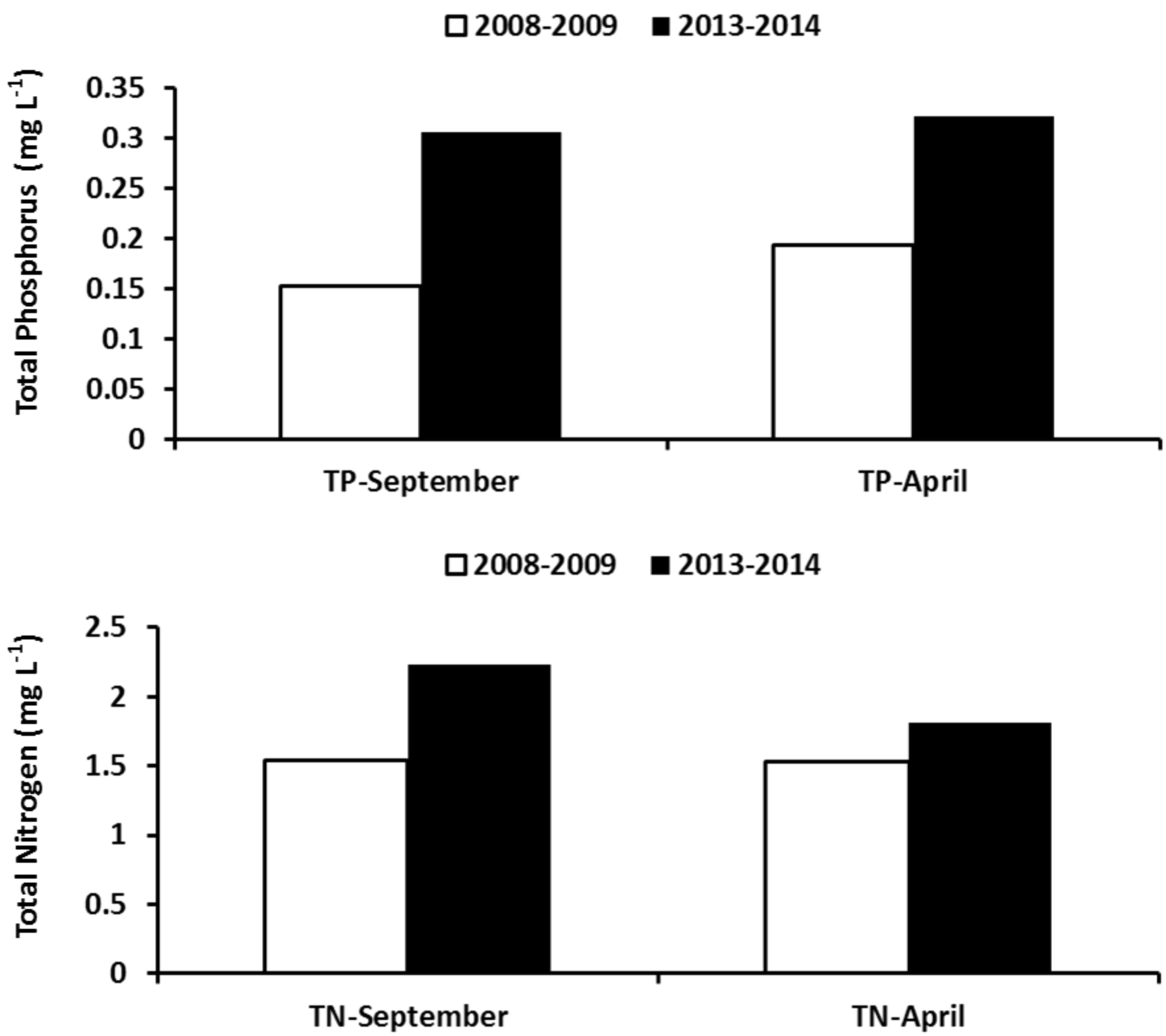

Figure 2.8 Total phosphorus (TP) and total nitrogen (TN) in April and September for 2008-2009 and 2013-2014.

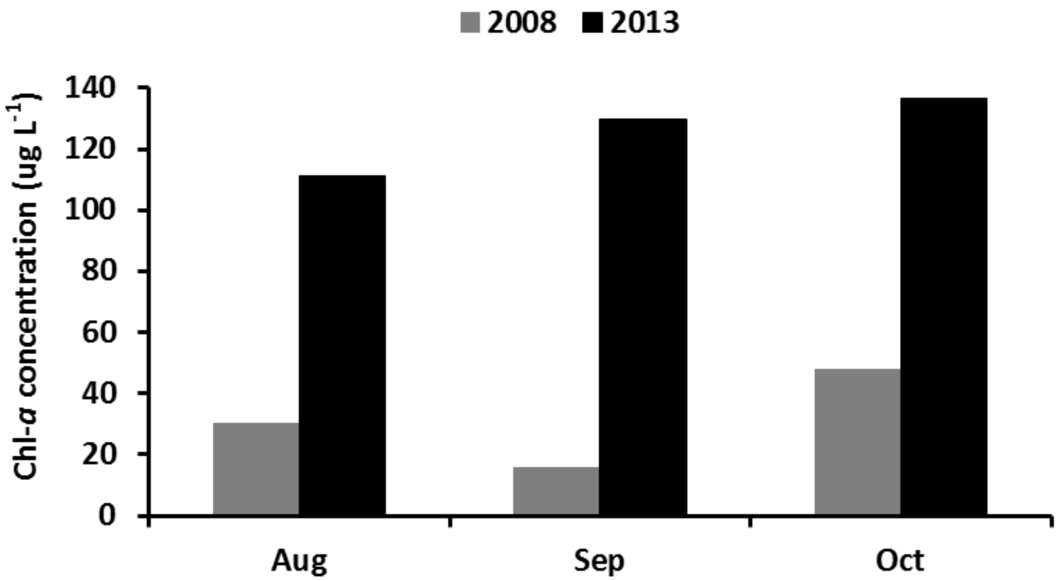

Figure 2.9 Comparison of chlorophyll *a* (Chl-*a*) concentration in University Lake from August to October in 2008 and 2003

2.4 DISCUSSION

2.4.1 Feasibility of using diel dissolved oxygen ranges as an index

Commonly used trophic state indices have been reported to have limitations in their application to shallow waters. These indices normally consider three parameters as critical: the concentrations of chlorophyll *a*, total phosphorus, and the light condition of water, normally given as Secchi disk transparency (Carlson, 1977; Chang and Chuang, 2001; Liou and Lo, 2005). The index boundary values of nutrients and chlorophyll *a* used for classifying trophic states are arbitrary, and they cannot truly reflect the association of nutrients with biological activities for different climate regions and ambient conditions. The application of Secchi disk is limited to deeper waters and has been reported to be impractical for shallow lakes (Joniak et al., 2009; Santhanam and Amal Raj, 2010). The fundamental concept of tropic state indices is to relate a water body's nutrient status to its biological productivity and potential dissolved oxygen

depletion. However, it is difficult to quantitatively associate any change in the nutrient and chlorophyll *a* concentrations with the actual change in biological productivity and dissolved oxygen condition. Incorporating comparison of diel DO in the current tropic classification theme can help identify the change in actual oxygen consumption.

Ranges in diel cycles of DO can work as an indicative variable for changes in trophic state. Although wide swings in DO concentration is considered one of the symptoms of eutrophication (Dodds et al., 1998), dissolved oxygen is normally not considered in trophic state determination. The parameter is used only for lakes that are deep enough to develop a cold bottom layer of hypolimnion during the summer (Walker, 1979) but little has been done for shallow lakes. Also, diel variations in DO concentrations have been used for photosynthesis/respiration ratios as a method to characterize trophic state (Hornberger et al., 1977), but due to the fact that it needs intensive monitoring of DO, it's not widely used (Dodds et al., 1998). In contrast, data from other studies have shown the difference in diel cycles of DO reflecting degraded water quality cause by nutrient increase (Wassenaar et al., 2010), but the degree of range varies depending on different geological locations. Our study shows a clear increase of total phosphorus, total nitrogen, and chlorophyll a concentrations in the lake in 2013-2014 compared to 2008-2009, indicating intensified eutrophication of the lake in the past five years. Concurrently, our findings of the change in diel cycles of DO between the two periods shows that daily DO fluctuation has increased in the past five years, especially during the summer and fall months, reflecting the change in the trophic state based on chlorophyll *a* and nutritional attributes.

2.4.2 Advantages of using ranges in diel DO over other methods

Dissolved oxygen is widely measured as a water quality parameter for natural waters, wastewaters, and treatment waters, but many studies only have point-by-time measurements. Comparison of single point-by-time measurements cannot well reflect changes in water quality compared to using range in diel DO. DO data summaries, such as those listed in U.S. Geological Survey (USGS) annual water-resources data reports, are reported as simple statistics like daily means, minimums, or variations. Others have reported DO violations as the percentage that the standard was violated, for instance the percentage that DO less than 5 mg L^{-1} (Isaac, 1991; Greb and Graczyk, 1995). However, neither simple statistics nor percentage of violations could correctly present the change of trophic state for University Lake. Similar facts can be found from data presented in other studies. For example, in a study for a eutrophic shallow lake in China, Wang and others (2007) reported a monthly DO fluctuating from 5.8 to 9.2 mg L^{-1} with an average of 6.5 mg L^{-1} in 1999 and from 5.0 to 11.3 mg L^{-1} with an average of 7.5 mg L^{-1} in 2003. Although their studied lake was becoming less and less eutrophic during their studied period, it's not well reflected by the comparison of monthly sampled DO (Wang et al., 2007).

Beyond that, if there is no adjustment to improve the sampling strategy, the simple comparison of point-by-time measurements of DO may still lead to a false interpretation of water quality change even though the sampling frequency is increased. Like data presented in this study, sampling one time a day at 10:00 cannot detect eutrophicated effects on DO (Table 3), while frequency analysis using intensive monitoring data for comparison also only has a very limited indication for a severe eutrophication. It suggests the necessity to use an improved DO sampling strategy, like collecting ranges of diel DO, for a better interpretation of water quality.

Comparison of simple statistics and frequency analysis in this study reported a reduced frequency of oxygen depletion, giving an impression of water quality improvement of the lake. Firstly, it could be attributed to physical changes of the studied lake, like uplifted water level. The increase of water level leads to a higher capability for oxygen storage and reduced oxygen consumption caused by sediments (Sondergaard *et al.* 1992). Also, according to a study by Miranda and others (2001), the probability that DO concentration below 1.5 mg L^{-1} at dawn changes dramatically if water level is below 2 meters, in which case even an increase of 0.1 meter can significantly decrease the frequency of severe oxygen depletion. Field data from that study also suggests that the change of water level has the greatest potential for reducing the incidence of the relatively frequent DO depletion that affect small lakes, or small area of large lakes (< 300 ha) (Miranda *et al.* 2001). Another reason resulting in an apparently better DO condition could be frequent hyperoxia. Since the studied lake was already eutrophic in 2008-2009 suffering from intensive oxygen depletions, effects from intensified eutrophication may not be reflected strongly in terms of DO depletion. In contrast, frequent hyperoxia became a more critical problem after five years. It increased the long term mean DO as well as decreased the frequency of oxygen depletion to some degree. In contrast, the effectiveness of using diel DO ranges as an indicator for the determination of trophic state changes is less disturbed by those factors.

2.4.3 Suggestions for collecting diel dissolved oxygen ranges

Based on our study, sampling twice a day, one at the lowest point of a diel DO cycle in the early morning and one at its peak in the late afternoon (e.g. 7:00 and 16:00-18:00 for our studied lake), would provide insight into a diel range. Compared to other alternatives, like DO frequency-duration analysis (Greb and Graczyk 1995), diel range measurements do not require

additional extensive, continuous records from monitoring equipment, which saves the cost for water quality management. This cost-effective adjustment for point-by-time measurements should be available for other water bodies of the similar type as well, but the collection time for diel bottoms and peaks should be determined depending on different geological regions. Also, to use it as a variable in trophic state determination, more data from other lakes in different climate region are needed for further study.

2.5 CONCLUSIONS

This study compared intensive DO records collected during two 1-year periods (2008-2009 and 2013-2014) in a eutrophic shallow lake in subtropical Louisiana, USA. The studied lake was found to be more eutrophic during 2013-2014 than during 2008-2009 according to the total phosphorus level and chlorophyll *a* concentration. Less dissolved oxygen depletion occurred in 2013-2014 but much more frequent hyperoxia was observed as well. Diel DO ranges seem to be a reliable variable in trophic state determination, especially during summer and fall for the studied lake. Further studies for data from other lakes of the similar type in different climate regions are also recommended to make the disl DO range a strong index for the change of trophic states.

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CHAPTER 3: A DETERMINISTIC MODEL FOR PREDICTING HOURLY DISSOLVED OXYGEN CHANGE: DEVELOPMENT AND APPLICATION TO A SHALOW EUTROPHICA LAKE

3.1 INTRODUCTION

Dissolved oxygen (DO) is needed by aquatic organism in water columns and organism in benthic substrates. Deficiency of DO in a water body can lead to mortality of the life forms, affecting chemical and biological processes in the ecosystem. Studies have shown that sensitive species of fish and invertebrates are negatively impacted if DO level is below 5 mg L^{-1} (e.g., Frodge et al., 1990; Diaz and Rosenberg, 2008), and that nitrogen and phosphorus transformations could be impeded when DO is lower than 2.5 mg L^{-1} (e.g., Kemp et al., 1990; Breitburg, 1992; Hamilton et al., 1997; Gray et al., 2002; Harrison et al., 2005; Stevens et al., 2006). Therefore, DO levels are commonly used as a key health indicator for water bodies and prediction of DO changes can provide helpful information to the management of aquatic systems.

DO concentrations in a water body can fluctuate largely within a very short period of time due to the dynamics of physical, chemical, and biological processes in the system. Photosynthesis and aeration add oxygen to a water body while respiration and degradation of organic matters consume oxygen. Due to the complexity, predicting DO change in a natural water body is challenging. Over the last two decades, there has been a rapid development of numerical models for predicting DO changes. These DO models were applied to water bodies with different characteristics in their climatic, hydrologic, morphometric, biologic conditions (Stefan and Fang, 1994; Chau, 2006). For instance, DO models were developed to predict DO changes in aquaculture ponds (Culberson and Piedrahita, 1995; Kayombo et al., 2000), natural rivers (Radwan et al., 2003; Boano et al., 2006; Williams and Boorman, 2012; Martin et al.,

2013), lagoons and lakes (Hull et al., 2008; Misra, 2011), and estuaries (Mandal et al., 2012). DO modeling for lake systems is becoming more and more significant because many lakes are strongly affected by anthropogenic stressors including modified inflow due to land use change, inputs of various pollutants and contaminants, overexploitation, invasive species, and climate change (Mooij et al., 2010).

Most DO modeling studies were conducted for deep lakes or reservoirs (James et al., 1997; Tundisi, 1990) in temperate regions where clearly definable thermal layers develop over seasons. In general, modeling efforts on DO dynamics in subtropical lakes is very limited, especially for those that are shallow, eutrophic lakes suffering periodic and/or episodic hypoxia. Few DO modeling studies were also done for tropical and subtropical coastal lagoons and estuaries (D'Autilia et al., 2004; Oren, 2009; Wan et al., 2012), but these water bodies have very different environmental conditions when compared with deep freshwater lakes in a temperate zone. The difference complicates DO models' applicability as some researchers (Stefan and Fang, 1994; Blauw et al., 2009) found that generic models work better for deep lakes but show many limitations for shallow dynamic environments. Furthermore, these models are highly site-specific in terms of climatic, physical, and biological conditions; They tend to perform poorly when applied to systems outside of the climate region for which they were developed even after re-parameterization (Pena et al., 2010).

In addition to the above limitations, most DO models are not capable to predict DO dynamics in a high-time resolution (i.e. hourly), which further constrains their application for eutrophic/hyper-eutrophic shallow water bodies that often suffer from sporadic algal blooms. Eutrophic water bodies are phytoplankton-rich and a sudden algal bloom can lead to severe oxygen depletion killing fish and other sensitive organisms. This is especially the case for

shallow urban lakes in tropical and subtropical regions, where the climatic and anthropogenic environments can accelerate eutrophication of waters. DO levels in eutrophic lakes in warm regions have been found to fluctuate rapidly during the day, dropping from oversaturation to hypoxia within a few hours (Rabalais et al., 2001; Yin et al., 2004). Prediction of DO dynamics in a high-time resolution can be a useful tool for both scientific research and management plans in preventing algal bloom in lakes and reservoirs. For instance, an hourly model could provide important information to managers about the probable effectiveness of various remedial actions at affordable costs (Pena et al., 2010).

This study aimed to develop a high time resolution model for predicting DO change in shallow freshwater lakes. To do so, intensive measurements on lake dissolved oxygen and other environmental factors were conducted in a shallow, eutrophic lake in subtropical Louisiana, USA over the period from August 2008 to July 2009. The primary purpose of the study is twofold: first, to construct an hourly, process-based DO model with a full coupling of empirical functions of photosynthesis, respiration, and reaeration; secondly, to gain deeper insights into the dynamic interplay among the processes and weather conditions.

3.2 METHODOLOGY

3.2.1 Site description

The field observations were made at University Lake in Baton Rouge, south Louisiana, USA (Latitude 30°24’50”N; Longitude 91°10’00”W) on the Louisiana State University (LSU) campus (Figure 3.1). The lake is 74.6 ha with a perimeter of about 6.7 km and an average depth of 0.9 meter. The lake was artificially developed from a swamp area in the 1930s as a public works project to create an open water environment. The most recent dredging was conducted in

1983 when large amounts of sediments and excess nutrients from surface runoff were removed (Reich Assoc., 1991). The drainage area of the entire lake watershed is about 187.4 ha (Reich Assoc. 1991, Xu and Mesmer, 2013) and land use of the watershed consists of residential, recreational, and university campus areas. A recent study found high concentrations of phosphorus (Mesmer, 2010) and chlorophyll *a* (Xu and Xu, in review).

South Louisiana has a humid-subtropical climate with long hot summers and short mild winters. Long-term annual temperature in the area was reported to be 20 °C, with monthly averages ranging from 11 °C in the coldest month (January) to 28 °C in the warmest month (July) (Xu and Mesmer, 2013). The annual average air temperature during the 12 month study period (August 2008 to July 2009) recorded at Ben Hur weather station, which is about 5 km southeast of the study lake, was 20°C, fluctuated from 10 °C in December 2008 to 26 °C in July 2009. During much of the 12- month study period, monthly average temperatures were lower than the long-term monthly averages. Long-term annual precipitation in the area was reported to be about 1477 mm, ranging from 159 mm in July to 81 mm in October (Xu and Mesmer, 2013). Total precipitation during the 12-month study period was 1253 mm, ranging from a low monthly total of 11 mm in October 2008 to a high of 232 mm in September 2008.

3.2.2 Field DO measurements and water sample collection

In the spring of 2008 an environment monitoring buoy (EMB) (YSI Inc., Yellow Springs, OH, USA) was deployed in the center of University Lake (Figure 3.1). The EMB was equipped with multi-probe data sondes (YSI 6920) that recorded dissolved oxygen at 15 minute intervals at about 60 cm below the water surface. The sondes also took a series of other water quality parameters including water temperature, pH, conductivity, turbidity, and chlorophyll *a*

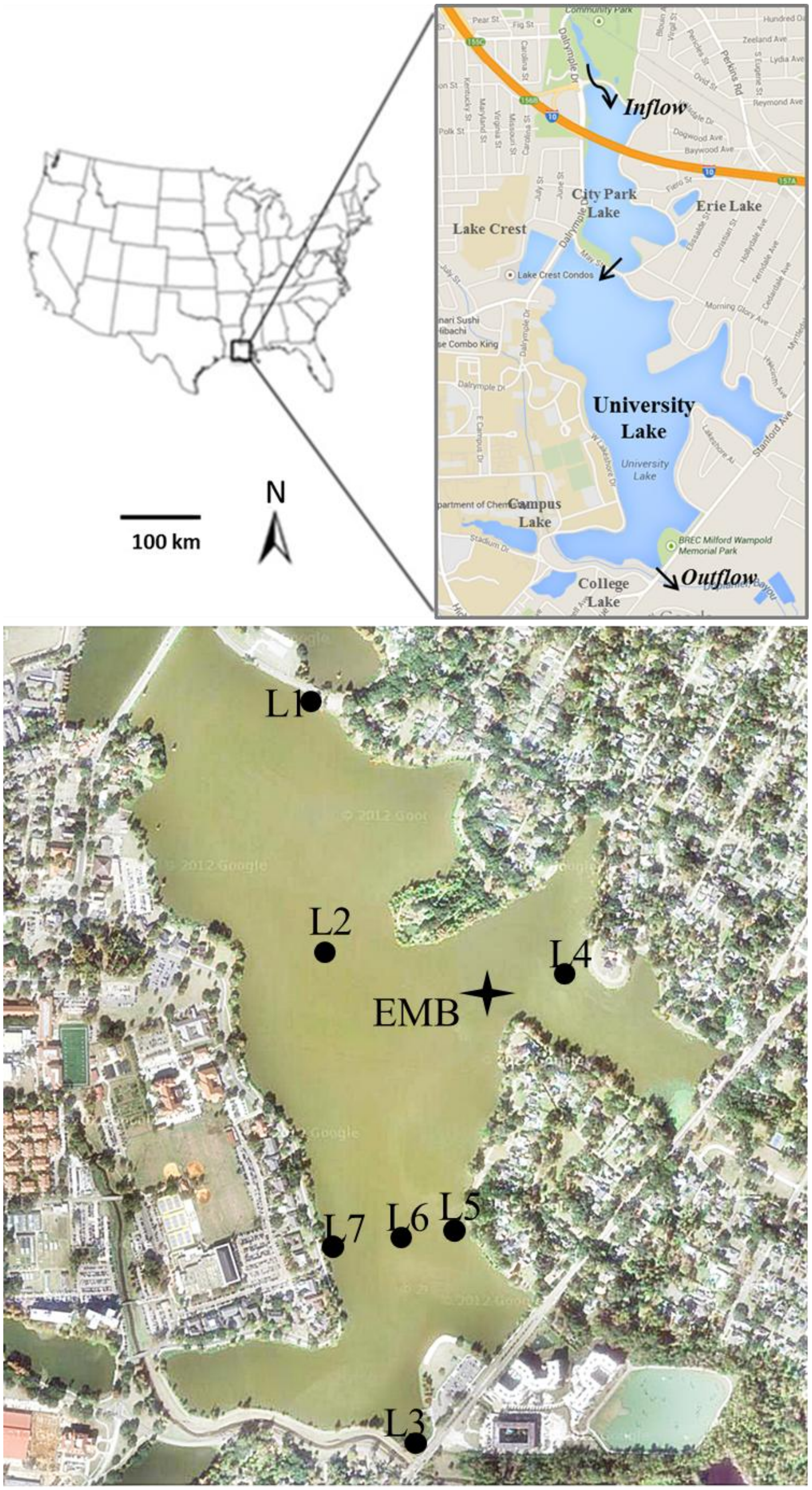

Figure 3.1 Geographical location of University Lake in Baton Rouge, Louisiana, USA (above), all sampling sites and the Environment Monitoring Buoy (EMB) in the lake.

concentration. During the study period from August 2008 to July 2009, the data sondes were calibrated monthly in laboratory.

In addition, monthly field trips were made to collect water samples for determination of biochemical oxygen demand (BOD). A total of seven locations were chosen (Figure 3.1): four of them were located near-shore while three of them were in open water. A 2000-ml water sample was collected from each site at 0.3 m below the water surface and was stored in a cooler with wet ice during the transportation for later laboratory analysis.

3.2.3 Laboratory BOD measurements

To estimate consumption of dissolved oxygen by biochemicals, 5-day BOD (BOD_5) of the water samples collected from the studied lake were measured at the Watershed Hydrology Laboratory, LSU School of Renewable Natural Resources. The measurements followed the protocol of a modified version of Section 5210B of APHA's 'Standard Methods for the Examination of Water and Wastewater' (APHA, 2005). Modifications to the standard method included a daily sample re-aeration if dissolved oxygen concentration was below 3.00 mg L^{-1} due to no dilution being performed. BOD samples were stored at room temperature (20 ℃ +/- 2 ℃) in an incubator (Thermo Scientific Imperial III Standard Incubator, Thermal Scientific Inc., Texas, USA) and DO of the samples were measured with an YSI 5100 dissolved oxygen meter (YSI Inc., Yellow Springs, OH, USA).

3.2.4 Climatic data collection

Hourly climatic records were gathered for the study period from a nearby weather station (Ben Hur Station, the Louisiana Agriclimatic Information System) located approximately 5 km southeast of the study site. The records included a series of weather parameters, such as air

temperature, precipitation, wind speed, humidity, solar radiation, and soil temperature. These data were used in the modeling for estimation of DO changes caused by photosynthesis and reaeration, as described below.

3.3 DEVELOPMENT OF A PROCESS-BASED DO MODEL

Dissolved oxygen level in a water body is affected by production and consumption sources. This can be expressed in a balance equation as follows:

$$dDO/dt = P + J - R - S_{BOD} - S_{SOD} \tag{1}$$

where *dDO/dt* is the change in DO in mg O_2 L^{-1} hr^{-1}, *P* is the oxygen production by photosynthesis in mg O_2 L^{-1} hr^{-1}, *J* is the oxygen diffusion rate in O_2 L^{-1} hr^{-1}, *R* is the respiration rate in mg O_2 L^{-1} hr^{-1}, S_{BOD} is the oxygen consumption by biochemical oxygen demand in mg O_2 L^{-1} hr^{-1}, and S_{SOD} is the oxygen consumed by sediment oxygen demand in mg O_2 L^{-1} hr^{-1}. Estimation for the sources and sinks is described below.

3.3.1 Oxygen production by photosynthesis

Photosynthesis is a process used by plants that releases free oxygen to the water body. It is affected by many factors including water temperature, intensity of photosynthetically active solar radiation (PAR), and dissolved nutrient concentration. In this model, photosynthesis is assumed as a first-order kinetic process related with chlorophyll *a* concentration. The formulation for oxygen production by photosynthesis is derived from Steele's equation (1962) represented by Bannister (1974) and Culberson and Piedrahita (1996):

$$P = \alpha_p * P_c * Chl\text{-}a \tag{2}$$

$$P_c = (\alpha_{par} * R_s) * P_{max} * e^{(1-\alpha_{par} * Rs)} \tag{3}$$

where α_p is a dimensionless photosynthesis adjustment coefficient, P_c is the rate of chlorophyll-a dependent oxygen production in mg O_2 mg Chl-a^{-1} hr^{-1}, *Chl-a* is the chlorophyll-a concentration in mg L^{-1}, R_s is the broadband solar radiation in kW m^{-2}, and α_{par} is the ratio of PAR to broadband solar radiation in m^2 kW^{-1} for the studied region which is often calculated as a constant ratio (Alados et al., 1995). P_{max} is the maximum oxygen production rate by photosynthesis at saturating lighting conditions (mg O_2 (mg Chl-a * hr)$^{-1}$). Chlorophyll *a* concentration represents the biomass of phytoplankton in the lake and is depending on trophic status (Gregor and Marsalek, 2004). It could indirectly reflect dissolved nutrient concentrations. Therefore there is no variable in this equation for nutrient limitations.

P_{max} has been estimated as a temperature dependent variable and is consistent with the Arrhenius equation (Megard et al., 1984):

$$P_{max} = 9.6 * 1.036^{(T-20)} \tag{4}$$

where T is water temperature in °C. Researchers (e.g., Stefan and Fang, 1994) successfully applied it for inland lakes in north central United States.

Combining Eqs. 2, 3 and 4, oxygen production through photosynthesis can be expressed as below:

$$P = \alpha_p * (\alpha_{par} * R_s) * [9.6 * 1.036^{(T-20)}] * e^{(1-\alpha_{par} * Rs)} * Chl\text{-}a \tag{5}$$

3.3.2 Re-aeration by wind regime

Re-aeration is another major oxygen source for water bodies. Water temperature can affect the capacity of dissolved oxygen saturation in a water body, while wind can accelerate oxygen dissolution. For lake systems, wind is considered as the driving force in regulating

surface turbulence, in contrast to the flow-induced turbulence that prevails in most streams (Gelda et al., 1996). Therefore, the equation for estimating physical re-aeration is derived from Gelda et al:

$$J = \alpha_j * (K_L/H) * (C_{sat} - C_s) \tag{6}$$

where α_j is the dimensionless re-aeration adjustment coefficient, K_L is the oxygen transfer coefficient in cm hr^{-1}, H is the thickness of surface layer in cm, C_{sat} is the saturated oxygen temperature in the surface layer at giver temperature in mg O_2 L^{-1}, C_s is the oxygen centration in the water in mg O_2 L^{-1}.

To compute oxygen transfer coefficient, the equation discussed by Crusius and Wanninkhof (2003) was used here for low wind speed over a lake, which is similar to the wind regime in the studied region:

$$For\ U < 3.7\ m/s\ K_L = 0.72U \tag{7}$$

$$For\ U \geqslant 3.7\ m/s\ K_L = 4.33U - 13.3$$

where U is the hourly wind speed at 10 m height above the lake in m s^{-1}, which is from Ben Hur station from Louisiana Agriclimatic Information System (http://weather.lsuagcenter.com/).

3.3.3 Respiration

Respiration is the reverse of photosynthesis which consumes oxygen in the water. In this study we assumed oxygen consumption by respiration as a first-order kinetics affected by external factors including water temperature and chlorophyll-a concentration. The equation derived from the study of Hull (2008) was used as an approximation:

$$R = \alpha_r * \theta_r^{(T-20)} * Chl\text{-}a\ (mg / (L * hr)) \quad (8)$$

where α_r is a respiration adjustment coefficient in hr^{-1}, θ_r is the temperature adjustment coefficient, T is the hourly water temperature in °C, and *Chl-a* is the chlorophyll-a concentration in mg L^{-1}. θr was reported as 1.045 by Ambrose et al. (1988) and successfully applied in some eutrophication models.

3.3.4 Biochemical oxygen demand

Biochemical oxygen demand in a water column is dependent on water temperature and available biochemical materials. In this study we used the equation from Stefan and Fang (1994) to estimate hourly change of BOD:

$$S_{BOD} = K_b * \theta_b^{(T-20)} * BOD / 24 \quad (9)$$

where K_b is the first-order decay coefficient in day^{-1}, θ_b is the temperature adjustment coefficient, and T is the hourly water temperature in °C. *BOD* is the daily biochemical oxygen demand representing available organic detritus that supplies the substratum for the oxygen consumption as oxygen equivalent. For estimation, in the model laboratory measurements for BOD_5 from monthly field trips were used to calculate average daily BOD and then used in the equation for that sampling month. Also, according to Stefan and Fang (1994), θ_b was set for 1.047 when water temperature was equal or greater than 20°C, while θ_b was set for 1.13 when water temperature was between 4°C and 20°C.

3.3.5 Sediment oxygen demand

Sediment oxygen demand (SOD) depends on the content of bottom muds and the area of the bottom muds contacting water. The equation for SOD can be given by Thomann and Mueller (1987):

$$S_{SOD} = S_{S20} * \theta_s^{(T-20)} / Z \tag{10}$$

where S_{S20} is the sediment oxygen demand at 20°C in mg O_2 m^{-2} hr^{-1}, Z is depth of the lake bottom sediment in meter, T is the water temperature in °C and θ_s is a temperature adjustment coefficient.

3.3.6 Dissolved oxygen transport equation

Combining the components, a one-dimensional DO model can be given as:

$$DO_{v,t} = DO_{v,t-1} + (dDO_v/dt)*dt \tag{11}$$

where $DO_{v,t}$ is DO concentration of V at time t in mg L^{-1}, $DO_{v,t-1}$ is DO concentration of V at time $t-1$ in mg L^{-1}, and dDO_v/dt is the rate of change in DO concentration in V during the time interval in mg L^{-1} hr^{-1}, which is:

$$\begin{aligned} dDO_v/dt = {} & \alpha_p * (\alpha_{par} * R_s) * [9.6 * 1.036^{(T-20)}] * e^{(1-\alpha_{par} * R_s)} * Chl\text{-}a \\ & + \alpha_j * (K_L/H) * (C_{sat} - C_s) \\ & - \alpha_r * \theta_r^{(T-20)} * Chl\text{-}a \\ & - K_b * \theta_b^{(T-20)} * BOD / 24 \end{aligned}$$

$- S_{S20} * \theta_s^{(T-20)} / Z$ (12)

Eqs. 11 and 12 are for hourly dissolved oxygen dynamics. Chlorophyll *a* concentration (*Chl-a*), water temperature (T), daily BOD, solar radiation (Rs) and wind speed (U) are model inputs, while adjustment coefficient for photosynthesis (α_p), re-aeration (αj) and respiration (α_r), temperature adjustment coefficient for SOD (θ_s), the ratio of PAR to broadband solar radiation (α_{par}), and rate coefficient for BOD (K_b) and SOD (S_{S20}) are calibration coefficients. Other required coefficients and parameters are from literature review.

3.3.7 Model run

The model was calibrated and validated on a monthly basis from August 2008 to July 2009 (except September 2008 due to insufficient data). Means of 15-minute records within an hour were used to represent hourly average. If more than two records in an hour were missing, data for that hour would be considered invalid. Only valid hourly data were used for calibration and validation. For each month, continuous valid hourly data were divided into two parts - one for calibration and the other for validation - and starting values were the first observed oxygen concentration. During model run, if simulated DO was less than 0, the predicted DO for that time point was set to 0. Model was run for calibration until optimal fit was met between observation and simulation. After all the parameters and coefficients were fixed by literature review and calibration, the model was tested for validation. All the calculations were performed by SAS Statistical Software package (SAS Institute, Cary, NC).

3.3.8 Model evaluation

Except graphical comparison between simulated DO and measured DO, coefficient of determination and Nash and Sutcliffe's (1970) model coefficient of efficiency (NSE) were used

as the criteria evaluating model results. The coefficient of determination (R^2) is defined as the squared value of Pearson's correlation coefficient (Moriasi et al. 2007). NSE is defined as:

$$\mathrm{NSE} = 1 - \left[\frac{\sum_{i=1}^{n} (DO_i^{obs} - DO_i^{sim})^2}{\sum_{i=1}^{n} \left(DO_i^{obs} - DO^{mean}\right)^2}\right] \tag{13}$$

where DO_i^{obs} is the ith DO observation for the time period being evaluated, DO_i^{sim} is the ith simulated DO value for the interval being evaluated, DO^{mean} is the mean of observed DO for the constituent being evaluated, and n is the total number of observations.

Model runs for first 24 hours were excluded from evaluation. All the calculations were performed by SAS Statistical Software package (SAS Institute, Cary, NC).

3.4 RESULTS

3.4.1 Model calibration

Most coefficients varied monthly without a clear trend except S_{S20}. It ranged between 0.0625 and 0.156 mg O_2 m^{-2} hr^{-1} (i.e. 1.5 to 3.74 mg O_2 m^{-2} day^{-1}), appearing high in the warm months and low in the cold months with a trend rising from winter to the spring, being high from middle spring to the end of summer, and a dropping in the fall to its bottom in the winter (Table 3.1).

Simulations showed good agreements between simulated DO and measured DO over the calibration period from August 2008 to July 2009. The rising/falling trends and the magnitude of peaks were well predicted for every month from December 2008 to July 2009 (Figure 3.2). The trend of DO dynamics was well reflected but discrepancy exists for magnitude of the peaks (e.g. August 22, 2008). However, simulations performed unsatisfactorily for October 2008, during

which large DO fluctuations and hypoxic events (Oct. 13th to Oct. 16th) occurred (Figure 3.2). Hourly NSE for DO in calibration runs showed a negative result for October 2008 (-0.38) and ranged from 0.31 to 0.70 for rest months (Table 3.2). R^2 was low for October 2008 (0.03) and varied from 0.45 to 0.77 for other months. Both NSE and R^2 values appeared to be higher in the winter and lower in the spring (Table 3.2).

3.4.2 Model validation

With the calibrated parameters, the DO model was applied to another continuous period in each calibrated month from August 2008 to July 2009 (except for September 2008). Overall, the modeling produced satisfactory simulation results in hourly DO change. Visual comparison showed good agreements between the observed and simulated DO for November 2008, December 2008, January 2009, February 2009 and May 2009 (Figure 3.3). The model overestimated DO peaks for a few months (October 2008 and June 2009). Depending on the evaluation criteria, NSE was negative for August 2008 (-0.078), October 2008 (-2.35) and April 2009 (-0.37), and ranged from 0.074 to 0.39 for the rest. R^2 values were between 0.20 and 0.58 (Table 3.2).

3.4.3 Major factors affecting DO modeling results

Data from calibration output were selected to discern major factors affecting modeling results. For each month in the studied period, model simulations showed that photosynthesis contributed 38.7% to 93.8% of total oxygen release, working as the overall dominant role in oxygen sources (Figure 3.4). Reaeration was less important in general but was as significant as photosynthesis in certain months (e.g. November 2008). Respiration consumed 14.5% to 83.4%, of oxygen each month in the lake, playing as the major oxygen consumer in general (Figure 3.4).

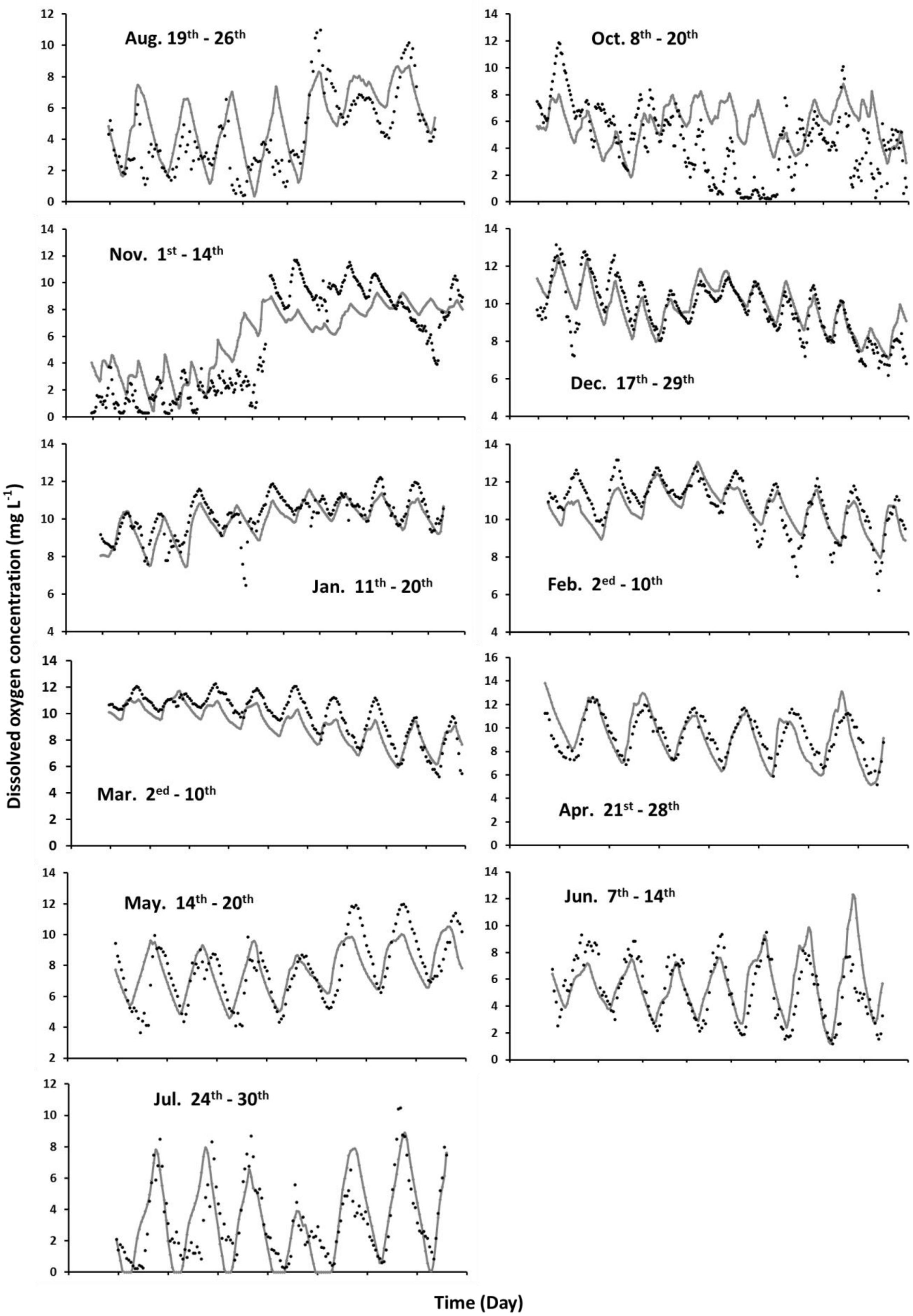

Figure 3.2 Dissolved oxygen hourly simulation for model calibration. Each tick mark interval on x-axis represents a whole day from 0:00 am to 23:59 pm.

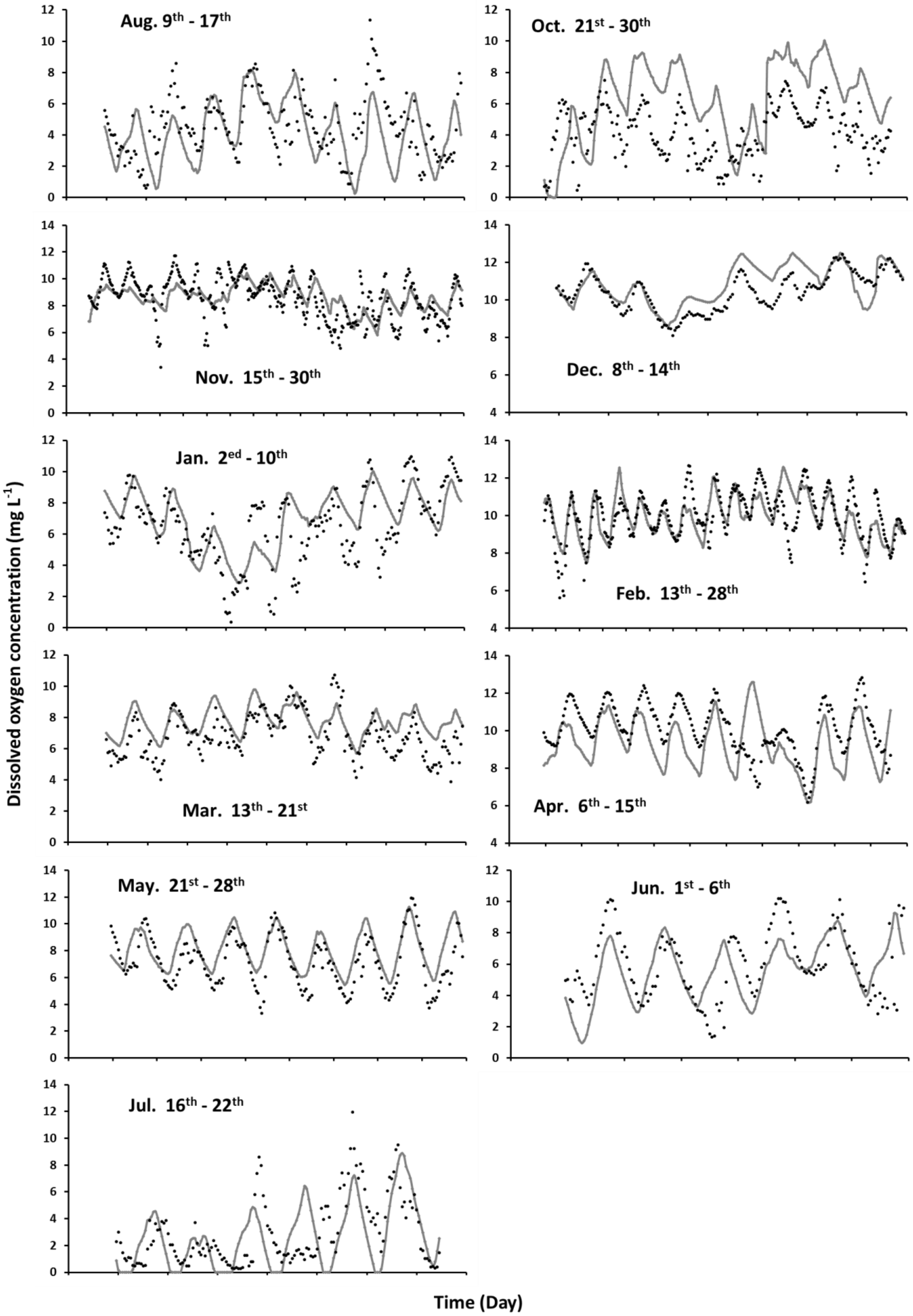

Figure 3.3 Dissolved oxygen hourly simulation for model validation. Each tick mark interval on x-axis represents a whole day from 0:00 am to 23:59 pm.

Table 3.1 Model parameters for each month during August 2008 and July 2009.

	Aug-08	Oct-08	Nov-08	Dec-08	Jan-09	Feb-09	Mar-09	Apr-09	May09	Jun-09	Jul-09	Source
α_p	3.0	1.4	1.5	2.0	1.9	3.0	3.0	5.0	2.8	2.2	2.6	a
α_{par}	3.24	6.48	8.83	4.86	3.24	2.92	3.82	1.36	1.62	2.78	2.5	a
α_j	4.0	3.0	1.0	1.0	1.0	2.0	2.5	1.5	2.0	3.0	1.0	a
α_r	8.33	5.00	3.21	3.33	7.29	3.54	6.25	2.66	4.43	6.25	7.5	a
K_b	0.30	0.30	0.30	0.20	0.10	0.30	0.34	0.62	0.11	0.11	0.36	a
Ss_{20}	0.146	0.0938	0.0625	0.0781	0.0625	0.0938	0.125	0.156	0.109	0.125	0.125	a
θ_s	1.17 for January and 1.07 for the rest											a
θ_b	1.047 when $T \geqslant 20$, 1.13 when $T < 20$											b
θ_r	1.045 for all studied period											b

a. calibration b. literature review

Table 3.2 Statistical results for calibration and validation of the deterministic model

Month	Calibration			Validation		
	n	NSE	*r*-squared	n	NSE	r-squared
August	178	0.31	0.45	216	-0.078	0.20
October	118	-0.38	0.03	231	-2.35	0.26
November	332	0.61	0.65	384	0.31	0.31
December	312	0.70	0.71	168	0.31	0.54
January	228	0.44	0.54	216	0.37	0.42
February	216	0.65	0.67	368	0.39	0.43
March	215	0.61	0.77	216	0.074	0.50
April	160	0.38	0.60	408	-0.37	0.25
May	168	0.46	0.46	193	0.34	0.58
June	180	0.43	0.50	144	0.14	0.27
July	160	0.50	0.60	156	0.15	0.30

The overall second largest oxygen consumer was SOD, which utilized 12.0% to 58.2% DO in each month of the year and was even more critical than respiration sometimes (e.g. August 2008) (Figure 3.4). In addition, driven by wind, oxygen could be released from water column when oversaturated. Oversaturation was not a significant part as oxygen sinks compared with respiration and SOD in summer and fall but appears to be much more important in winter and spring (Figure 3.4). During model calibration, simulation results were not sensitive to variation in oxygen consumed by BOD.

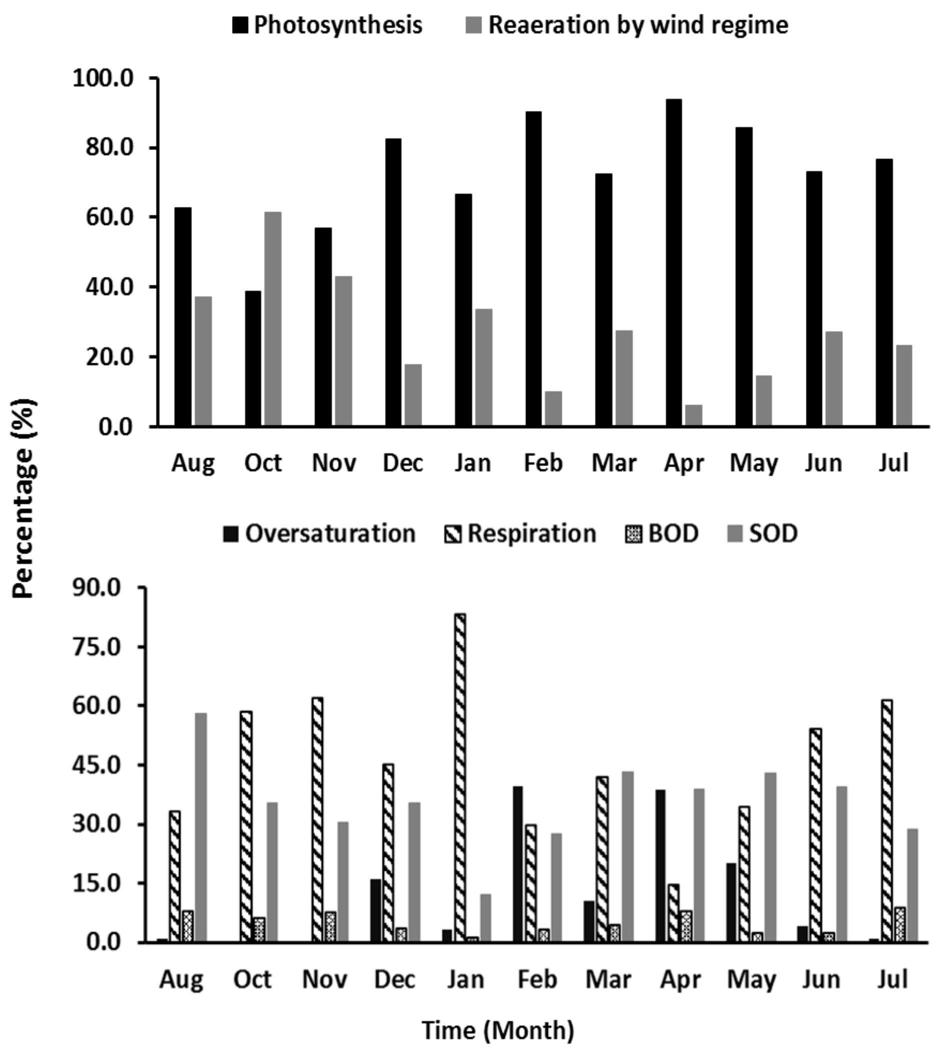

Figure 3.4 Components of oxygen sources (above) and sinks in model calibration.

Based on the level of chlorophyll *a* concentration, the studied lake was eutrophic throughout the year (data not presented). However, water temperature was a more important factor in the determination of changes in photosynthesis compared to chlorophyll *a* concentration. Beyond that, hourly oxygen production by photosynthesis went up and down along with the change of hourly solar radiation, but most times its trends had obvious drops at daily peaks of irradiation for the all seasons (Figure 3.5).

The percentage of oxygen replenishment from reaeration in total oxygen sources (J_{source}%) and percentage of oxygen release by oversaturation in total oxygen sink (J_{sink}%) in every month fluctuated with the change of monthly wind speed (Figure 3.6). However, sometimes J_{source}% went along with change of wind speed but sometimes went against it. In contrast, J_{sink}% always went along with fluctuations of monthly wind speed (Figure 3.6). In months when wind mostly promoted reaeration, hourly oxygen production by reaeration was positively related with the change of hourly wind speed (Figure 3.7 above). However, when wind speed mostly promoted oversaturation, trends for hourly wind speed and the amounts of oxygen released from oversaturation were opposite (Figure 3.7 below).

3.5 DISCUSSION

3.5.1 Model performance

Overall, the model showed a good prediction of diel DO trend over time. The model performed better for the winter months than for the summer months, showing the difficulty in modeling rapid changes in DO that can occur frequently in eutrophic water bodies. Similar problems have been found in other studies (e.g. Chaudhury et al., 1998). In a model with a lower

time resolution (i.e. daily), a rapid change in DO during the day cannot be well reflected when data are averaged.

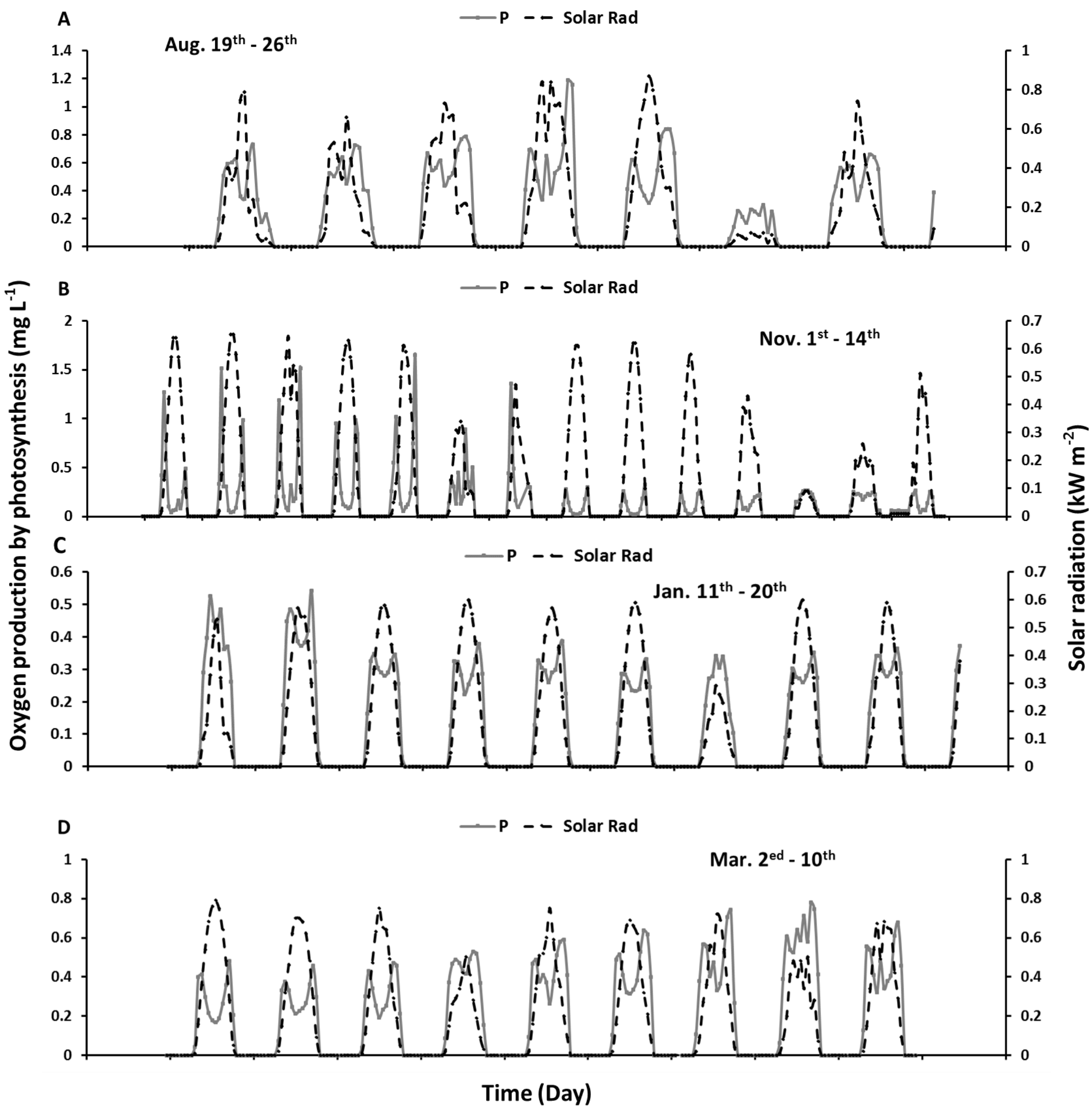

Figure 3.5 Comparison of hourly oxygen production by photosynthesis and intensity of solar radiation for selected days representing: A) summer, B) fall, C) winter, D) spring. Each tick mark interval on x-axis represents a whole day from 0:00 to 23:59.

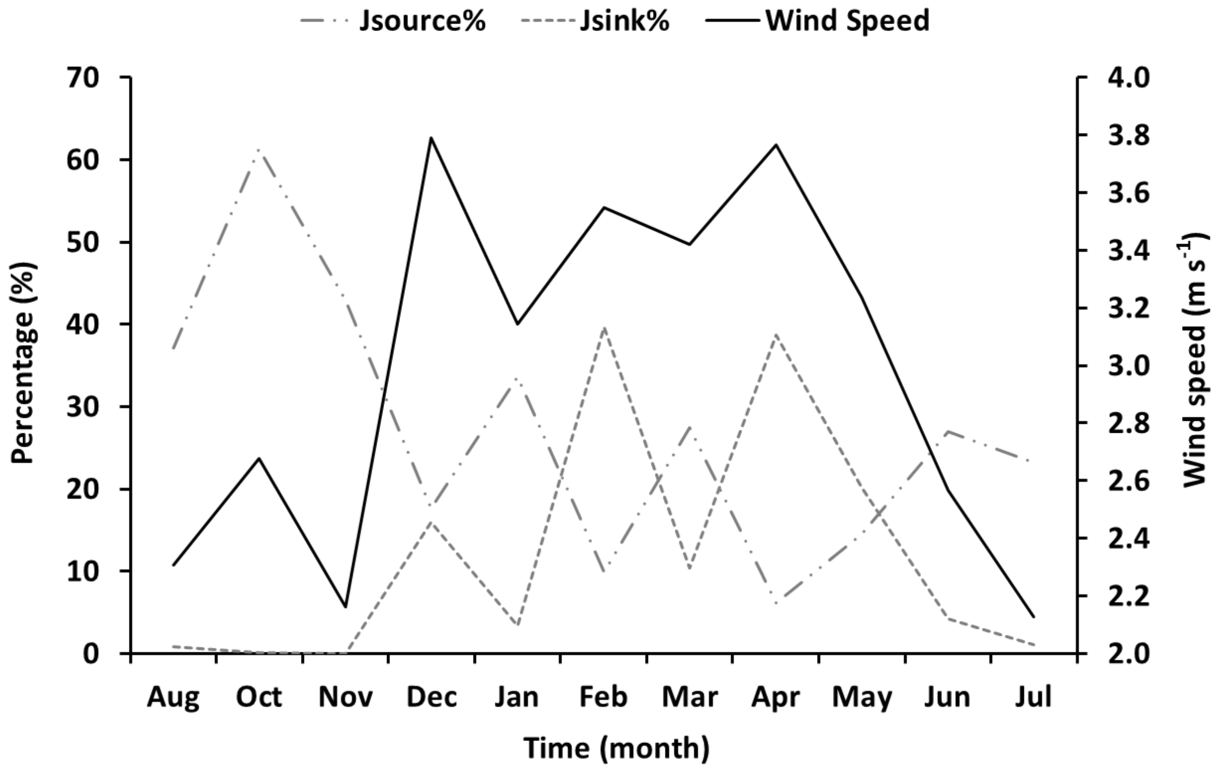

Figure 3.6 Comparison among average monthly wind speed, percentage of oxygen replenishment by reaeration in total oxygen sources (Jsource%) and percentage of oxygen release by oversaturation in total oxygen sink (Jsink%) in every month.

In water quality modeling studies, comparison of modeled results with observed records is mostly done at daily or monthly time intervals. Evaluation for hourly based modeling results using field measurements in water quality is very rare. We used both Nash and Sutcliffe's (1970) model coefficient of efficiency (NSE) and coefficient of determination for evaluation. Nash and Sutcliffe's model coefficient of efficiency have been widely used to evaluate model performance for streamflow, surface runoff, sediments or nutrients. (Legates and McCabe, 1999), but most of published literature reported daily or monthly NSE (Moriasi et al., 2007). Based on a monthly time step, NSE that is equal or greater than 0.5 is considered as satisfactory, equal or greater than 0.65 is taken as good, and equal or greater than 0.75 is rated as very good (Moriasi et al., 2007). Coefficients of determination has been widely used as well, and typically values of R^2 greater

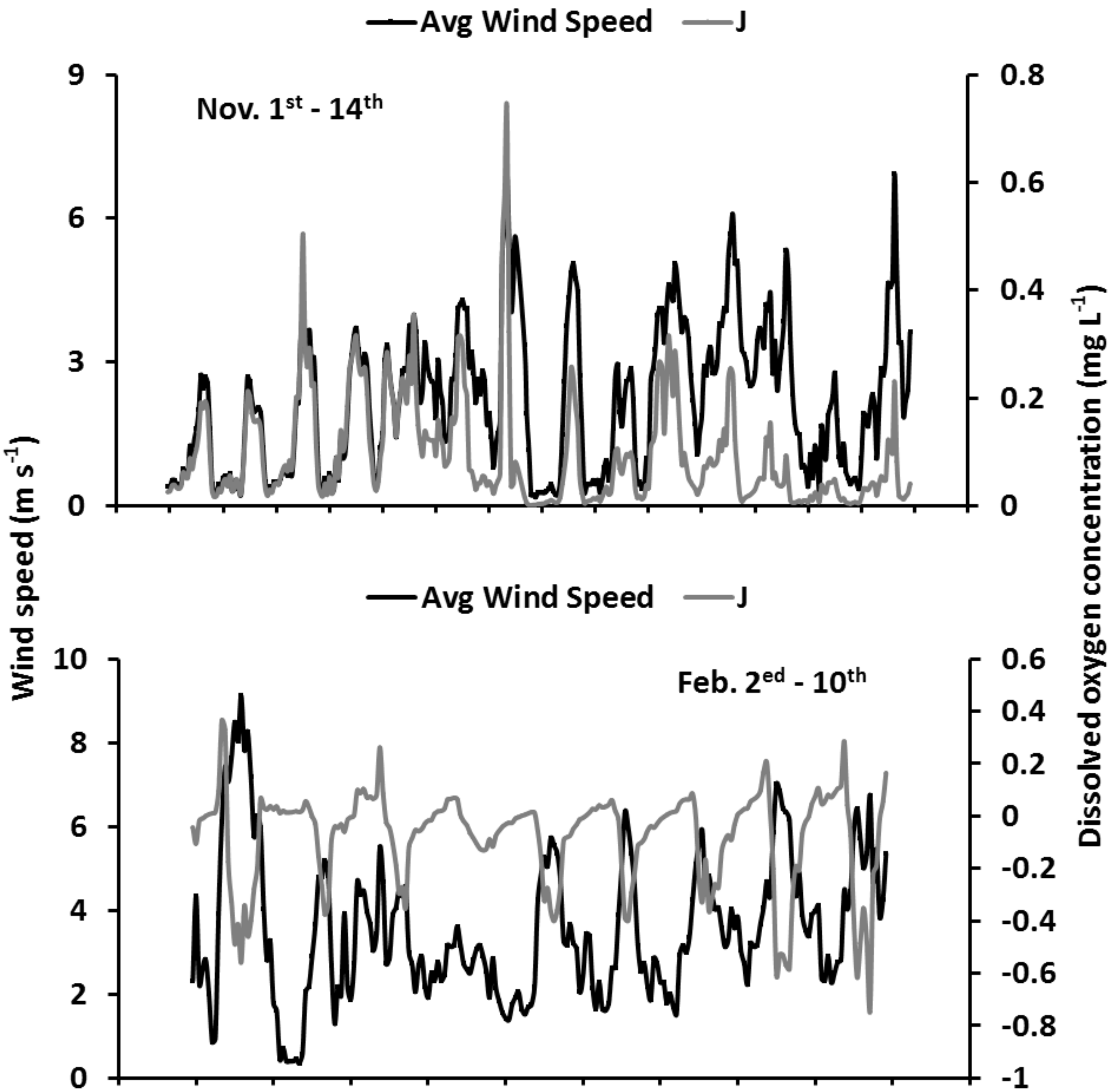

Figure 3.7 Comparison of hourly wind speed and oxygen production/loss by reaeration (positive part in secondary y-axis)/oversaturation (negative part in secondary y-axis) in November 2008 and February 2009.

than 0.5 are considered acceptable for models on a daily or monthly time step (Santhi et al., 2001; Van Liew et al., 2003; Moriasi et al., 2007). Due to the fact that averaging values significantly decreases the variation, models with higher time resolution were always reported with lower

NSE and R^2 (Fernandez et al., 2005; Singh et al., 2005; Wu and Xu, 2006; Van Liew et al., 2007). Some researchers (Motovilov et al., 1999; Van Liew et al., 2003) reported NSE values between 0.36 to 0.75 as satisfactory and greater than 0.75 as good on a daily time step. Therefore, based on our results, we propose to consider an NSE value of less than 0.30 as unsatisfactory, an NSE value between 0.30 to 0.60 as satisfactory, and an NSE value of greater than 0.60 as good for DO modeling at the hourly-time resolution. Similarly, for the coefficient of determination, values of R^2 equal or greater than 0.45 and 0.70 can be considered acceptable and good, respectively, for high-time resolution DO modeling.

3.5.2 Critical model parameters

Sediment oxygen demand is a major factor consuming DO in aquatic environments (Truax et al., 2005; Martin et al., 2012). The parameter was incorporated in our DO model, but field SOD data was not available for the studied period. In this study, we used a published empirical equation (S_{S20}) to estimate SOD. Stefan and Fang (1994) chose 2.0 mg O_2 m^{-2} day^{-1} from literature review for S_{S20} of shallow eutrophic lakes in the generic model they developed, and it was successfully applied for their study. Since University Lake was eutrophic throughout the studied period and even close to hyper-eutrophic in summer and fall (data not presented), the calibrated value for S_{S20} raging 1.5 to 3.74 mg O_2 m^{-2} day^{-1} is considered reasonable for this study. The seasonal trend of S_{S20} was driven by water temperature since biological activity in the sediment was inhibited in the cold months.

Water temperature is a driving force in the model. It is more important than chlorophyll *a* concentration for photosynthesis, has an impact on all biological processes for oxygen sinks, and indirectly affects reaeration by deciding oxygen saturation levels. Other weather parameters, like solar radiation and wind speed, also strongly affect model simulations. However, compared with

water temperature which has been well studied in former studies, relationships between solar radiation and photosynthesis and between wind speed and reaeration in DO modeling are not clearly understood, especially in a high-time resolution model.

The obvious marked slow-down for photosynthesis during the hours of maximum irradiation could be attributed to photorespiration, which has been reported in other studies as well. Field and laboratory experiments in a shallow lake in Italy also shows that primary production slowed down obviously at the peak of solar radiation, especially in spring and summer (Hull, 2008). Photorespiration occurs in the photosynthetic tissues and is completely distinct from ordinary respiration, which is essentially mitochondrial (Beardall, 1989; Hull, 2008). Culberson and Piedrahita (1995) reported that up to 10% of oxygen production by photosynthesis could be consumed because of photorespiration. The photorespiration process is neglected in most of DO models, and it can only be directly observed in models with high-time resolution. Although the model developed in this study clearly reflected the photorespiration process, it seems that the degree of the slow-down in photosynthesis is overestimated sometime (e.g. November 2008, Figure 3.5), indicating that more improvements are needed to simulate photorespiration specifically. Successful trials includes Culberson and Piedrahita's study (1995) in which an individual equation for photorespiration was added in the primary production in their DO model for an aquaculture pond and successful simulations were yielded. For DO models with high-time resolution, especially for eutrophic water bodies, considerations for the photorespiration process are recommended.

To our knowledge, all published DO modeling studies consider wind as a contributing source. In our modeling study for this eutrophic/hyper-eutrophic shallow lake, we found that the relationship between wind and oxygen dissolution is complex - Wind contributed to adding

oxygen into the lake water when dissolved oxygen levels were low; however, wind seemed to release oxygen from the lake water into the atmosphere when the water was oversaturated. This reversed functionality of wind has not been considered in the current dissolved oxygen modeling. For most current daily or monthly DO models, it is very uncommon that averaged daily or monthly DO concentrations become oversaturated. However, for eutrophic lakes, a few hours in a day can often cause saturation and oversaturation, indicating the importance of considering the reversed wind-DO functionality in high-time resolution modeling. Although stronger wind would accelerate the turbulence between the water-air interface, when DO is replenished and becoming closer to saturation equilibrium, wind is no longer acting as the driving force for reaeration. In addition, when DO is oversaturated, the widely accepted formula for reaeration, which is also the formula where we derived from in this study, shows that wind could strongly promote oxygen release from water column. Both Figure 3.6 and 7 shows that the effects of oversaturation are strong, and it's against the common sense that stronger wind is always good for reaeration. Based on the results of their DO modeling study for coastal shallow waters, Hull et al. (2008) postulated that wind could contribute in achieving dissolved oxygen supersaturation levels. Therefore, they suggested adding an increment to the saturation value caused by the wind stress, and the value of the increment should be determined by laboratory tests. However, for high-time resolution DO modeling, further studies are needed to quantitatively describe the mechanisms between wind speed, reaeration, and/or DO release under various conditions of DO saturation.

3.5.3 Other options for improving model performance

In addition to changing the assumption for the one-dimensional model that water column is assumed well mixed due to its shallow depth, some options are available to improve model

performance, for instance the collection of additional field data. Due to the significance of reaeration for oxygen sources in summer/fall and oversaturation for oxygen sinks in spring/winter (Figure 3.4), the accuracy of the major driving force-wind speed- is becoming very critical as a model input. Reports from a previous study (Fontaine et al., 2001) suggested that site specific climatological data including wind speed and solar radiation could help to provide better estimates. Therefore, the model developed in this study could be better parameterized and calibrated if wind speed were collected at the studied site instead of a nearby weather station. This may also help improve the model performance for October 2008 since calibration results indicated that reaeration was dominant as oxygen sources for this particular month (Figure 3.4).

3.6 CONCLUSIONS

This study developed an hourly deterministic model of dissolved oxygen and applied the model to a subtropical eutrophic shallow lake for a 1-year period. The model incorporated important source and sink components of dissolved oxygen for a lake system, such as photosynthesis, re-aeration, respiration, biochemical oxygen demand, and sediment oxygen demand. It is the first DO modeling with such a high-time resolution and for such a long period of time. Overall, the model produced satisfactory results, providing a modeling approach for predicting rapid, sporadic hypoxic events. The model performed better for winter months than for summer months, showing our current knowledge gap and the difficulty in accurately quantifying the relationship between solar radiation and photosynthesis and the relationship between wind speed, reaeration and oxygen release under variable saturation conditions in DO modeling.

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CHAPTER 4: RAPID FIELD ESTIMATION OF BIOCHEMICAL OXYGEN DEMAND IN A SUBTROPICAL EUTROPHIC URBAN LAKE WITH CHLOROPHYLL A FLUORESCENCE

4.1 INTRODUCTION

In the United States, about 44% of all lakes and 59% of man-made lakes are classified to be in fair or poor biological condition (USEPA, 2009). The main reason for the water quality degradation has been attributed to excess nutrients and organic inputs to the lake water bodies, which can lead to algal bloom and hence dissolved oxygen (DO) depletion (Carpenter et al., 1998). This could be especially serious for urban lakes where the large impervious surface of the urban environment increases nutrient runoff and waste discharges with oxygen consuming chemicals (Whitehead et al., 2009).

Oxygen is needed for aquatic life and the amount of oxygen dissolved in a water body is therefore an important water quality parameter. Low DO has been identified as a serious water quality problem (Caraco and Cole, 2002). When DO falls below 5 mg L^{-1}, sensitive species of fish and invertebrates can be negatively impacted, and at DO levels below 2.5 mg L^{-1}, an oxygen depletion stage known as hypoxia, most fish species could be negatively impacted (Frodge et al., 1990). Hypoxia in water bodies is a growing problem worldwide that is associated with negative impacts on not only sensitive species of fish and invertebrates, but also on metal, nitrogen and phosphorus transformations (Kemp et al., 1990; Breitburg, 1992; Hamilton et al., 1997; Gray et al., 2002; Harrison et al., 2005; Stevens et al., 2006).

One factor leading to low DO is organic pollution that can adversely affect the health of the aquatic system by consuming a large amount of dissolved oxygen in water resulting in hypoxic conditions. Normally, organic consumption of dissolved oxygen in an aquatic system is

presented as biochemical oxygen demand (BOD). BOD measures the amount of oxygen consumed within a certain period of time by bio-degradable organic matter in a water column. Therefore, BOD of an aquatic system is an important parameter frequently used in assessment of water quality, as well as for developing management strategies for water quality protection (Basant et al., 2010). BOD measurements are commonly given as a 5- to 20-day test, with a 5-day test being the most common period, also known as BOD_5. As a laboratory based biodegradation test, it delays analysis of potential pollution events. If BOD can be estimated rapidly using a real time monitoring technique, it would be of great usefulness to environmental regulators in predicting the degree of organic pollution and taking prompt actions.

Fluorometric methods have long been used to investigate chlorophylls' reaction to toxic chemical compounds (e.g. Christoffers and Ernst, 1983; Brack and Frank, 1998). Several recent studies have used fluorescence techniques as a portable tool for rapid determination of the presence of biodegradable organic matter. It is a rapid testing technique that does not use chemical reagents and requires little sample preparation (Hudson et al., 2008). Fluorescence spectroscopy, such as excitation–emission matrix (EEM) spectroscopy, has been used in several studies on dissolved organic matter in natural waters including marine waters (Coble, 1996), rivers (Patel-Sorrentino et al., 2002; Hudson et al., 2008), ground waters (Baker and Genty, 1999) and lakes (Cammack et al., 2004) in laboratory. Some researchers tested the possibility of using fluorescence as a surrogate for BOD (Cârstea et al., 2012). This method has been successfully applied to identify microbial communities in water and to establish the correlation between a waterbody's BOD_5 and the microbial activity in it (Baker and Inverarity, 2004; Hudson et al., 2008; Kwak et al., 2013). In the recent decade, studies have been conducted on the relationship between BOD_5 and tryptophan-like fluorescence ($\lambda_{excitation}$ = 280 nm, $\lambda_{emission}$ 350 nm) for waters

collected from rivers (Comber et al., 1996; Baker and Inverarity, 2004; Hudson et al., 2008), sewage (Comber et al., 1996; Reynolds and Ahmad, 1997; Ahmad and Reynolds, 1999; Reynolds, 2002; Baker and Curry, 2004; Hudson et al., 2008) and industrial effluents (Comber et al., 1996; Hudson et al., 2008). Some researchers (e.g., Kwak et al., 2013) developed an algorithm to predict BOD_5 of water samples using a fluorescence reading. Up to now, this approach has been applied in the laboratory mostly to wastewater samples with a wide range of BOD_5 concentrations (Kwak et al., 2013).

Many urban water bodies are monitored by local communities and volunteers. A rapid BOD testing method with fluorescence can be not only time- and cost-saving, but it offers a tool for predicting potential oxygen depletion. To our knowledge, no report exists on a numeric relation between BOD and field chlorophyll *a* fluorescence ($\lambda_{excitation}$ = 460 nm, $\lambda_{emission}$ 685 nm) measurements. Many urban lakes receive large quantities of storm runoff from turf and paved surfaces. In some cases the turf has received fertilizer treatments. Some of the fertilizer, along with grass clippings and leaf litter, may be mobilized due to rainfall or irrigation and can then flow into nearby water bodies. Therefore, urban lakes can be especially affected by organic pollutants or the eutrophication caused by them. Determining BOD with field fluorescence measurements can be a cost-effective tool for rapid assessment of water quality.

This study was conducted in a shallow, eutrophic urban lake over the period from October 2012 to September 2013. The objectives of this study were to: 1) assess trends of BOD, chlorophyll fluorescence and chlorophyll *a* concentration in the lake environment, 2) develop a numeric relationship between BOD and fluorescence, and 3) test other ambient factors that may affect BOD in the similar environment.

4.2 METHODS

4.2.1 Site description

The study was conducted at University Lake, located in Baton Rouge, Louisiana, USA (Latitude 30°24’50”N; Longitude 91°10’00”W) on the Louisiana State University (LSU) campus (Figure 4.1). The lake itself is 74.6- ha, surrounded by five small lakes. The perimeter of University Lake is about 6.7 km, with an average depth of 0.9 meter. The entire lake watershed has a drainage area of about 187.4 ha (Reich Assoc., 1991; Xu and Mesmer, 2013). Climate in the region is humid-subtropical, with long hot summers and short mild winters. University Lake has one primary surface inflow and one surface outflow, excluding periods of runoff, both of which are via overflow dams. The entire watershed of University Lake is mainly for urban use including residential, recreational and institutional purposes. University Lake and the surrounding small lakes were developed from swamps in the 1930s as a public works project to create an open water environment. The most recent dredging was conducted in 1983 when large amounts of sediments and excess nutrients from surface runoff were removed (Reich Assoc., 1991). The lake has been reported as eutrophic, as its water showed high concentrations of nitrogen and phosphorus (Mesmer, 2010).

4.2.2 Field measurements

In this study, six sampling locations were identified to represent the lake (Figure 4.1). Location 1 was near a heavy traffic road. Location 2 was at a pier near the outflow dam of the lake next to a parking area. Locations 3 and 4 generally represented the deep water area of the lake. Location 5 was the only site at the eastern part of the lake and location 6 was near the inflow of the Lake, close to a 2-lane busy highway.

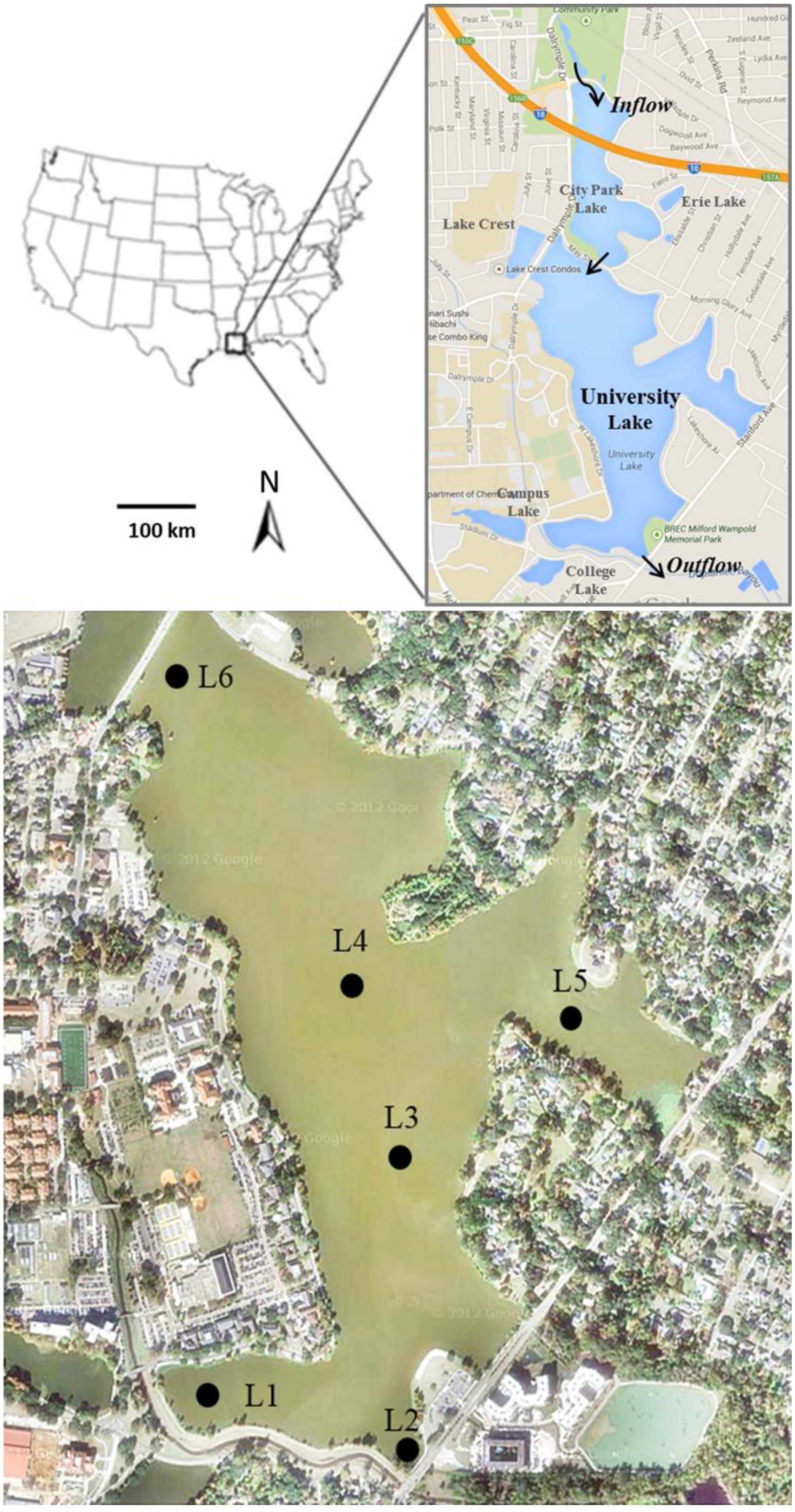

Figure 4.1 Geographical location of University Lake in Baton Rouge, Louisiana, USA (above) and sampling sites (1 – 6) in the lake.

From October 2012 to September 2013, biweekly field trips were made to conduct *in-situ* measurements on fluorescence and water quality at the six sampling sites. Fluorescence was measured with an AquaFluor® handheld fluorometer (Turner Designs, CA, USA) and was reported as arbitrary fluorescence units (AFU). An AFU is a unit of measurement used for *in vivo* chlorophyll analysis which is the detection of chlorophyll in live algal cells in water. In this technique, the excitation light from the fluorometer passes through the untreated sample of water, causing the chlorophyll within the cells to fluorescence. Then the fluorometer reports the normalized variable fluorescence after a 5s scan.

During each field trip, a set of *in-situ* water quality parameters was measured at the six sites using an YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA). The parameters included water temperature, pH, conductivity, and dissolved oxygen. In addition, a 2000-ml water sample was collected from each site and the samples were stored in a cooler with wet ice during the transportation for later laboratory analysis. At five near-shore sites (i.e. L2, L5 and L6; Figure 4.1), measurements were taken about 3 meters from the shoreline on the lake bottom and water samples were taken by a sampler at about 10 cm below water surface. For the three far-shore sites (i.e. L1, L3 and L4; Figure 4.1), water samples were collected using a kayak at about 10 cm below water surface and measurements were taken at 35 cm below the surface.

4.2.3 Laboratory measurements

Water samples were taken from various locations in the lake and at different dates to develop a relationship between fluorometer reading and chlorophyll *a* concentration. Extraction and analysis of chlorophyll *a* from the water samples were done at the Wetland Biogeochemistry Analytical Services, LSU Department of Oceanography and Coastal Sciences, using a Turner Designs TD-700 Fluorometer (Turner Designs, Sunnyvale, CA, USA) following the protocols of

Arar and Collins (1997). Extracted chlorophyll concentrations (μg L^{-1}) were then correlated with *in vivo* chlorophyll fluorescence (AFU) from the AquaFluor® handheld fluorometer. A strong linear relationship has been found for the studied lake between *in-vivo* chlorophyll fluorescence (AFU) and extracted chlorophyll *a* concentration (μg L^{-1}), which can be given as follows:

$$Chl\text{-}a = 0.3944 * AFU + 1.0039 \qquad (r^2 = 0.9827) \tag{1}$$

Water samples from each sampling dates were analyzed at the Watershed Hydrology Laboratory, LSU School of Renewable Natural Resources, for 5-day and 10-day biochemical oxygen demands, reported as BOD_5 and BOD_{10}, respectively. Laboratory procedure followed a modified version of Section 5210B of APHA's 'Standard Methods for the Examination of Water and Wastewater' (APHA, 2005). The modification to the standard method included a daily sample re-aeration if dissolved oxygen (DO) concentration was below 3.00 mg L^{-1} due to no dilution being performed. BOD samples were stored at room temperature (20 ℃ +/- 2 ℃) in an incubator (Thermo Scientific Imperial III Standard Incubator, Thermal Scientific Inc., Texas, USA). In the laboratory, DO of all BOD samples were measured with an YSI 5100 dissolved oxygen meter (YSI Inc., Yellow Springs, OH, USA).

Starting from June 2013, biochemical oxygen demand was measured every day to determine the reduction rate in biochemical oxygen consumption of the lake water samples. At the same time, additional samples were also used for a daily fluorescence measurement to assess the relationship between oxygen consumption and the change in water fluorescence; these samples were stored in separate BOD bottles.

4.2.4 Ambient data collection and analysis

To document ambient lake water conditions, daily climatic records from a near-by weath er station (Ben Hur Station, the Louisiana Agriclimatic Information System) were gathered for th e study period. The weather station is located approximately 5 km east of the study site, and the weather records included daily rainfall, maximum air temperature, and minimum air temperature (Table 4.1).

Table 4.1 Monthly weather data for University Lake in Baton Rouge, USA, from July 2008 to June 2009 and from October 2012 to September 2013.

	Parameters	Mean	Max	Min	Std.
2008-2009	Monthly Max Air Temp. (°C)	25.9	33.3	17.9	5.6
	Monthly Min Air Temp. (°C)	14.1	22.4	5.4	6.5
	Monthly Precipitation (mm)	103.9	230.9	11.2	70.5
2012-2013	Monthly Max Air Temp. (°C)	25.0	32.3	17.6	5.9
	Monthly Min Air Temp. (°C)	13.0	22.7	1.2	7.4
	Monthly Precipitation (mm)	156.4	397.0	13.7	98.4

Regression analysis was employed to determine the relationship between biochemical oxygen demand (BOD, mg L^{-1}) and *in-situ* fluorescence in AFU. The general equation for data collected from all six sites is given as follows:

$$BOD = b + k * AFU \tag{2}$$

where *b* and *k* are the regression parameters. Best fitting parameters were found with the SAS Statistical Software package (SAS Institute, Cary, NC). All statistical analysis was performed.

4.3 RESULTS AND DISCUSSION

4.3.1 Seasonality of fluorescence and chlorophyll a concentration

From October 2012 to September 2013, the studied shallow urban lake showed a large variation in the chlorophyll *a* fluorescence, with a range from 17.2 AFU to 406.5 AFU (Table 4.2). The fluorometric unit appeared highest in August and lowest in February, displaying a trend of AFU rising from the winter months to the summer months and then declining from the fall into the winter (Table 4.2). Considerable variation in AFU existed also among the sampling sites, and the variation was significantly lower in the winter months than in the summer months (Table 4.2).

Concurrently, chlorophyll *a* concentrations fluctuated greatly over the year, ranging from 7.8 μg L^{-1} to 161.3 μg L^{-1} with an average of 47.5 μg L^{-1} during the studied period (Table 4.3). The highest concentration occurred in August 2013 and the lowest was found in February 2013 (Table 4.3). Chlorophyll *a* concentration was consistently low during the late winter and early spring, rose up rapidly in the late spring, and reached the peak in the late summer blooms following a decline in late fall (Table 4.3). Variation in chlorophyll *a* concentration was significantly lower in the late winter and early spring and was significantly higher in the late summer blooms (Table 4.3).

Based on a 1-year monitoring of nutrient inputs from stormwater into University Lake, Mesmer (2010) reported an average concentration of total nitrogen (TN, sum of organic nitrogen + nitrate nitrogen + nitrite nitrogen + ammonia nitrogen) of 3.14 mg L^{-1} and an average concentration of total phosphorus (TP) of 0.383 mg L^{-1}. Based on both Carlson's Trophic State Index for lake waters (1977) and the classification for stream trophic state proposed by Dodds et

Table 4.2 *In-Situ* fluorescence, mean and standard deviation from 6 sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013.

	Fluorescence (AFU)							
Date	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean	STD
10/26/2012	189.6	201.4	242.4	261.5	182.9	267.3	224.2	37.4
11/13/2012	176.5	173.5	178.7	176.4	193.7	139.5	173.1	17.9
11/29/2012	152.5	167.3	176.9	174.7	167.4	142.5	163.6	13.4
12/12/2012	102.6	85.0	90.3	84.3	101.5	76.7	90.1	10.2
01/28/2013	93.8	75.4	76.9	70.4	65.0	68.8	75.0	10.1
02/15/2013	17.2	20.8	26.4	31.5	30.1	27.3	25.5	5.5
03/01/2013	42.8	46.7	49.3	43.1	43.2	41.1	44.4	3.0
03/19/2013	30.6	27.5	28.3	25.8	28.9	40.5	30.3	5.2
04/01/2013	60.2	61.4	66.0	62.3	61.5	58.0	61.5	2.6
04/15/2013	68.0	93.3	96.8	71.7	95.0	59.6	80.7	16.2
04/29/2013	41.2	67.1	80.0	43.8	59.5	44.7	56.1	15.5
05/13/2013	39.4	43.9	50.4	51.9	49.0	39.9	45.8	5.4
05/30/2013	147.0	139.9	120.1	105.6	112.1	104.7	121.6	18.0
06/10/2013	133.8	89.9	73.6	93.0	61.2	69.9	86.9	26.0
06/25/2013	214.4	198.5	182.8	207.8	152.4	164.4	186.7	24.7
07/19/2013	196.2	345.6	318.0	212.3	232.7	185.9	248.5	67.0
08/02/2013	362.1	227.3	249.0	284.0	295.0	332.0	291.6	50.2
08/19/2013	268.5	222.0	262.3	318.7	293.3	237.7	267.1	35.4
09/09/2013	310.7	406.5	370.4	389.5	381.5	258.7	352.9	56.6
09/29/2013	370.3	291.1	332.2	248.0	292.6	261.0	299.2	45.5
Mean	150.9	149.2	153.5	147.8	144.9	131.0	146.2	23.3

Table 4.3 Means and standard deviations of chlorophyll *a* concentration from 6 sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013.

	Chlorophyll *a* (μg L^{-1})							
Date	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean	STD
10/26/2012	75.8	80.4	96.6	104.1	73.1	106.4	89.4	13.5
11/13/2012	70.6	69.4	71.5	70.6	77.4	56.0	69.3	6.5
11/29/2012	61.1	67.0	70.8	69.9	67.0	57.2	65.5	4.8
12/12/2012	41.5	34.5	36.6	34.3	41.0	31.3	36.5	3.7
01/28/2013	38.0	30.7	31.3	28.8	26.7	28.2	30.6	3.7
02/15/2013	7.8	9.2	11.4	13.4	12.9	11.8	11.1	2.0
03/01/2013	17.9	19.4	20.4	18.0	18.1	17.2	18.5	1.1
03/19/2013	13.1	11.8	12.2	11.2	12.4	17.0	12.9	1.9
04/01/2013	24.7	25.2	27.0	25.6	25.3	23.9	25.3	0.9
04/15/2013	27.8	37.8	39.2	29.3	38.5	24.5	32.8	5.8
04/29/2013	17.3	27.5	32.5	18.3	24.5	18.6	23.1	5.6
05/13/2013	16.5	18.3	20.9	21.5	20.3	16.7	19.0	2.0
05/30/2013	59.0	56.2	48.4	42.7	45.2	42.3	48.9	6.5
06/10/2013	53.8	36.4	30.0	37.7	25.1	28.6	35.3	9.4
06/25/2013	85.6	79.3	73.1	83.0	61.1	65.8	74.6	8.9
07/19/2013	78.4	137.3	126.4	84.7	92.8	74.3	99.0	24.1
08/02/2013	143.8	90.7	99.2	113.0	117.4	131.9	116.0	18.1
08/19/2013	106.9	88.6	104.5	126.7	116.7	94.8	106.3	14.0
09/09/2013	123.5	161.3	147.1	154.6	151.5	103.0	140.2	22.3
09/29/2013	147.1	115.8	132.0	98.8	116.4	103.9	119.0	17.9
Mean	60.5	59.8	61.6	59.3	58.2	52.7	58.7	8.6

al. (1998) this shallow urban lake should be considered as eutrophic. When classifying trophic state of lake waters, although TN, TP, and Secchi depth are considered, priority is often given to the estimation associated with chlorophyll *a* since it is the most accurate parameter for predicting algal biomass (Gregor and Marsalek, 2004). Based on Carlson's TSI, the boundary value of chlorophyll *a* between eutrophic and hypereutrophic is 56 μg L^{-1}. Accordingly, University Lake was hypereutrophic throughout the summer and fall as the chlorophyll *a* concentrations during the period were constantly above 66 μg L^{-1}.

The seasonality of chlorophyll *a* concentration assessed in this study is in agreement with findings from other studies conducted in temperate and subarctic shallow eutrophic lakes. For example, in a study conducted by French and Petticrew (2006) on shallow eutrophic lakes located in subarctic north-central British Columbia, chlorophyll *a* concentrations ranged from < 1 μg L^{-1} in the winter and spring months to 112 μg L^{-1} in the late summer and early fall months during 1997 - 1998; In another study conducted by Schalles and others (1998) on an eutrophic lake in a temperate climate, high chlorophyll *a* concentrations (up to 280 μg L^{-1}) were found during the late summer and early fall months, with the lowest chlorophyll *a* concentration (20 μg L^{-1}) occurring in the winter and early spring months during 1995 and 1996. Although the range of chlorophyll *a* concentrations among these studies and ours were different, it appears that in all these studies chlorophyll *a* concentrations showed a similar seasonal trend and were strongly affected by temperature. Interesting to note is the difference in chlorophyll *a* concentration of these eutrophic lakes during the winter time. Surface water freeze occurs in high-latitude lakes during winter, which may reduce light penetration and cause chlorophyll *a* concentration down to a very low level, while eutrophic lakes in warm regions show higher levels of chlorophyll *a*

concentration in the winter months. The results imply that lakes in warm climate can be especially prone to urban pollution and algal bloom.

4.3.2 Seasonal fluctuation of biochemical oxygen demands

During the period from October 2012 to September 2013, 5-day BOD levels in the lake waters ranged from 1.3 mg L^{-1} to 17.6 mg L^{-1}, with an average of 7.6 mg L^{-1} (Table 4.4). In general, levels of 10-day BOD were higher with an average of 12.7 mg L^{-1}, fluctuating from 2.3 mg L^{-1} to 30.2 mg L^{-1}. As with AFU and chlorophyll *a*, BOD_5 and BOD_{10} peaked both in August and reached their minima in February (Table 4.4). There was a rising trend from the winter months to the summer months, following a drop into the fall (Figure 4.2). Similar to the fluctuations of AFU and chlorophyll *a* concentration, variation of BOD_5 and BOD_{10} among the sampling sites was significantly lower in the winter months than in the summer months (Table 4.4).

The seasonal fluctuation in BOD observed in this study represents general characteristics for the range and seasonality in this shallow urban lake. In a previous study on dissolved oxygen during 2008-2009 in the same lake, Xu and Mesmer (2013) reported a slightly higher 5-day BOD average (7.2 mg L^{-1}) with a similar seasonal trend. Also, the BOD ranges of this eutrophic lake are comparable to the findings from other shallow eutrophic lakes in similar climate regions. For instance, from their study on a subtropical man-made lake in India, Arora and Mehra (2009) reported a BOD_5 range between 4.0 mg L^{-1} and 12.0 mg L^{-1} (average: 6.8 mg L^{-1}) from January 2000 to December 2001; In another study on a subtropical freshwater lake in China, Wang and others (2007) reported a BOD_5 dynamics fluctuating from 3.2 mg L^{-1} to 9.1 mg L^{-1} with an average of 6.0 mg L^{-1} from 1999 to 2003. The difference in BOD range among these and our

studies could be attributed to urban pollution levels, as well as to ambient conditions such as rainfall and temperature.

Table 4.4 Means and standard deviations of BOD_5 and BOD_{10} from 6 sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013.

Collection Date	BOD_5 / BOD_{10} (mg L^{-1})							
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean	STD
10/26/2012	10.4/18.3	8.7/16.4	9.5/16.9	8.5/15.9	6.6/13.3	8.7/16.3	8.7/16.2	1.25/1.64
11/13/2012	7.1/13.8	7.1/14.1	7.2/14.4	7.7/14.7	7.0/13.6	5.9/7.3	7.0/13.0	0.60/2.80
11/29/2012	8.1/12.9	8.5/12.8	8.3/13.0	8.3/12.0	7.0/11.6	7.9/12.3	8.0/12.4	0.55/0.59
12/12/2012	4.6/8.3	5.1/8.7	5.3/8.8	5.3/8.8	5.8/9.5	5.1/8.1	5.2/8.7	0.39/0.48
01/28/2013	6.5/9.3	9.0/12.4	6.2/8.7	8.5/11.8	8.4/11.5	8.1/10.9	7.8/10.8	1.16/1.47
02/15/2013	1.3/2.3	1.5/2.6	1.7/2.9	1.8/3.2	1.6/2.9	3.7/5.7	1.9/3.2	0.89/1.22
03/01/2013	2.7/4.6	2.9/4.8	2.7/4.6	2.7/4.4	2.6/4.5	3.1/5.0	2.8/4.6	0.20/0.22
03/19/2013	2.5/3.9	3.1/4.5	3.2/4.6	2.9/4.1	2.8/4.3	4.2/6.2	3.1/4.6	0.59/0.84
04/01/2013	5.1/7.6	4.8/7.3	5.3/7.9	4.7/7.1	5.1/7.5	5.1/7.7	5.0/7.5	0.20/0.27
04/15/2013	4.5/6.9	4.6/7.5	4.4/7.4	4.3/7.1	4.6/7.6	4.1/6.7	4.4/7.2	0.19/0.36
04/29/2013	3.7/5.6	3.7/6.1	3.6/5.7	3.8/5.9	3.8/5.8	3.8/5.7	3.7/5.8	0.10/0.18
05/13/2013	6.7/8.4	6.2/8.0	6.4/8.1	5.7/7.4	6.6/8.3	5.5/7.2	6.2/7.9	0.50/0.50
05/30/2013	8.4/12.3	6.9/10.2	6.9/10.3	7.0/10.1	7.5/11.1	6.3/10.1	7.1/10.7	0.70/0.87
06/10/2013	6.4/10.7	5.8/10.4	5.7/9.9	5.8/10.2	6.1/10.1	5.4/9.6	5.9/10.1	0.35/0.38
06/25/2013	10.8/17.7	7.5/12.1	8.9/14.6	7.7/13.6	6.6/11.6	7.9/13.4	8.2/13.8	1.46/2.20
07/19/2013	15.7/25.4	12.5/22.5	11.4/20.0	13.5/17.5	11.1/18.8	13.1/22.7	12.9/21.1	1.66/2.91
08/02/2013	17.6/28.0	14.1/24.6	16.4/28.1	12.5/22.6	14.9/24.2	11.5/22.1	14.5/24.9	2.30/2.58
08/19/2013	15.9/28.3	13/23.7	14.8/25.6	16.7/30.2	14.1/25.8	13.2/25.2	14.6/26.5	1.47/2.35
09/09/2013	17.6/29.5	16.8/29.5	13.0/25.0	13.8/26.4	13.9/25.8	14.1/25.3	14.9/26.9	1.86/2.07
09/29/2013	12.3/20.8	9.8/17.2	8.9/15.5	11.9/19.3	8.4/15.8	13.5/24.2	10.8/18.8	2.06/3.35
Mean	8.4/13.7	7.6/12.7	7.512.6	7.6/12.6	7.2.12.2	7.5/12.6	7.6/12.7	0.92/1.36

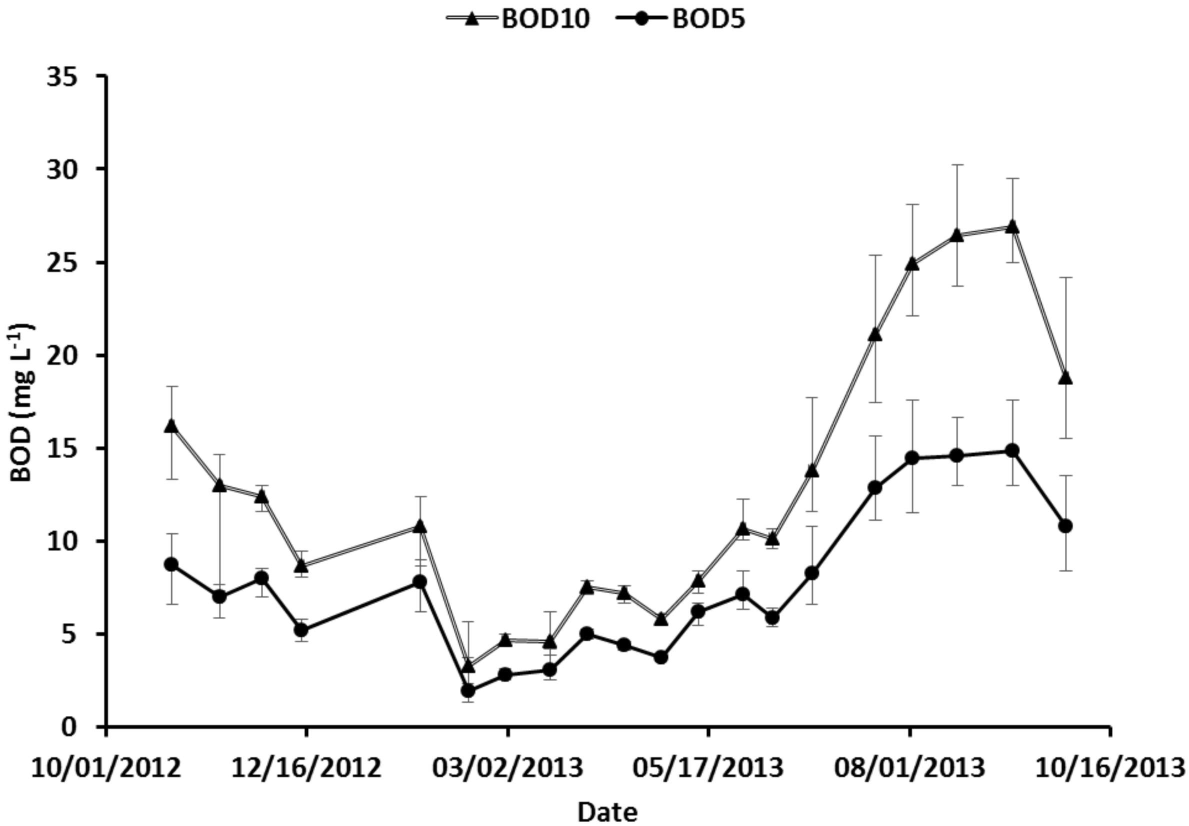

Figure 4.2 Mean, maximum and minimum BOD_5/BOD_{10} from 6 sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013. Means are plotted as solid dots/triangles with error bars showing maximum and minimum BOD_5/BOD_{10}.

During the study period, a total of 48 rainfall events with a rainfall amount greater than 0.254 mm were identified in one week before each fieldwork. There appeared a negative correlation between rainfall amount and BOD_5 (Figure 4.3). At the same time, water temperature appeared to have a positive effect on BOD_5, which may have confounded the negative effect by rainfall to some degree (Figure 4.4). Multiple regression analysis (Table 4.5) indicated that a stronger correlation exists when water temperature (T) is included as the second independent variable to determine BOD_5 ($r^2 = 0.88$, Cp = 2.5), when compared to the condition that AFU is the single independent variable ($r^2 = 0.87$, Cp = 2.1). Also, correlations appear to be stronger

when rainfall is considered as another independent variable for BOD_5-RFU or BOD_5-(FRU, T) relationships, but in general the effects of rainfall are not very obvious.

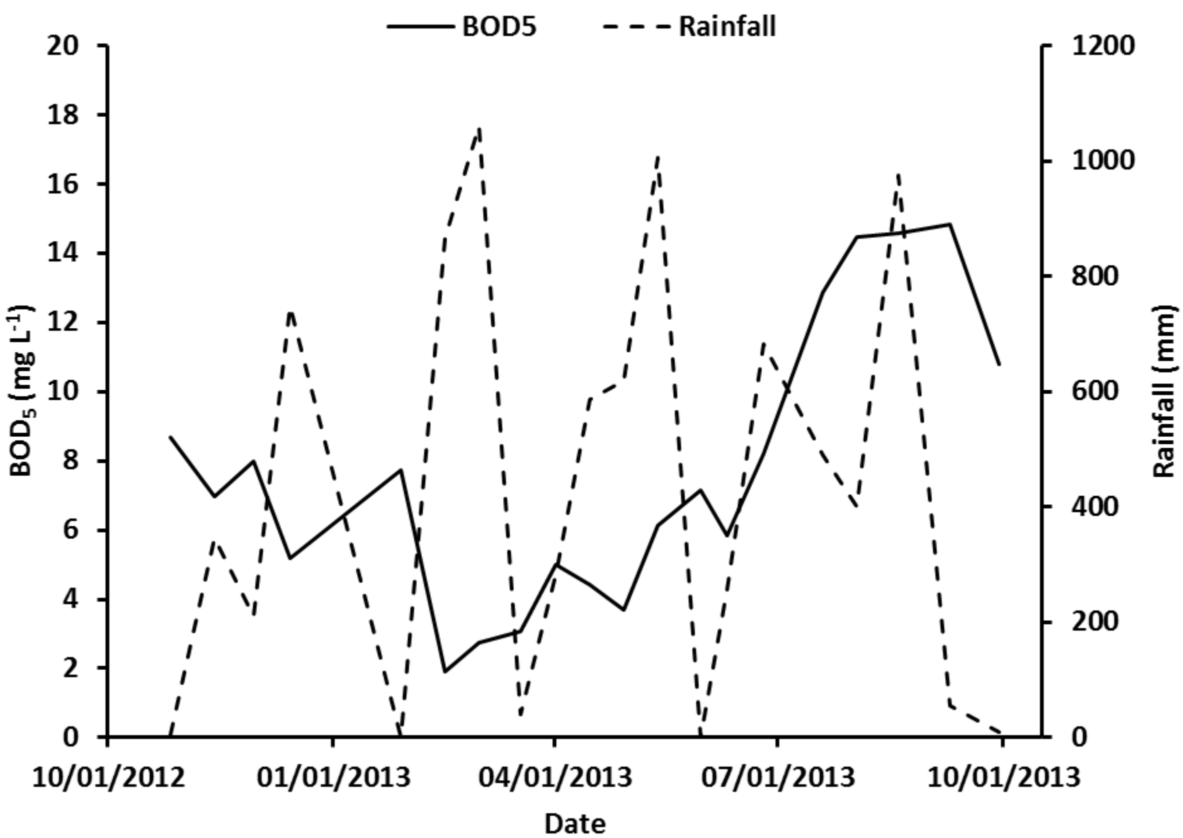

Figure 4.3 Rainfall effect on BOD_5 in University Lake, Baton Rouge, USA, from October 2012 to September 2013. Rainfall amounts were the sum of all the rainfall one week before each of the sampling dates from Ben Hur station. Missing data for May 30th, 2013 is due to the fact that there is no record for second half of that month. BOD_5 showed on the figure is the mean for the entire University Lake.

At our studied lake, Mesmer (2010) found a lower variation in BOD (5.4 – 9.5 mg L^{-1}) for 2008 - 2009. In this present study we found much lower BOD in the 2012/2013 winter months, during which the total precipitation (803 mm) was three times higher than during the 2008/2009 winter months (269 mm). High rainfall can cause more surface runoff, which could result in a higher input of pollutants into the lake.

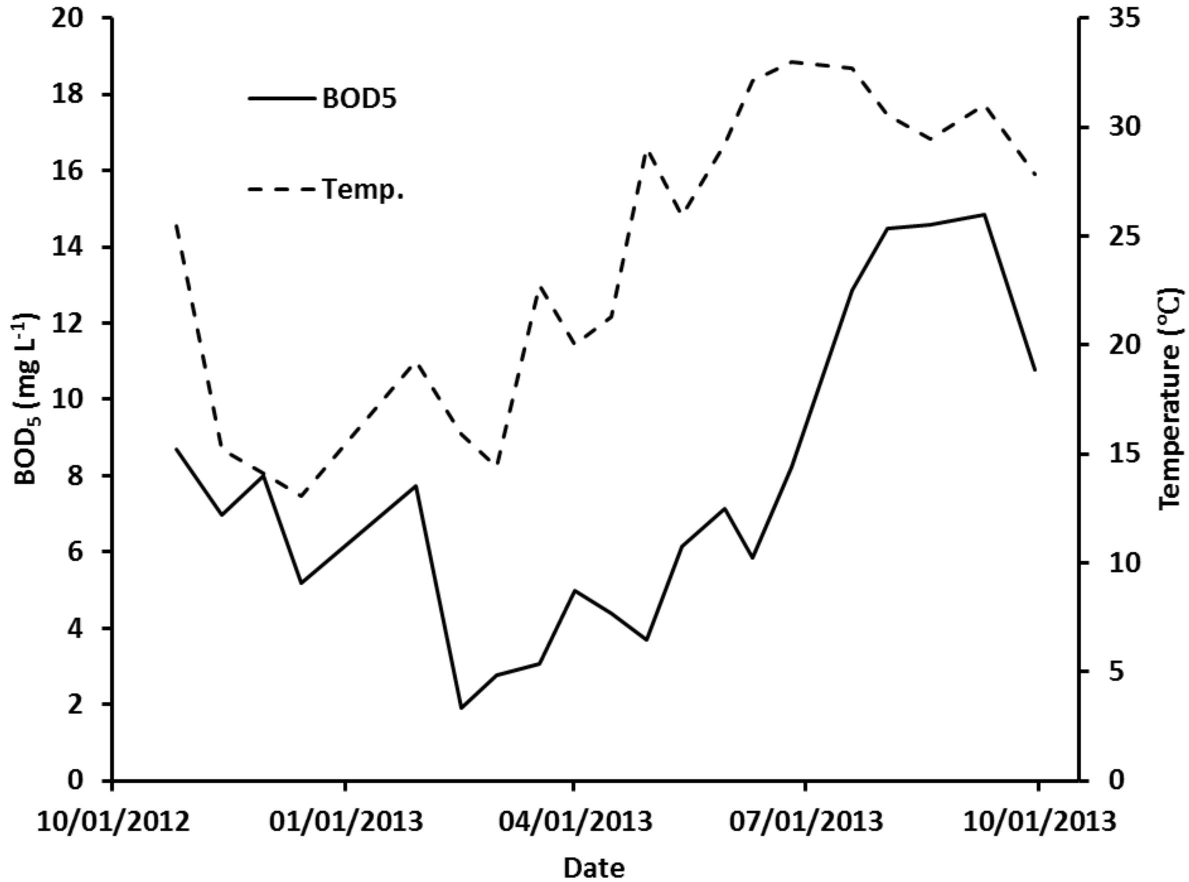

Figure 4.4 Temperature effect on BOD_5 in University Lake, Baton Rouge, USA, from October 2012 to September 2013. Temperature was the *in-situ* water temperature and BOD_5 showed on the figure is the mean for the entire University Lake.

Table 4.5 Multiple regression models for BOD_5 in mg L^{-1}, AFU, water temperature (T) in ℃, and rainfall in cm. All data used are the mean from 6 sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013.

dependent variable	C(p)	R-Square	Variables in Model
	2.1490	0.8678	AFU
	2.4878	0.8806	AFU T
	3.5692	0.8722	AFU Rainfall
BOD_5	4.0000	0.8843	AFU T Rainfall
	68.5159	0.3715	T Rainfall
	70.0016	0.3446	T
	107.2388	0.0575	Rainfall

4.3.3 Relationship between biochemical oxygen demand and chlorophyll-a concentration, and between biochemical oxygen demand and fluorescence

A close, positive relationship was found between chlorophyll *a* concentration and biochemical oxygen demand (Figure 4.5). The relationship appeared to be stronger with the 10-day BOD measurements (r^2 = 0.83) than with the 5-day BOD measurements (r^2 = 0.76). Chlorophyll *a* concentration was calculated with the *in-situ* fluorecense measurements (see Eq. 1). Therefore, a close, positive relationship between AFU and biochemical oxygen demand also existed (Figure 4.6). This relationship was found for all sampling sites throughout the study period (Table 4.6), with a regression coefficient ranging from 0.71 to 0.90.

The close relationship between chlorophyll *a* concentration and biochemical oxygen demand indicates that the studied shallow urban lake is autochthonous, i.e. rich of phytoplankton. Higher chlorophyll *a* concentrations indicate greater total phytoplankton biomass, whereas lower chlorophyll *a* concentration represents less phytoplankton biomass (Beutler et al., 2002). Daily BOD and chlorophyll *a* concentration showed a close negative daily relationship (Figure 4.7), representing the daily increase of BOD with the daily decline of chlorophyll *a* concentration during the five or ten-day measurement period. It is apparent that the die-off of phytoplankton has been the main consumption of oxygen which is correlated to the changes in BOD.

With high chlorophyll *a* concentration which is the most important variable to determine the lake trophic state, not only LSU University Lake but also many other eutrophic lakes are supposed to be autochthonous. In that case, organic pollutants responsible for BOD are mainly formed within the water system, through derivation from polymerisation and degradation of existing dissolved organic matter, release from living and dead organisms and through microbial syntheses within the body water (Thomas, 1997; Cârstea, 2012). By the origin, this type of

organic pollutants is very different from allochthonous organic pollutants in the sewage in the wastewater plants. Allochthonous organic pollutant is the fraction that is formed outside the water system and transported inside through discharge of human wastes, farm wastes, leachates and so on (Hudson et al., 2007; Cârstea, 2012).

Table 4.6 Regression parameters in the relationship between BOD and *in-situ* fluorescence measurements of water (see Eq. 2) at 6 sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013.

	Site	k	b	R-square	n
BOD_5	1	0.042	2.065	0.81	20
	2	0.033	2.639	0.79	20
	3	0.031	2.719	0.71	20
	4	0.034	2.577	0.81	20
	5	0.031	2.754	0.75	20
	6	0.033	3.111	0.76	20
BOD_{10}	1	0.072	2.789	0.84	20
	2	0.063	3.378	0.84	20
	3	0.060	3.381	0.77	20
	4	0.066	2.899	0.90	20
	5	0.061	3.385	0.87	20
	6	0.069	3.528	0.81	20

The positive relationship between chlorophyll *a* concentrations and biochemical oxygen demand has been reported by a few studies for shallow eutrophic lakes. In a study conducted in temperate eutrophic Lake, Taihu Lake, in China, Wang and others (2007) reported a significantly positive correlation between phytoplanktom biomass and COD, BOD and TP in spring, summer and autumn. Zhang and Qin (2001) invested the same lake and pointed out that COD and BOD

values were closely correlated with phytoplankton biomass in the most eutrophic part of Taihu Lake that was strongly affected by anthropogenic activities. However, until now, we found no report of a quantitative equation that uses chlorophyll *a* concentration to predict BOD or vise verse.

The relatively high accuracy for predicting BOD with chlorophyll *a* concentration found in our study indicates that *in-situ* chlorophyll *a* fluorencese can be a cost-effective, rapid approach in urban water quality monitoring. By application of the chlorophyll fluorescence (i.e., $\lambda_{excitation}$ = 460 nm, $\lambda_{emission}$ 685 nm) for the real-time monitoring of water quality in eutrophic lakes, chlorophyll *a* concentrations and BOD can be estimated simultaneously *in-situ* in few seconds without sample preparation and laboratory analysis such as EEM spectroscopy. Since the relationship exists due to the autochthonous organic pollutants, it should work well in eutrophic water bodies, which fills in the blank for former fluorescence spectroscopy studies that focus mainly on Tryptophan-like fluorescence ($\lambda_{excitation}$ = 280 nm, $\lambda_{emission}$ 350 nm) in the sewage including mostly allochthonous organic pollutants (Reynolds and Ahmad, 1997; Ahmad and Reynolds, 1999; Reynolds, 2002; Baker and Curry, 2004; Baker and Inverarity, 2004; Hudson et al., 2008).

Variability in the AFU/BOD relationship existed and should be taken into consideration. As Table 5 shows, even within a small lake, the sites have different AFU/BOD relationships, and the correlations of AFU with BOD are stronger at some sites than others. This coincides with similar characteristics for variations of BOD, AFU and chlorophyll *a* of being higher at their peaks in the summer months and lower on the bottoms in the winter months that indicates a locally distinct distribution of phytoplankton, especially in the algae bloom time, in the studied lake. For a larger water body or lakes in different climate regions, enormous variability can exist

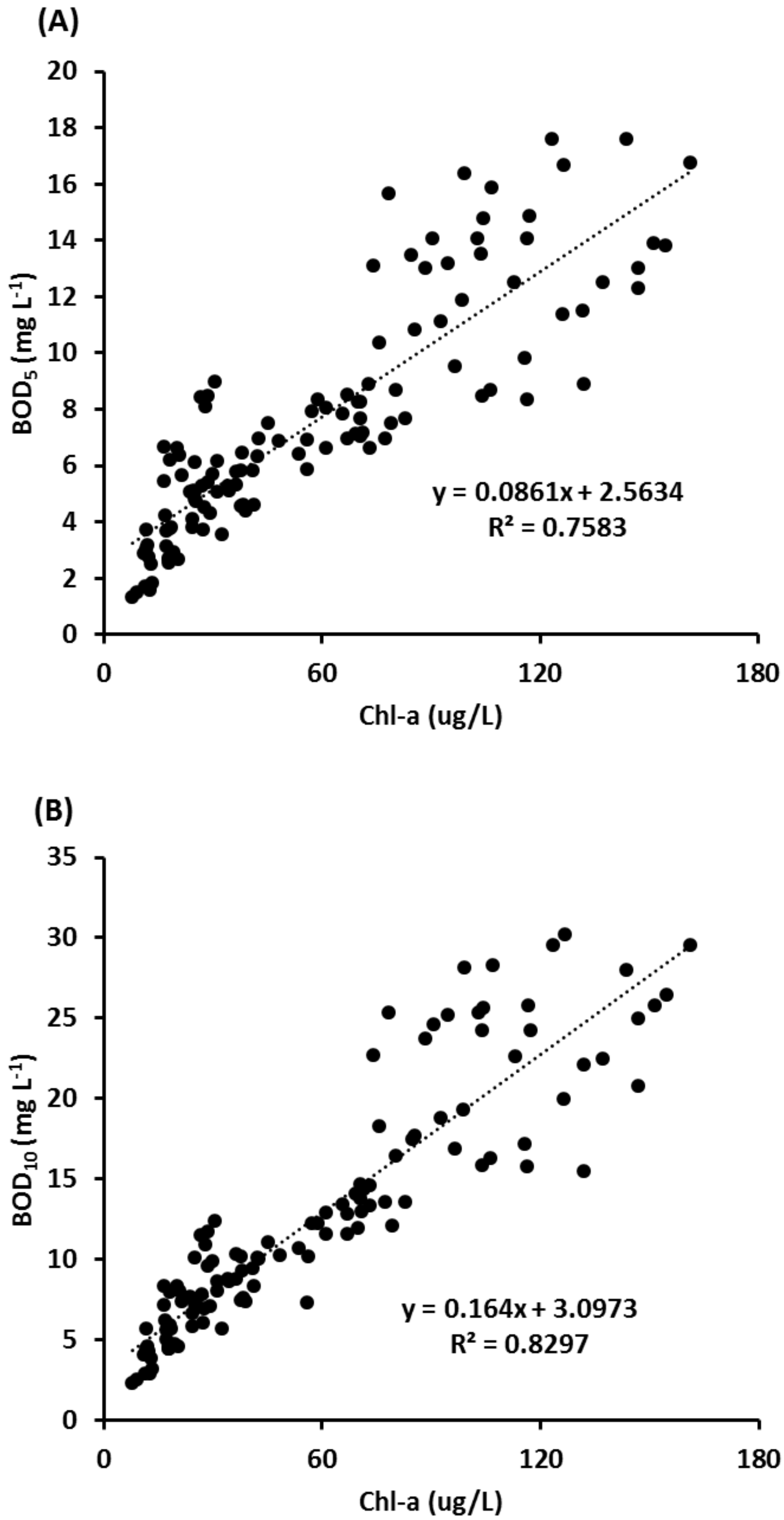

Figure 4.5 Relationships of (A) BOD_5 and chlorophyll *a* concentration, and (B) BOD_{10} and chlorophyll *a* concentration fluorescence for University Lake, Baton Rouge, USA.

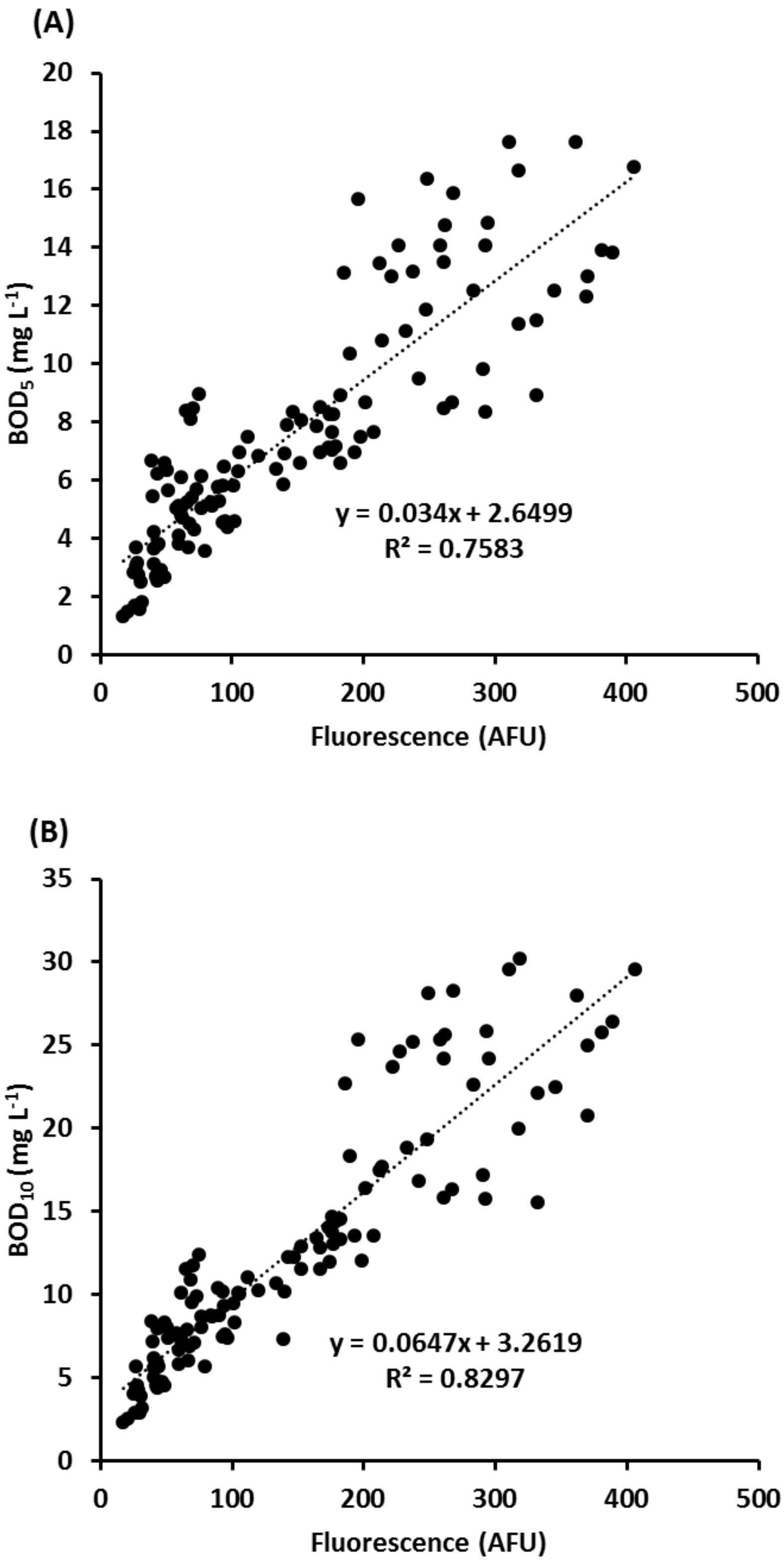

Figure 4.6 Relationships of (A) BOD_5 and *in situ* fluorescence and (B) BOD_{10} and *in situ* fluorescence for University Lake, Baton Rouge, USA.

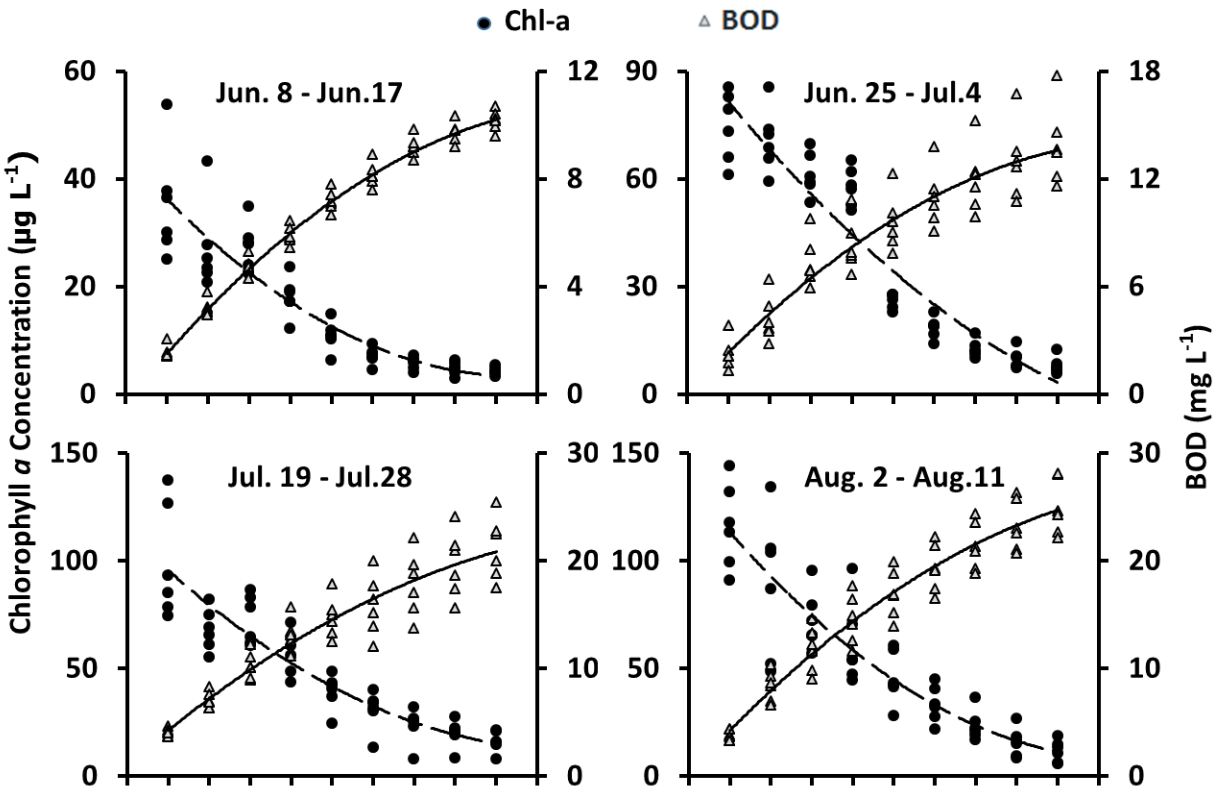

Figure 4.7 Trend of daily BOD and corresponding daily chlorophyll *a* concentrations measured one day ahead of BOD for samples on (A) June 10th, 2013 (B) June 25th, 2013 (C) July 19th, 2013 (D) August 2^{ed}, 2013. Solid line is the trendline for daily BOD while dashed line is the trendline for daily fluorescence with r-square above them. Each tick mark interval on x-axis represents a day.

in both the surface water and effluents/runoffs to it, causing more difference in the AFU/BOD relationship. Similar local variability is also mentioned in a study for relationship between Tryptophan-like fluorescence and BOD_5 by Hudson and other researchers from water samples collected in South West England area (~1700 km^2) (Hudson et al., 2007). They applied a geographically weighted regression to present the geographical variability. Here it is suggested that the comparison between site specific and local fluorescence /BOD_5 relationships and whole watershed fluorescence /BOD_5 relationship should be applied to further support the application of chlorophyll fluorescence in water quality assessment.

Ambient conditions such as rainfall and water temperature may also partially affect BOD variation. This agrees with previous studies in the same lake. Seasonal BOD_5 trend in 2008-2009 showed smaller variation than the one in this study (Xu and Mesmer, 2013), which can be explained by a larger variation of water temperature and rainfall during this study period (Table 4.1). In addition to temperature and rainfall, other ambient factors that can affect water light conditions, such as cloudiness and radiation, may influence field fluorescence reading, therefore causing variation in the BOD-fluorenscene relation. Except for ambient conditions, other possible factors that would affect the BOD-fluorenscene relation pointed out by other researcher includes pH, and salinity due to the influence in fluorophore and intramolecular reactions (Carstea, 2012). However, those factors did not show significance in this study.

4.4 CONCLUSIONS

This study assessed the range and seasonal fluctuation of field chlorophyll fluorescence, chlorophyll *a* concentration, 5-day and 10-day biochemical oxygen demands in a subtropical, eutrophic urban lake during the period from October 2012 to September 2013. Based on the measurements, we developed a simple model for predication of biochemical oxygen demand with field chlorophyll fluorenscene measurements. The prediction model produced relatively high accuracy in estimating 5-day and 10-day BODs. This fluorometric approach can be especially applicable to eutrophic waters as it effectively detects chlorophyll concentrations. The study is the first trial to have used field chlorophyll fluorescence for rapid BOD estimation through a numeric relationship. We suggest that this approach be further tested for eutrophic waters in subtropical and other climate regions.

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CHAPTER 5: SUMMARY

This thesis research conducted intensive dissolved oxygen monitoring and a long-term water quality analysis in a eutrophic shallow lake in a subtropical region. The research comprised three studies to: (1) characterize diel DO cycles and utilize the characteristics to determine the changes in trophic state and water quality; (2) develop a deterministic model that can predict hourly change in DO of a water body with high-time resolution weather parameters; and (3) develop a rapid field method for predicting BOD using chlorophyll *a* fluorescence. Major findings from this research are summarized below.

The study aiming at using DO for the determination of trophic state change and water quality degradation showed higher average daily DO levels during 2013-2014 than during 2008-2009, especially in the summer and fall months. The frequency of oxygen levels below 5 mg L^{-1} was also less frequent during 2013-2014 than during 2008-2009, giving an impression of water quality improvement of the lake. However, a comparison of diel DO cycles between the two periods revealed a clear intensification of eutrophication in the lake system. Changes in the nutrient level and chlorophyll *a* concentration from 2008-2009 to 2013-2014 also supported the finding. At the same time, diel DO discrepancy seems to be a good indicator for water quality degradation, since it is less disturbed by other factors like uplifted water level and increased hyperoxia.

The modeling study developed a one-dimensional, deterministic DO model for estimating the hourly change of source and sink components of DO, such as photosynthesis, re-aeration, respiration, BOD and sediment oxygen demand. Overall, the modeling yielded successful results of simulating high-time fluctuation of DO in the studied lake. The model showed its highest

predictability during winter months and showed good predictability for extreme algal bloom events. Photosynthesis and respiration were dominant components in the model. However, the model performed poorly when re-aeration dominated as a major oxygen source. This may be improved through collections of site specific climatological data and a more detailed equation for the primary production.

The study on rapid field estimation of BOD showed a clear seasonal trend of both BOD measurements (BOD_5 and BOD_{10}) being high during the summer and low during the winter. There was a linear, positive relationship between chlorophyll *a* fluorescence and BOD, and the relationship appeared to be stronger with the 10-day BOD ($r^2 = 0.83$) than with the 5-day BOD ($r^2 = 0.76$). BOD dropped each day with declining Chlorophyll *a* fluorescence, suggesting that die-off of phytoplankton has been the main consumption of oxygen in the studied lake. Ambient conditions such as rainfall and water temperature may have partially affected BOD variation.

Knowledge for eutrophic shallow lakes in the subtropical region is still limited compared to more intensive studies for deep stratified lakes, and this thesis research is only an ongoing step to fill in the blank. Long term monitoring is continuing to be collected on University Lake for future analysis of water quality of shallow eutrophic water bodies.

APPENDEX: KEY SAS CODE FOR MODELING

Key code for the calibration in December 2008 is presented here as an example:

```
/* December Cali*/

Libname DO 'C:\Zhen_Xu\Manuscript\DO\DOModel';

data work.C12monthlypre;
	set DO.caliPre;
	ap = 4.86;
	up = 2;
	uj = 1;
	aR = 80/24;
	Kb = 0.20;
	Qs = 1.07;
	S20 = 2.5/24;
	H = 60;
	QR = 1.045;
	Z = 1.2;
	where '15DEC2008:23:00:00'dt <= datetime <= '29DEC2008:23:00:00'dt;
	n+1;
	if n=1 then DO = DOConc; else DO=.;
run;

data work.C12monthly;
	Temp = DO;
	set work.C12monthlypre;
	if Temp ne . then do;
	 Change = ((ap * Rs) * Pmax * (exp(1-ap * Rs)) * Chl)*up
	   + ((KL/H) * (Csat - Temp))*uj
	   - aR * QR**(T-20) * Chl
	   - Kb * Qb**(T-20) * BOD / 24
	   - S20 * Qs**(T-20) / Z;
	 DO = Temp + Change;
	end;
	else
	Temp = lag1(DO);
run;

ods graphics on;

proc corr data=work.C12monthly;
	var DO;
	with DOConc;
```

```
	where '16DEC2008:23:00:00'dt <= datetime <= '29DEC2008:23:00:00'dt;
run;

ods graphics off;

symbol1 interpol=none value=squarefilled color=vibg height=1;
symbol2 interpol=join value=diamondfilled color=depk height=1;

axis1 ;
axis2 label=(angle=90 "Concentration");
axis3 order=('16DEC2008:23:00:00'dt to '29DEC2008:23:00:00'dt by dtday) ;

legend1 repeat=1 label=none frame;

title1 'Dec.2008';

proc gplot data=C12monthly;
	plot (DOConc DO)*Datetime / overlay legend=legend1
	haxis=axis3 vaxis=axis2;
run;

/*
libname ReEX 'C:\Zhen_Xu\Manuscript\DO\ResultsP1.xlsx';

Data ReEX.R12V;
	set work.C12monthly;
	where '16DEC2008:23:00:00'dt <= datetime <= '29DEC2008:23:00:00'dt;
	keep Datetime DO DOConc;
run;

libname ReEX clear;
*/
```

VITA

Zhen Xu was born in 1988 in Zhengzhou City, Henan Province, China. He graduated from the College of Idaho in 2012, earning his Bachelor of Science degree in environmental studies with a concentration on chemistry. He moved to Baton Rouge, Louisiana, in August 2012 to pursue his Master of Science degree at Louisiana State University in Renewable Natural Resources concentrating on watershed hydrology. He plans on pursuing his doctorate to further investigate the nature of hydrological processes and their influence on water quality.