

Rapid field estimation of biochemical oxygen demand in a subtropical eutrophic urban lake with chlorophyll *a* fluorescence

Zhen Xu · Y. Jun Xu

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Abstract Development of a technique for rapid field estimation of biochemical oxygen demand (BOD) is necessary for cost-effective monitoring and management of urban lakes. While several studies reported the usefulness of laboratory tryptophan-like fluorescence technique in predicting 5-day BOD (BOD₅) of wastewater and leachates, little is known about the predictability of field chlorophyll fluorescence measurements for BOD of urban lake waters that are constantly exposed to the mixture of chemical compounds. This study was conducted to develop a numeric relationship between chlorophyll *a* fluorescence and BOD for a eutrophic urban lake that is widely representative of lake water conditions in the subtropical southern USA. From October 2012 to September 2013, in situ measurements at the studied lake were made every 2 weeks on chlorophyll *a* fluorescence and other water quality parameters including water temperature, pH, dissolved oxygen, and specific conductivity. Water samples were taken for 5-day BOD and 10-day BOD (BOD₁₀) analysis with and without incubation. The results showed a clear seasonal trend of both BOD measurements 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.

Keywords Water quality monitoring · Biochemical oxygen demand · Chlorophyll *a* · Field fluorescence · Water quality · Eutrophication

Introduction

In the USA, about 44 % of all lakes and 59 % of man-made lakes are classified to be in poor biological condition (US EPA 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, sensitive species of fish and invertebrates can be negatively impacted, and at DO levels below 2 mg/L, an oxygen depletion stage known as hypoxia, most fish species could be

Z. Xu · Y. J. Xu (✉)
School of Renewable Natural Resources, Louisiana State
University Agricultural Center,
Baton Rouge, LA 70803, USA
e-mail: yjxu@lsu.edu

negatively impacted (Frodge et al. 1990). Hypoxia in water bodies is a growing problem worldwide that is associated with negative impacts not only on sensitive species of fish and invertebrates, but also on metal, nitrogen, and phosphorus transformations (Kemp et al. 1990, Breitbart 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 DO in water, resulting in hypoxic conditions. Normally, organic consumption of DO 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 biodegradable organic matter in a water column. Therefore, BOD of an aquatic system is an important parameter frequently used in the 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 BOD₅. 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 managers and regulators in predicting the degree of organic pollution and taking prompt actions.

Fluorometric method has 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 laboratory 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). 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 water body's BOD₅ 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 BOD₅ and tryptophan-like fluorescence ($\lambda_{\text{excitation}}=280$ nm, $\lambda_{\text{emission}}=350$ 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 BOD₅ of water samples using a fluorescence reading. Up to now, this approach has been only applied in laboratory settings mostly to wastewater samples with a wide range of BOD₅ 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 ($\lambda_{\text{excitation}}=460$ nm, $\lambda_{\text{emission}}=685$ 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.

Methods

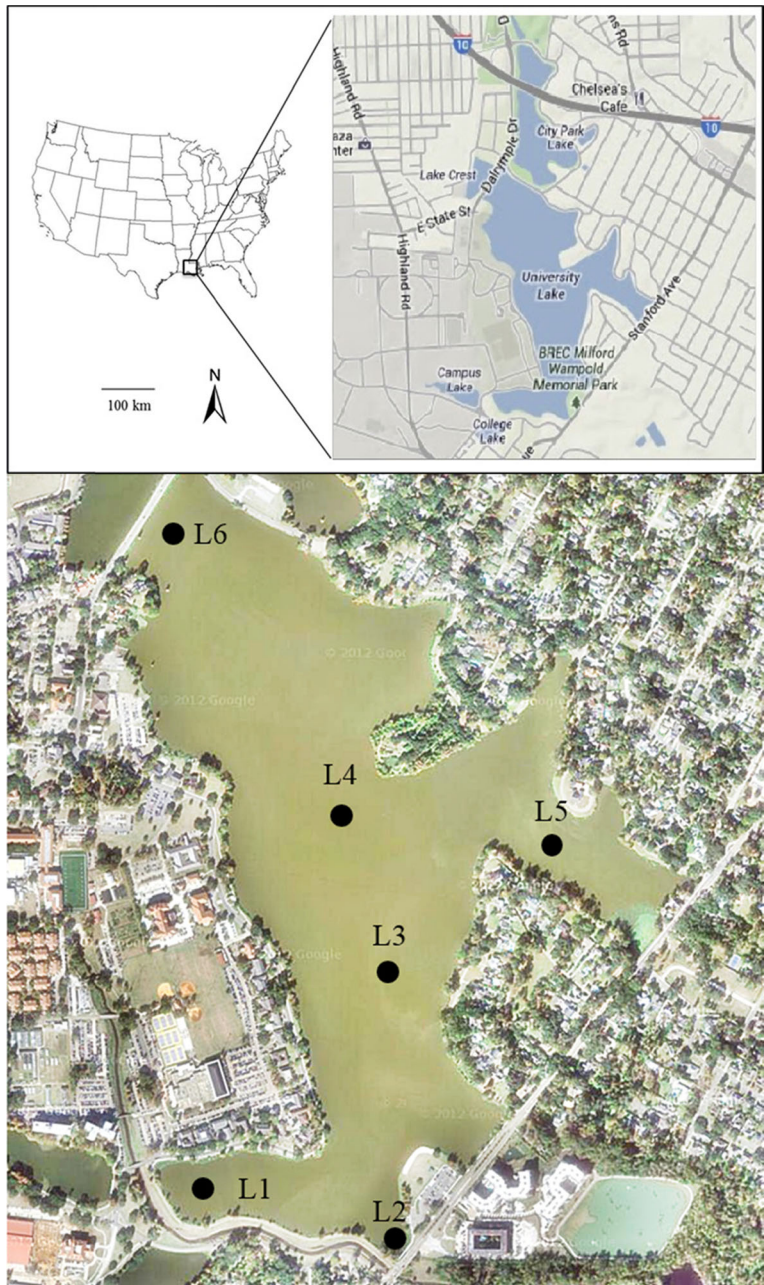
Site description

The study was conducted at University Lake, located in Baton Rouge, LA, USA (latitude 30° 24' 50" N; longitude 91° 10' 00" W) on the Louisiana State University

(LSU) campus (Fig. 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 m. 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

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



reported as eutrophic, as its water showed high concentrations of nitrogen and phosphorus (Mesmer, 2010).

Field measurements

In this study, six sampling locations were identified to represent the lake (Fig. 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 two-lane busy highway.

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 (AFUs). 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 fluoresce. Then, the fluorometer reports the normalized variable fluorescence after a 5-s 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 DO. 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 three near-shore sites (i.e., L2, L5, and L6; Fig. 1), measurements were taken about 3 m 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; Fig. 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.

Laboratory measurements

Water samples were taken from the six 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 (in µg/L) 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 (Chl-*a*, in µg/L), which can be given as follows:

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

Water samples from each sampling date were analyzed at the Watershed Hydrology Laboratory, LSU School of Renewable Natural Resources, for 5- and 10-day BODs, reported as BOD₅ and BOD₁₀, 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 DO concentration was below 3.00 mg/L due to no dilution being performed. BOD samples were stored at room temperature (20±2 °C) in an incubator (Thermo Scientific Imperial III Standard Incubator, Thermal Scientific Inc., TX, USA). In the laboratory, DO of all BOD samples was measured with an YSI 5100 DO meter (YSI Inc., Yellow Springs, OH, USA).

Starting from June 2013, BOD 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.

Ambient data collection and analysis

To document ambient lake water conditions, daily climatic records from a near-by weather station (Ben Hur Station, the Louisiana Agrilclimatic Information System) were gathered for the 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 1).

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

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

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 analyses were performed.

Results and discussion

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 to 406.5 AFU (Table 2). The fluorometric unit appeared highest in September 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 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 2).

Concurrently, chlorophyll *a* concentrations fluctuated greatly over the year, ranging from 7.8 to 161.3 µg/L with an average of 47.5 µg/L during the studied period (Table 3). The highest concentration occurred in September 2013, and the lowest was found in February

2013 (Table 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 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 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 and an average concentration of total phosphorus (TP) of 0.383 mg/L. Based on both Carlson’s Trophic State Index for lake waters (1977) and the classification for stream trophic state proposed by Dodds et 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. Accordingly, University Lake was hypereutrophic throughout the summer and fall, as the chlorophyll *a* concentrations during the period were constantly above 66 µg/L.

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 (2007) on shallow eutrophic lakes located in subarctic north central British Columbia, chlorophyll *a* concentrations ranged from <1 µg/L in the winter and spring

Table 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

Table 2 In situ fluorescence, mean, and standard deviation from six sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013

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

months to 112 $\mu\text{g/L}$ in the late summer and early fall months during 1997–1998; In another study conducted by Schalles et al. (1998) on an eutrophic lake in a temperate climate, high chlorophyll *a* concentrations (up to 280 $\mu\text{g/L}$) were found during the late summer and early fall months, with the lowest chlorophyll *a* concentration (20 $\mu\text{g/L}$) 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.

Seasonal fluctuation of BODs

During the period from October 2012 to September 2013, 5-day BOD levels in the lake waters ranged from 1.3 to 17.6 mg/L, with an average of 7.6 mg/L (Table 4). In general, levels of 10-day BOD were higher with an average of 12.7 mg/L, fluctuating from 2.3 to 30.2 mg/L. As with AFU and chlorophyll *a*, BOD₅ and BOD₁₀ peaked both in August and reached their bottoms in February (Table 4). There was a rising trend from the winter months to the summer months, following a drop into the fall (Fig. 2). Similar to the fluctuations of AFU and chlorophyll *a* concentration, variation of BOD₅ and BOD₁₀ among the sampling sites was significantly lower in the winter months than in the summer months (Table 4).

Table 3 Means and standard deviations of chlorophyll *a* concentration from six sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013

Date	Chlorophyll <i>a</i> (µg/L)							Mean	STD
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6			
Oct. 26, 2012	75.8	80.4	96.6	104.1	73.1	106.4	89.4	13.5	
Nov. 13, 2012	70.6	69.4	71.5	70.6	77.4	56.0	69.3	6.5	
Nov. 29, 2012	61.1	67.0	70.8	69.9	67.0	57.2	65.5	4.8	
Dec. 12, 2012	41.5	34.5	36.6	34.3	41.0	31.3	36.5	3.7	
Jan. 28, 2013	38.0	30.7	31.3	28.8	26.7	28.2	30.6	3.7	
Feb. 15, 2013	7.8	9.2	11.4	13.4	12.9	11.8	11.1	2.0	
Mar. 01, 2013	17.9	19.4	20.4	18.0	18.1	17.2	18.5	1.1	
Mar. 19, 2013	13.1	11.8	12.2	11.2	12.4	17.0	12.9	1.9	
Apr. 01, 2013	24.7	25.2	27.0	25.6	25.3	23.9	25.3	0.9	
Apr. 15, 2013	27.8	37.8	39.2	29.3	38.5	24.5	32.8	5.8	
Apr. 29, 2013	17.3	27.5	32.5	18.3	24.5	18.6	23.1	5.6	
May 13, 2013	16.5	18.3	20.9	21.5	20.3	16.7	19.0	2.0	
May 30, 2013	59.0	56.2	48.4	42.7	45.2	42.3	48.9	6.5	
Jun. 10, 2013	53.8	36.4	30.0	37.7	25.1	28.6	35.3	9.4	
Jun. 25, 2013	85.6	79.3	73.1	83.0	61.1	65.8	74.6	8.9	
Jul. 19, 2013	78.4	137.3	126.4	84.7	92.8	74.3	99.0	24.1	
Aug. 02, 2013	143.8	90.7	99.2	113.0	117.4	131.9	116.0	18.1	
Aug. 19, 2013	106.9	88.6	104.5	126.7	116.7	94.8	106.3	14.0	
Sept. 09, 2013	123.5	161.3	147.1	154.6	151.5	103.0	140.2	22.3	
Sept. 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	

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 DO during 2008–2009 in the same lake, Xu and Mesmer (2013) reported a slightly higher 5-day BOD average (7.2 mg/L) 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 BOD₅ range between 4.0 and 12.0 mg/L (average 6.8 mg/L) from January 2000 to December 2001. In another study on a subtropical freshwater lake in China, Wang et al. (2007) reported a BOD₅ dynamics fluctuating from 3.2 to 9.1 mg/L with an average of 6.0 mg/L 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.

During the study period, a total of 48 rainfall events with a rainfall amount greater than 0.254 mm were identified in 1 week before each fieldwork. There appeared a negative correlation between rainfall amount and BOD₅ (Fig. 3). At the same time, BOD appeared to have a positive relationship with temperature (Fig. 4). This may be a result of increased biological activities with increasing temperature. However, the relationship between BOD and temperature within a same season is weak ($r^2=0.3$). Multiple regression analysis (Table 5) indicated that a stronger correlation exists when water temperature (T) is included as the second independent variable to determine BOD₅ ($r^2=0.88$, $C_p=2.5$), when compared to the condition that AFU is the single independent variable ($r^2=0.87$, $C_p=2.1$). Also, correlations appear to be stronger when rainfall is considered as another independent variable for BOD₅-AFU or BOD₅-(AFU, T) relationships, but in general, the effect of rainfall is not very obvious.

Table 4 Means and standard deviations of BOD₅ and BOD₁₀ from six sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013

Collection Date	BOD ₅ /BOD ₁₀ (mg/L)							
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean	STD
Oct. 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
Nov. 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
Nov. 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
Dec. 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
Jan. 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
Feb. 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
Mar. 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
Mar. 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
Apr. 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
Apr. 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
Apr. 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
May 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
May 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
Jun. 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
Jun. 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
Jul. 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
Aug. 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
Aug. 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
Sept. 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
Sept. 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	7.5/12.6	7.6/12.6	7.2/12.2	7.5/12.6	7.6/12.7	0.92/1.36

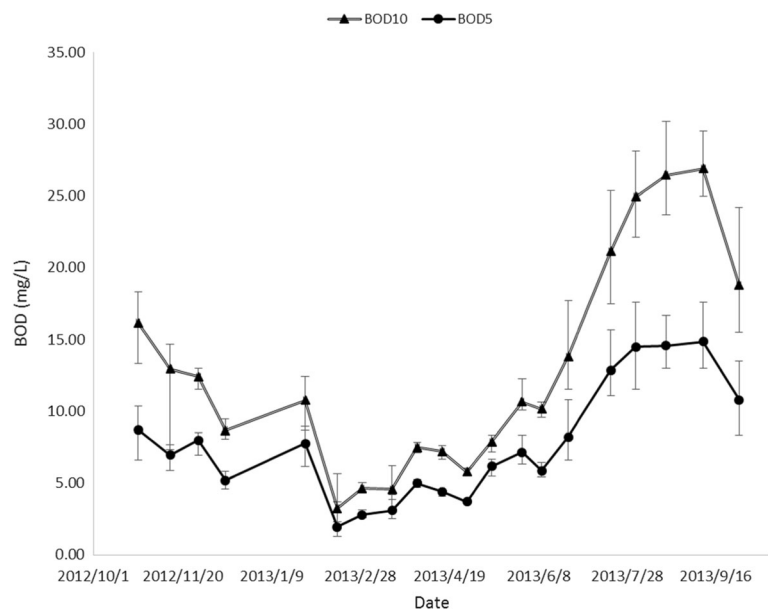
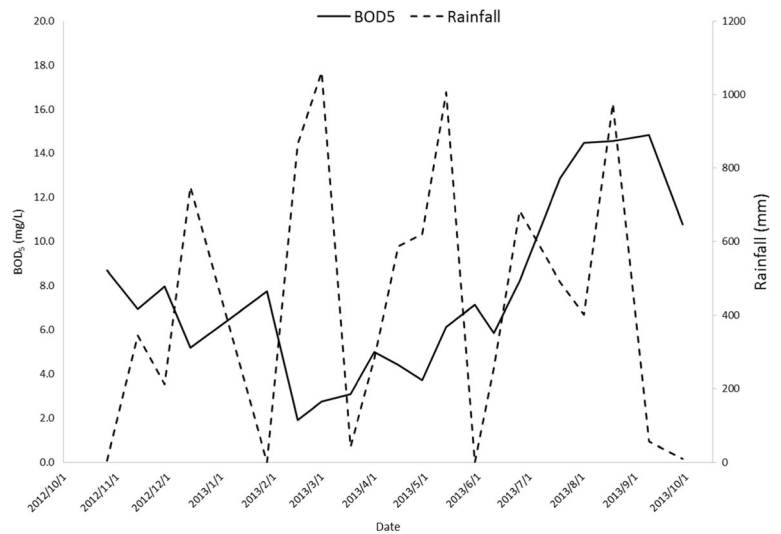
Fig. 2 Mean, maximum, and minimum BOD₅/BOD₁₀ from six sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013. Means are plotted as *solid dots/triangles* with *error bars* showing maximum and minimum BOD₅/BOD₁₀

Fig. 3 Rainfall effect on BOD₅ in University Lake, Baton Rouge, USA, from October 2012 to September 2013. Rainfall amounts were the sum of all the rainfall 1 week before each of the sampling dates from Ben Hur station. Missing data for May 30, 2013, is due to the fact that there is no record for the second half of that month. BOD₅ 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) 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.

Relationship between BOD and chlorophyll *a* concentration and between BOD and fluorescence

A close, positive relationship was found between chlorophyll *a* concentration and BOD (Fig. 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 fluorescence measurements (see Eq. 1). Therefore, a close, positive relationship between AFU and BOD also existed (Fig. 6). This relationship was found for all sampling sites throughout the study period (Table 6), with a regression coefficient ranging from 0.71 to 0.90.

The close relationship between chlorophyll *a* concentration and BOD indicates that the studied shallow urban lake is autochthonous, i.e., rich of phytoplankton. Higher chlorophyll *a* concentrations indicate greater

Fig. 4 Temperature effect on BOD₅ in University Lake, Baton Rouge, USA, from October 2012 to September 2013. Temperature was the in situ water temperature, and BOD₅ showed on the figure is the mean for the entire University Lake

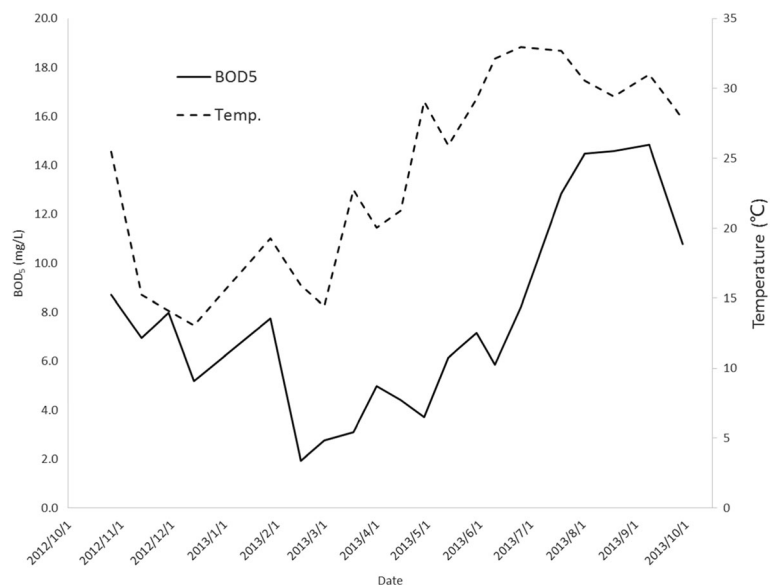


Table 5 Multiple regression models for BOD₅ (in mg/L), AFU, water temperature (*T*) (in °C), and rainfall (in cm)

Dependent variable	C(p)	R ²	Variables in model
BOD ₅	2.1490	0.8678	AFU
	2.4878	0.8806	AFU <i>T</i>
	3.5692	0.8722	AFU rainfall
	4.0000	0.8843	AFU <i>T</i> rainfall
	68.5159	0.3715	<i>T</i> rainfall
	70.0016	0.3446	<i>T</i>
	107.2388	0.0575	Rainfall

All data used are the mean from six sampling sites in University Lake, Baton Rouge, USA, from October 2012 to September 2013

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

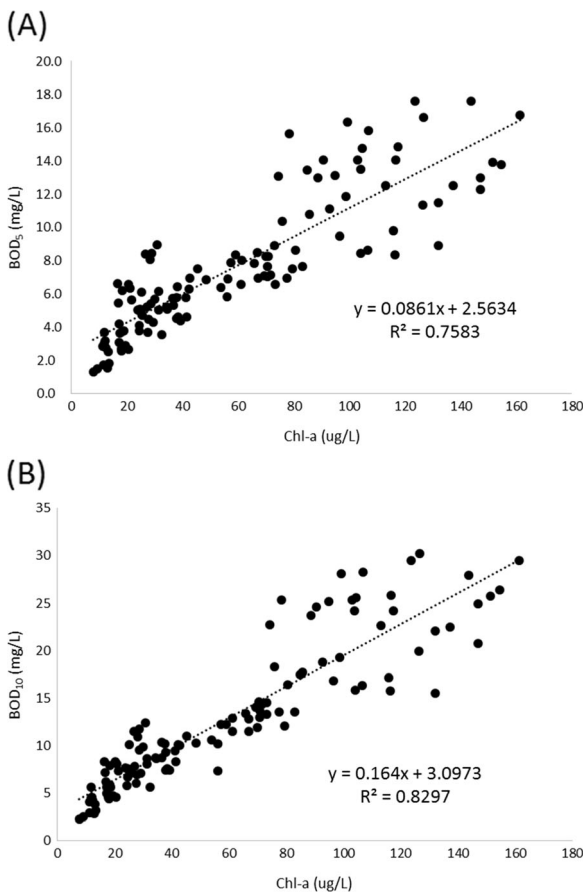


Fig. 5 Relationships of **a** BOD₅ and chlorophyll *a* concentration, and **b** BOD₁₀ and chlorophyll *a* concentration for University Lake, Baton Rouge, USA

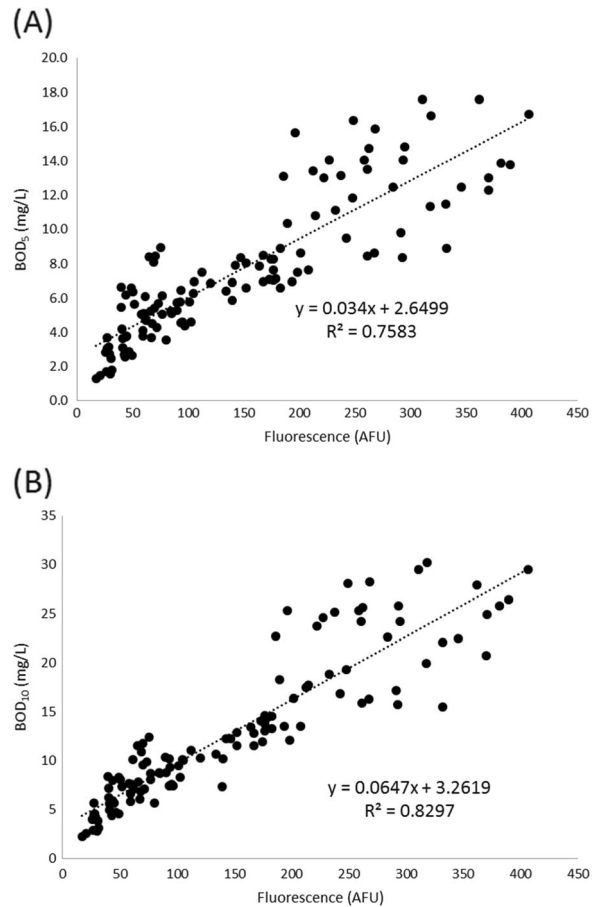


Fig. 6 Relationships of **a** BOD₅ and in situ fluorescence and **b** BOD₁₀ and in situ fluorescence for University Lake, Baton Rouge, USA

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

	Site	<i>k</i>	<i>b</i>	R ²	<i>n</i>
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

(Fig. 7), representing the daily increase of BOD with the daily decline of chlorophyll *a* concentration during the 5- or 10-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.

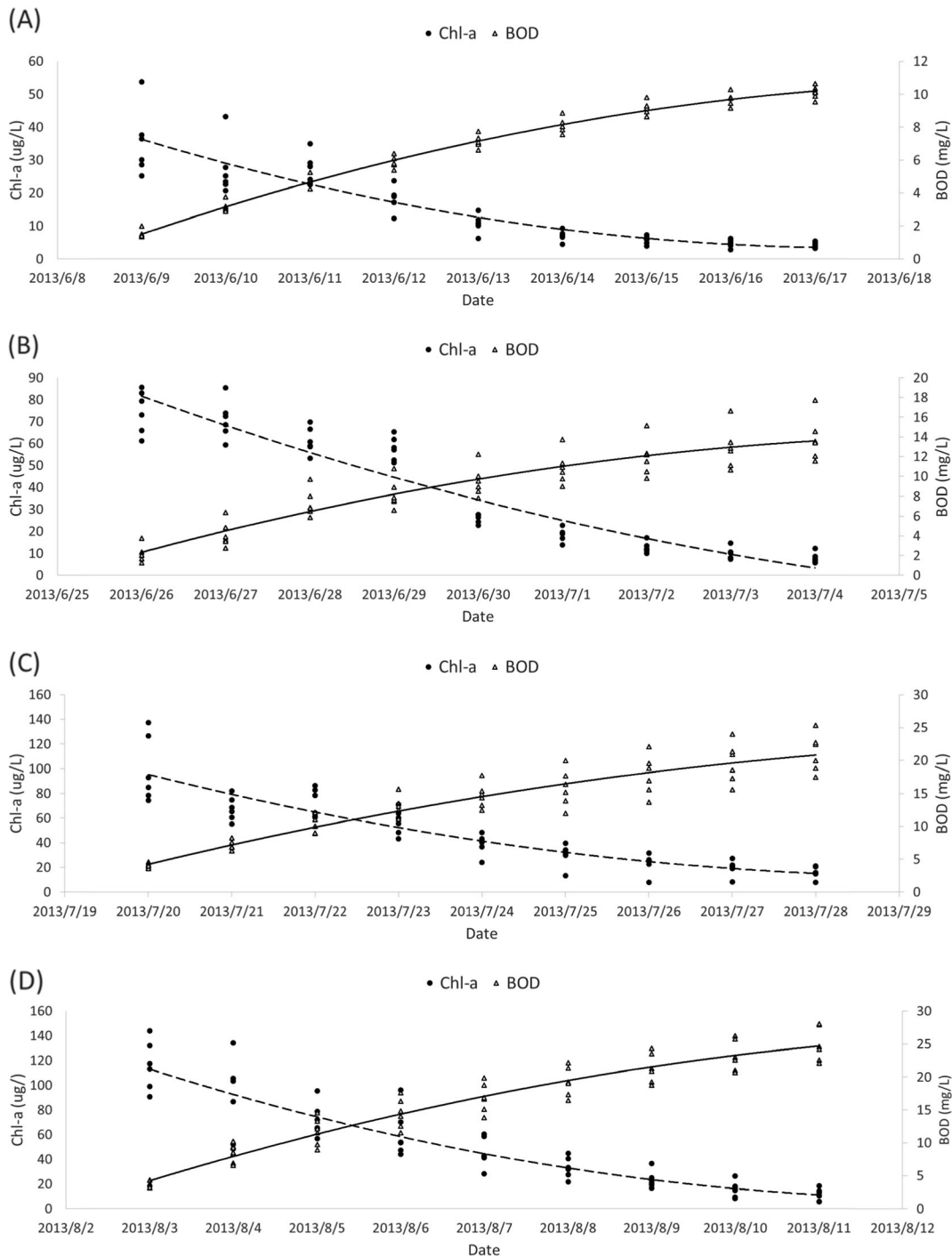


Fig. 7 Trend of daily BOD and corresponding daily chlorophyll *a* concentrations measured 1 day ahead of BOD for samples **a** June 10, 2013, **b** June 25, 2013, **c** July 19, 2013, and **d** August 2,

2013. *Solid line* is the trend line for daily BOD while *dashed line* is the trend line for daily fluorescence with R^2 above them

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 polymerization 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).

The positive relationship between chlorophyll *a* concentrations and BOD has been reported by a few studies for shallow eutrophic lakes. In a study conducted in temperate eutrophic lake, Taihu Lake, in China, Wang et al. (2007) reported a significantly positive correlation between phytoplankton biomass and COD, BOD, and TP in spring, summer, and autumn. Zhang and Qin (2001) investigated 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 vice versa.

The relatively high accuracy for predicting BOD with chlorophyll *a* concentration found in our study indicates that in situ chlorophyll *a* fluorescence can be a cost-effective, rapid approach in urban water quality monitoring. By application of the chlorophyll fluorescence (i.e., $\lambda_{\text{excitation}}=460$ nm and $\lambda_{\text{emission}}=685$ 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 ($\lambda_{\text{excitation}}=280$ nm, $\lambda_{\text{emission}}=350$ 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 algal bloom time, in the studied lake. For a larger water body or lakes in different climate regions, enormous variability can exist 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 BOD₅ by Hudson and other researchers from water samples collected in South West England area (~1700 km²) (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/BOD₅ relationships and whole watershed fluorescence/BOD₅ 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 the finding from a previous study (Xu and Mesmer 2013) conducted in the same lake during 2008–2009. Seasonal BOD₅ trend in 2008–2009 showed smaller variation than the one in this present study, which can be explained by a larger variation of water temperature and rainfall during this study period (Table 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–fluorescence relation. Except for ambient conditions, other possible factors that would affect the BOD–fluorescence relation pointed out by other researcher include pH and salinity due to the influence in fluorophore and intramolecular reactions (Cârstea 2012). However, those factors did not show significance in this study.

Conclusions

This study assessed the range and seasonal fluctuation of field chlorophyll fluorescence, chlorophyll *a*

concentration, and 5- and 10-day BODs 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 BOD with field chlorophyll fluorescence measurements. The prediction model produced relatively high accuracy in estimating 5- 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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