

Estimation of surface water quality in a Yazoo River tributary using the duration curve and recurrence interval approach

Ying Ouyang, Prem B. Parajuli and Daniel A. Marion

ABSTRACT

Pollution of surface water with harmful chemicals and eutrophication of rivers and lakes with excess nutrients are serious environmental concerns. This study estimated surface water quality in a stream within the Yazoo River Basin (YRB), Mississippi, USA, using the duration curve and recurrence interval analysis techniques. Data from the US Geological Survey (USGS) surface water monitoring station located in Deer Creek east of Leland from the YRB were selected for the analysis. Results showed that the water quality constituents, namely water temperature, specific conductivity (SC) and dissolved oxygen (DO), in this stream were found not to be the major concerns as the percentages of the time when these constituents did not meet their criteria were very low. Our results further revealed that the water temperature and SC increased as time elapsed, indicating the potential global warming and contamination impacts in this stream. In contrast, the DO and pH decreased as time elapsed, postulating a potential increase in biochemical oxygen demand and an acidic trend in this stream. Over the last decade, the average recurrence intervals when the water temperature, SC, and DO did not meet their criteria or minimum conditions were around 1 year. Using a target DO value of 429 kg d^{-1} proposed by the Mississippi Department of Environmental Quality, results from this study showed that there was about 25% of the time when the DO load did not meet the target value. This study suggests that the duration curve and recurrence interval analysis techniques are useful statistical tools for water quality trend estimation.

Key words | dissolved oxygen, load duration curve, recurrence period, specific conductivity, water quality

INTRODUCTION

Contamination of surface water with harmful chemicals and eutrophication of rivers and lakes with excess nutrients are a global environmental concern. Agricultural, industrial, and urban activities are considered as being major sources of chemicals and nutrients to aquatic ecosystems (Dodds & Welch 2000; Ouyang *et al.* 2011). In excess, biologically available nutrients can lead to diverse problems such as toxic algal blooms, low dissolved oxygen, fish kills, and loss of biodiversity. Harmful chemicals can seriously degrade aquatic ecosystems and impair the use of water for drinking, industry, agriculture, recreation, and other purposes (Ouyang 2005).

The Yazoo River Basin (YRB) is the largest river basin in Mississippi, USA and has a drainage area of about $34,600 \text{ km}^2$ (Figure 1). This basin is separated into two distinct topographic regions: the Bluff Hills and the Mississippi Alluvial Delta (Guedon & Thomas 2004; MDEQ 2003; Shields *et al.* 2008). The Bluff Hills region is a hilly upland area where streams originate from the oak-hickory forests and pasture lands which dominate the rural landscape. The Delta Region, on the other hand, is a flat, lowland area of slow moving streams and an extensive system of oxbow lakes. This Delta Region is a highly

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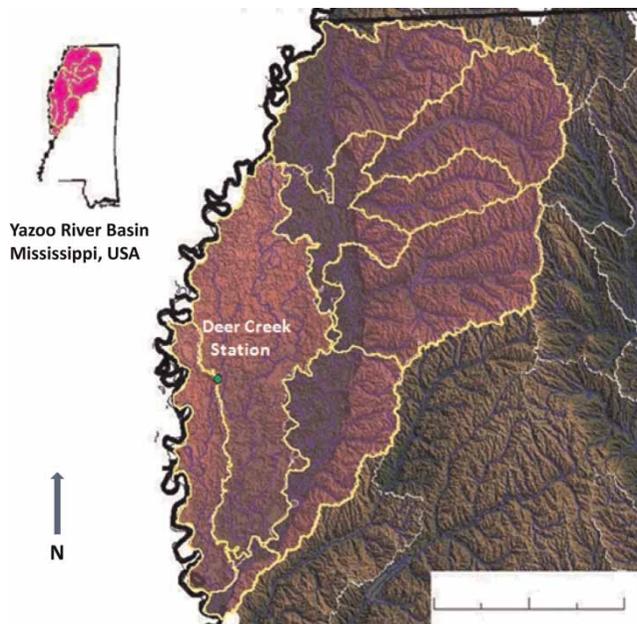


Figure 1 | Location of the Deer Creek surface water monitoring station within the Yazoo River Basin, Mississippi, USA.

productive agricultural area and is known for its cotton, corn, soybeans, rice, and catfish (MDEQ 2003).

Surface water pollution within the YRB includes contaminants such as excess nutrients, heavy metals, sediments, and herbicides which come from both point and non-point sources, and are the results of storm water runoff, discharge from ditches and creeks, groundwater seepage, aquatic weed control, naturally-occurring organic inputs, and atmospheric deposition (Nett *et al.* 2004; Pennington 2004; Aulenbach *et al.* 2007; Alexander *et al.* 2008; Shields *et al.* 2008). The degradation of water quality due to these contaminants has resulted in altered species composition and decreased overall health of aquatic communities within the river basin. With increased understanding of the importance of drinking water quality to public health and raw water quality to aquatic life, several efforts have been devoted to restoring the health of the YRB during the last several decades and preventing further pollution. To support these efforts, a surface water quality monitoring network within the YRB has been operated by US Geological Survey (USGS) and Yazoo Mississippi Delta Joint Water Management District for decades. The primary monitoring objectives are to identify water quality problems, describe seasonal and spatial trends for developing qualitative and

quantitative models of freshwater ecosystem, and determine permit compliance. Since its inception, the monitoring network has become a critical data source for assessing surface water pollution within the YRB. However, these datasets have not been fully explored to determine surface water quality trends in the basin. In recent years, multivariate statistical tools such as principal component analysis and factor analysis have been widely applied to analyze water quality variations in streams and aquifers (Ouyang *et al.* 2006; Skeppstrom & Olofsson 2006). Although these statistical tools are useful for identifying key and indicator water quality constituents, their applications to detect the temporal trends of water quality constituents are, however, somewhat limited. To this end, the duration curve and frequency distribution analysis techniques were employed in this study.

The duration curve and frequency distribution (or return interval) analysis techniques are commonly used in water flow (or discharge) estimations (Smakhtin 2001; Laaha & Blöschl 2007; Ouyang 2012). The flow duration curve is a relationship between any given discharge value and the percentage of time that this flow is equaled or exceeded. A flow duration curve can be constructed by organizing the flow time series values in a decreasing order, assigning flow values to class intervals, and counting the number of occurrences (time steps) within each class interval. Cumulated class frequencies are then calculated and expressed as a percentage of the total number of time steps in the record period. Finally, the lower limit of every discharge class interval is plotted against the percentage points (Maidment 1993; Smakhtin 2001). In contrast, a flow frequency distribution analysis shows the proportion of years when a flow is exceeded. The proportion of years is equivalent to the mean interval in years, which also are referred to recurrence interval that the river falls exceeds a given discharge. The flow frequency distribution analysis is normally constructed based on a series of annual values for the flow characteristic in question (e.g., annual maximum, 7-day annual minimum), which are extracted from the available continuous flow series (one value from every year of record) (Harris & Middleton 1993; Midgley *et al.* 1994). The flow duration curve shows the proportion of time during which a flow is exceeded, whereas the flow frequency distribution analysis displays the proportion of years when a flow is exceeded.

Although the duration curve and frequency distribution analysis techniques have been widely used for flow estimations, very few efforts have been devoted to applying these techniques for water quality load estimations. Total maximum daily loads (TMDLs) are generally developed by states when the concentrations of water quality pollutants exceed the designated water quality standards. The TMDL allows quantifying maximum allowable loads from various pollutant sources to meet the water quality goals. Several methods are used to quantify TMDLs such as simple regression-based models or complex simulation models but the load duration curve is one of the simplest and commonly used methods (Shirmohammadi *et al.* 2006; Johnson *et al.* 2009). The duration curve provides a quick visual assessment of water quality conditions and determines the percentage of time a flow or load is exceeded.

Characterization of surface water quality trends is an important aspect for evaluating stream pollution due to natural or anthropogenic inputs. Understanding surface water quality trends assists resource managers in identifying emerging water quality concerns, planning remediation efforts, and evaluating the effectiveness of remediation. The aim of this study was to apply the duration curve and frequency distribution analysis technique to evaluate the trends of surface water quality constituents, namely water temperature, specific conductivity (SP), dissolved oxygen (DO), and pH, in a stream within the YRB. Our specific objectives were to estimate: (1) the percentage of time when each constituent did not meet Mississippi state water quality criterion or minimum condition; (2) the recurrence interval when each constituent did not meet its criterion occurred; and (3) the load duration curve and frequency distribution of DO. It should be pointed out that the approach presented in this study could also be used for analyzing other water quality constituents from other locations provided there are sufficient field data available.

METHODS

Data source

Data used in this study were obtained from the USGS surface water monitoring station #0728875070 (latitude

33°24'04", longitude 90°53'31") located on Deer Creek east of Leland, Mississippi, USA (hereafter referred to as Dear Creek Station, Figure 1). This station has a drainage area of about 207 km² (http://waterdata.usgs.gov/nwis/dv?referred_module=sw&site_no=0728875070) and the land use is dominated by agriculture and forestry. The station record provides the daily discharge data for a period from 2001 to 2012 and the daily water temperature, SC, DO, and pH data for a period from 2001 to 2010. The discharge and water quality data for calendar year from 2001 to 2010 were used in this study. To scrutinize the change in surface water quality trends over time, the period of data records was further divided into a 3-year increment (i.e., 2001–2004, 2004–2007, and 2007–2010) for each water quality constituent. This increment allowed us to examine the percentage of time a constituent did not meet a prescribed value as time elapsed. A 3-year rather than 1-year increment was chosen because a 3-year value is statistically more meaningful than 1-year value. The Deer Creek Station is the only stream flow monitoring station within the YRB where such data are available.

Duration curve and frequency distribution analysis

The duration curve analysis was used to identify the percentage of the time a water quality constituent equaled or exceeded a prescribed value (e.g., Mississippi State water quality criterion), whereas the frequency distribution analysis was employed to determine the probability and recurrence interval of a water quality constituent at a prescribed value. These analyses were accomplished with the Hydstra Model (Version 10.3.2, Kisters Inc.). In this study, the duration curve analysis was accomplished using the Hyflow function from the Hydstra Model, while the frequency distribution analysis was done using the Hydist function from the Hydstra Model. Water quality data were extracted to tabular output using the Hyflow function, and all values were sorted and stored in a list. This list was then treated as a frequency histogram, and values were interpolated to obtain the desired quantiles. A flow-weighted distribution was also produced, in which quantiles were calculated by finding the item in the list where the cumulative value was equal to the quantile multiplied by the total value for the entire list. This distribution showed the percentage of

the total water quality value exceeding the nominated value. The frequency distribution analysis provided the probability and annual recurrence interval for each water quality constituent. In this study, the Pearson Type III distribution function was used for analysis. A load duration curve was also constructed for DO in this study. This curve was accomplished first by multiplying the stream discharges with the DO concentrations to obtain the DO loads, and then by constructing the load duration curve using the Hyflow function.

RESULTS AND DISCUSSION

Exceedance estimation

Figure 2 shows the duration curves for water temperature, DO, SC, and pH. These duration curves were obtained using the daily mean data (except for temperature which used maximum daily values) over the entire period from 2001 to 2010 for the

Deer Creek Station. Over the past 10 years, the percentages of the time were 2% for water temperature higher than its criterion of 32.2 °C, 97% for DO exceeding its criterion of 5 mg L⁻¹, 8% for SC above the value of 500 µmhos cm⁻¹, and 90% for water pH larger than its middle point of 7.5. These criteria or minimum conditions (except for SC and pH), developed by the Mississippi Department of Environmental Quality (MDEQ 2003), are outlined in Table 1. As stated in Table 1, there shall be no substances added to increase the SC above 1,000 µmhos cm⁻¹ for freshwater streams like Deer Creek. As the observed maximum SC in the Deer Creek is only about 700 µmhos cm⁻¹, the SC is not a concern for Deer Creek at all. Based on MDEQ (2003), Deer Creek is not listed among those having alternative Designated Use Classifications. Therefore, the Classification for Deer Creek would be as a Fish and Wildlife stream. A value of 500 µmhos cm⁻¹ for SC in Figure 2 was selected solely for the purpose to show how the SC changed over time (noted that for the alternative Designated Use Classifications streams

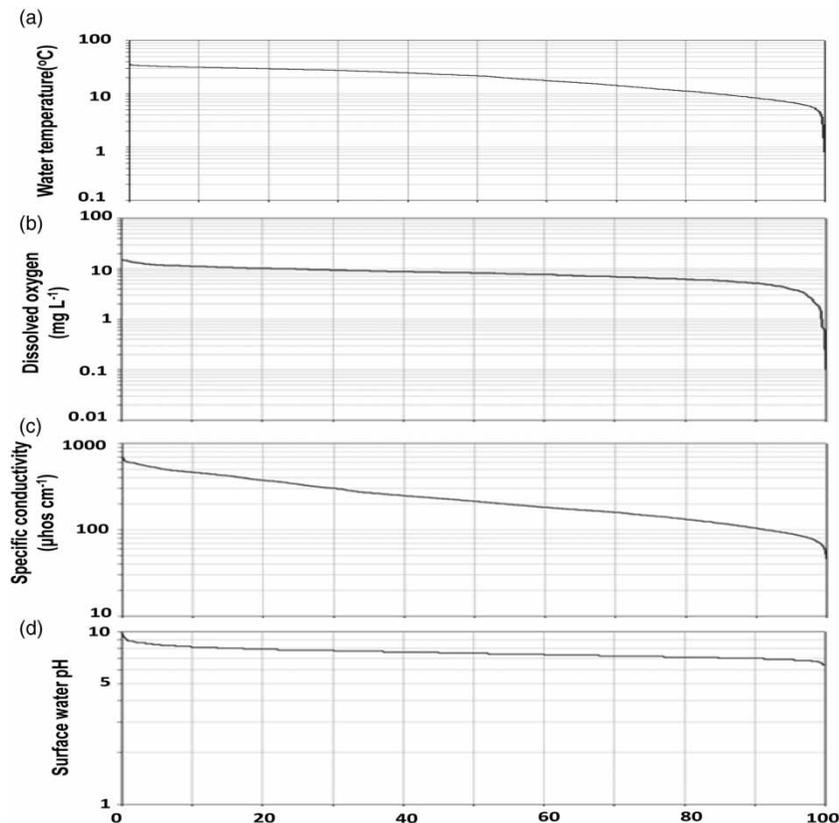


Figure 2 | Duration curves for water temperature, specific conductivity, dissolved oxygen, and pH at the Deer Creek Station for the calendar years from 2001 to 2010. All data are the daily mean values except for water temperature which are the daily maximum values.

Table 1 | Mississippi State surface water quality criteria applicable to Deer Creek for constituents used in this study (MDEQ 2003) and the percentage of time these criteria were not achieved for 2001 to 2010. The Designated Use Classification for Deer Creek is Fish and Wildlife

Constituent	Criteria description	Percentage of time not achieved
Temperature	The maximum water temperature shall not exceed 90°F (32.2 °C) in streams, lakes, and reservoirs. In addition, the discharge of any heated waters into a stream, lake, or reservoir shall not raise temperatures more than 5°F (2.8 °C) above natural conditions for temperatures.	4
Specific conductance	There shall be no substances added to increase the conductivity above 1,000 µmhos cm ⁻¹ for freshwater streams.	0
Dissolved oxygen	Dissolved oxygen concentrations shall be maintained at a daily average of not less than 5.0 mg/l with an instantaneous minimum of not less than 4.0 mg/l.	3
pH	The normal pH of the waters shall be 6.0 to 9.0 and shall not be caused to vary more than 1.0 unit within this range. Variations may be allowed on a case-by-case basis if the Commission determines that there will be no detrimental effect on the water body's designated uses as a result of the greater pH change.	5 (pH ≥ 7.5)

in Mississippi, the criterion for SC is 500 µmhos cm⁻¹). For pH, the 'normal' value is assumed to be 7.5, which is the median (i.e., 50% quantile) of the mean daily value for the period from 2001–2010 (Figure 2). A pH range of 6.5 to 8.5 defines a 1.0-unit variance from the normal value. As pH was never observed to fall below 6.5 (Figure 2), the only instances when the pH criterion was not achieved occurred when pH exceeded 8.5.

Water temperature can affect stream ecosystem directly and indirectly. The metabolic rate, food and oxygen demand, and waste release of most aquatic organisms increase in warm water. The amount of DO in water is partly controlled by temperature with more oxygen in cold water than in warm water. As water temperature rises, the rate of photosynthesis of the aquatic plants may increase if there are adequate amounts of nutrients. Our analysis showed that the water temperature in Deer Creek exceeded the 32.2 °C criteria 4% of the time over the last 10 years (Figure 2(a)).

Oxygen is a necessary element to all forms of life, and DO measures the amount of gaseous oxygen dissolved in an aqueous solution. Oxygen enters into water by diffusion from the surrounding air, by aeration (charging water with oxygen gas), and as a byproduct of photosynthesis. As the DO level in water drops below 5 mg L⁻¹, aquatic life is stressed (<http://www.state.ky.us/nrepc/water/wcpdo.htm>). Similar to the case of water temperature, the DO in this stream was primarily sufficient most of the time as it had 97% of the time above 5 mg L⁻¹ over the last 10 years (Figure 2(b)).

Specific conductivity is a measure of the water's ability to conduct electricity and thereby is a measure of the water's ionic activity and content. For a given temperature, the higher the concentration of ionic (dissolved) constituents such as total dissolved solid and salinity, the higher the SC will be. Used the prescribed value of 500 µmhos cm⁻¹ and compared with the cases of DO and temperature, the SC in this stream increased relatively more frequent as it had 8% of the time above 500 µmhos cm⁻¹ over the last 10 years (Figure 2(c)) although the SC is not a concern for Deer Creek. The relative acidity or alkalinity of a stream is indicated by its pH. Figure 2(d) indicates that about 5% of the time pH exceeded 8.5 over the last 10 years. Based on our prescribed pH value, the surface water pH is in good shape for this stream.

Figure 3 shows the time trends for exceedance of water quality standards in Deer Creek. Water temperature was above its criterion of 32.2 °C 2% of the time from 2001–2004, 6% from 2004–2007, and 8% from 2007–2010 (Figure 3(a)), suggesting that water temperature increased as time elapsed. Although the exact reason for warmer stream temperature remains to be investigated, a possible explanation would be the effect of global warming. Similarly, the percentage of time that SC exceeded the value of 500 µmhos cm⁻¹ increased as time elapsed (Figure 3(b)). This is partially explained by the fact that water temperature increased during this time period. Another contributing factor might be that the total dissolved solid content in this stream increased due to erosion; however, there were

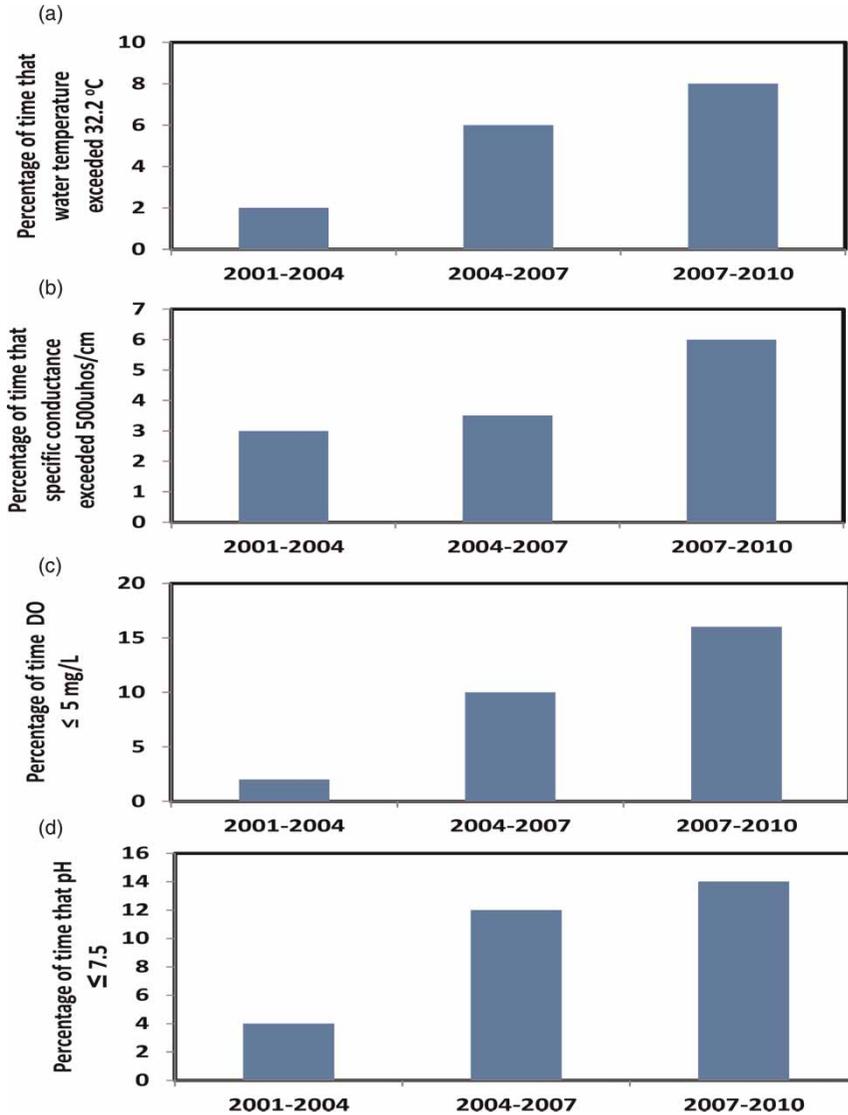


Figure 3 | Percentage of water quality constituents did not meet their criteria during a 3-year increment at the Deer Creek Station for the calendar years from 2001 to 2010.

insufficient data for total dissolved solid in this stream to test this assumption.

Unlike the cases of water temperature and SC, the percentage of time that the DO did not meet its criterion of 5 mg L⁻¹ was 98% from 2001–2004, 90% from 2004–2007, and 84% from 2007–2010. In other words, the percentage of time that the DO was less than or equalled 5 mg L⁻¹ was 2% from 2001–2004, 10% from 2004–2007, and 16% from 2007–2010 (Figure 3(c)). This trend indicates that the DO level in Deer Creek declined as time elapsed during the period from 2001 to 2010. This could occur as a result

of more biochemical oxygen demands due to the pollution of the stream. In addition, warmer water also reduced DO.

Recurrence and load estimation

The average recurrence intervals for water temperature, SC, pH, and DO at Deer Creek are given in Figure 4. The average recurrence interval is 1.004 years for water temperature at 32.2 °C (Figure 4(a)), 1.11 years for SC at 500 µhos cm⁻¹ (Figure 4(b)), 1.01 years for DO at 5 mg L⁻¹ (Figure 4(c)), and 1.01 years for pH at 7.5 (Figure 4(d)) over the last

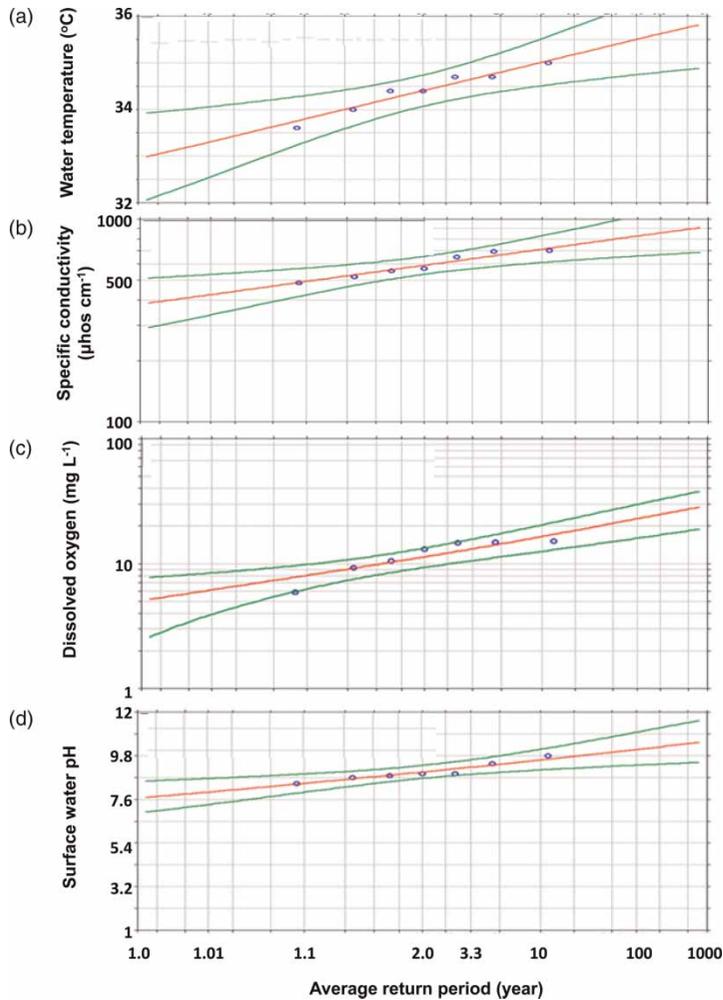


Figure 4 | Frequency distributions of water quality constituents at the Deer Creek Station for the calendar years from 2001 to 2010. The middle line denotes the average return period for the water quality constituents, whereas the two lines above and below the middle line represent the 95% interval.

10-year period. Therefore, these water quality constituents might not be the big concerns as their extremes occurred only once a year or less.

Very few efforts have been devoted to performing the load duration curve analysis for water quality constituents although this analysis is very important for TMDL implementation (Kim *et al.* 2012). Kim *et al.* (2012) argued that the TMDL approach should consider water quality characterizations based on overall flow conditions rather than on a single flow event. The load duration curve, which involves overall flow conditions, could provide a good opportunity for determination of appropriate TMDL targets.

Dissolved oxygen load duration curve and its frequency distribution (recurrence interval) are given in Figure 5.

Although there was no TMDL target for DO in this stream, the TMDL target for DO in the Black Bayou Watershed, a nearby stream within the YRB, is 429 kg d^{-1} (or 945.4 lb d^{-1}) (MDEQ 2003). The DO target for Black Bayou was obtained using the product of a mean daily discharge of $2.485 \text{ m}^3 \text{ s}^{-1}$ (as compared with $2.0 \text{ m}^3 \text{ s}^{-1}$ for Deer Creek) and a mean daily DO concentration of 2 mg L^{-1} . If the Black Bayou TMDL was applied to Deer Creek, the DO load would not meet this target about 25% of the time during 2001 to 2010 (Figure 5(a)). For the DO load at this target (429 kg d^{-1}), the average recurrence interval was 1.1 years (Figure 5(b)). It should be noted that the load duration curves for water temperature, SC, and pH were not computed because these constituents were

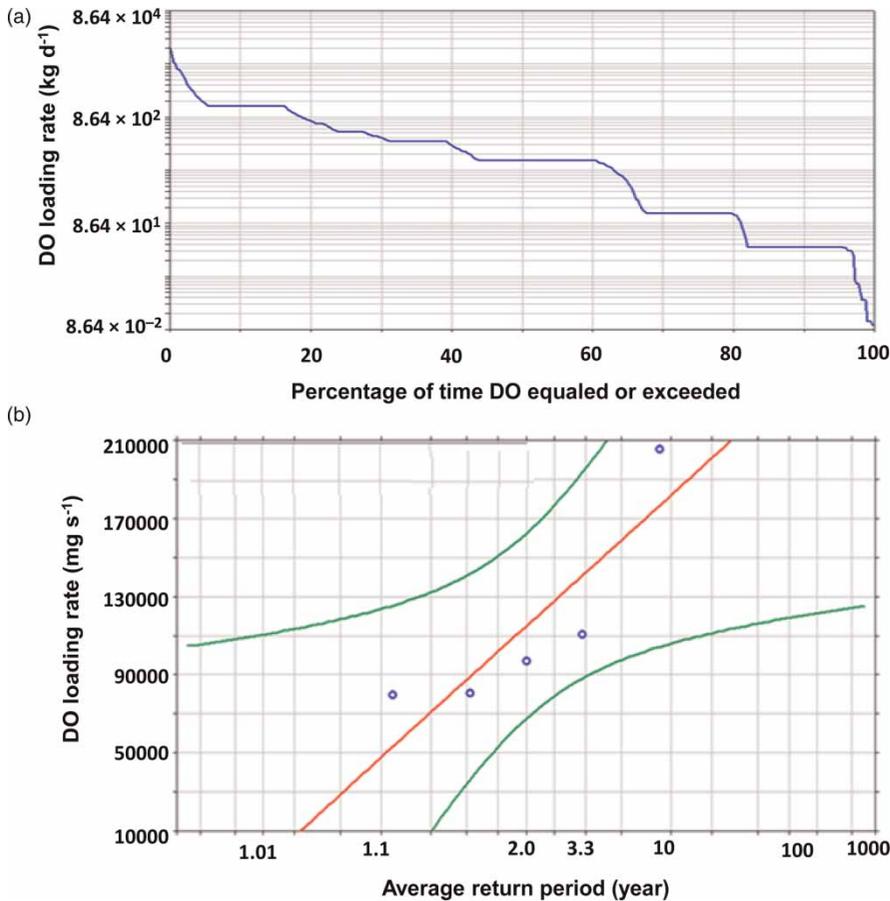


Figure 5 | Dissolved oxygen load duration curve and frequency distribution at the Deer Creek Station for the calendar years from 2001 to 2010.

not quantified in mass and the loadings of these constituents were physically meaningless.

SUMMARY

In this study, surface water quality data collected from 2001 to 2010 for water temperature, SC, DO, and pH from the Deer Creek Station in the YRB, Mississippi were analyzed, using the duration curve and recurrence interval analysis techniques. The percentage of the time when a water quality constituent did not meet its criterion or minimum condition was estimated. The recurrence period (or interval) when a water quality constituent equaled or exceeded its criterion or minimum condition was evaluated. The criteria or minimum conditions used in this study were developed by the Mississippi Department of Environmental Quality (MDEQ 2003).

Over the last decade, the percentages of the time were 2% for water temperature higher than its criterion of 32.2 °C, 3% for DO below its criterion of 5 mg L⁻¹, and 8% for SC above a prescribed value of 500 μmhos cm⁻¹. Results showed that these water quality constituents might not be the major concerns as the percentages of the time when these constituents did not meet their criteria or minimum conditions were very low.

The average recurrence interval in this stream was 1.004 years for water temperature at 32.2 °C, 1.11 years for SC at 500 μmhos cm⁻¹, 1.01 years for DO at 5 mg L⁻¹, and 1.01 years for pH at 7.5 over the last 10-year period. It further confirmed that these water quality constituents might not be the big concerns as their extremes occurred only once a year or less. The water temperature and SC increased but the DO decreased in the stream as time elapsed during the past decade. In addition, the stream had an acidic tendency as time elapsed.

There was about 25% of times that the DO load did not meet the TMDL target (429 kg d^{-1}). For the DO load at this target, the average recurrence interval was 1.1 years. Therefore, more efforts have yet to be accomplished to increase the DO load in the stream.

It should be noted that the water quality constituents (i.e., water temperature, DO, pH, and specific conductivity) selected in this study are not the major adverse environmental concerns in the YRB. For a comprehensive estimation of water quality trends in the YRB using the duration curve and return interval techniques, the water quality constituents such as excess nutrients, heavy metals, sediments, and herbicides, which are the major pollutants in YRB, are necessary although our attempts to locate such a dataset were unsuccessful.

Very few efforts have been devoted to applying the load duration curve and return interval techniques for water quality trend analysis. Further study is, therefore, warranted for applying these techniques for water quality trend analysis, especially for those watersheds where the datasets for excess nutrients, heavy metals, sediments, and herbicides are available.

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