

Atmospheric influences on water quality: a simulation of nutrient loading for the Pearl River Basin, USA

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Abstract Knowledge of water quality conditions is essential in assessing the health of riverine ecosystems. The goal of this study is to determine the degree to which water quality variables are related to precipitation and air temperature conditions for a segment of the Pearl River Basin near Bogalusa, LA, USA. The AQUATOX ecological fate simulation model is used to estimate daily total nitrogen, total phosphorus, and dissolved oxygen concentrations over a 2-year period. Daily modeled output for each variable was calibrated against reliably measured data to assess the accuracy. Observed data were plotted against simulated data for controlled and perturbed models for validation, and stepwise multiple regression analysis was used to quantify the relationships between the water quality and meteorological variables. Results suggest that daily dissolved oxygen is significantly negatively correlated to concurrent daily mean air temperature with a total explained variance of 0.679 ($p < 0.01$), and monthly dissolved oxygen is significantly negatively correlated to monthly mean air temperature with a total explained variance of 0.567 ($p < 0.01$). Total mean monthly phosphorus concentration is significantly positively related to

the previous month's precipitation with a total explained variance of 0.302 ($p < 0.01$). These relationships suggest that atmospheric conditions have a strong influence on water quality in the Pearl Basin. Therefore, environmental planners should expect that future climatic changes are likely to alter water quality.

Keywords Water quality · Riverine ecosystem · AQUATOX · Louisiana hydroclimatology · Climate

Introduction

Streams are crucial lifelines and integral components of the communities that they intersect. The assets that streams provide collectively create a deep and natural dependence on fluvial ecosystems that is amplified when these ecosystems are endangered by both natural and anthropogenic forces. The current conditions and influences on a stream must be known before a plan for preservation and/or restoration, under various scenarios of changing environmental conditions, can be implemented (Maret et al. 2008).

While understanding and controlling the anthropogenic forces that endanger water quality is essential, it is also important to recognize the natural forces that impact water quality. The interplay between atmospheric variables (e.g., precipitation and air temperature) that

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may affect streamflow (McCabe and Wolock 2002), oxygen availability (Mimikou et al. 2000), total suspended sediment (TSS) concentrations (Walling and Fang 2003), and nutrient loadings (McKee et al. 2003; Bricker et al. 2008; Liu et al. 2009; Rabalais et al. 2009) can be critical. For example, the concentration of nutrients such as phosphorus and nitrogen from an agricultural site in a nearby stream depends on the timing and amount of precipitation (Bricker et al. 2008; Maret et al. 2008).

These same nutrients may also be deposited from the atmosphere. Atmospheric particulate matter is commonly examined to assess air quality (e.g., Pérez et al. 2010), but air quality may also play an important role in water quality conditions (Sundarambal et al. 2010). Sundarambal et al. (2010) utilized PM₁₀ (particulate matter $\leq 10 \mu\text{m}$ in diameter) concentrations to create a pollutant standards index and concluded that high concentrations of nitrogen and phosphorus resulted in wet atmospheric deposition and may subsequently impact water quality.

Atmospheric water quality relationships have been established in many areas (Zwolsman and Bokhoven 2007; Liu et al. 2009; Richardson et al. 2009), but these relationships vary somewhat between locations (Liu et al. 2009). Many studies allude to a rainfall–runoff association as well as the impact of land use (Kazi et al. 2009; Lee et al. 2009). Rainfall–runoff/land use relationships in addition to atmospheric impacts create a complex system that necessitates the use of water quality models.

Water quality models are essential tools used by biologists, ecologists, wildlife managers, and system modelers to develop total maximum daily loads (TMDLs), assess ecological risks, and determine water quality thresholds that must be met to avoid impaired waterway status under federal and state regulations (Chapra 2003). The integrated eutrophication and contaminant fate and effect model known as AQUATOX predicts pollutant fates and how they impact an entire ecosystem (Park et al. 1988, 2005). The biological components included in AQUATOX also enhance the utility and complexity of the model by including potential biotic indicators of anthropogenic and natural changes within the ecosystem (Karr and Chu 2000). The multidimensional and integrative nature of AQUATOX gives many of the same capabilities as other models, such as the River and Stream Water Quality Model (QUAL2K, Chapra et al. 2007),

Environmental Protection Division River 1 (Martin and Wool 2002), and Water Quality Analysis Simulation Program (Wool et al. 2004), while also incorporating equations that allow it to model various fish and plant species including phytoplankton as well as sediments and nutrients (Park et al. 2008).

AQUATOX is one of the many modeling systems available within the Environmental Protection Agency's (EPA's) Better Assessment Science Integrating point and Non-point Sources (BASINS) platform. The AQUATOX interface is user-friendly without requiring the extensive data sets of other models; it includes pre-loaded sites in various geographic settings that already have regionally similar environmental conditions and pollutants (Sourisseau et al. 2008). Its ability to run in conjunction with the Hydrologic Simulation Program—FORTRAN (HSPF) watershed model allows AQUATOX to incorporate land use and nutrient loadings (e.g., nitrogen and phosphorus) to predict water quality indicators (Park et al. 2005).

AQUATOX has been used for informing state and federal agencies as well as local governments and community planners (Park et al. 1995; Rashleigh 2003). The federal Clean Water Act of 1972 (USA) outlined a set of laws that were intended to regulate water pollution (P.L. 92-500). The Clean Water Act established water quality standards based on the intended uses of a water body (e.g., fishing, recreation, agriculture, and water supply). If these standards are not met, then the body of water is designated as “impaired” and placed on the 303(d) impaired water body list. If a water body is placed on the 303(d) list, then a TMDL must be developed to consider plans for reducing pollutant levels below the necessary standard (Bourgeois-Calvin et al. 2004). AQUATOX is useful in creating TMDLs, solving impairment issues, and identifying the changes needed in concentrations of various variables to meet and exceed these regulations (Carleton et al. 2009). AQUATOX has also been used to show how adjusted levels of phosphorus, TSS, and nitrogen can impact other water quality indicators such as algae and benthic chlorophyll *a* (Carleton et al. 2009). These indicators are used to infer overall water quality conditions and areas of improvement relative to necessary standards and inform TMDL development. The lag times between the implementation of best management practices and water quality improvement can also be monitored through a multitude of approaches (Meals et al. 2010).

Study area and research questions

The Pearl River Basin (PRB) is the focus of this study. Measured daily and monthly discharge are used to simulate daily water quality conditions in a small segment of the Pearl from the northeastern corner of Washington Parish to Bogalusa, LA (Fig. 1), an area with reliable and continuous environmental data, as described in the next section. This segment of the PRB is of particular importance because, unlike many streams in the surrounding region, the absence of constraining levees in this section of the PRB allows the river to support a vibrant diversity of flora and fauna in large areas of submerged and semi-submerged bottomland forests, swamplands, and marsh. The river is also sufficiently wide and deep in this area to support extensive boating and recreational fishing activities.

In addition, environmental monitoring and modeling of the PRB is of particular importance because the river is included on the 303(d) list of impaired waterways due to excessive nutrient levels (nitrogen and phosphorus), mercury concentrations, sediment loadings, and pesticide concentrations (MDEQ 2010). Overexploitation or increased degradation could have immediate ramifications but also create future concerns, especially considering the increasingly erratic nature of meteorological and climatological events such as floods, droughts, heat waves, and cold bursts in this region. Thus, the research questions for this study are as follows:

1. Can water quality be modeled effectively in the PRB with available data?
2. Are precipitation and air temperature, which are both related to streamflow (Jordan et al. 1997; Harmel et al. 2006), potentially associated with specific water quality parameters in the PRB?

Materials and methods

Data

Data were acquired from multiple sources and platforms. Watershed subsegments (“hydrologic units”), hydrography and catchment data (National Hydrography Dataset (NHD) Plus), and meteorological station data were downloaded using the

BASINS environmental analysis system (USEPA 2007). All related hydrography and catchment data from the NHD Plus were downloaded for the study area including flow lines, areal features such as catchment basins/sub-basins, and water body features such as lakes. Data from 323 meteorological stations in the PRB, including precipitation, potential evapotranspiration, and air temperature, were available in most locations as potential independent variables for stepwise multiple regression model inclusion.

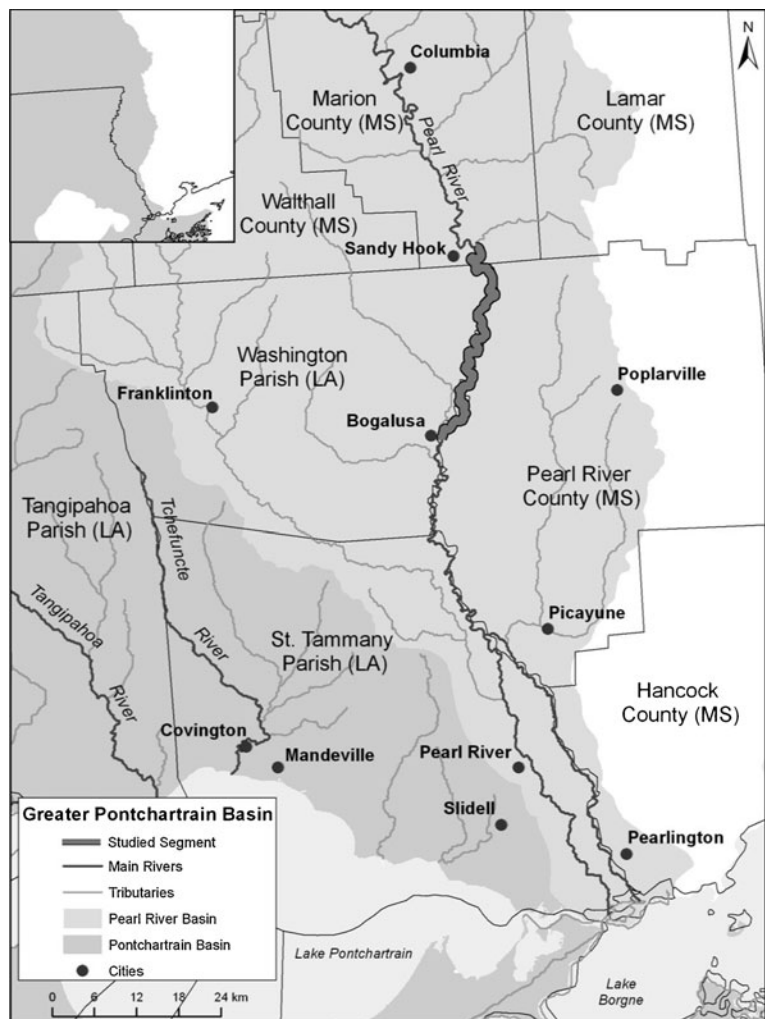
Additional data were downloaded to examine the relationships between streamflow, precipitation, air temperature, and multiple water quality parameters: i.e., total nitrogen (TN; in milligrams per liter), total phosphorus (TP; in milligrams per liter), dissolved oxygen (DO; percent saturation), pH, and water temperature. The geospatial attributes of gages for evaluating streamflow (GAGES) data set includes 6,785 US Geological Survey stream gages in the conterminous USA with time series extending to as wide as 1950–2007 (<http://esapubs.org/archive/ecol/E091/045/default.htm>). Stream gage data for the segment of the PRB in the study region were extracted from the original GAGES database. Daily precipitation and air temperature data for Bogalusa were downloaded from the National Climatic Data Center (<http://www.ncdc.noaa.gov/>). Water quality monitoring data were downloaded from the USEPA's Storage and Retrieval (STORET) Legacy database (<http://www.epa.gov/storet/>) and included monthly values of TN, TP, DO, pH, and water temperature. Daily TN, TP, and DO were simulated and pH and water temperature were used as model input variables to aid in the simulation of the other daily water quality variables.

Methods of simulation and statistical analysis

Historical records from each data set were analyzed statistically and graphically to determine whether a relationship exists between air temperature and precipitation and the three water quality parameters in the PRB. AQUATOX (Release 3) was utilized to simulate multiple stressors in the PRB system (Carleton et al. 2009) including TN, TP, and DO.

The AQUATOX simulation was set to begin in January 1997 and end in December 1998, to correspond with the period of optimal data coverage and

Fig. 1 The segment of the Pearl River used for the AQUATOX simulation



quality in the study area. Initial nutrient and detritus conditions were unchanged from the default values because they are sensitive to subsequent loadings rather than initial conditions. All plant and invertebrate simulations and initial conditions remained unchanged from default values as well because the defaults are set to a generic stream in the southeastern USA. Bass, catfish, and carp fish species were added to the simulation because they represent the dominant fish species in the PRB (Louisiana Sportsmen 2005, <http://www.louisianasportsman.com/>).

Various AQUATOX parameters were set based on the chosen stream segment along the Louisiana/Mississippi border (Table 1). For the stream surface, “riffle” was set to 10 % and “run” was set to 90 % because most of this segment of the Pearl River has a moderate

current and smooth surface. Monthly water temperature readings for the time period were imported to create a time-varying temperature series; the initial water temperature (January) was set to 13.5 °C based on the mean from available data. Photoperiod was computed from latitude, average light was set to 285 ly day⁻¹, and annual light range was set to 336 ly day⁻¹. Annual mean and range for light loadings were based on solar information from the airport at McComb, Mississippi. Observed pH (monthly) was imported and initial pH conditions were set to 7.0 based on January means concurrent with the start date for the AQUATOX simulation. Monthly values for TN, TP, and DO were imported as inflow loadings for model simulation.

Table 1 Description of stream segment between Sandy Hook, Mississippi, and Bogalusa, Louisiana

Description	Value
Segment length	28.1 km
Surface area	7,109,300 m ²
Mean depth	2.86 m
Maximum depth	4.29 m
Channel slope	0.0003 mm ⁻¹
Water volume	20,332,598 m ³
Phytoplankton retention (distance to outfall)	96 km
Latitude	30.89°N
Altitude (mean)	60 m

As a part of model calibration, an initial control run for model simulation was performed in “spin-up mode” to allow the initial biotic conditions to be used from the previous iteration. Model calibration was performed using root mean square error (RMSE) statistics and *R*-squared values. Observed values were also plotted against simulated values for visual comparison. A third control run was performed without using spin-up mode, and an additional “perturbed” model was also run for comparison to the control run.

Statistical analysis

Daily output time series data for TN, TP, and DO were then exported from AQUATOX, and a single database was created that also included concurrent daily and lagged (1 to 5 days) air temperature (maximum, minimum, and mean) and precipitation readings. A monthly time series database was also created from the original water quality variables acquired from EPA's STORET Legacy database and the atmospheric readings for that specific day of the month were added to the database. One-month lags for monthly mean atmospheric data were also added to the monthly database. After data manipulation and aggregation were completed, a Shapiro–Wilk test was performed on each of the water quality and atmospheric variables to test for normality. A logarithmic (log base 10) transformation was applied to non-normal data to create a potentially more meaningful set of values. Both Pearson and Spearman bivariate correlation were used to identify significant ($\alpha < 0.05$) correlations (two-tailed test) between atmospheric conditions and water quality.

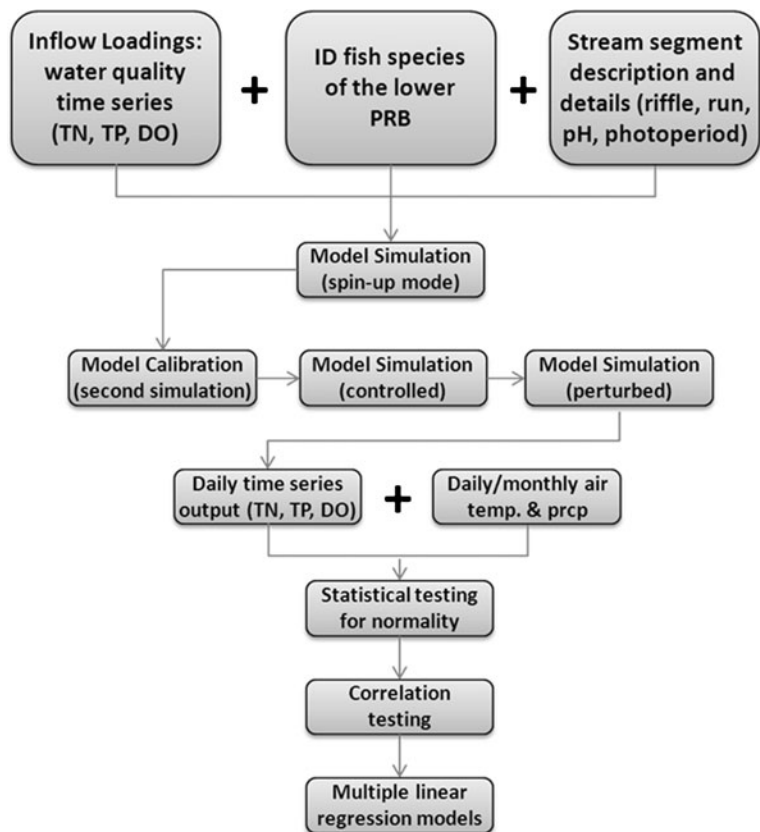
Six stepwise multiple linear regression models were then generated to determine which atmospheric variables exert the most influence on daily (and then subsequently monthly) values of each of the three water quality variables. Standardized predicted values and standardized residuals were recorded along with Cook's and Leverage distance values. A probability of *F* was set at 0.05 for entry into the model and 0.10 for removal. Multi-collinearity statistics were also included to examine inter-variable relationships. A detailed flow-chart of the methodology is illustrated in Fig. 2.

Results and discussion

AQUATOX accurately simulated monthly mean TN, TP, and DO values. Calibration statistics are listed in Table 2. *R*-squared values were significant at $\alpha < 0.01$ for all modeled variables. Visual comparison of observed and modeled values revealed that TN consistently overpredicted for that month by an average of 0.4 mg L⁻¹. For this reason, the model was rerun with an initial TN value that was 0.4 mg L⁻¹ lower than the initial value used in the previous model run. Initially, simulated TN values ranged between 0.8 and 1.4 mg L⁻¹, while adjusted simulated values in the new model ranged from 0.4 to 1.0 mg L⁻¹. Accuracy metrics for the newly simulated TN values produced a higher *R*-squared value and lower RMSE.

AQUATOX also plotted non-simulated monthly variables. Daily streamflow values, which were a major component of simulation runs, fluctuated from a low level of 35 m³ s⁻¹ to a high level of 110 m³ s⁻¹. Streamflow was minimized between July and November and maximized from January to May each year, reflecting in part a seasonal trend of higher precipitation in the winter and spring and lower precipitation in the summer and fall. Although evapotranspiration was not represented directly, it likely contributed to lower streamflow values in the summer and fall months. Observed monthly mean water temperature (Fig. 3) and pH levels (Fig. 4) showed the expected seasonal trends, with lower values of the latter (~6.2) occurring in the late winter and early spring months and higher values (~7.6–8.2) occurring in the summer and fall months. However, these pH levels were not necessarily consistent from year to year with a value of 7.3 in early December 1997 and a value of 6.5 in December 1998.

Fig. 2 Methodology for AQUATOX model simulation and subsequent statistical analysis



TN maximized at 1.08 mg L^{-1} in the winter months, with a secondary peak between 0.72 and 0.78 mg L^{-1} in the summer months. TN concentrations were lowest in the spring and fall months with values less than 0.45 mg L^{-1} (Fig. 5). Simulated TN followed a similar pattern. TP did not exhibit a seasonal pattern but instead maximized at 0.20 mg L^{-1} in June 1997 and minimized at 0.01 mg L^{-1} in January 1998 with values averaging between 0.06 and 0.08 mg L^{-1} at most other times (Fig. 6). Simulated TP accurately reflected the trends and actual values of

observed TP with a maximum (minimum) departure from those observed of 0.02 mg L^{-1} ($<0.005 \text{ mg L}^{-1}$). Simulated TP values ranged between 0.01 and 0.20 mg L^{-1} . Simulated DO (ranging between 6.14 and 11.25 mg L^{-1}) also closely reflected the overall trends and actual observed values of DO (Fig. 7). Two observed DO values were $\sim 0.7 \text{ mg L}^{-1}$ higher than the simulated values, but some observed values were also slightly lower so it was determined that the simulation was reasonable, especially when considering the seasonal trends of high values in the winter and low values in the summer.

Atmospheric conditions and water quality values were also analyzed to determine whether a statistically significant relationship exists between the two. The Shapiro–Wilk test revealed that all daily atmospheric and water quality variables were non-normal, with p values of less than 0.01 . Monthly variables for TN and DO were not found to deviate significantly from normality, while all other monthly values were non-normal ($p < 0.01$).

Table 2 Accuracy metrics for modeled monthly water quality variables

Variables	RMSE	R-squared values
TN ($n=26$)	0.050 ^a	0.909 ^a
TP ($n=26$)	0.003 ^a	0.991 ^a
DO ($n=26$)	0.320 ^a	0.945 ^a
TN (2nd simulation) ($n=26$)	0.047 ^a	0.922 ^a

^aSignificance at the 0.01 level

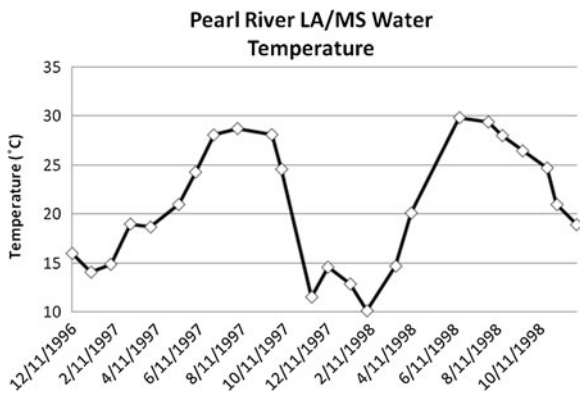


Fig. 3 Observed water temperature for the Pearl River near Bogalusa, LA

Not surprisingly, daily DO was significantly negatively correlated to daily maximum, minimum, and mean air temperatures, and mean monthly DO was correlated with monthly mean air temperature at concomitant time periods (Table 3) after all non-normal data were transformed via log transformation. Monthly TP was found to be significantly correlated to the previous month's precipitation (Table 3).

Regression models were created to determine the degree of influence of air temperature and precipitation on water quality variables. Monthly TP vs. the previous month's precipitation had an adjusted *R*-squared value of 0.302 ($p < 0.01$) (Table 3; Eq. 1). Because minimum, maximum, and mean air temperatures are naturally autocorrelated, only the mean daily air temperature and precipitation were selected for the daily DO regression model. The regression model revealed an adjusted *R*-squared value between daily DO and mean air temperature of 0.679 ($p < 0.01$)

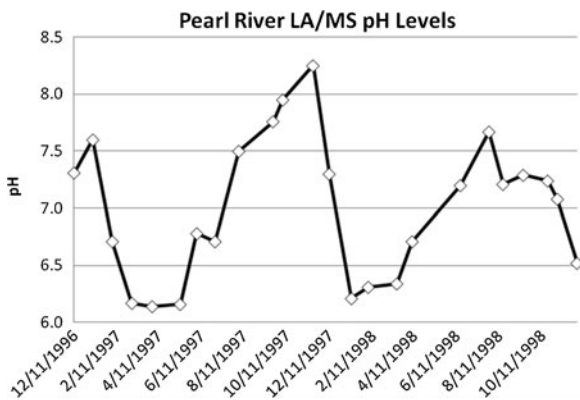


Fig. 4 Observed pH levels for the Pearl River near Bogalusa, LA

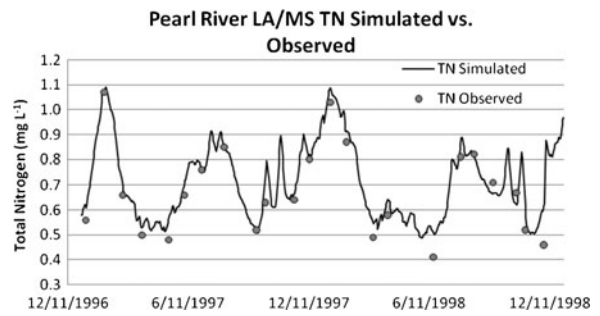


Fig. 5 Perturbed AQUATOX daily simulations and observed monthly values of TN

(Eq. 2) and an adjusted *R*-squared value of 0.567 ($p < 0.01$) (Eq. 3) between monthly DO and mean air temperature (Table 3).

$$\begin{aligned}
 TP_{monthly}(\text{milligrams per liter}) & \\
 &= 0.001(P_{previous\ month\ total}(\text{milliliters})) \\
 &+ 0.046 \tag{1}
 \end{aligned}$$

$$\begin{aligned}
 DO_{daily}(\text{milligrams per liter}) & \\
 &= -0.136(T_{mean}(\text{degree Celsius})) + 10.935 \tag{2}
 \end{aligned}$$

$$\begin{aligned}
 DO_{monthly}(\text{milligrams per liter}) & \\
 &= -0.158(T_{mean}(\text{degree Celsius})) + 11.492 \tag{3}
 \end{aligned}$$

The average monthly precipitation for the period between 1997 and 1998 (143 mm or 5.61 in.) was near the normal value of 134.0 mm (5.34 in.). However, the high inter-monthly precipitation variability (modeled

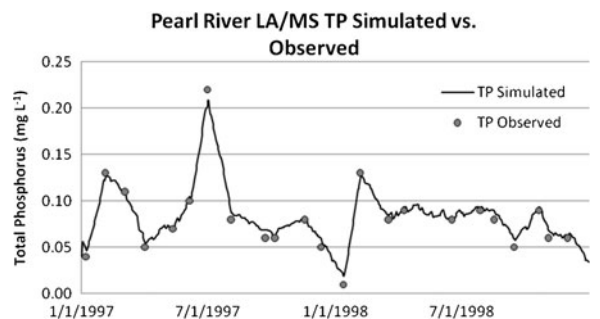


Fig. 6 Perturbed AQUATOX daily simulations and observed monthly values of TP

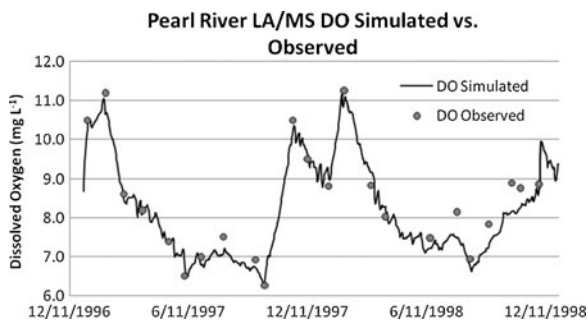


Fig. 7 Perturbed AQUATOX daily simulations and observed monthly values of DO

and actual) inferred that results estimate conditions caused by a high variability in rainfall. Seasonal trends in TN and DO signaled a strong association to atmospheric features, although some of those relationships were not found to be statistically significant. Air temperature explained the majority of DO variance, while the previous month's precipitation explained almost one third of the variability in TP levels. A lack of similar findings for TN does not mean that they do not exist. Higher concentrations of TN can be expected in the winter and summer months, while lower concentrations can be expected in the spring and fall months. A prominent peak in DO in winter and in pH in the late summer/early fall was observed. These patterns could infer lagged relationships between atmospheric features and water quality parameters. These relationships are not confirmed but warrant more investigation. The lack of a seasonal pattern for TP may suggest that it is more regulated by instantaneous conditions, thus inferring that extreme weather events such as heavy rains may be linked more closely than seasonal climatological trends to TP concentrations.

Table 3 Correlation and regression values for selected atmospheric and water quality variables

Relationships	Correlation coefficients	Adjusted R-squared
Previous month precipitation and monthly TP	0.47, $p < 0.05$	0.302, $p < 0.01$
Mean daily air temperature and daily DO	-0.79, $p < 0.01$	0.679, $p < 0.01$
Mean monthly air temperature and monthly DO	-0.77, $p < 0.01$	0.567, $p < 0.01$

The correlation between TP and precipitation was not unexpected because a key determinant of water quality is streamflow (Jordan et al. 1997; Harmel et al. 2006). Precipitation and nutrient/sediment loads from runoff vary drastically across different land covers, and agricultural areas are usually the source of higher phosphorus loadings (Inamdar et al. 2001). Changes in streamflow may have a net negative effect on water quality (Mimikou et al. 2000); thus, the direct positive correlation between TP and precipitation may infer a secondary correlation between TP and streamflow.

While the only statistically significant correlation to precipitation was TP, there is evidence from prior research that precipitation and other water quality indicators may be linked. Streamflow, and consequently precipitation, affects oxygenation and aeration (Neto et al. 2007) as well as the timing and nutrient concentrations (Jordan et al. 1997) of runoff. Additionally, Mimikou et al. (2000) found that increases in air temperature coupled with decreases in precipitation in a catchment in central Greece resulted in severe summer drought and significant impairment to water quality—specifically to DO and ammonium levels. Collectively, these findings suggest that streamflow–nutrient load relationships should be studied more thoroughly.

The apparent relationships between atmospheric conditions and certain water quality parameters affirm that a watershed simulation model in conjunction with general circulation model-based predictions of long-term climatic variables for the PRB is needed. Some recent work has been focused on the impact of climatic change on aquatic systems (Zwolsman and Bokhoven 2007; Towler et al. 2010). Basin-scale watershed models such as the Soil and Water Assessment Tool (Stone et al. 2001; Wu and Xu 2006; Xu et al. 2006) and the HSPF (Göncü and Albek 2010) can examine environments at a broader spatial scale than AQUATOX and have been used to model the effects of climatic change throughout entire watersheds. Xu et al. (2006) specifically examined watersheds in southeastern Louisiana and found that increases in air temperature caused decreases in streamflow, but corresponding increases in precipitation had the potential to cause drastic increases in streamflow, potentially resulting in a net effect of widespread flooding.

Conclusions

AQUATOX provided an excellent simulation of daily values for multiple water quality variables based solely on monthly time series records. The study found that climate does impact certain water quality variables in the studied segment of the PRB. Major observations were that:

1. AQUATOX accurately interpolated monthly data into daily data, thus allowing for a more in-depth data analysis in a location (Bogalusa) with limited data availability.
2. One-month-lagged precipitation within the PRB is closely linked to TP, and both daily and current monthly mean air temperature are associated with DO concentrations in the Pearl River.

Disparities between TN, TP, and DO at other stations in the PRB should be examined in future studies because individual stations are influenced by industrial and other local emissions related to urban transport, maritime activities, and land use. Additionally, more research studies should be conducted to discover other potential relationships between climate and water quality so that future studies related to climatic change will be well-informed when analyzing multiple water quality variables (Delpla et al. 2009; Whitehead et al. 2009; Carvalho et al. 2012). Ecological risk assessment and impact assessment of changes in water quality are usually only addressed in a reactive manner when water quality impairment has already occurred, but when considering climatic change there will be a need to be proactive in managing potential challenges instead of merely predicting potential problems (Johnson and Weaver 2009).

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