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Empirical Modelling of Dissolved Oxygen against Pollution Parameters in Coastal Water in Different Seasons

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ABSTRACT

An empirical modelling study of dissolved oxygen (DO) against six pollution parameters: biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrate, total phosphate, total solids and temperature, analysed from field samples was carried out for wet and dry seasons of April 2006 – January 2007. Modelled equations were developed from each parameter using regression analysis to predict DO within the two seasons; the best fitted equation was reported in each case with their corresponding R^2 values and the validity ranges evaluated for model calibration. The resulting DO values predicted from the modelled equations were validated by comparison with field data and found to correlate better in the dry season for data obtained based on BOD, COD, nitrate and phosphate. Also, the validity ranges of the models developed from these anthropogenic pollution parameters were wider during the dry season. However, total solids (TS) and temperature used to measure contributions from physical and natural conditions to DO modelling depicts a better simulation during the wet season for the TS prediction due to an increase in natural effects witnessed in the wet season than the dry one. Temperature had the lowest R^2 values due to reduced natural temperature variations in the tropical region. Thus, the predictions of DO based on anthropogenic, abstracting pollution parameters are better done in the dry season.

Keywords: anthropogenic activities, regression analysis, simulation, wet and dry seasons

INTRODUCTION

Oxygen dissolved in the aquatic habitat is indispensable to fish and other living organisms in the zone. The survival of these important aquatic resources depends on the availability of dissolved oxygen (DO) for their metabolic activities. Fish require the highest level of DO while invertebrates require lower and bacteria the least.

DO is an important water quality parameter needed for aquatic life support is however affected by a number of physical conditions (James 2002) and pollutants from anthropogenic activities (de Bashan and Bashan 2004; Kotti *et al.* 2005). Light penetration is needed for photosynthesis by phytoplankton and other sea plants to produce oxygen; tidal waves and currents affect the dissolution rate of atmospheric oxygen in the water system by its turbulent mixture while temperature increase of the water system inversely affects DO content (Deas and Lowney 2000). These are among the physical conditions that affect dissolution of oxygen in the water system of coastal areas. These physical conditions vary spatially, temporally and seasonally and their consideration helps to understand the state of DO in a zone.

Further, disposal of sewage into water bodies, agricultural practices (e.g. the use of fertilizers) and other anthropogenic activities introduce organic matter and nutrients (nitrate and phosphate) into the water system. The introduction of these nutrients aid the growth of algae and seed weeds (eutrophication) which in turn increase the organic matter content of the water. The decomposition of organic matter from the disposed sewage and the dead algae is done by aerobic metabolism of micro-organisms which feed on the biomass through an oxidative process using up the dissolved oxygen as oxidant. Thus, DO which should support aquatic life, is removed by adverse anthropogenic activities.

Therefore, DO is an important empirical standard for evaluating water pollution and the quality of water bodies and the support of such for aquatic life. DO content must then be maintained in such a way that it does not go below a certain desirable minimum concentration. To therefore analyse for and ensure this concentration, modelling of DO in relation to parameters affecting it will be a useful and imperative tool. This will assist in planning, managing, formulation of policies and monitoring activities that will conserve the environment.

There are very limited works in the literature on modelling of DO (Altunkaynak *et al*. 2005; Yuan *et al*. 2007) in coastal waters while much emphasis has been laid on other water quality parameters (e.g. metals and organic micropollutants). Likewise, deterministic approaches were adopted in most of the models that exist (Park and Lee 2002; Suh *et al*. 2004; Ghosh and Mujumdar 2006). However, a recent trend in modelling reveals that it is nearly impossible to totally understand the boundaries and the forces guiding the behaviour of a parameter as needed in a deterministic or mechanistic model especially in coastal waters (BDMF 2000; James 2002). Also, the complexity of a model does not imply accuracy since much of the assumptions made in its formulation can cause significant deviation. Thus, an empirical understanding of the pattern of a water quality parameter like DO is necessary in relation to other parameters that influence it based on observed field data. This is increasingly becoming as important as the deterministic approach.

Therefore, this study presents an empirical modelling of DO in relation to other pollution indicators that affect it. Pollution parameters considered were biochemical oxygen demand (BOD) and chemical oxygen demand (COD), nitrate-nitrogen, total phosphate, total solids and temperature. The calibrations of the modelled equations were also presented to obtain the parameter boundaries suitable for accurate prediction while the validity of the equations were determined by the comparison of modelled values with field observed values.

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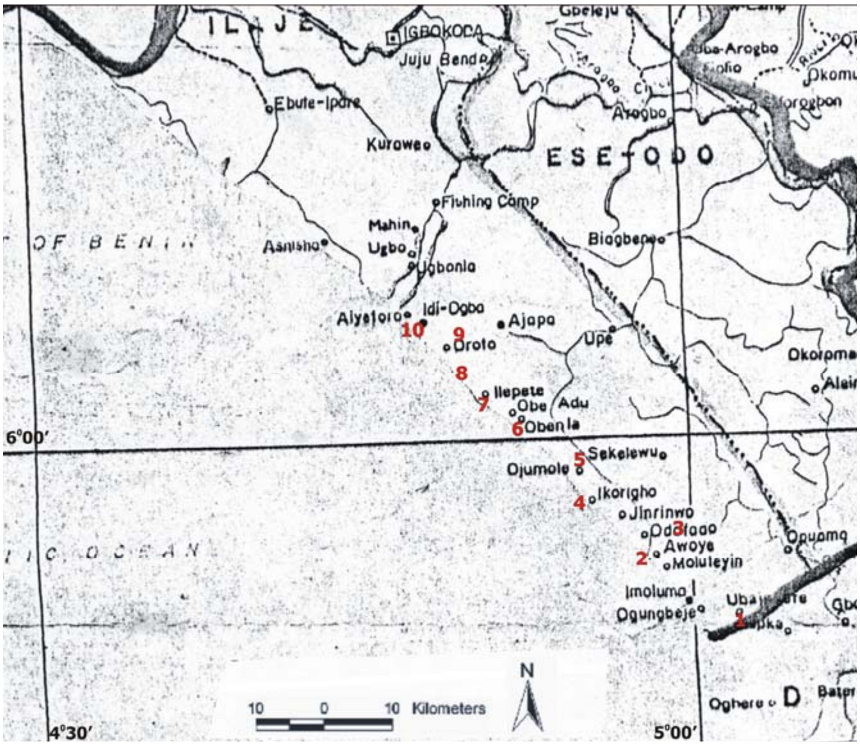

Fig. 1 Map of the Coastal Area of Ondo State and the sampling points.

EXPERIMENTAL

Sampling site

The coastal area of Ondo State, Nigeria (lat. 5° 50′ N, 6° 09′ N and long. 4° 45′ E, 5° 05′ E) was used as the sampling site for the study. The water at the coast is brackish with a sharp salinity range of 1.22–33.8 during the dry season and 23.73–31.51 during the wet season. The salinity of the coastal water varies inversely with the increasing distance of sampling spot away from the estuary discharge point which is at Awoye (Lat. 5° 54′ N, Long. 4° 59′ E). Salt water incursion and the movement of high tidal waves from the ocean into the sampling sites were more noticeable during the wet season than the dry season and dilution of salinity by atmospheric precipitation was also common during the wet season. These made the salinity range of the water very close during the wet season due to better mixing. The average rainfall index during the wet season was about 2500 mm while for the dry season it was 850 mm. There are various settlements across the length of the coast with farming and fishing as the major occupations of the inhabitants of the area. Domestic waste and sewage from all the settlements are discharged directly into the water untreated and the coast has a Chevron platform for crude oil exploration. The sampling sites are represented in **Fig. 1** and their description with coordinates and related activities may be found in **Table 1**.

Sample collection and preservation

The water samples were collected from a commercial speedboat with its engine switched off to reduce agitation. The collections of the samples for DO determination were done into quick-fit, narrow-necked glass bottles (300 ml) and covered with a quick-fit glass stopper. Prior to sampling, the bottles were treated by washing and soaking in 0.1 M HNO_3 for 48 h before washing with distilled water and soaked in iodine solution for 4 h to remove microbes. Samples were collected at 10 cm below the water surface avoiding entrapment or dissolution of atmospheric oxygen by allowing the water to overflow the volume of the bottles and replacing the stoppers under the water surface with reduced agitation. At each sampling point the temperature of the water samples were immediately measured while samples for other parameters were collected into high density polyethylene bottles and preserved in an ice chest at 4°C. The samples collected for DO determination were kept at temperature of collection but microbial activities were arrested by adding 1 ml of conc. H_2SO_4 and 1 ml alkali iodide azide solution (prepared with 500 g NaOH, 135 g NaI dissolved in 1 L distilled water and adding 10 g NaN_3 in 40 ml of distilled water). The DO values were determined in all samples within 8 h of collection.

Chemical analysis

DO was determined in each sample by the liberation of iodine which was then titrated with standardized sodium thiosulphate (Azide Modification of Winkler's Titration). The liberation of iodine involved the careful opening of sample bottles and the addition of 2 mL manganous sulphate (2.15 M) and 3 mL alkali iodide solution. The stopper was carefully replaced and the sample thoroughly mixed by inverting the bottle several times to give a milky precipitate which turns brownish yellow. The precipitate was allowed to settle and 2 mL conc. H_2SO_4 was added by lowering the pipette tip slightly below the water surface. The stopper

Table 1 Names and locations of sampling points.

Site	Name	Location	Activities
1	Ukua	Lat. 5° 50′N Long 5° 04′E	Chevron Oil exploration platform
2	Awoye	Lat. 5° 54′N Long 4° 59′E	Estuary discharge point
3	Odo Nla	Lat. 5° 55′N Long 4° 58′E	Settlement/farming
4	Ikorigho	Lat. 5° 57′N Long 4° 56′E	Settlement/farming
5	Ojumole	Lat. 5° 59′N Long 4° 55′E	Settlement/farming
6	Obe Nla	Lat. 6° 01′N Long 4° 52′E	Settlement/farming
7	Ilepete	Lat. 6° 02′N Long 4° 51′E	Settlement/farming
8	Ilowo	Lat. 6° 03′N Long 4° 50′E	Settlement/farming
9	Ibijinmi	Lat. 6° 04′N Long 4° 49′E	Settlement and fishing camp
10	Idi Ogba	Lat. 6° 06′N Long 4° 48′E	Settlement

Table 2 Results of Modelled Equation using Regression analysis with the best fitting.

Equation number	Season	Equation*	R^2	Validity range (mg/L)	Parameter related
1	Wet	DO = 12.23 – 5.07In BOD	0.56	0.5 – 10	DO and BOD
2	Dry	DO = 3.83 + 0.57In BOD	0.78	0.5 – 25	DO and BOD
3	Wet	DO = 19.95 – 4.62log COD	0.55	50 – 40,000	DO and COD
4	Dry	DO = 5.46log COD – 9.91	0.76	100 – 30,000	DO and COD
5	Wet	log DO = 4.13 – 2.97$e^{nitrate}$	0.57	0.05 – 0.40	DO and Nitrate
6	Dry	DO = 3.10 + 1.35$e^{nitrate}$	0.40	0.05 – 2.00	DO and Nitrate
7	Wet	DO = 23.91 – 8.32log Phos	0.53	10 – 700	DO and Phos.
8	Dry	DO = 5.12log Phos – 4.97	0.62	10 – 5000	DO and Phos.
9	Wet	DO = 364.55 – 34.18In TS	0.79	27,500 – 40,000	DO and Total Solid
10	Dry	DO = 2.42 + 0.25In TS	0.49	500 – 40,000	DO and Total Solid
11	Wet	DO = – 2.375T^2 + 135.13T – 1912	0.29	26.5 – 30.5°C	DO and Temp.
12	Dry	DO = 0.85T^2 – 51.675T + 788.43	0.43	27.5 – 33.5°C	DO and Temp.

* The units of the parameters used in the equation were in mg/L except temperature (°C).

was gently replaced and the bottle inverted several times to dissolve the precipitate and liberate iodine to give a yellowish solution. The liberated iodine was titrated with freshly prepared $Na_2S_2O_3$ (0.025 N) which had been earlier standardized with standard KIO_3 using 1% starch solution as an indicator in each case (APHA 1995). BOD was determined in all samples using a dilution method and Winkler's titration at day 1 and 5 after incubation. The details of the method for BOD determination and other parameters (total solids, COD, nitrate, and total phosphate) determined were as reported in the Standard Method for Examination of Water and Wastewater (APHA 1995).

MODELLING PROCEDURE

The empirical modelled equations were generated in relation to each of the parameters and in different seasons. Regression analysis was adopted as the modelling tool using SAS Inc. and SPSS ver. 11 software. The chemical analysis data obtained from field samples were used as input data and the software used to derive equations. The equation reported in each case was the best fitted obtained and their R^2 values were reported. The modelled equations obtained were calibrated to obtain the validity range of the dependent variables (i.e. the pollution parameters) and they were tested against field observed values to validate the models.

RESULTS AND DISCUSSION

The results of the equations generated, the validity range, and the R^2 values for the empirical modelling of DO in the two seasons are presented in **Table 2**. The fitness of the equation generally showed medium to slightly strong correlations (less that 0.80) because of the complex nature of the factors that affect DO concentration in coastal zones. The observed field values depend on combination of all anthropogenic factors and some natural ones.

Organic matter content modelling of DO

Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are direct measures of organic matter content in water bodies and are sources of abstraction of DO in a water system. Increasing BOD and COD concentrations are not desirable for good water quality that will support aquatic lives and various other uses.

The expressions relating DO to BOD (equations 1 and 2; **Table 2**) follow a natural logarithm of BOD as the independent variable for the two seasons investigated. The validity range of the expression for the dry season (0.5–25.0 mg/L) was wider than that of the wet season (0.5–10 mg/L) and the R^2 values obtained show a better fitness during the dry season (0.78) relative to the wet season (0.56). Likewise, the empirical modelled equation of DO relative to COD as an independent variable best fit into a logarithmic equation of base 10 (equations 3 and 4; **Table 2**) with a wider validity range of 50–40,000 mg/L for the wet season than 100–30,000 mg/L for the dry. The measures of fitness of these expressions (R^2) were better for the dry (0.76) than the wet season (0.55). It thus implies that the modelling of DO based on organic matter content is better done in the dry season than the wet. The high tide and wave current are much more prominent in the wet season and the atmospheric dilution from rain water must have been responsible for the great deviation observed in the wet season. These natural phenomena therefore play significant roles in DO content variation in coastal waters.

Furthermore, the comparative graphs of the modelled DO and the field observed ones for BOD for the two seasons (**Fig. 2A, 2B**) and that of the COD (**Fig. 3A, 3B**) clearly confirm an earlier observation that variations in parameters in the wet season were more affected by increased perturbation which has a tendency of reducing their fitness to simulation (Agunbiade *et al*. unpublished). The comparative results of the dry season were nearer and better than those of the wet season based on the reported R^2 values (**Table 2**). In the wet season, there were obvious deviations in the modelled values of DO and the field data especially at sites 5 and 3 for both BOD and COD simulation. There is a likelyhood of increased discharge of organic matter or other abstraction sources of DO during the field validation process at these sites. However, the dry season comparative graph reveals that the modelled values were nearer to the observed values as one moved away from the estuary point (site 2) where advection was higher to where it was lower. This confirms the important role of agitation of the water bodies on DO content enhancement while domestic and agricultural waste discharge observed at sites close to settlements and farming activities play major roles in DO abstraction.

Modelling DO from nutrient contents

Nutrient contents get into the water systems from sewage discharge, domestic waste discharge, fertilizer applications, death and decay of some nitrogen- or phosphorus-enriched plants, among others. The nutrients investigated in this study were nitrate-nitrogen and total phosphate. The two parameters aid the growth of algae, phytoplankton and seaweeds which increase biomass content of the water system thus depleting DO content indirectly. Therefore, minimizing nutrient content is desirable for improved water quality.

The prediction of DO based on nitrate concentration in coastal water was found to fit into exponential functions for the seasons investigated (equations 5 and 6; **Table 2**). The validity ranges were at concentration of 0.05–0.40 mg/L for the wet season and a wider concentration of 0.05–2.00 mg/L for the dry season. The R^2 values showed a slightly better fitness during the wet season (0.57) than the dry season (0.40) but a reverse situation was observed in the total phosphate simulated equation which followed the earlier trends of simulation from other parameters. The phosphate-based models for both seasons followed a logarithmic function of base 10 (equations 7 and 8; **Table 2**) with a validity range of 10–700 mg/L for the wet season and much wider range of 10–5000 mg/L during the dry season. It could therefore be proposed that nutrient simulation of DO in the dry season in coastal water gives better results than the wet season as observed by organic matter simulation.

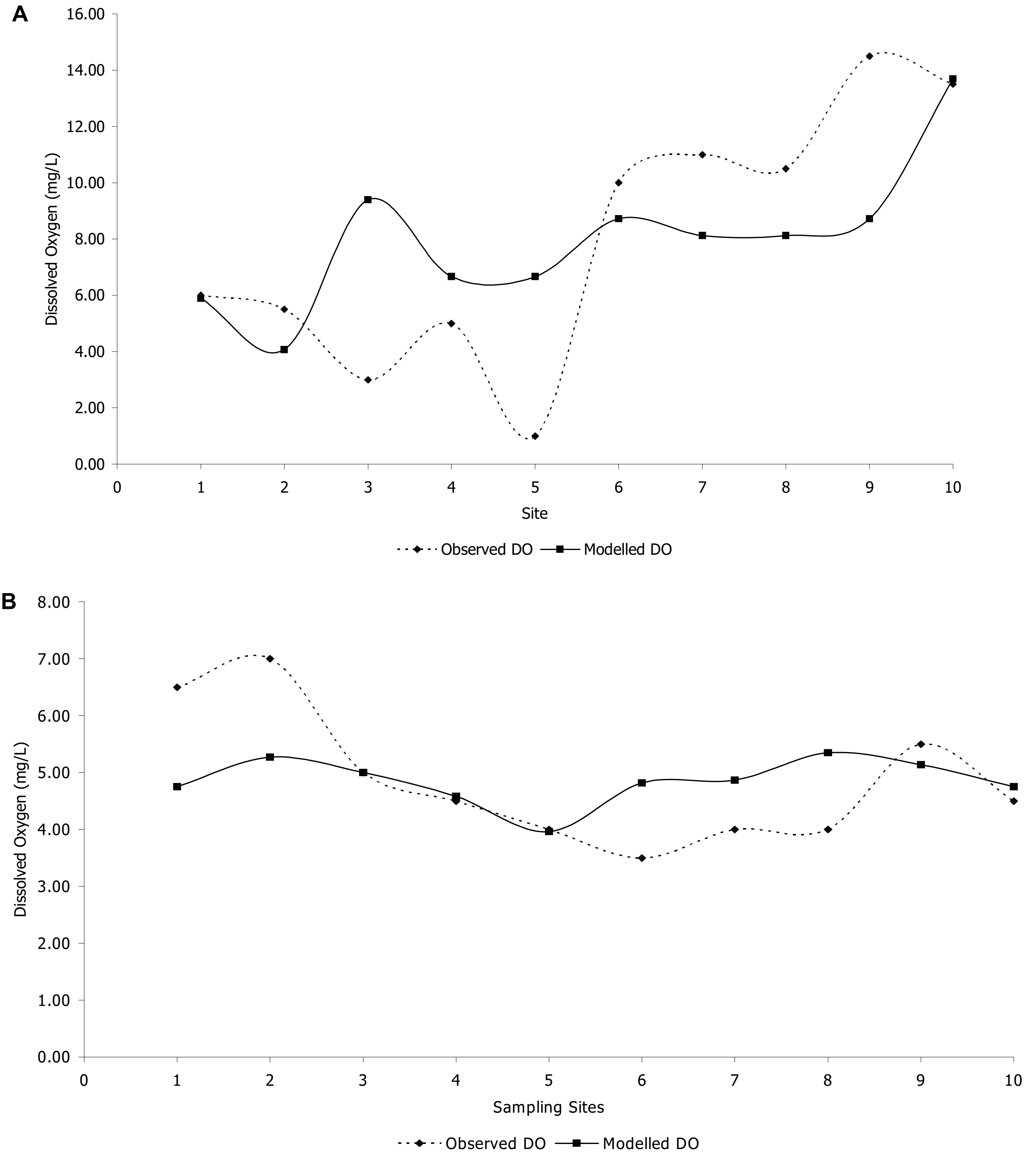

Fig. 2 (**A**) Comparative graph of field observed DO to the BOD modelled DO for the Wet Season. (**B**) Comparative graph of field observed DO to the BOD modelled DO for the dry season.

The comparative graph of modelled DO from the nitrate against the observed field data during the wet season (**Fig. 4A**) did not show the observed deviation noticed in site 5 as in earlier cases which implies that the proposed DO abstracting condition during wet season model validation is related to nitrate content in the site. Moreover, the comparative nitrate graph of the dry season (**Fig. 4B**) depicts a closer and better prediction during the dry season while the total phosphate comparative graph (**Fig. 5B**) for the dry season also correlated better the modelled and observed value that was obtained in the wet season (**Fig. 5A**). This wet season graph also indicated an obvious deviation in sites 3, 5 and 10. Thus, the trend of modelling DO based on organic matter data and that based on nutrient parameters in coastal water systems are very related because both are means abstraction of DO concentration in the environment.

Modelling DO from physical conditions

Physical conditions that affect DO are light penetration, turbulence (water current and tide) and temperature. The dissolution of atmospheric oxygen is aided by turbulence while light penetration affects production of oxygen by aquatic plants by photosynthesis. TS concentration was used to measure these two physical parameters. The assumption is that the incursion of saline water from the ocean is a measure of turbulence involved which at the same time contributes dissolved solids and the degree of the water agitation involved will determine the amount of suspended solids introduced by re-suspension of bottom sediment, eroded soil and other source contributions of suspended solids. Likewise, the quantity of suspended solids determines the light scattering ability of the water in the system. Thus, TS which

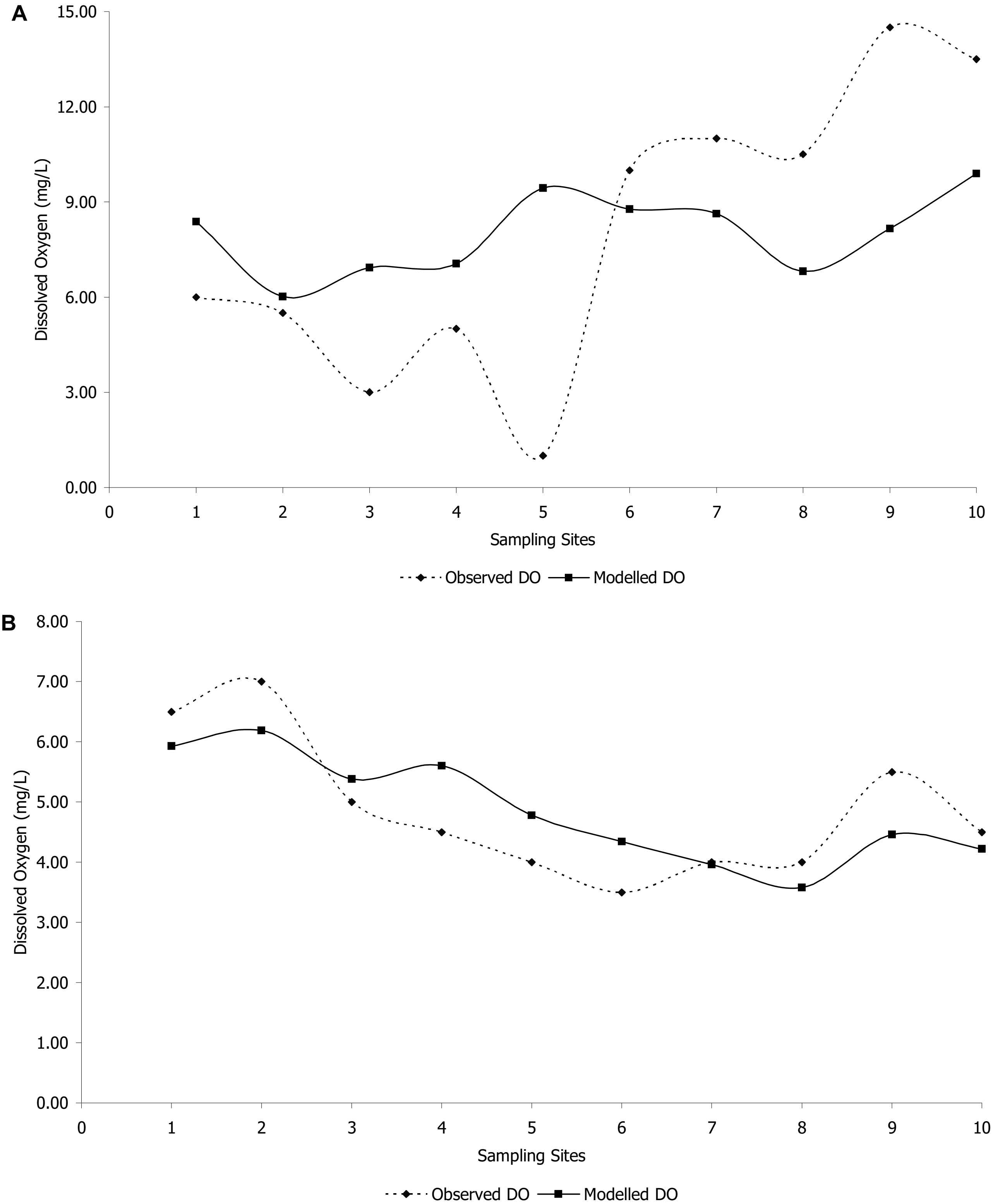

Fig. 3 (**A**) Comparative graph of field observed DO to the COD modelled DO for the wet season. (**B**) Comparative graph of field observed DO to the COD modelled DO for the dry season.

is a combination of dissolved and suspended solids, could give a strong indication of turbulence and light penetration degree which affect DO content.

The results of modelling DO from TS as independent variable presented in equations 9 and 10, **Table 2** follows a natural logarithm function for the two seasons with a better fitness during the wet season ($R^2 = 0.79$) that the dry season ($R^2 = 0.49$). This was a clear departure from the trend observed earlier under the simulation of organic matter and nutrients. The validity range of the wet season model was much narrower (27,500–40,000 mg/L) than the range of 500–40,000 mg/L obtained for the dry season. This is because the increased incursion of saline water in the wet season improved the mix of the coastal water narrowing TS variation compared to the dry season when sharp variation was observed away from the estuary discharge point. This observed seasonal variation in solid concentration as the distance increased from the estuary discharge point serves as a strong basis for proposing that natural and physical conditions likewise play obvious significant effects on DO simulation in coastal waters and could be better appreciated during wet seasons. Further, the comparative DO graph simulated based on TS concentration for the wet season (**Fig. 6A**) shows a much better relationship between the modelled

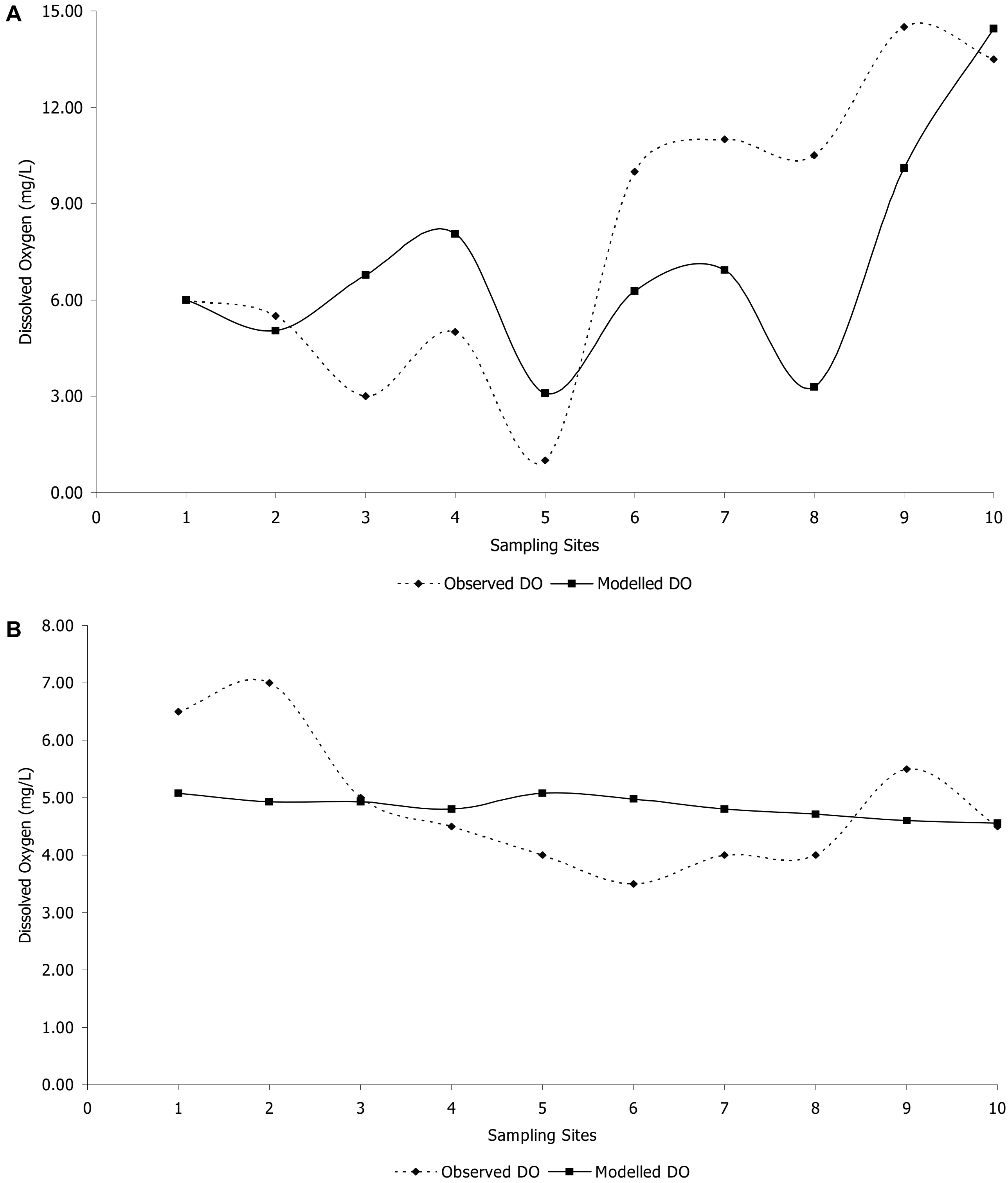

Fig. 4 (**A**) Comparative graph of field observed DO to the Nitrate modelled DO for the Wet Season. (**B**) Comparative graph of field observed DO to the Nitrate modelled DO for the dry season.

and observed DO and no deviation at site 5 as observed in earlier models. It thus implies that DO is depleted by discharge that are related to TS and nitrate at that site during the model validation period. Meanwhile, a comparative graph of the dry season (**Fig. 6B**) did not relate much. The modelled values did not vary much as the distance changes from the estuary but variations were observed in the field data. Thus, DO prediction from TS during the wet season is more precise. This is because TS measure parameters that related with DO improvement in water sources (turbulence) much more that its abstraction and this parameter is commonly witnessed in the wet season with increased volume of water in the coast.

Finally, the DO was simulated with respect to temperature variation in the coast. Temperature has an inverse relationship with DO concentration in the water system and equally affects the rate of metabolism of aquatic life which relates to DO concentration (Deas and Lowney 2000). The results of DO-modelled equation from temperature for the wet and dry seasons are presented as equations 11 and 12, **Table 2** respectively. The validity ranges were between 26.5–30.5°C for the wet season and 27.5–33.5°C for the dry season. The temperature ranges obtained in this study are due to the values observable in the coastal region of tropical areas of Africa. The fitness of the equations gave very low R^2 values because sharp temperature changes are not wit-

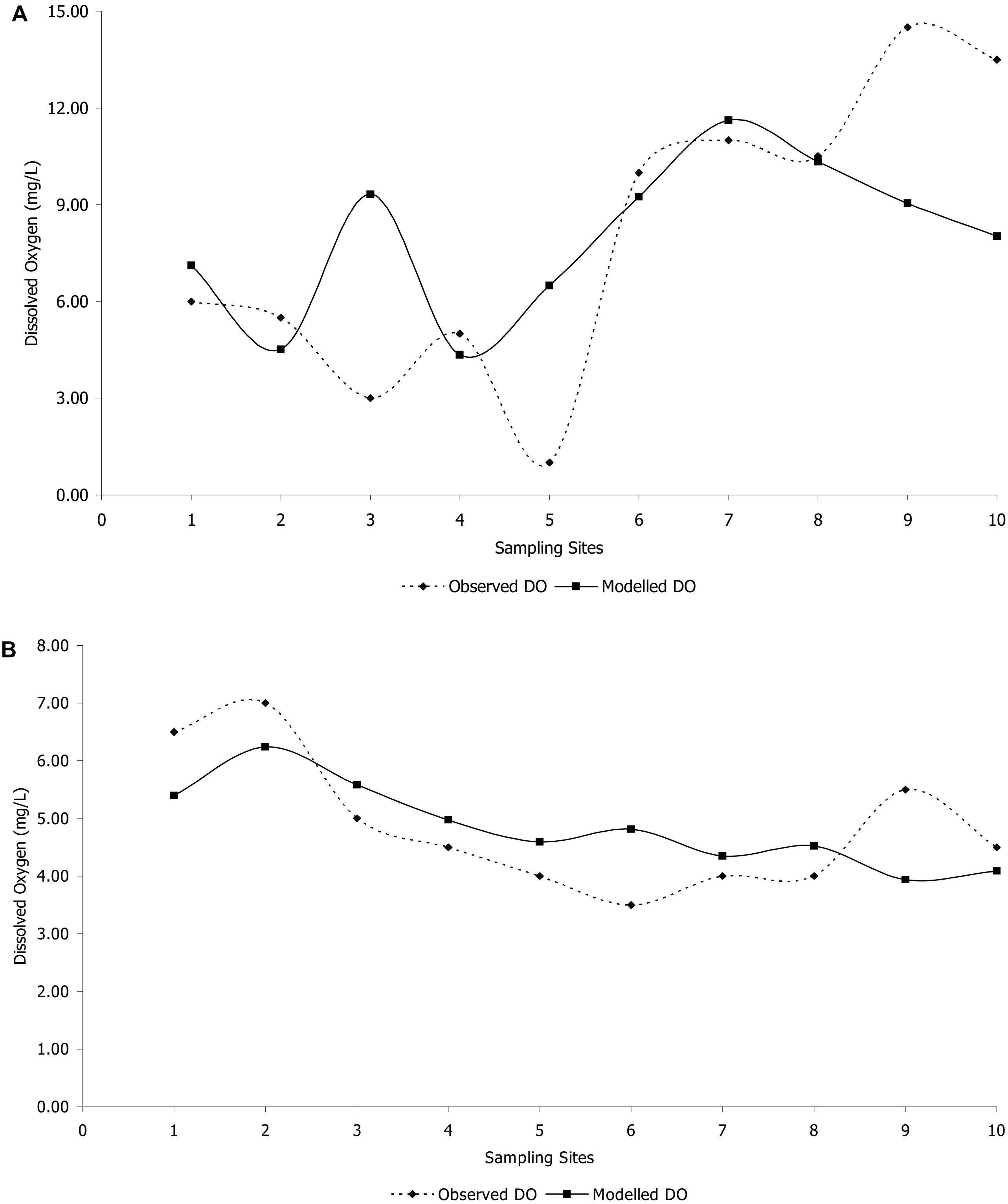

Fig. 5 (**A**) Comparative graph of field observed DO to the Phosphate modelled DO for the Wet Season. (**B**) Comparative graph of field observed DO to the Phosphate modelled DO for the dry season.

nessed in tropic as in temperate regions. Temperature in the tropics does not go as low as a single digit or negative which makes natural temperature changes affect DO prediction less except for remarkable anthropogenic activity such as the discharge of hot industrial effluent into a water system. Thus, the observed expression only depicts the contribute-ons from natural temperature variation. However, the comparison of R^2 between seasons and the graphs **(Fig. 7A, 7B)** showed a relatively better correlation during the dry season when temperature variation is relatively sharper between sunrise and sunset than in the wet season.

CONCLUSION

The prediction of DO based on anthropogenic pollution parameters measured as organic matter and nutrient gave a better correlation and wider validity during the dry season when natural effects were reduced indicating the possibility of more precise DO simulation in this season when abstraction of DO is focussed. However, TS used to evaluate DO relative to natural pollution sources fit the wet season better when turbulence, atmospheric precipitation and increased turbidity from soil erosion are more pronounced.

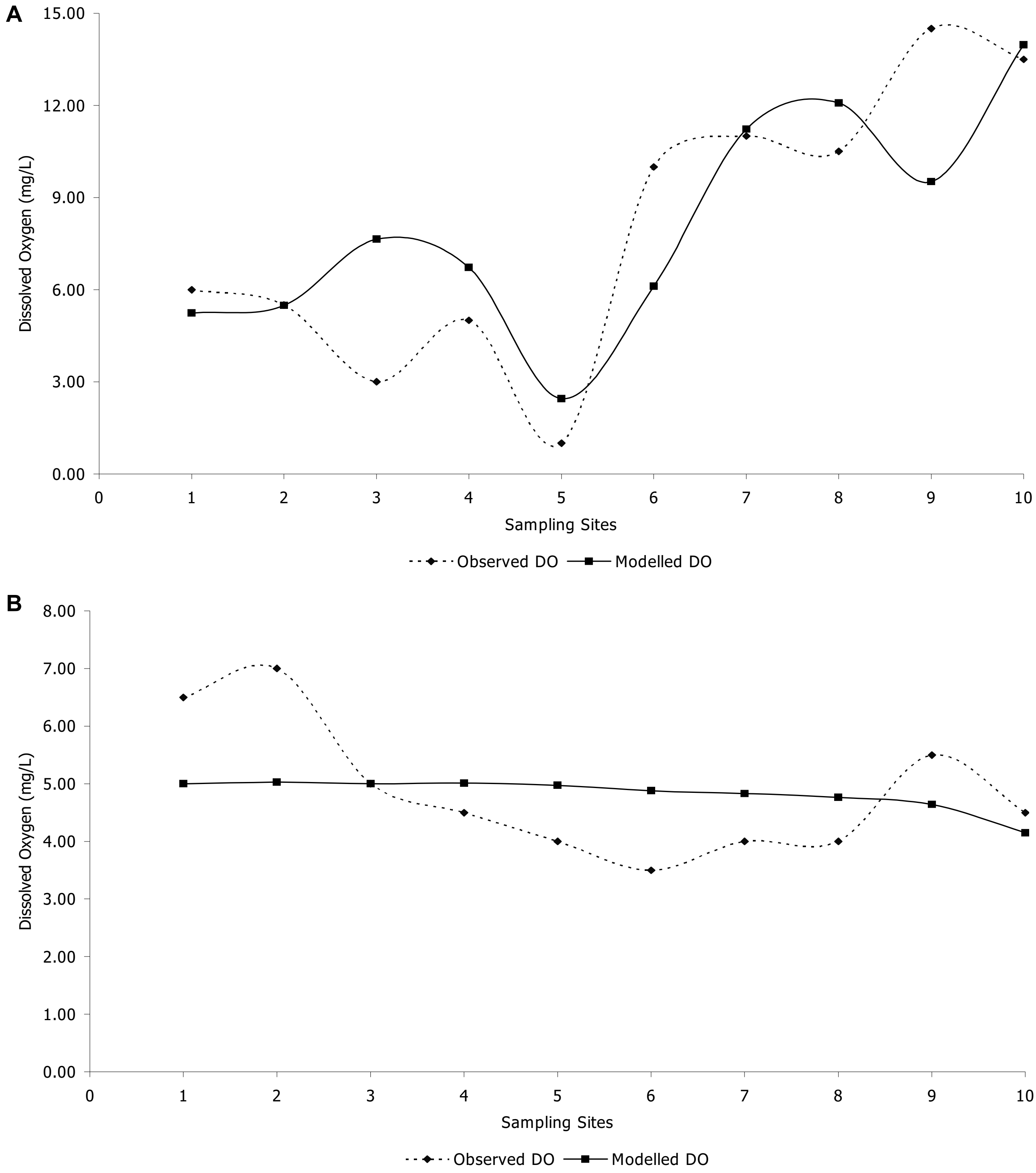

Fig. 6 (**A**) Comparative graph of field observed DO to the Total Solid modelled DO for the Wet Season. (**B**) Comparative graph of field observed DO to the Total Solid modelled DO for the dry season.

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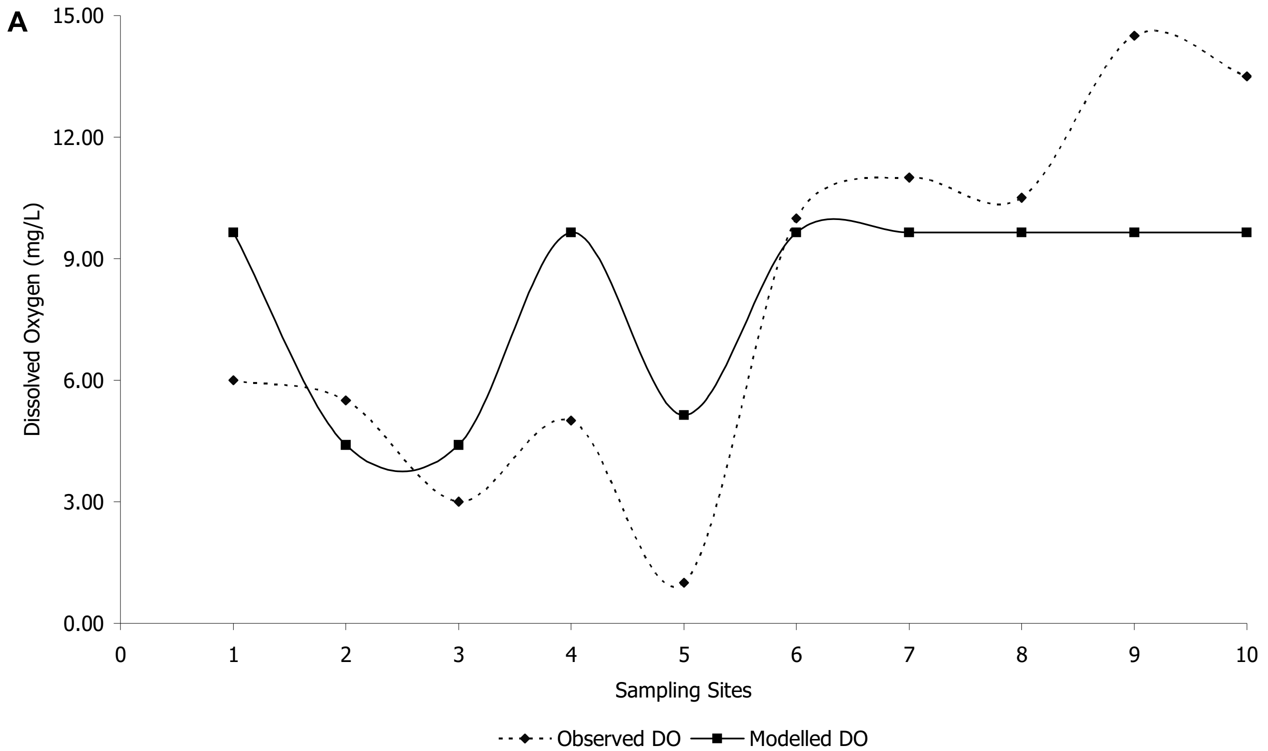

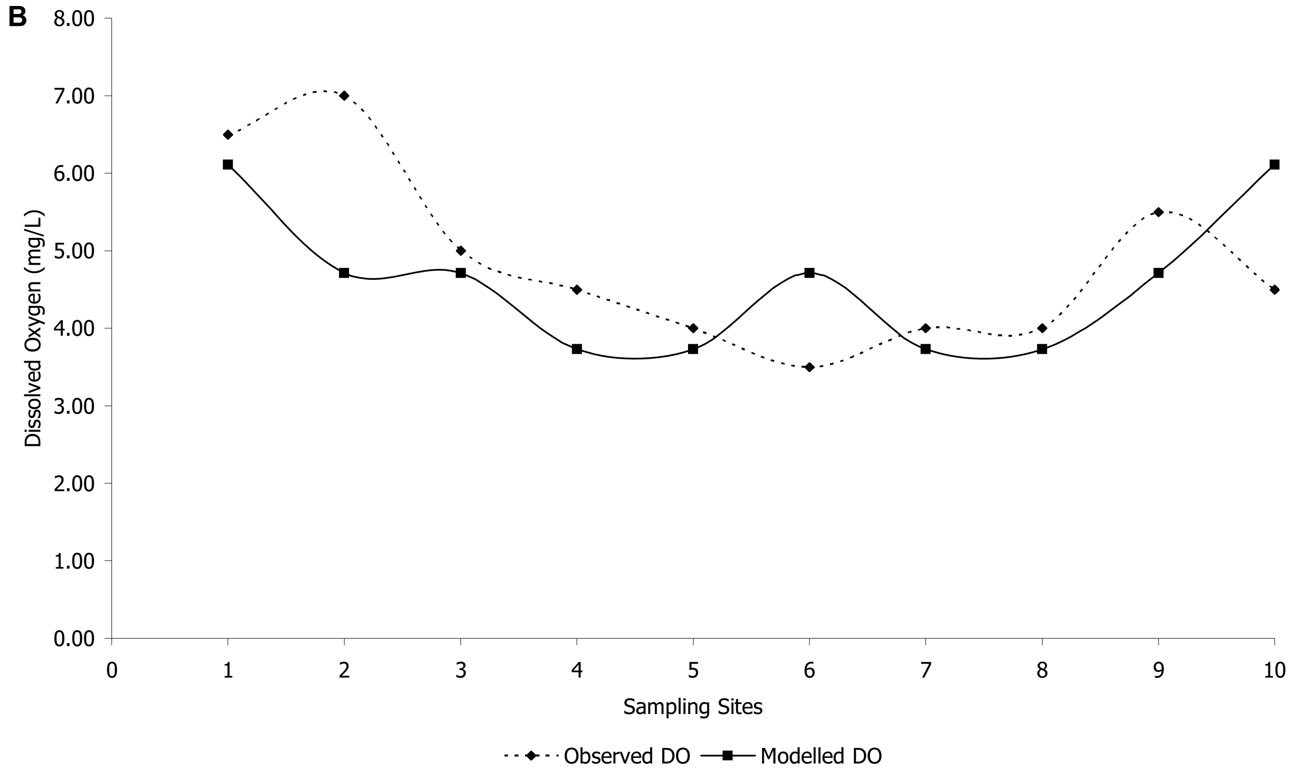

Fig. 7 (**A**) Comparative graph of field observed DO to the Temperature modelled DO for the Wet Season. (**B**) Comparative graph of field observed DO to the Temperature modelled DO for the dry season.