MODELING WATER QUALITY IN RIVERS: A CASE STUDY OF BEYLERDERESI RIVER IN TURKEY

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(Received 21st Sep 2015; accepted 23rd Jan 2016)

Abstract. River pollution is a major environmental problem that has negative consequences for humans and wildlife alike. To prevent its consequences, the sources and severity of pollution must be determined by monitoring water quality in river basins, followed by the measures necessary to control the contamination. Models and computer simulation of water quality are important tools for predicting adverse effects of pollution along a stream, and they can help guide practical investments in stream health. In water quality models, parameters that are determined through optimization rather than through trial and error are required to ensure the reliability of the model. In this study, a continuous stirred tank reactor (CSTR) approach was used to model Beylerderesi stream as a dynamic model, and the kinetic parameters were determined through optimization. For the optimization step, the Sequential Quadratic Programming method was used. The model predictions indicated good agreement with experimental data. The Mean Absolute Percentage error values for dissolved oxygen and biochemical oxygen demand were calculated as 0.95 % and 1.39 %, respectively. Statistical analysis showed differences between river and effluent samples for all parameters measured.
Keywords: *river modeling, river water quality, dynamic simulation, parameter estimation, optimization*

Introduction

Water pollution is gradually becoming a major issue in lakes and rivers. Water quality models can be useful tools for simulating and predicting pollutant transport (Bai et al. 2011; Huang et al., 2012; Wang et al., 2013). Surface water quality models have made enormous progress from estimating single factors of water quality to representing multiple drivers and aspects of water quality, from steady-state to dynamic models, from point source models to models that couple point and non-point sources, and from zero-dimensional models to one-, two-, and three-dimensional models (Wang et al., 2011). These models can be categorized by researchers based on water body types, the methods used to establish the models, the water quality coefficients, model properties, water quality components, reaction kinetics, and spatial dimension. However, all water quality models have constraints (Wang et al., 2013), so new models or modifications of existing models continue to emerge.

Mathematical models of water quality have been important in evaluating the impact of wastewater discharge into surface waters in recent years (Yetik et al., 2014). In addition, there have been major developments in water quality modelling for rivers. A review by Rauch et al. (1998) described the state of the art in river water quality modelling. The water quality models can be classified from many perspectives, according to model complexity, the simulation methods employed, and the number and type of water quality indicators incorporated. Cox (2003) noted that water quality modelling was a globally active area of research but that only

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1401_383395

few papers describe specific models. The majority of the papers reported applications of QUAL2E.

Some important surface water quality models, such as the Streeter-Phelps, QUASAR, QUAL, WASP, CE-QUAL-W 2, BASINS, and MIKE models have been widely used for studies (Fan et al., 2009; Morley, 2007). QUAL2EU, WASP7, and QUASAR models are the most suitable for simulating dissolved oxygen concentrations along rivers and streams (Kannel et al., 2011). Most advanced surface water quality models have been created by developed countries (The U.S. EPA website). A few surface water quality models that have been widely used are summarized in *Table 1*. Characteristic features of these models are also shown in *Table 1*.

Table 1. *A list of select surface water quality models and their characteristics (Wang et al., 2013).*

Models	Model version	Characteristics
Streeter-Phelps	S-P model, Thomas BOD-DO model, O'Connor BOD-DO model, Dobbins-Camp BOD-DO model.	-focuses on oxygen balance -first-order decay of BOD -one-dimensional steady-state models.
QUAL	QUAL I, QUAL II, QUAL2E, QUAL2E UNCAS, QUAL 2K	-suitable for dendritic rivers -non-point source pollution -one-dimensional steady-state or dynamic models.
WASP	WASP1-7 models	-suitable for water quality simulation in rivers, lakes, estuaries, coastal wetlands, and reservoirs -one-, two- or three-dimensional models.
QUASAR	QUASAR model	-suitable for dissolved oxygen simulation in larger rivers -one-dimensional dynamic model
MIKE models	MIKE11, MIKE 21, MIKE 31	-suitable for water quality simulation in rivers, estuaries, and tidal wetlands -one-, two- or three-dimensional models.
BASINS models	BASINS 1, BASINS 2, BASINS 3, BASINS 4,	-multipurpose environmental analysis systems -integrates point and non-point source pollution -suitable for water quality analysis at the watershed scale.

The QUAL2E model is a flexible and accurate water quality model that has been widely applied in controlling pollution in watersheds and water quality management. This model has been used in medium-sized rivers to track the fate and transport of targeted pollutants (Ning et al., 2000; Pelletier et al., 2006; Zhu et al., 2015).

Karadurmus and Berber (2004) proposed a dynamic modelling strategy based on the QUAL2E model coupled with a parameter estimation technique. The suggested strategy assumes that a river reach can be modeled as a single continuous stirred-tank reactor (CSTR). For such reaches, the model predicts values and compares them to the field data for 10 quality metrics. Except for the total coliform, total chloride and BOD_5, good agreement was obtained. In subsequent research, a reach was represented by a series of CSTRs rather than a single one, and the number of water quality model parameters identified was increased (Yuceer et al., 2007). Yuceer et al. (2007) also compared their own models to QUAL2E on the basis of experimental data collected in the Yesilirmak

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river in Turkey (Yuceer et al., 2007). In addition to the River Stream Dynamic Simulation (RSDS) software previously developed in MATLAB, our research group used the model by Yuceer et al. (2007) as the water quality model, and incorporated it into a GIS platform (Yetik et al., 2014).

In this study, serially connected CSTRs were used for the dynamic modeling of the water flow. Beylerderesi river is examined in a dynamic model, and the kinetic parameters were estimated by optimization.

Materials and Methods

Field Observations and Data Collection

For both field observations and data collection, the concentrations of water-quality parameters related to pollution in the river were determined either on site by portable analysis systems or in the laboratory from samples taken in the field. The experimental data for parameter estimation were obtained from sampling stations along the Beylerderesi River near the city of Malatya in Turkey. The concentrations of nine water quality variables that correspond to the state variables of the model and indicate the level of pollution in the river were determined either on-site by portable analysis systems or in the laboratory after careful conservation. For in situ measurements, four samples were taken and analyzed, and the mean of these four values was used. To determine BOD, samples were carefully preserved in the field and taken to the laboratory for analysis. Further details are presented in Karadurmus and Berber (2004).

Water quality constituents were measured at various locations along a 20 km section of the river. The sampling locations were matched to the water flow such that the volume element sampled at location zero (i.e., from the starting point at Şahnahan station) was followed downstream. This sampling scheme was designed to resemble tracking an element that is moving downstream at the same velocity as the main flow. After the starting point, samples were taken 0.5, 11 and 20 km downstream. The discharge site of an organized industrial zone II wastewater treatment plant is located 500 m downstream of the starting point, and a cesspool is discharged 11 km downstream of the starting point. Thus, this study models nutrient and contaminant discharged from these two sources. In the simulations, the addition of these discharges was considered to be a continuous disturbance to the system, and their water quality effects were determined. *Table 2* reveals the properties of the Beylerderesi river immediately before and after the discharge sites.

Table 2. *Properties of the Beylerderesi river immediately before and after the discharge sites*

Parameters	Beylerderesi-before mixing	organized industrial zone II wastewater treatment plant discharge	11. km	cesspool discharge	20. km
Temperature (^oC)	15.2	21.5	16.4	18.5	15.8
pH	8.11	8.27	8.19	7.70	8.38
Conductivity (µS/cm)	402	5520	945	871	1313
Flow rate (m^3/s)	4.20	0.22	4.44	0.010	4.45
Ammonia Nitrogen (mg/L)	0.013	0.233	0.025	8.60	0.048
Nitrite Nitrogen (mg/L)	0.012	0.058	0.016	0.075	0.016

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Nitrate Nitrogen (mg/L)	2.05	0.826	1.99	0.492	1.97
Organic Nitrogen (mg/L)	1.4	4.356	1.53	32.8	1.56
Organic Phosphorus (mg/L)	0.028	1.0	0.068	2.25	0.077
Dissolved Phosphorus (mg/L)	0.018	0.86	0.056	1.943	0.062
Dissolved Oxygen (mg/L)	9.17	7.5	8.9	5.10	9.0
BOD_5 (mg/L)	11	56	10.3	28	8.0
Total Chloride (mg/L)	7.95	976	32.4	44.6	21.9

Figure 1 shows the sampling stations used to collect the experimental data for dynamic simulation of the Beylerderesi river.

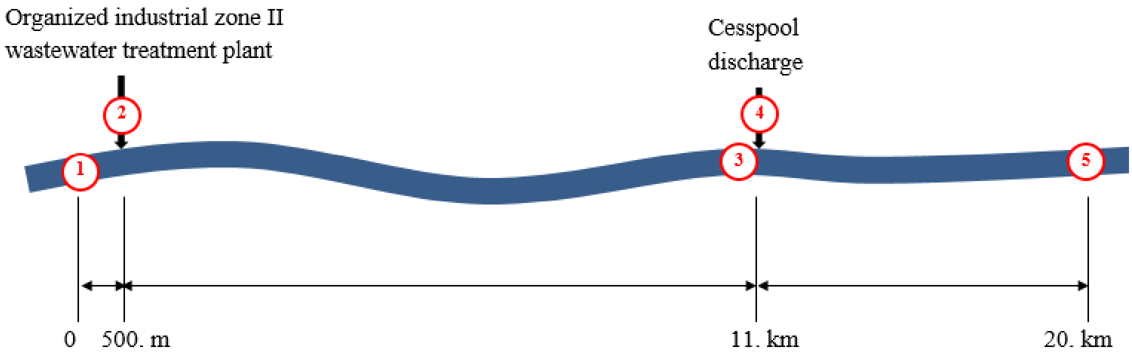

Figure 1. *Sampling stations*

Serially connected CSTRs are used to represent the flow of water and dissolved substances in dynamic modelling. Each reactor forms a computational element and is connected sequentially to similar elements upstream and downstream.

The following assumptions were employed for model development:

- The flow was well-mixed in cross sections of the river
- Dendritic streams were well-mixed
- There was constant channel cross section and stream flow
- The chemical and biological reaction rates were constant within the computational element.

All of the chemical, biological and physical reactions and interactions that might occur in the stream were considered. The modelling strategy employed in this study stems from that of the QUAL2E water quality model (Brown, 1987). Differential-Algebraic equations of the river model used in this study were taken from our previous study (Yuceer et al., 2007).

As representative elements of water quality from the perspective of environmental pollution, the following constituents were included in the model: ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, organic nitrogen, biochemical oxygen demand,

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dissolved oxygen, organic phosphorous, dissolved phosphorus and chloride. The mass balance equation for each of these constituents was written, and several algebraic equations describing phenomena such as the conversion of different forms of nitrogen were included. The model thus simulates stream flow and 9 water quality constituents. Descriptive equations for the modeled properties and constituents were established in light of the stream's water volume (Yuceer et al., 2007).

A HACH-HQ40d multi-model digital portable oxygen meter was used for the analysis of dissolved oxygen. Ammonia nitrogen, nitrite nitrogen and nitrate nitrogen were measured with a HACH (Model DR3900) portable spectrophotometer. The Kjeldahl method was used to determine total nitrogen. The organic nitrogen was calculated as the difference between the total nitrogen and the sum of ammonia, nitrite and nitrate forms. Phosphorous was analyzed with colorimetric ascorbic acid amino reduction and molibdovanado phosphate in the same spectrophotometer. BOD_5 analysis was performed in the laboratory, after careful transportation of the samples, with a manometric method in a HACH spectrophotometer. The chloride analysis was performed in a HACH spectrophotometer for chloride. The 9 state variables were determined from field measurements.

Optimization Studies

A nonlinear, constrained parameter estimation strategy has been incorporated into the simulation so that Sequential Quadratic Programming (SQP) can be used for optimization. SQP algorithms have had demonstrable success in constraint optimization (Yuceer et al., 2007; Yuceer et al., 2008; Balku et al., 2009; Atasoy et al., 2013). This method updates the Hessian matrix of the Lagrangian function, solves the quadratic programming subproblem and uses a line search and merit function calculation at each iteration. The estimation was based on minimizing the objective function defined in Eq. (1), the difference between the predictions and observed data during the transient period of observations.

$$J = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(y_{c_{ij}} - y_{o_{ij}} \right)^2 \qquad \text{(Eq. 1)}$$

Where y_c is the computed value, y_o is the observed value, n is the total number of state variables and m is the total number of observations in time for the particular station.

The model parameters of the Beylerderesi river were estimated via SQP optimization. A MATLAB code was written for parameter estimation. For the dynamic simulations, we used a stiff Runge–Kutta type explicit integrator along the river.

Statistical Analysis of Data

Statistical analyses are often used to characterize water quality in rivers. The physicochemical and bacteriological characteristics of various rivers have been analyzed (Abdul-Razak et al., 2009; Maglangit et al., 2014; Ewemoje et al., 2014; Khan and Nath, 2014, Yurtseven et al., 2016).

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DOI: http://dx.doi.org/10.15666/aeer/1401_383395

To assess the contamination of the Beylerderesi River using physicochemical parameters, the data obtained were analyzed by means of the Statistical Package for Social Sciences (SPSS) version 22 (trial version). A one-way Analysis of Variance (ANOVA) was used to compare three or more means. A one-way ANOVA (alpha = 0.05) was used to assess the difference between water quality sampling stations. ANOVA results were considered to be a significant difference at $p<0.05$ for all sites.

Results and Discussions

The described model was based on the measurements of 9 state variables characteristic of streams and pollution loads (ammonium, nitrite, nitrate, and organic nitrogens, and dissolved organic phosphorus, 5-day biochemical oxygen demand, dissolved oxygen, and chloride). Model predictions and field data were compared along a 20 km reach of the river. In the simulations, the addition of two discharge sites was considered to be a continuous disturbance to the system, and their effect the water quality was determined. *Figures 2–10* show the profiles of nine pollutants, Ammonia-N, Nitrite-N, Nitrate-N, Organic-N, Organic-P, Dissolved-P, BOD_5, Dissolved Oxygen (DO), Coliform and Chloride along a 20 km reach downstream from point-source inputs.

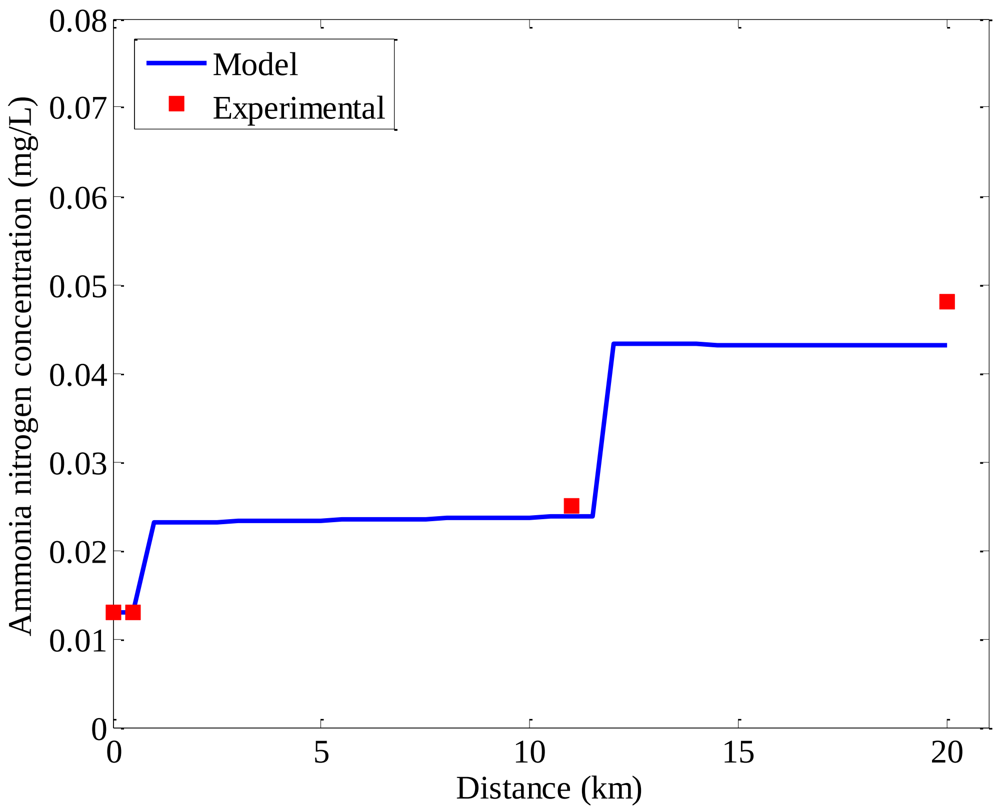

Figure 2. *Ammonia nitrogen profile in a 20 km section*

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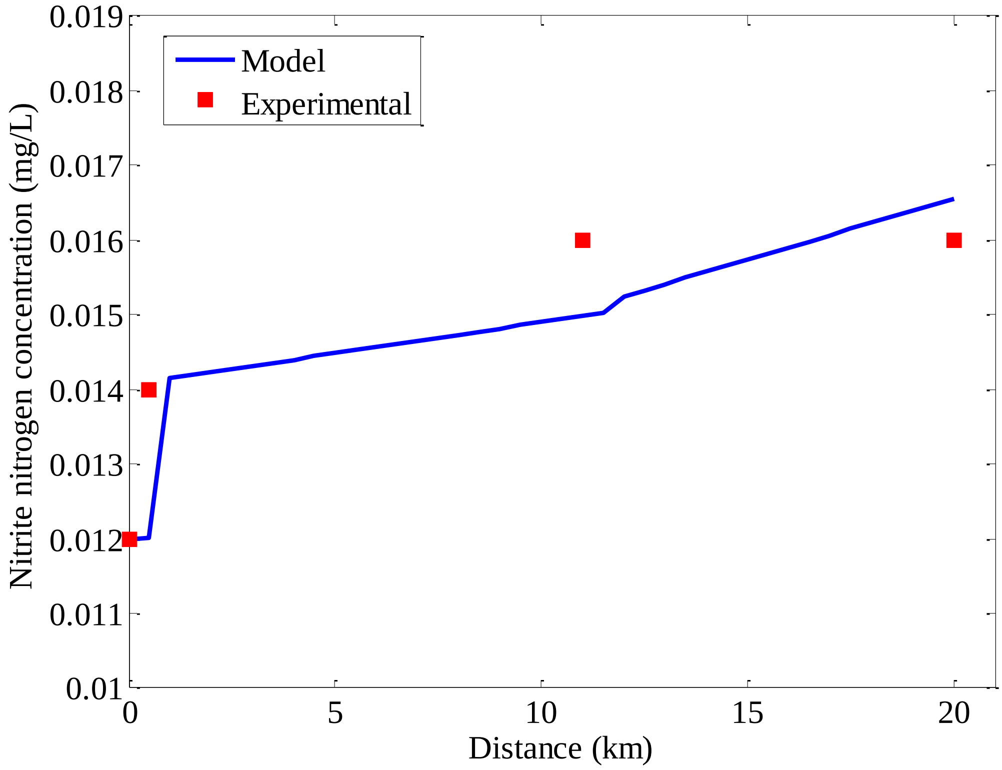

Figure 3. *Nitrite nitrogen profile in a 20 km section*

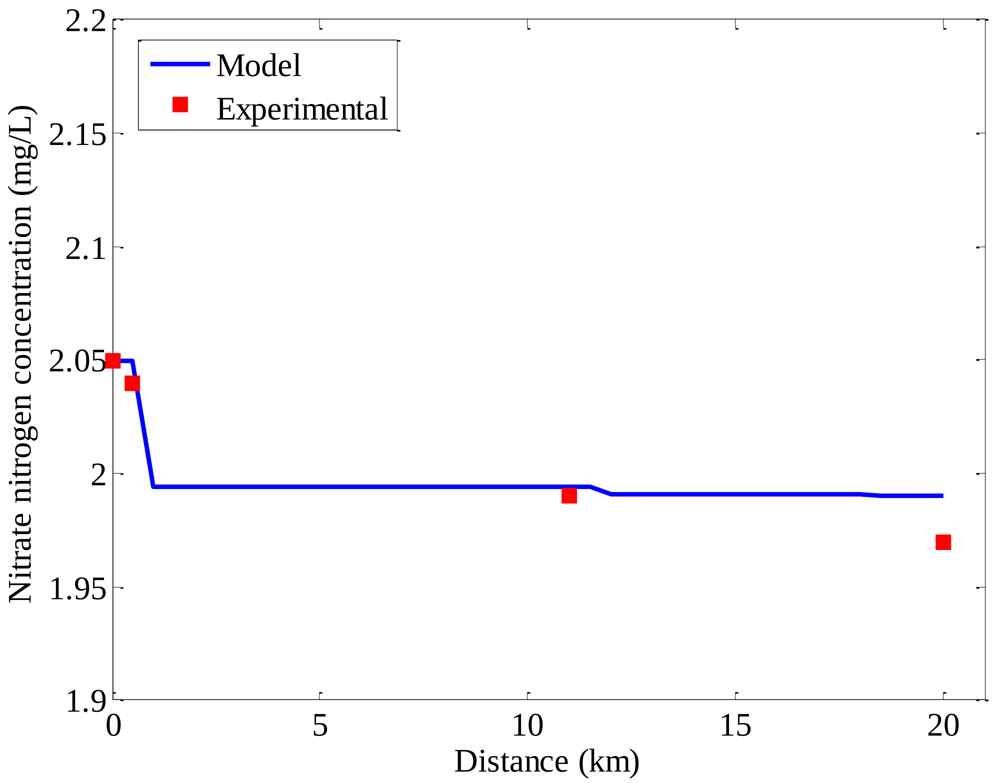

Figure 4. *Nitrate nitrogen profile in a 20 km section*

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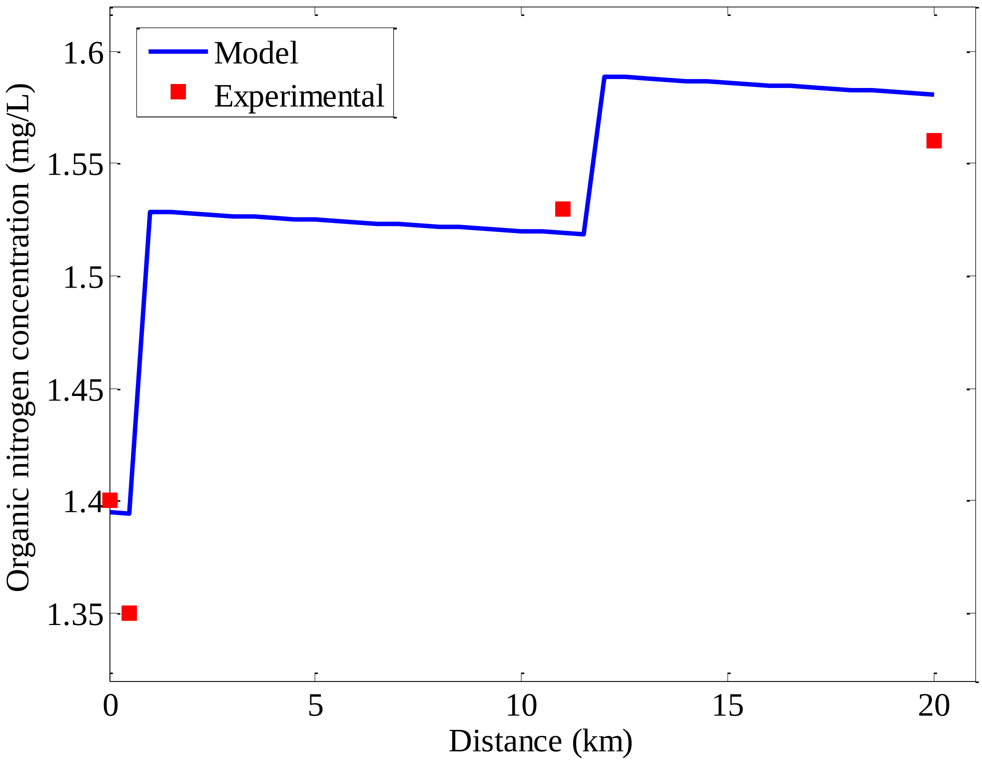

Figure 5. *Organic nitrogen profile in a 20 km section*

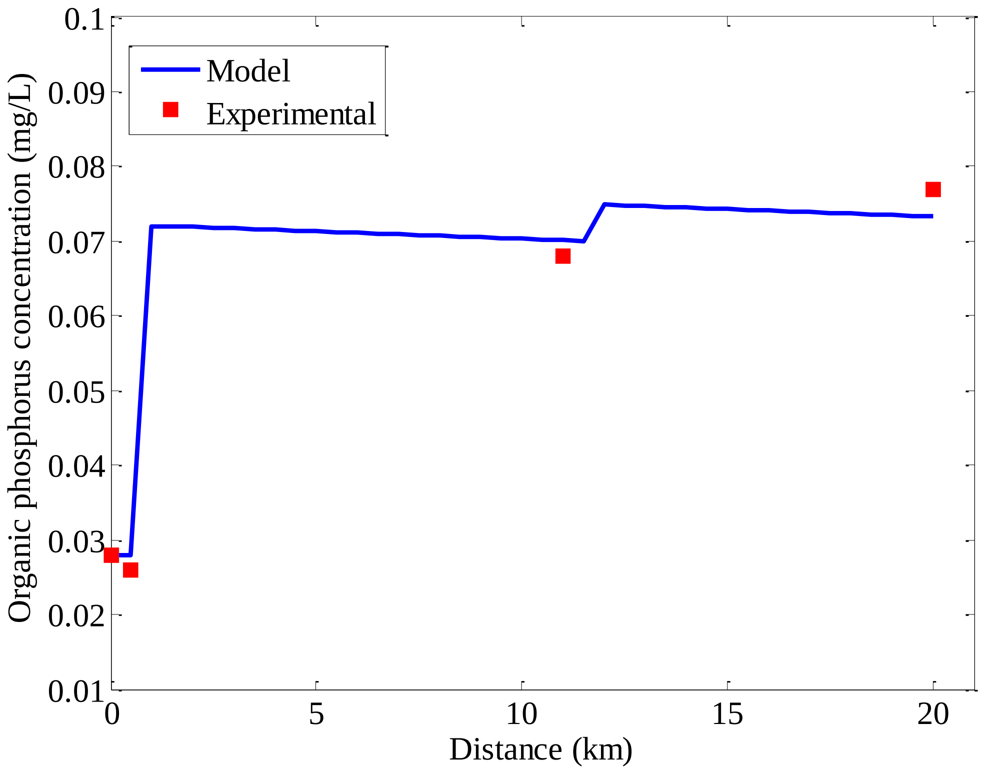

Figure 6. *Organic phosphorus profile in a 20 km section*

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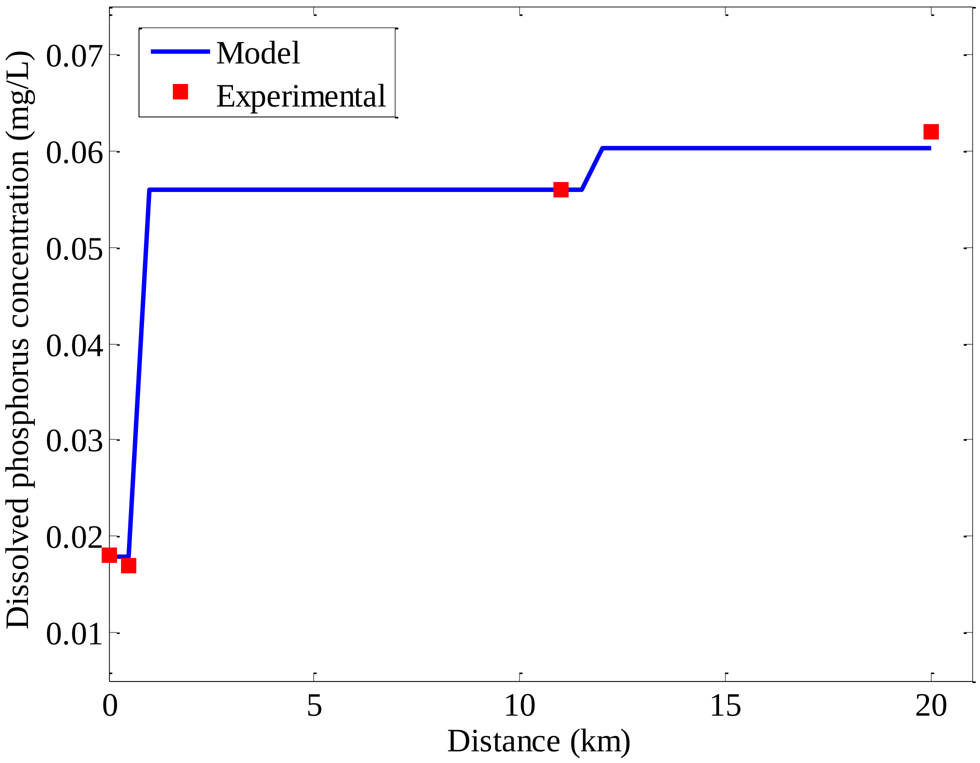

Figure 7. *Dissolved phosphorus profile in a 20 km section*

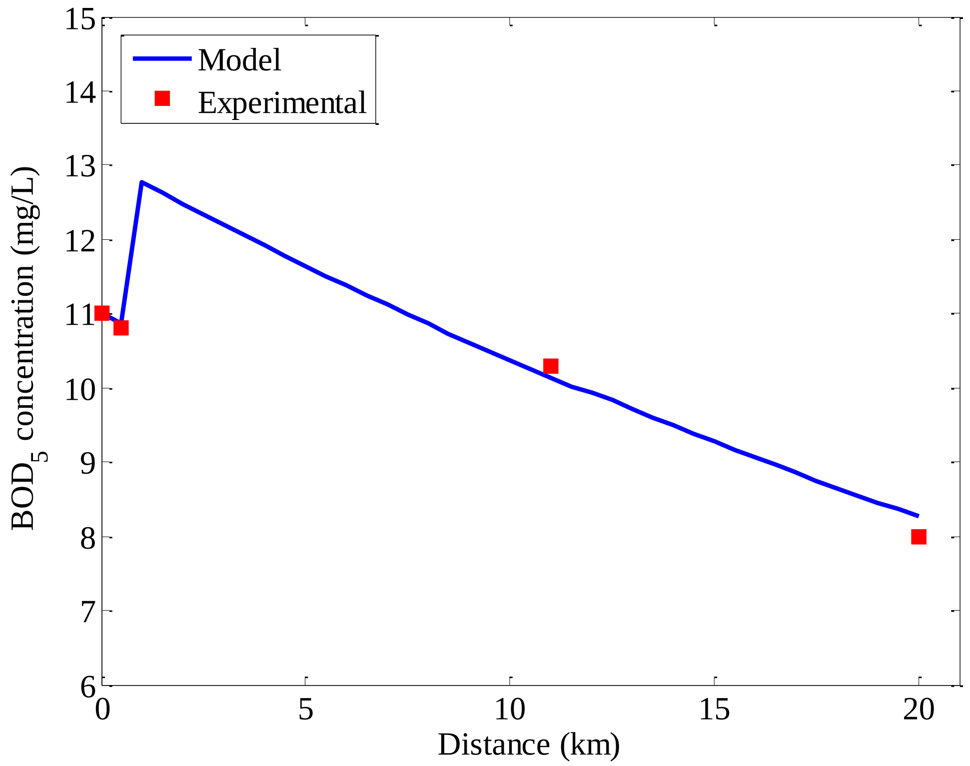

Figure 8. *BOD5 profile in a 20 km section*

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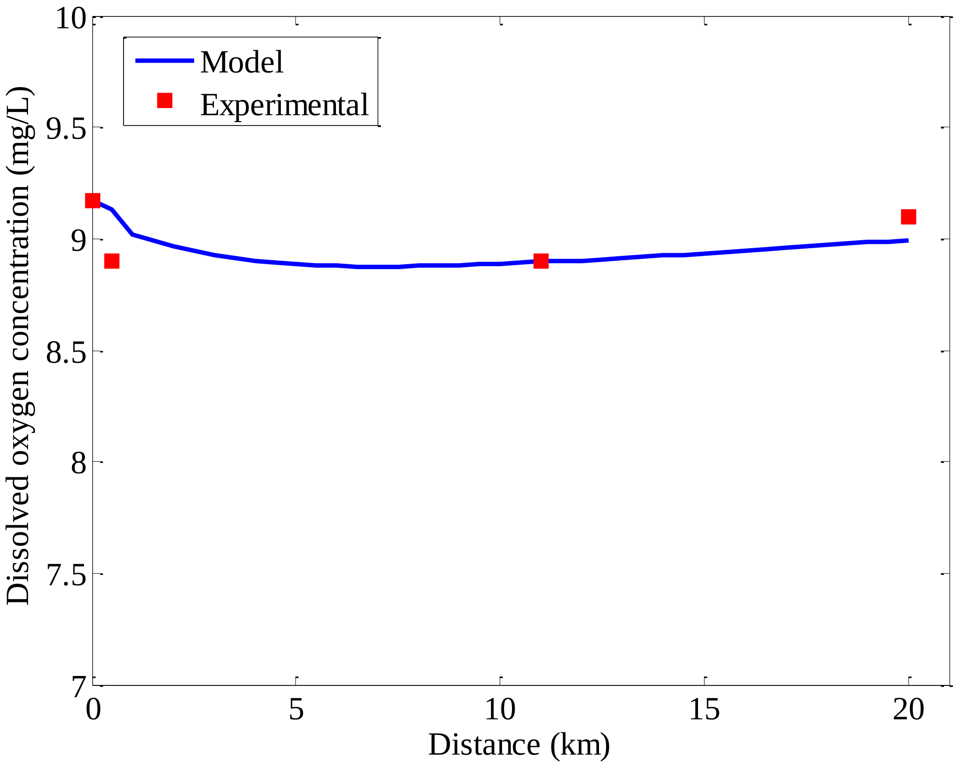

Figure 9. *Dissolved oxygen profile in a 20 km section*

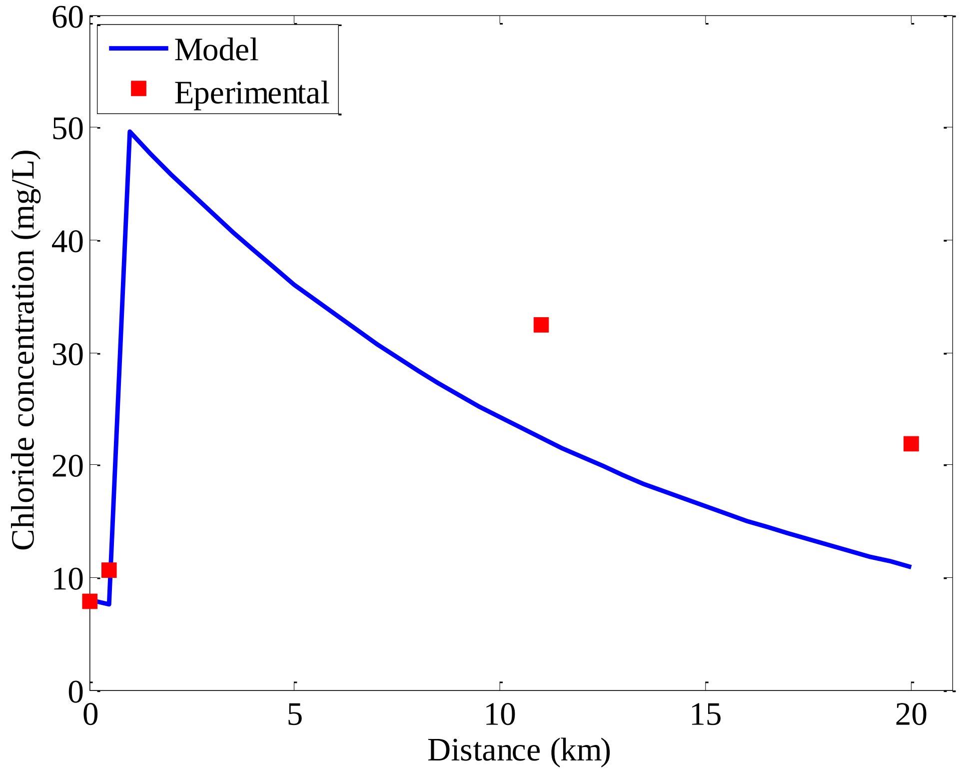

Figure 10. *Chloride profile in a 20 km section*

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For statistical evaluation and comparison, Mean Absolute Percentage Error (MAPE) values were calculated for the dynamic simulation, as in Equation (2):

$$\mathrm{MAPE}\ (\%) = \frac{1}{N}\left(\sum_{n=1}^{N}\frac{|X_{exp_n} - X_{obs_n}|}{X_{exp_n}}\right)\cdot 100 \qquad \text{(Eq. 2)}$$

where N is the number of measurements, X_{exp} is the experimental value, and X_{obs} is the observed value.

A dynamic simulation and parameter estimation strategy were suggested in a previous study (Balku et al., 2009). According to this suggestion, modeling was based on the assumption that the segments of river between sampling stations were serially connected completely stirred tank reactors (CSTRs). In that research, the CSTRs provided automatically generated, reliable estimates of water quality model parameters without trial-and-error simulations. The results are given in *Table 3* for the nine pollution variables considered. It can be seen from this table that the mean absolute average percentage error values were relatively small for most of the state variables. Therefore, the same dynamic simulation procedure was used for the current model, which offered a valuable model calibration tool for easily and reliably estimating the model parameters for river basins.

Table 3. *Mean Absolute Percentage Error (MAPE %) values for comparison of pollution variables*

Water Quality Variables	**(MAPE, %)**
Ammonia Nitrogen	3.85
Nitrite Nitrogen	5.99
Nitrate Nitrogen	0.43
Organic Nitrogen	1.43
Organic Phosphorus	3.88
Dissolved Phosphorus	2.15
BOD_5	1.39
Dissolved Oxygen	0.95
Chloride	27.4

Statistical analysis of data is shown in *Table A.1* (Appendix). The table shows the values of the physicochemical parameters of the discharge from the wastewater treatment plant, the discharge of cesspool effluent and river water samples. There was significant variation in all parameters ($P<0.05$) between the river and effluents samples. The temperature, pH, conductivity, ammonia nitrogen, nitrite nitrogen, organic nitrogen, organic phosphorus, dissolved phosphorus and total chloride levels significantly increased ($p=0$) in the downstream direction. Nitrate nitrogen, BOD_5 and dissolved oxygen values decreased in the downstream direction.

Overall, the downstream parameter values were relatively higher than the upstream parameters, which could be attributed to wastewater and cesspool discharge containing organic waste entering the river.

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Conclusions

The mean absolute percentage errors obtained by comparing simulation results with field data along 20 km of stream indicated a good agreement between modeled values and the experimental data. Two of the most important indicators of stream health, its dissolved oxygen and biochemical oxygen demand, had average absolute error values of 0.95 % and 1.39 %, respectively. The statistical analysis suggests that the measured values of the samples from the river were significantly different from those of the effluent samples.

This study may help predict the effects of planned industrial investments on water quality and help in the preparation of Environmental Impact Assessments.

Acknowledgements. This work was supported by the Inonu University Research Fund [Project Number: İ.Ü.B.A.P. 2011-17 and 2011-141].

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ELECTRONIC APPENDIX

Appendix 1. Statistical analysis of data

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