

## QUALITY MANAGEMENT OF ZARRINEH RUD RIVER FOR AGRICULTURAL IRRIGATION USING QUAL2K SIMULATION MODEL

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### Highlights

- ▶ Establishment of the wastewater treatment plant for villages surrounding the Zarrineh Rud river downstream of Miandoab's plain.
- ▶ Standard wastewater discharge from Miandoab's wastewater treatment plant by province water and Wastewater Company.
- ▶ Controlling the agricultural fertilizer and pesticides consumption in the Zarrineh Rud river basin according to existed standards by supervision of agricultural organization in the province
- ▶ Establishment of the wastewater treatment plant for treating the wastewaters from the sugar factory and slaughterhouse of Miandoab and their discharge according to the standards of the department of environment.

**Abstract.** Zarrineh Rud river is one of the most important rivers in northwest of Iran. In this study, QUAL2K simulation model was used. The simulation parameters in this study were collected from 5 sampling stations. The results showed that the amount of oxygen saturated solution of Zarrineh Rud river varied between 7–8 mg / l, which is higher than the maximum standard value required. The results showed that BOD could increase by 16%, respectively, and should decrease by 70%. The station S5 at the river downstream with 3.53 mg/L DO deficit was the most critical point, and the 26th kilometer of the river with a DO deficit of 2.05 mg/L was the most critical point for maintaining the aquatic life; therefore, some scenario must be developed for waste load reduction at this station. In order to improve the quality of Zarrineh Rud river, construction of a wastewater treatment plant is necessary for Miandoab sugar factory.

**Keywords:** water quality, modeling, QUAL2K, Zarrineh Rud river, aquatic, Iran.

### Introduction

From ancient times till now, the human being seeks to water resources and their control and management. Currently, regarding the ever-increasing demand for drinking water, agriculture and industry on the one hand, and climatic changes and water scarcity from others, require to deploy advanced methods for water resources management. As one of the vital surface water resources and valuable ecologic resources, rivers have multiple roles and functions like drinking water supply, water transportation, industry and urban demands, water transportation, fishing, fisheries, visual and aesthetic values (Jalili, 2020). Understanding the causal relationship

between river water quality and waste loading is the first action to determine the self-purification capacity of a river. This relationship is affected by different physical factors such as flow rate, flow velocity, depth of water, movement time, temperature, and chemical biochemical properties like sediment oxygen demand (SOD), photosynthesis, algae respiration, and nitrification (Ghorbani et al., 2022). Besides these features, the rate of different reactions should be considered in studying this relationship (Sajjadi et al., 2019). For identifying the expected reaction of the river against the pollutant discharges, different mathematical models should be developed. These models not only allow the prediction of future loading effects but also estimate the water quality in response to

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the conditions not monitored in the past (e.g., a critical condition in low flow rate) (Fataei et al., 2011).

Rivers are valuable water resources, and their health condition and preservation survive the life of all creatures used them. The sustainable application of each function must be based on protective principles and sustainable deployment from the river, and oversight to the river capacity can lead to water pollution and threaten the ecosystem's life (Hakimpour, 2005). The ever-increasing development of agricultural and industrial activities and impressive volume of urban sewage cause the pollution of water resources, especially rivers. Rivers' pollution is one of the crucial problems of water resources and relates to the economic development and life quality in many countries worldwide (Chapra et al., 2008). Controlling, monitoring, and predicting the variation of qualitative parameters in quality management of rivers demonstrate that involved people and analysts inevitably need approaches, techniques, and models that are close to the nature of the problem as far as possible and are in more conformance with the environment. The qualitative method for simulating rivers, owing to their features, can provide suitable and fruitful procedures to recognize and analyze river pollution in as detail as possible, followed by arguments, controls, and correct decisions about qualitative management of water (Tajrish, 2001). The qualitative modeling allows us to acquire a clear understanding of the reaction of a water body against tensions arising from the waste load and can help us plan and make decisions in the framework of qualitative guidelines (Oliveira et al., 2013). QUAL2Kw model has also been used for simulating the seasonal changes of self-purification in the Karun river. In this study, a region of length 113 km was selected in the river, and BOD, DO, nitrate, and chloroform contents were examined to simulate the water quality of the river considering different scenarios by decreasing and increasing the flow rate of river and pollutant sources (Moghimi Nejad et al., 2017). Also, another study has been conducted on the Dez river to investigate its self-purification capacity showing its 98% self-purification capacity (Ebadati, 2017). QUAL2Kw simulation model was used to examine the self-purification capacity of Divandarreh river; also, AME and root-mean-square-error were applied to evaluate and validate the model's results (Babakhani et al., 2019). In another study conducted on the Jajar river (Indonesia), results indicated no natural purification process in this river. In other words, the experiments on water samples in each inlet section show the waste existence, which is verified by unacceptable results for DO and BOD concentration parameters (Nugraha et al., 2020). It should be noted that the leakage from the river to groundwater is one of the critical phenomena required to be evaluated in rivers and is a necessary tool for pollutant elimination (Semenov et al., 2019).

In another study, a water quality modeling system was developed for the Gaoping river basin in Taiwan. Results showed that suspended solids play an essential role in calculating the water quality index (WQI) of the river, and

they were a critical factor for calculating WQI, especially at the upstream part of the basin in water-abundant seasons. This was because soil erosion leads to an increase in the concentration of suspended solids in the water after floods that occur in water-abundant seasons, and the high flow rate of the river causes the discharge of pollutants from non-point sources ammoniacal nitrogen at the upper parts of the river. Also, results showed that an integrated approach could directly link a river's flow velocity, water quality, and pollution index (Lai et al., 2013). The self-purification capacity has been implied as to the main factor in predicting the Bhavani river health in India. A river of length 215 km was considered in this study, and oxygen was introduced as the most influential factor in the self-purification capacity of river (Devi, 2017). A combined program of modeling and WASP qualitative simulation was utilized for evaluating the effects of plants in the Reedy river in South Carolina on eliminating the effluents discharged from sewage treatment plants both qualitatively and quantitatively. All variables used in TMDL were applied in the first simulation, and in the second simulation, the model included the complete elimination of effluents of sewage treatment plants discharged into the river. Results showed that eliminating effluents cause the removal of 70% of waste load by upstream plants and a 66% removal of waste load downstream. Based on the daily flow rate values, it was predicted that all nitrogen, phosphorous, and mass loads would be reduced on average in seven years (Privette & Smink, 2017).

Huang used the SWAT model to evaluate the effect of land cover and land use on the water resources of the northern river basin in China. Results demonstrated a good agreement between simulated and observed data both daily and monthly and the monthly amount of phosphorous and ammoniacal nitrogen loads (Huang et al., 2013). In another research work conducted to identify the pollution sources and evaluate their effects on the Galing river in Malesia using numerical simulation models, results showed that Galing river has low-quality water due to the discharge of domestic and industrial wastewater, which is categorized as class 4 in terms of river water quality. The prediction model revealed that an 80% decrease in the river waste load could enhance river water quality to class 2 (Lee et al., 2017). In another study, the QUAL2Kw model is applied to evaluate the reaction of the Sertima river in Portugal to different waste loads such as nitrogen and phosphorous. The comparison between the measured and simulated flowrates indicated that it is necessary to decrease the actual load of phosphorous and nitrogen by 5–10 times to enhance the class of river from eutrophic to mesotrophic (Oliveira et al., 2013).

In evaluating self-purification capacity in Juma river, China, the self-purification capacity was introduced as one of the critical factors affecting river health (Tian et al., 2011). Measurements performed for examining the self-purification capacity showed that biological sampling could complete the physio-chemical analysis of water quality (Gonzales et al., 2014). Different types of qualitative

models have been evolved for simulating rivers, reservoirs, bays, and groundwater. QUAL2K is among the models mainly used for simulating river systems. In recent decades, different simulation models have been employed for the qualitative management of rivers. In these methods, the river is divided into some segments, and this can be done where an abrupt change occurs in river flowrate or its water quality, such as the points at which wastewaters are discharged, or secondary branches of river are joined. Accordingly, the intended parameters of governing equations are calculated in each segment and assumed to be constant in the river's length. QUAL2K is extensively applied for simulating the water quality in rivers. This model can consider the river systems branch-wise or with its secondary branches; also, it can simulate river in 1D with the non-uniform steady-state flow and take into account both the point and nonpoint loading effects. QUAL2K can also simulate variation daily with lower than 1-hour time steps (Kerachian, 2012). A study by Melo on the Rio Inhandava river concluded that, considering these issues recognize and evaluate the potential of local water resources is necessary, since the river Inhandava is inserted in the north-northeastern state of Rio Grande do Sul, in the Uruguay river basin and watershed belongs to Apuaê-Inhandava. The data were inventoried quality of studies conducted in Rio were considered diffuse agricultural loads, animal waste and sewage. To assess the water quality of the Rio Inhandava, the computer model was used QUAL2Kw. The calibrated model QUAL2Kw, became an instrument to in the management of water resources, since the analysis of the results showed the selfpurification in downstream river study (Melo et al., 2020). In other study analyzes the river's carrying and load capacity using the QUAL2Kw model approach. The river is located in Bengkalis Regency, Bukit Batu District. Modeling simulations were done with by using a scenario to determine the burden of pollution that occurs. The results of this study shows that the Bukit Batu river needs to reduce pollution loads by more than 70%. However the land carrying capacity is in the surplus category, thus it shows the availability of land in the Bukit Batu sub-district's sufficiency to meet the needs for agriculture

production (Saily & Setiawan, 2021). Yustiani compare water quality in Indonesia. The method used in this study is data collection in the form of calculating the rate of deoxygenation carried out in rivers in several urban areas based on previous studies. This assessment includes the amount of deoxygenation rate, calculation, and determination method. Based on the studies conducted, the method recently used is laboratory treatment. The comparison between the use of laboratory tests and empirical formulas shows a vast difference (Yustiani, 2021).

Since Zarrineh Rud river is among the essential arteries of water supply for Urmia lake in northwestern Iran and catches different pollutant streams in its path, the present study aims to evaluate the daily waste load of this river for environmental management of cold-water fish species using QUAL2K model.

## 1. Methods

### 1.1. Study region introduction

This river is located at geographical coordinates of  $45^{\circ} 45' - 47^{\circ} 24' N$  and  $35^{\circ} 40' - 37^{\circ} 28' E$ . Different point and non-point sources of pollution such as Miandoab sugar factory wastewater, effluent flowed out of Miandoab wastewater treatment plant, slaughterhouse wastewater, and agricultural effluents and urban wastewaters of nearby villages are discharged into the river and decrease its water quality. In the present study, a subsection of the river between the Nourozlu diversion dam and the river discharge into Urmia Lake, about 57.5 km in length, was selected for evaluating the water quality of Zarrineh Rud river using the QUAL2K model (Figure 1). River quality management has mostly relied on simulation models in recent decades. In these approaches, the river is initially separated into many intervals, which can be divided into times when the river's flow rate or quality changes suddenly, such as at the point where incoming wastewater is discharged or when sub-bifurcation rivers enter. Accordingly, the governing equations' parameters are determined at each interval and are commonly taken as constants. To simulate river water quality, the QUAL2K model is increasingly utilized.

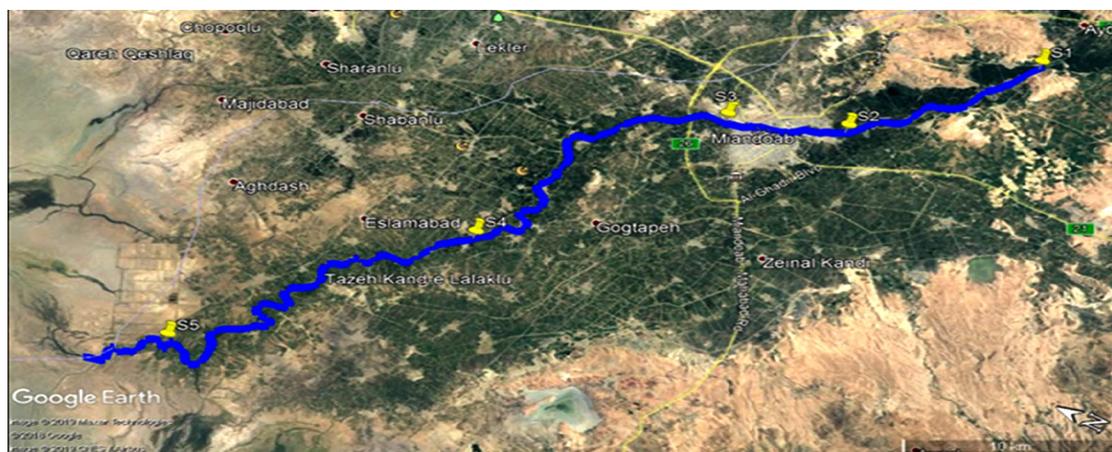


Figure 1. Location of sampling stations in the study area of Zarrineh Rud river

One of this model’s features is that it may conceive of the system as a branch with sub-branches. It can also simulate a river in one dimension with non-uniform continuous flow and take into account both spot and non-spot loading effects. In less than an hour, the QUAL2K model can simulate changes daily. The QUAL2K simulation model is one of the most commonly utilized in river system simulations. Qualitative specifications of sampling stations in May and August 2019 are presented in Tables 1 and 2. The evaluation of model output results (model calibration) was performed by varying the oxidation coefficient of BOD and reaeration coefficient applying RMSE measure; then, coefficients with the lowest RMSE were selected as the best parameters for the model calibration.

Table 1. Quality characteristics of Zarrineh Rud river sampling stations in May 2019

Station name	Station Position (km)	T(C°)	pH	NO <sub>3</sub>	BOD	PO <sub>4</sub>	DO
S1	57.5	25	7.8	1.2	3.8	0.2	7.2
S2	49.5	21	7.9	2.1	3	0.46	5.6
S3	40.14	12	7.6	3	5.1	0.3	6
S4	23.08	18	7.85	4.2	3.9	1.53	5.5
S5	0.2	19.5	7.7	5.6	3.7	1.76	5.2

Table 2. Quality characteristics of Zarrineh Rud river sampling stations in August 2019

Station name	Station Position (km)	T(C°)	pH	NO <sub>3</sub>	BOD	PO <sub>4</sub>	DO
S1	57.5	23.9	6.69	2.7	5	0.32	5.68
S2	49.5	22.1	7.61	3.6	4	0.63	5.50
S3	40.14	23.4	7.77	5.7	9.5	0.94	5
S4	23.08	26.1	7.85	8.1	10.5	2.60	4
S5	0.2	25.7	7.9	9.3	6.5	2.40	3.50

QUAL2K model divides a segment of the river into several numerical elements and conducts the hydrologic balance in terms of flow rate (m<sup>3</sup>/s), thermal balance in terms of temperature (°C), and mass balance in terms of concentration (mg/L) for each element. The 1D equation of mass transfer, convection-diffusion is the constitute equation governing the QUAL2K model, which can be expressed numerically for every qualitative parameter in terms of time and position. For each qualitative parameter, the equation can be defined as follows (Fataei et al., 2014).

$$\frac{dc_i}{dt} = \frac{Q_{i-1}}{V_i}c_{i-1} - \frac{Q_i}{V_i}c_i - \frac{Q_{ab,i}}{V_i}c_i + \frac{E'_{i-1}}{V_i}(c_{i-1} - c_i) + \frac{E'_i}{V_i}(c_{i+1} - c_i) + \frac{W_i}{V_i} + S_i + \frac{E'_{hyp,i}}{V_i}(c_{2,i} - c_i),$$

where: *c* – concentration (g/m<sup>3</sup>); *E* – *i* + 1.*i* scatter coefficient between elements (m<sup>3</sup>/d); *Q* – water flow (m<sup>3</sup>/d);

external load *i* (g/d); *V* – element volume *i* (m<sup>3</sup>); source of reaction and mass transfer (g/m<sup>3</sup>d); *T* – time (d).

## 2. Results

The evaluation results of the qualitative simulation model (model calibration) of Zarrineh Rud river in spring based on the square root mean square error (RMSE) method between the simulation data and the observational data are presented in Table 3. As mentioned above, the most proper coefficient for model calibration is selected based on the lowest RMSE. Therefore, the best oxidation coefficient of BOD was obtained with RMSE of 0.14, and the best reaeration coefficient of the river was determined as 8.5 with RMSE of 0.24, and then both of them were applied to model calibration.

Table 3. Results of quantitative comparison between QUAL2K model and observational data for Zarrineh Rud river in spring

	Oxidation coefficient of BOD (observational data)				Reaeration coefficient of DO (observational data)			
	2	3	4	5	8.5	15	22	33
RMSE	0.99	0.43	0.14	0.51	0.24	0.87	1.01	1.15

The trend of variation in parameters of electrical conductivity (EC), Nitrate (NO<sub>3</sub>), and pH in sampling stations of Zarrineh Rud river was evaluated in the spring and summer seasons of 2019 in comparison with FAO standards for irrigation of agricultural products. According to conducted investigations, the results of electrical conductivity parameter is less than 700 µhms/cm in all stations except the S5 station in the spring season. Therefore, the quality of Zarrineh Rud river water for agricultural irrigation usage is without any limitation according to FAO standards. Also, the pH variation for Zarrineh Rud river water is in the range of 6.5–8.5 (the allowable limit for agricultural irrigation) in all stations in both spring and summer seasons of 2019. The nitrate variation of the Zarrineh Rud river is in the range of the maximum allowable limit for consumption in agricultural irrigation in all stations in the spring and summer seasons of 2019. With this description, it can be concluded that the quality of Zarrineh Rud river water regarding under investigation parameters is suitable for irrigation of agricultural products.

### 2.1. Analysis of Inorganic Suspended Solids (ISS)

The graph of simulation of inorganic suspended solids (ISS) for Zarrineh Rud river in spring and summer seasons of 2019 is presented in Figures 2 and 3. As it can be seen, there is a good correlation in all stations in the spring season except S4 and S5 stations. The value of the concentration of inorganic suspended solids of Zarrineh Rud river is 125, 152 milligrams per liter in station S1 in spring and summer in order. The concentration of this parameter has been increased a little in both seasons by the entrance of agricultural drain water. The maximum

increase has happened in 46-kilometer distance point by the entrance of sugar factory wastewater. This parameter value at the mentioned point has reached 150 and 174 milligrams per liter in spring and summer in order. There has not been any important occurrence in the deposition of these materials in the remaining parts of the river considering the density of suspended material and flow rate of the river. The concentration of these materials has been stable approximately down to the end of the river and has been reached 151 and 173 milligrams per liter in station S5 in spring and summer in order.

### 2.2. Analysis of Water Acidity (pH)

The graph of observed data and output data for the simulation model of Zarrineh Rud river from the outlet of

Norouzlu regulating dam down to Uromia lake has been shown for the parameter of pH in Figures 4 and 5. It should be explained that pH is an important parameter in water and it impacts most of the chemical and biological reactions of water. In other words, the reactions in water happen in a special range of pH. Also, different utilizations of water including drinking, agricultural, aquaculture consumptions are applicable in the standard range of 6.5–8.5. Usually, the pH of sewages and agricultural drained water is in the range of alkalinity and therefore decreases the pH of accepting water a little. As it can be seen, observed data have a good correlation with model simulation graph in both spring and summer seasons of 2019. The model simulation graph shows in the spring and summer seasons the pH variation of the Zarrineh Rud river has a stable trend approximately and does not show noticeable changes.

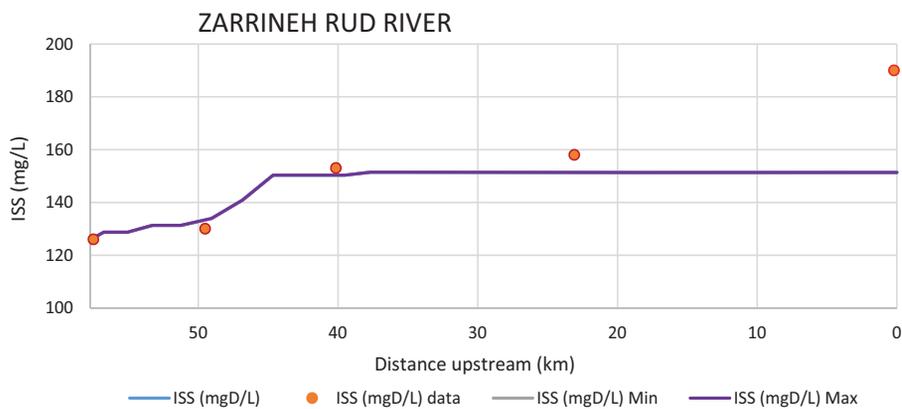


Figure 2. Simulation graph of suspended solids in Zarrineh Rud river in May 2019

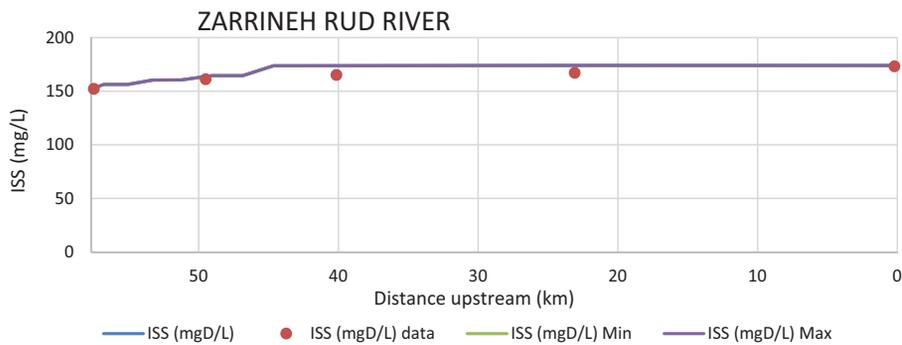


Figure 3. Simulation graph of suspended solids in Zarrineh Rud river in August 2019

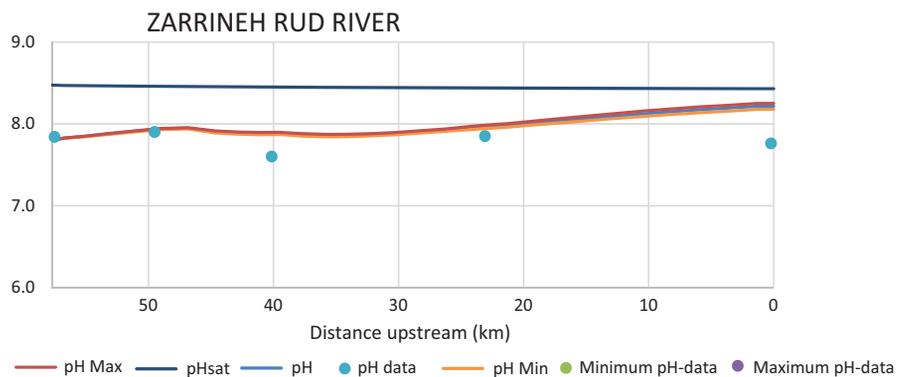


Figure 4. pH simulation graph of Zarrineh Rud river in May 2019

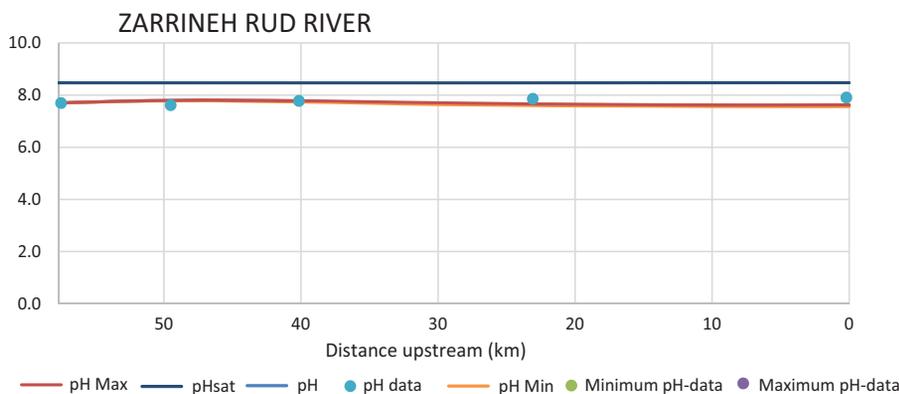


Figure 5. pH simulation graph of Zarrineh Rud river in August 2019

Only in the spring season, it shows a small increase in pH at locations close to the entrance of agricultural drained water. By looking at the graphs, it can be seen that the pH value of the Zarrineh Rud river is at the standard level.

### 2.3. Analysis of Nitrate (NO<sub>3</sub>)

The factors of increasing the nitrate amount in water resources are mainly human wastewater and agricultural drain water and it is defined as a middle form of nitrogen. Nitrate changes to (N<sub>2</sub>) form during a process entitled denitrification and exits the water in the gas form. Despite the nitrification process which is done in presence of oxygen and the aeration coefficient of the river has a positive impact on the reduction of ammonium, the denitrification process happens without the presence of oxygen, and aeration of the river does not have an impact on its conversion. Therefore, the denitrification process usually is very slow and occurs rarely in the rivers that are flowing and always taking up oxygen by natural aeration. As it can be seen, there is a good correlation between observed data and model simulation graph in all stations except station S5 in the spring and summer seasons. As it was mentioned before, the existence of no correlation between the S5 station and output graph of the simulation model can be due to the entrance of a contamination source or

sources in this distance which increases the nitrate of the river (Figures 6 and 7).

### 2.4. Analysis of Ammonium (NH<sub>4</sub>)

The ammonium ion is the primary form of nitrogen in the aquatic environment. The presence of ammonium in water is related to human and agricultural pollutions such as urban and rural sewage and agricultural drain water. Ammonium in the presence of dissolved oxygen transforms to nitrite and then nitrate during the nitrification process. Therefore, the reduction of ammonium amount is accompanied by the increase of nitrate concentration in the rivers. This process is done more quickly in the case that the aeration coefficient of the river is high. The simulation graph of the variation in ammonium concentration shows a decreasing trend in the spring season and its value has reached from 510 µgr/l in the headwater of the river before the discharge of municipal wastewater of Miandoab city in 39 kilometers distance point to the value of 480 µgr/l. The discharge of municipal wastewater of Miandoab city has increased the value of this parameter to 511 µgr/l again. The decreasing trend of ammonium due to the high flow rate and also high aeration coefficient of the river in the spring season has been continued down to the end of the river and has reached to value of 351 µgr/l. The concentration graph

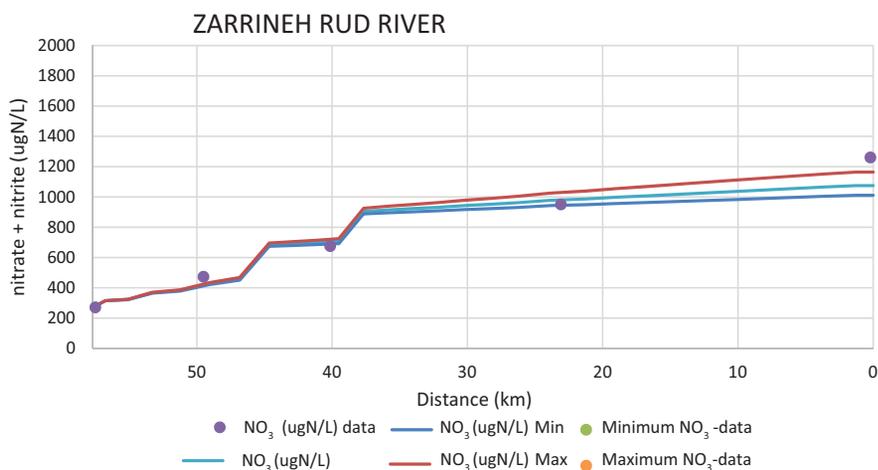


Figure 6. Simulation graph of nitrate in Zarrineh Rud river in May 2019

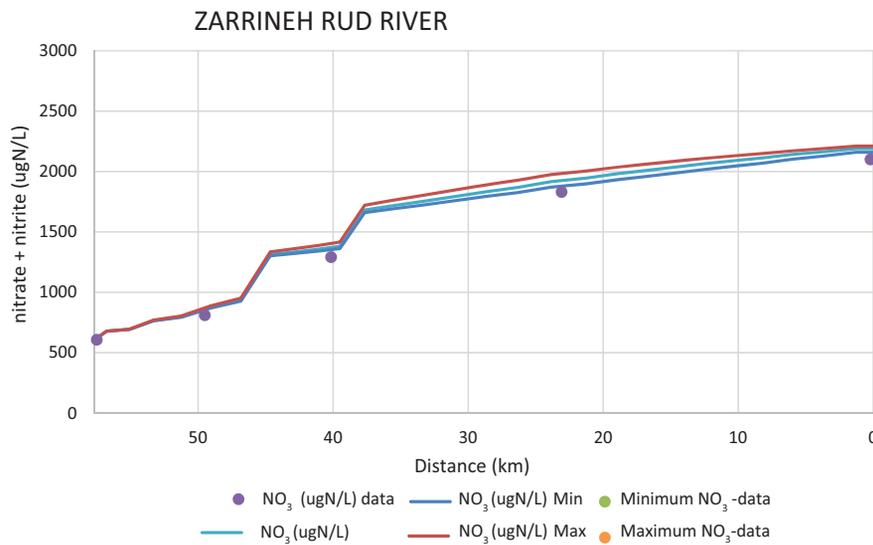


Figure 7. Simulation graph of nitrate in Zarrineh Rud river in August 2019

of ammonium simulation graph variation is different in the summer season relative to the spring season. The evaluation of hydraulic details of output simulation's current of Zarrineh Rud river in the summer season shows that the aeration coefficient of this river is relatively lower in the summer. One of its important reasons is the low flow rate. Therefore, the river in the distance between river headwater (Norouzlu dam outlet) up to point in the kilometer of 39 does not have appropriate self-purification due to discharge of agricultural and urban pollutants and hence it cannot do quick nitrification. The concentration of ammonium increased from 746  $\mu\text{gr/l}$  to 960  $\mu\text{gr/l}$ . This increase is more severe and quicker in the point of 39 kilometers distance, and at the point of 37 kilometers distance increases to 1222  $\mu\text{gr/l}$ . Again, from the point of 37 kilometers distance the decreasing trend of ammonium is started which is due to the nitrification process and decreasing of concentration of pollutants in the downstream of Miandoab, and it reaches 660  $\mu\text{gr/l}$  at the end of the river (Figures 8 and 9).

### 2.5. Analysis of Electrical Conductivity (EC)

The graphs of the simulation model of electrical conductivity (EC) for the Zarrineh Rud river in the spring and summer seasons of 2019 have been shown in Figures 10 and 11. As it can be seen, there is a good correlation between the graph of observed data and the model simulation graph up to 38 kilometers distance. But, after the point of 38 kilometers distance, the observed data in the summer season (stations number 4 and 5) does not correlate with the graph of the model's output and passes over it. Its reason can be the discharge of pollutant sources that have not been detected and applied in the model. It should be explained that the most important factor for electrical conductivity in surface waters is agricultural drain water. Other pollutant sources such as residential sewage have lower electrical conductivity compared to agricultural drain water and only if the discharge rate of mentioned sewages would be high, they can influence the electrical conductivity of the river. Hence, it is probable that by the

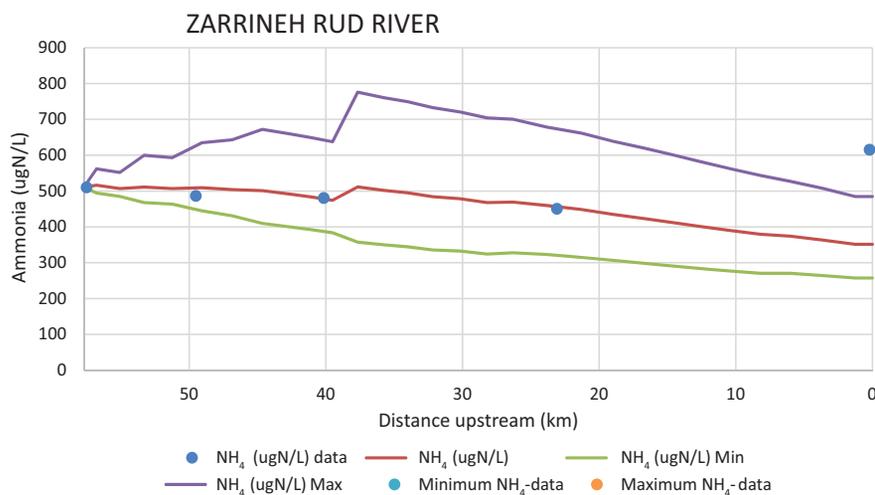


Figure 8. Ammonium simulation graph for Zarrineh Rud river in May of 2019

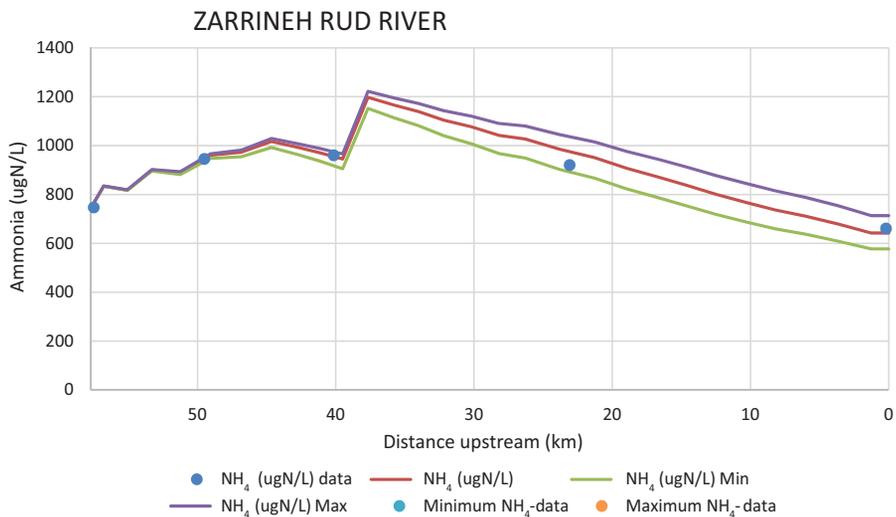


Figure 9. Ammonium simulation graph for Zarrineh Rud riverr in August of 2019

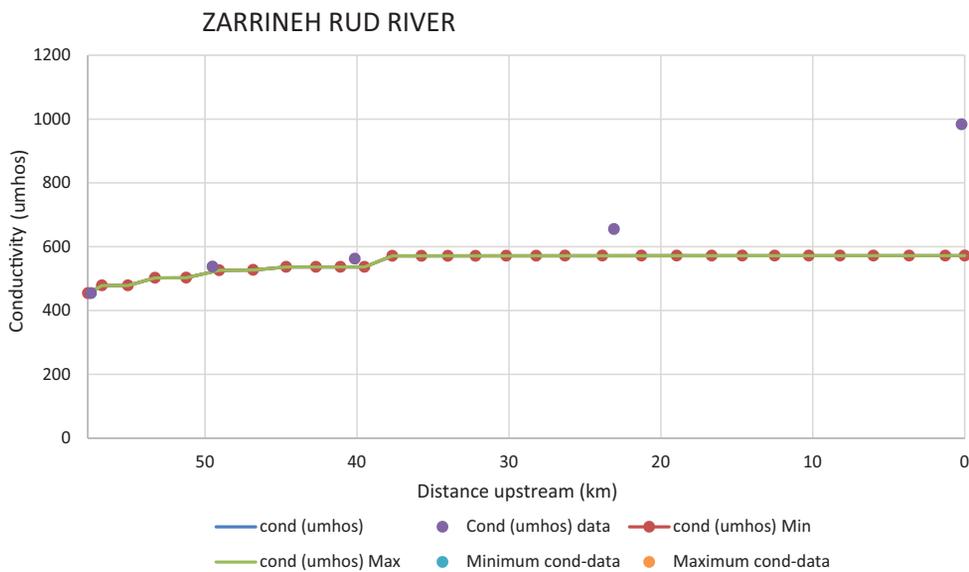


Figure 10. Electrical conductivity simulation graph for Zarrineh Rud river in May 2019

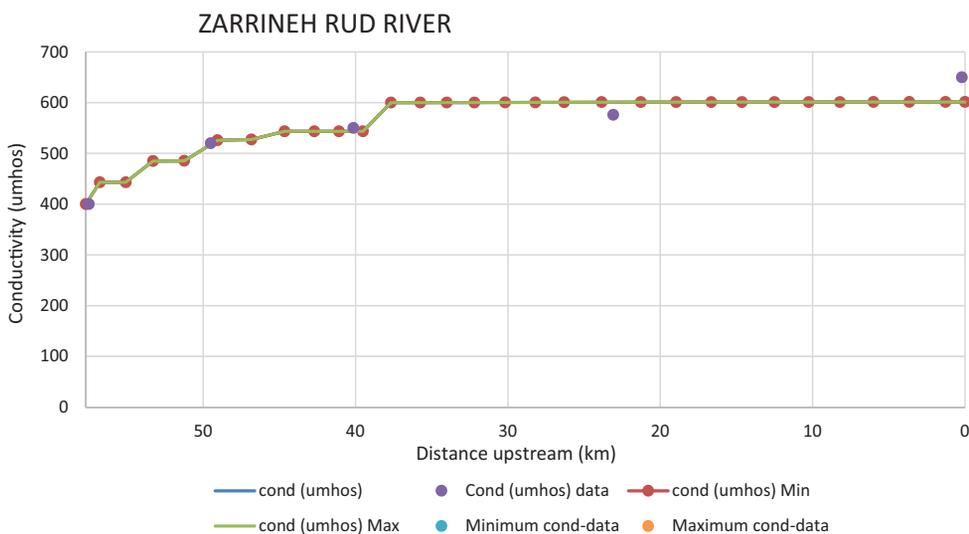


Figure 11. Electrical conductivity simulation graph for Zarrineh Rud river in August 2019

development of irrigation and draining network of Mian-doab plain especially in lower parts of the city, the agricultural drain water for adjacent lands to the river is discharged in non-centralized form and increases the mentioned parameter leading to non-correlation status with model simulation graph in this area. The value of electrical conductivity of Zarrineh Rud river in the river headwater (outlet of Norouzlu regulating dam) in the spring and summer seasons were 400 and 454  $\mu\text{hms/cm}$  in order. This value has a rising trend up to the 38 kilometers distance point where most of the influential pollutants on electrical conductivity such as drain water from agricultural activities, livestock slaughterhouse, sugar factory, and municipal sewage are discharged into the river. But, from this point afterward, the model simulation graph in both spring and summer seasons is not increased which is due to the reduction of the concentration of entering pollutants. The concentration amount of that stays constant down to the end of the river (station S5) and in the spring and summer is equal to 571 and 602  $\mu\text{hms/cm}$  in order. In general, the

value of electrical conductivity of the Zarrineh Rud river is in the natural limit and is in the standard range that is required for agricultural, aquacultural needs and is in the standard range for preserving the life of aquatic ecosystem creatures.

### 2.6. Analysis of Dissolved Oxygen (DO)

Simulation graphs for variation trend of dissolved oxygen (DO) for Zarrineh Rud river in spring (May) and summer (August) of 2019 have been presented in Figures 12 and 13. As it can be seen, observed data except station 5 in the spring gets correlated with the model simulation graph with a little difference. As it was mentioned before, in the recent case, the probability of the existence of undetected centralized and non-centralized pollutant sources which increases the consumption of dissolved oxygen in this range has led to a little difference in simulation model results. The amount of dissolved oxygen in river headwater (outlet of Norouzlu regulating dam) in the spring and summer seasons were 7.2 and 5.68 mg/l in order. In both

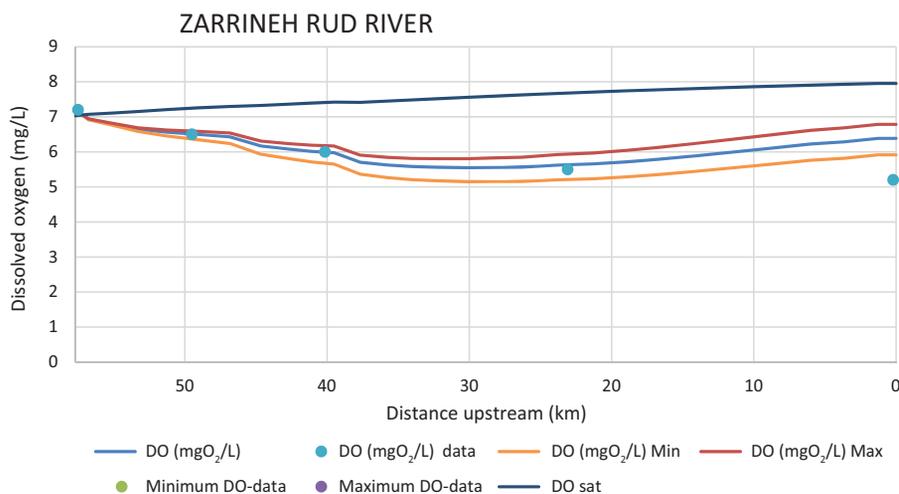


Figure 12. The graph of dissolved oxygen simulation for Zarrineh Rud river in May 2019

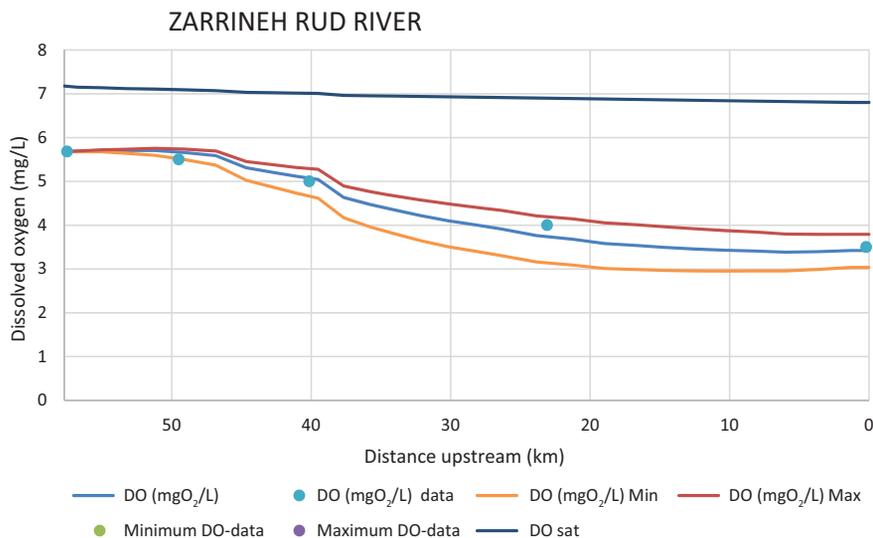


Figure 13. The graph of dissolved oxygen simulation for Zarrineh Rud river in August 2019

graphs, the trend of variation of dissolved oxygen is a decreasing trend which is due to entrance of pollutant sources such as drain water from agricultural activities, live-stock slaughterhouse, sugar factory and wastewater from Miandoab city and its municipal sewage-treatment plant and also wastewater from neighboring villages. Despite the entrance of different pollutant sources to the river, the value of dissolved oxygen has been decreased relatively. But, the aeration coefficient of the river and self-purification capacity of the river has been at a level that these pollutants were not able to decrease the dissolved oxygen value more. The minimum environmental standard of the river for dissolved oxygen is equal to 5 milligrams per liter. Therefore, the results of the simulation model show higher values for dissolved oxygen.

### 2.7. Analysis of Biochemical Oxygen Demand (BOD)

The graph of biochemical oxygen demand simulation (BOD) and observed data in the spring and summer seasons of 2019 have been presented in Figures 14 and 15. As it can be seen, there is a good correlation between observed data and model simulation graph in all stations except station S5 in the spring season. The main reason for rising BOD in rivers is human's sewage, food processing wastewater, and animal's excreta. The agricultural drain

water usually has a very lower BOD. BOD of Zarrineh Rud in river headwater in the spring and summer seasons are 3.8 and 5 mg/l in order. Up to the point with 46 kilometers distance in the river, there is no other specific pollutant source except agricultural drain water that can influence the increase of the BOD value of the river. Therefore, this parameter has been decreased due to the self-purification of the river and the oxidation of organic materials, especially in the spring. We can see two cases of quick and severe increase of BOD of Zarrineh Rud river in the simulation graph. The first case is related to the discharge location of sugar factory wastewater in the 46 kilometers point, in which the graph in the spring season has been increased from 3 to 6.2 mg/l and in the summer season from 4 to 10.76 mg/l. The second case is related to the location of wastewater of Miandoab sewage treatment-plant in 38 kilometers point, in which the BOD of Zarrineh Rud river has been increased from 5.1 to 6.84 mg/l in the spring season and from 9.5 to 13.35 mg/l in the summer season. In the distance between 46 kilometers point to 38 kilometers point, the graph has decreasing trend due to non-existence of an important pollutant source with high BOD and also self-purification of the river because of increase in aeration coefficient. In the continuation of the river, we are observing the decrease in BOD of the river which is due to very good reeration of the river and high

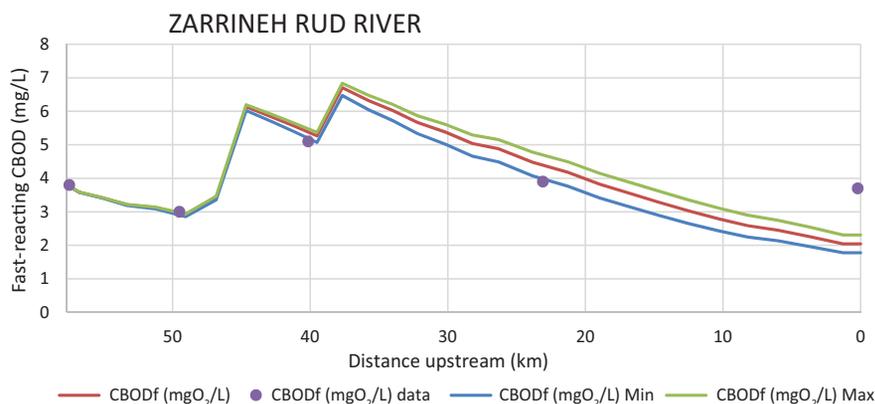


Figure 14. BOD simulation graph for Zarrineh Rud river in May 2019

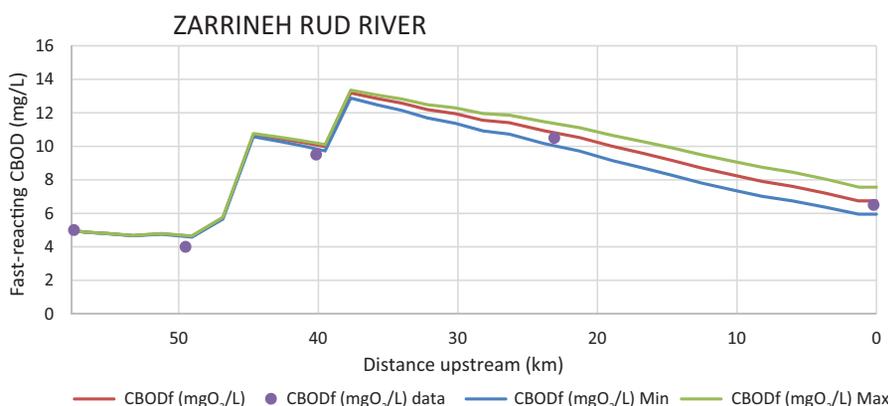


Figure 15. BOD simulation graph for Zarrineh Rud river in August 2019

self-purification capacity despite the entrance of different pollutant sources such as raw sewage water of villages adjacent to the river, and non-centralized agricultural drain water in lands around the river. The BOD value at the end of the river in spring reaches 2 mg/l and in summer it reaches 6.5 mg/l. The maximum environmental standard value of BOD for a river is 5 mg/l. It can be seen that from 46 kilometers distance point up to 38 kilometers point in the river, BOD value has surpassed the environmental standard limit.

### 2.8. Analysis of inorganic phosphor (PO<sub>4</sub>)

The obtained graph from the phosphate simulation model and observed data graph of Zarrineh Rud river in spring and summer seasons of 2019 have been presented in Figures 16 and 17. As it can be seen, observed data have a good correlation with model simulation graph. Non-correlated cases are related to the S5 station in the spring season and the S4 station in the summer season in which the phosphate concentration of observed data is more than its value in the modeling graph. Its reason can be due to a

pollutant source that enters into the river in that area, but it was not detected in this research and it was not applied in the model. The mentioned pollutant source is probably a momentary source. The phosphate value in the spring and summer seasons in the river headwater was 67 and 108 µg/l in order. By entering the pollutant sources up to the point at 38 kilometers distance of the river, the phosphate amount shows a gradually increasing trend, and its value before discharging of Miandoab city municipal wastewater in the spring and summer has reached 40 and 315 µg/l in order. The maximum value of phosphate rise is located at the Miandoab city municipal wastewater discharge location and its value reaches suddenly to 492 and 805 µg/l in spring and summer in order close to the point at 38 kilometers distance. By considering this point that the most important sources of phosphate in surface water resources are agricultural drain water which contains chemical fertilizers and human origin sewages, it can be seen that noticeable changes of phosphate have occurred in the simulated graph at the 38 kilometers distance point by entering sewage of Miandoab city into the river. It

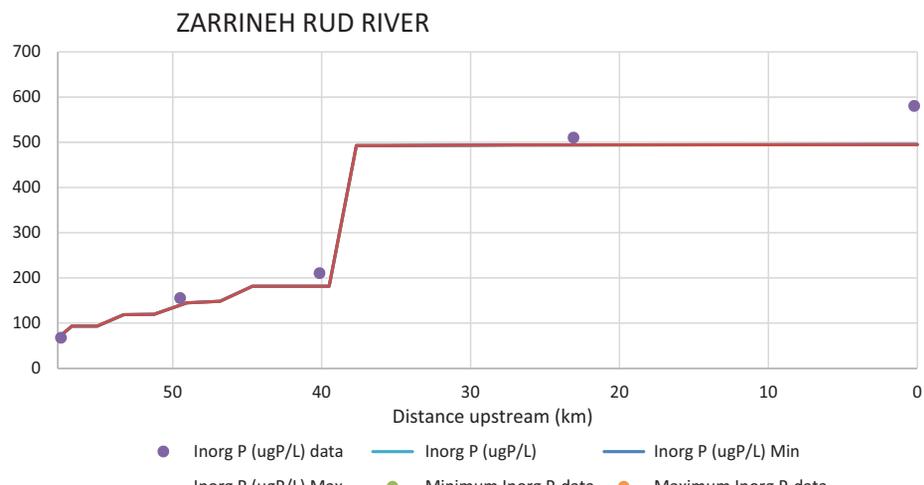


Figure 16. Inorganic phosphor simulation graph of Zarrineh Rud river in May 2019

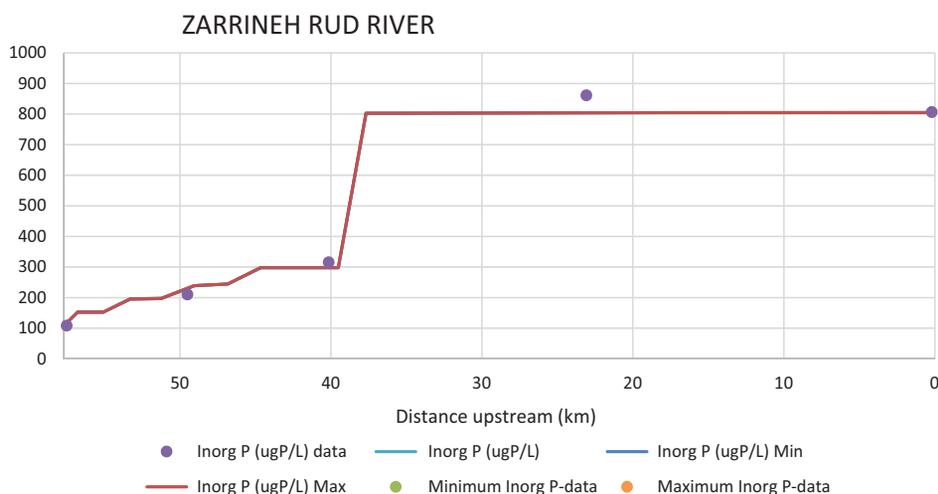


Figure 17. Inorganic phosphor simulation graph of Zarrineh Rud river in August 2019

should be explained that despite some quality parameters whose concentration reduction is a function of river aeration coefficient, the most important factor of phosphate reduction in water is related to its deposition speed.

### 3. Discussion

Different models have been invented for the simulation of the quality of rivers water. But, the QUAL2K model has been used in this research by considering the higher performance and capabilities of this model in simulating the quality of water resources. Parameter of inorganic suspended solids (ISS) has the highest value of 12 percent in human sewages of river's neighboring villages due to no sewage treatment and no removal of suspended particles. ISS has its lowest value of 0.1 percent in sugar factory wastewater in the Zarrineh Rud river. 23.6 percent of inorganic suspended solids for Zarrineh Rud river is related to entering pollutant sources and 76.4 percent of that is related to Zarrineh Rud river in upper sections of Norouzlu dam i.e. before studied area.

Considering this point that the mass of all investigated quality parameters in this research is changing in an aquatic environment during physicochemical and biological reactions. However, the conditions are different about ammonium and nitrate parameters, because ammonium transforms to nitrate during the nitrification process. Therefore, for determining the share of each pollutant source for these parameters especially for nitrate, the nitrification process has reduced the ammonium amount along the river and has added to the nitrate concentration. In other words, part of nitrate share in the river is related to the nitrate concentration available in river headwater, and some other part is related to the discharged pollutant sources into the river, and another part is related to nitrate added from the ammonium transformation process. Considering the non-separable capability of the mentioned cases, in this research only rationing the current conditions is evaluated. Therefore based on that, agricultural drain water and wastewater of Miandoab sewage treatment plant with 16.4 and 14.6 percent have the maximum share and sugar factory wastewater with 2.1 percent has the minimum share of pollution in Zarrineh Rud river. Therefore, the pollutant sources of Zarrineh Rud river have 43.37 percent of pollution share without considering nitrate increase during nitrification process, and 56.63 percent is related to nitrate available in upstream of river and is increasing from transforming ammonium form of nitrogen to nitrate.

For ammonium parameter, wastewater of Miandoab city sewage-treatment plant and agricultural drain water with 23.1 and 16.5 percent in order have the maximum share of ammonium pollution in the Zarrineh Rud river and sugar factory wastewater with 1.5 percent has the minimum share of it. From the total pollution load of ammonium in the Zarrineh Rud river, 53.13 percent is related to entering pollutant sources and 46.87 percent is related to the upstream of the river above the studied area. The

results show that the agricultural drain water with 18.4 percent has the most share from Zarrineh Rud river pollutants related to electrical conductivity (salinity) in the studied area and sugar factory wastewater with 0.1 percent has the least share of that. Altogether, 30.5 percent of the electrical conductivity of rivers is related to pollutant sources, and the rest of that (69.5 percent) is related to the upstream above the studied area (before Norouzlu regulatory dam).

Evaluation of share of pollution by biochemical oxygen demand (BOD) in Zarrineh Rud river shows that wastewater of Miandoab sewage-treatment plant with 25.8 percent has the maximum share of BOD pollution and agricultural drains with 0.1 percent have the minimum share. Also, the sewage of the Miandoab slaughterhouse with 17.36 percent has the maximum impact in the rise of BOD in the Zarrineh Rud river after the wastewater from the sewage-treatment plant. Altogether the pollutant sources of Zarrineh Rud river have a 65.76 percent share in the rising of BOD and the rest of BOD (34.24 percent) is related to before of S1 station (before Norouzlu regulatory dam).

The most share of phosphate in pollutants in Zarrineh Rud river is related to wastewater of Miandoab sewage-treatment plant with 56.1 percent share and after that, it is related to the discharged agricultural drains with 11.5 percent share containing consumed fertilizer in the agricultural sector of Miandoab plain, and the least share of phosphate pollution is related to sugar factory with 0.7 percent share. Altogether, the total share of available phosphate from pollutant sources in the Zarrineh Rud river is 74.37 percent and 25.63 percent of phosphate is related to the section before studied area i.e. before Norouzlu regulatory dam.

Evaluation of simulation results for DO parameters along the Zarrineh Rud river showed that the river has appropriate aeration capacity. Despite the discharge of many pollutant sources such as the sugar factory of Miandoab, livestock slaughterhouse, wastewater of Miandoab municipal sewage-treatment plant, sewage from villages adjacent to the river, drain water from Miandoab plain drains, the re-aeration of the river has preserved the amount of oxygen in a high level. Generally, the Zarrineh Rud river has a high re-aeration capability, and dissolved oxygen in it stands in good status.

Generally, results from a qualitative evaluation of Zarrineh Rud river using a quality simulation model of QUAL2K show that the quality of water in this river has been decreased in the study period which is related to entering pollutant sources such as agricultural drains, sewage of populated areas like urban, and rural sectors. The evaluation of the trend of changes in quality parameters of Zarrineh Rud river in sampling stations showed that the amount of electrical conductivity of the river is appropriate in spring and summer. Dissolved oxygen of river in all stations in the spring season is in the allowable range and it is more than the allowable standard limit for stations S4 and S5 in the summer season. Also, the BOD

concentration, ammonium, and nitrate are at the standard level for all stations in both seasons, but in stations S3, S4, and S5, they are more than the standard limit of the river ecosystem for preserving aquatic life.

Obtained results from the total maximum daily load (TMDL) of Zarrineh Rud river from upstream pollutant sources to provide minimum standard in the river ecosystem in the critical point of the river (26 kilometers) showed that in the spring season the BOD pollutant discharging rate from point and non-point sources of river's upstream can be increased 16 percent and in the summer season it should be decreased 70 percent so the required standard level be achieved. Also, for reaching the optimum load of pollution related to  $\text{NH}_4$  from point and non-point sources upstream of the river an increase of 68 percent in pollution load of  $\text{NH}_4$  in the spring season, and a decrease of 57 percent in the summer season are required. The results of performed investigations by other researchers showed that the quality of river water in summer and winter seasons considering simulated quality parameters such as BOD,  $\text{NO}_3$ , and ammoniac nitrogen has worse conditions relative to other seasons. Also, researchers determined in the evaluation and selection of a program for improving the quality of water in the Basin of Taihou Lake in China using QUAL2K that the mentioned model can be used as an effective tool in water quality improvement programs (Miri, 2010). In general, the quality of river water in headwater is good, but, along the river, its quality has been decreased due to the entrance of pollutant sources such as agricultural drains, sewage of populated urban and rural centers, and this decrease in quality was correct in the evaluation of the basin too. Therefore, due to the high self-purification capability of the upper sections of the Zarrineh Rud river, the pollutant sources could not decrease the quality of water more except in few cases. In the evaluation of the capability of accepting pollution in Ghareh-Aghaj river using QUAL2K software concluded that in general, the amount of oxygen of studied river is in standard level considering the actual and simulation results (Najafi & Mahmoudpour, 2012). This matter shows that the self-purification ability of the river was high (Najafi & Mahmoudpour, 2012). But, Najafi after evaluation of the quality of Gharahsou river in Kermanshah using QUAL2K concluded that the amount of dissolved oxygen is lower than the allowable limit of 5 milligrams per liter in general, and the most critical point is located after Kermanshah city by entering wastewater and sewage of this city into Gharahsou river. The results of quality evaluation of Zarrineh Rud river for environmental management of cold water fishes using a quality simulation model of QUAL2K shows that the quality of river water has been decreased in the study period which is due to the entrance of agricultural drain water, sewages of populated urban, and rural centers (Chang, 2004). As two other researchers have mentioned, the increase in human activities has increased the share of pollution from sub basins in the output pollution load of the river. But, due to the high flowing rate of the current in the river, and

the high self-purification capability of it under influence of reoxygenation and reduction of water depth along the river, the self-purification speed has been increased (Chang, 2004; Carney, 2009). The obtained results by are confirming the impact of residential, agricultural, dairy farming sectors on the quality of Karaj river water too (Abdilizadeh, 2015).

In this study, due to limitations in the quality data of the river, other quality parameters, especially algae and phytoplankton, and also influential parameters in the model, such as the sediments in the river bed were not evaluated.

## Conclusions

Studies conducted by other scholars indicated that the river's water quality is of lousy condition in simulated qualitative parameters such as BOD,  $\text{NO}_3$ , and ammoniacal nitrogen in summer and winter compared to other seasons (Abdilizadeh, 2015). Generally, the river's water quality was good in Sarab; however, by moving in the river's length, its quality reduced due to the discharge of pollution sources like agricultural drainages and sewages of urban and rural areas, and this was hold in this study too. Nevertheless, because of the high self-purification capacity of the Zarrineh Rud river, pollution sources could not significantly reduce the water quality for cold-water fishes except in some specific cases.

Generally, the results of the qualitative study of the Zarrineh Rud river using the QUAL2K qualitative simulation model demonstrate that the water quality of this river is satisfactory at the point of overflow; however, the quality of the river is degraded due to the entry of polluting sources such as agricultural drain-seepage and wastewater from urban and rural population centers. The river, on the other hand, has a great capacity for self-purification, particularly in the spring owing to increased intensity and downstream of the city due to re-aeration and a decrease in water level along the river, which enhances the pace of self-purification. The entry of these contaminants will not have a significant impact on the quality of the water.

Although some pollutant sources, particularly decentralized pollutant sources such as agricultural effluents and rural wastewater along the river in the Miandoab area, could not be recognized and tested, the model could simulate the real quality conditions of the Zarrineh Rud river quite well. As a result, the QUAL2K model was shown to be an appropriate model for qualitative simulation of the Zarrineh Rud river. The findings of model calibration using correction of river re-oxygenation coefficients, organic matter oxidation coefficients (BOD), nitrification coefficient ( $\text{NH}_4$ ), nitrate denitrification coefficient ( $\text{NO}_3$ ), change of phosphate precipitation rate coefficient ( $\text{PO}_4$ ), inorganic suspended solids (ISS), and quantitative evaluation of the model using the square root mean square error (RMSE) indicated that compared to spring, the simulation model showed the lowest inaccuracy in summer. As a result, the coefficients employed in the summer are quite reliable in other seasons.

In the autumn, the simulation model's findings revealed that the observational data and the model's output diagrams are in good agreement. The model was then tested using the RMSE approach, which revealed that the coefficients employed in summer were extremely accurate.

Since the main reasons for pollution of Zarrineh Rud river are the discharge of raw urban and rural wastewaters, sewages of the slaughterhouse, Sugar factory wastewater, and agricultural drainage water of Miandoab's plain through drainages, the recommended approaches that can be applied to allocate the daily waste load in Zarrineh Rud river for environmental management of agricultural irrigation species are as follows:

1. Establishment of the wastewater treatment plant for villages surrounding the Zarrineh Rud river downstream of Miandoab's plain.
2. Standard wastewater discharge from Miandoab's wastewater treatment plant by province water and Wastewater Company.
3. Controlling the agricultural fertilizer and pesticides consumption in the Zarrineh Rud basin according to existed standards by supervision of agricultural Jihad organization in the province
4. Establishment of the wastewater treatment plant for treating the wastewaters from the sugar factory and slaughterhouse of Miandoab and their discharge according to the standards of the department of environment.

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