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Investigation of self-purification capacity and water quality of Haraz river during dry and wet season

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GRAPHICAL ABSTRACT



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1. Introduction

ABSTRACT

Rivers are one of the primary water resources for agricultural, drinking, industrial and environmental applications; thus, assessment of the river water quality has a great significance. This study aims to evaluate the self-purification capacity of the Haraz river and identify critical areas with the lack of dissolved oxygen along the river. Also, the QUAL2K model, IRWQI and NSFWQI indexes were applied for the determination of water quality. In this study, primary pollutant sources including urban areas, industrial centers, farmlands and multiple cold-water fish farms that their water usage and discharge have severe consequences on the quality and quantity of the river's stream were identified and located. This model was built and calibrated for four seasons with data from six sampling stations of Haraz river. Based on this study, upstream of Haraz river has adequate self-purification capacity in comparison to its midstream and downstream, especially in the Amol city area, lack of dissolved oxygen was observed and self-purification capacity considerably reduced. The critical areas of Haraz river in spring and winter seasons are downstream and the estuary region, while in summer and autumn, critical areas are increased in Amol city. In general, as the elevation decreases, the water quality decreases. Only in upstream areas (near the Poloor village and before the Chelav station), water quality is in the average condition, but near the Caspian sea, the condition of Haraz river is worrying due to the existence of contamination sources.

In most of the countries around the world, including Iran, the water quality of rivers has been altered by social and industrial development and proceed into excessive contamination. The apparent contradiction between limitation of water resources and this issue in one hand and ever-increasing demand for water resources in societies, on the other hand, vitalize permanent monitoring, control, and treatment of surface water (Taheri-Tizro et al. 2014; Fatemi. 2015).Haraz River has great

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importance due to the economic and social dependence of the north part of Iran to this river. This river located in a region which is populated by tourists from all over the country. The concentration of restaurants, fish farming, water harvesting for irrigation of agricultural farms and extraction of sand close to this river are essential issues in Haraz watershed (Kavyan and Namdar et al. 2016). Basically, in the watershed of rivers, due to human activities, especially agricultural activity, the augmentation of different organic substances in the river is predictable and indeed, a high concentration of phosphate and

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other nutrients caused by fertilizers is observable. Each year the migration of birds to the watershed of Haraz river is diminished and uncontrolled development of fish farming, stone workshop in riverside and uncontrolled floods exacerbate the critical condition of the river. Study the self-purification capacity of the river determine not only the current condition of water quality of the river but also the critical points and could be an asset for sustainable development and increasing efficiency in this river (González and Almeida et al. 2014).

In recent years, the application of environment system models for assessment and selection has achieved great attention. These models, which mostly have different superiority in processing, required input data, assumptions, and modeling capabilities, could have valuable outputs if they are chosen for an appropriate purpose. Models with satisfying results from the simulation of dissolved oxygen concentration along the river are SIMCAT (TOMCAT Qual2E 4 Qual2K WASP7 and QUASAR (Kannel and Kanel et al. 2011). The comparison of these models showed that SMCAT and TOMCAT have a simple structure but are appropriate for rapid assessment of the impact of point discharge pollutions. QUAL2E water quality model developed during the earlier stages had many limitations. To overcome these limitations, some researchers developed the QUAL2K model (Park and Lee. 2002). The modifications in QUAL2K include the expansion of computational structures and the addition of new constituent interactions like algal BOD, denitrification and DO change caused by fixed plants (Idris and Abdu et al. 2016). Assessment of river water quality can also be done based on the WQI, developed by the US National Sanitation Foundation (NSF) (Effendi and Wardiatno. 2015). The NSFWQI is a common index for surface water quality classifications. The NSFWQI index has been used in some studies to show the existing water quality condition of rivers (Misaghi and Delgosha et al. 2017). IRWQI is another index for water quality assessment. The IRWQI index is used in Iran, which assesses the water quality based on physical and chemical properties. This indicator often shows water safety from non-disease parameter aspects (Aazami and Moradpour et al. 2018). This investigation is the first comprehensive assessment of the water quality of Haraz river during the dry and wet season for years 2018 and 2019. The six stations were considered and samples were carefully collected and tested for each station. The QUAL2K model, IRWQI and NSFWQI indexes were applied for the determination of water quality. Then, the self-purification capacity and critical points of Haraz river according to variation of dissolved oxygen were determined. In the simulation of the self-purification capacity of Haraz river, alongside data from six stations, the qualitative information of

point pollution sources along the river was used. The point pollution sources include sand extraction workshops and five huge fish farming farms along the river, which are embedded in the model and impact of other pollution sources considered by data from sampling stations.

2. Material and methods

2. 1. Study Area

Haraz river stems from Lar valley in the south of Damavand and Ghazi kola valley and Dare jungle runoffs discharge into this river. Also, streams from Ziaro and Lasem, which originated from the western mountain of Ghazghanchay, enter this river. Tributaries in Delarsetagh villages enter the Haraz river (Mazandaran Regional Water Organization, 2015). Haraz river flows in a broad valley to the this river supplies agricultural water for Amol north. citv. Freydoonkenar, part of Babol and Noor cities. Amol and Freydoonkenar are the most important cities which are developed on the cone of this river. This river has a variable slope in the mountain area. The slope of Haraz river is 13:1000 from the boundary of the mountain to the north of Amol city and in Amol city reaches 7:1000 (Department of Environmental Protection, 2008). Precipitation in the watershed of Haraz river is in the form of rain and snow (especially in the mountains). The annual average precipitation in the year 2014 was 698.6 mm. The majority of precipitation is in the plain area, which is at a higher altitude than the mountain area (Meteorological Organization of Mazandaran Province, 2014). The Haraz watershed begins from Damavand mountains and extends to the Sorkhrood region in the Caspian Sea. Figs. 1 and 2a represent the Haraz river map and streams joining this river alongside a digitized map of Haraz watershed. There are over 20 fish farming, 15 sand extraction workshops, tens of agriculture farms and industrial areas and around 40 villages which their wastewater and solid waste directly or indirectly are discharged to this river. Urban and rural wastewater include sewage, wastewater from bathrooms and surface domestic wastewater from washing cities. Also, solid waste and sewage of over 20 restaurants which are located close to the course of the river are discharged directly to the river that contains fat, food residual, hard degradable materials (like plastics, cans and so forth) and pathogenic pollution (such as microbes, bacteria, fecal coliform, viruses). Does Not only human waste enter the river from restaurants and other tourist centers along the road but also industrial and mine workshops discharge a considerable amount of this kind of a waste to Haraz river.



Fig. 1. Map of Haraz river and waterways, which are leading to it.

Industrial pollution around the river includes meat and dairy product factories near Emamzade Abdollah station, secondary treatment unit of burned oil factory (Polkhand) and Amol Asphalt plant (Amol-Mahmoodabad ring road). Also, wastewater from sack weaving, juicer and canned are discharged to a tributary of Haraz river, which is passed Mahmood Abad city. Contamination caused by the exploitation of mines leads to precipitation in the river, increasing turbidity and lessening dissolved oxygen concentration in the river (Varol and Gökot et al. 2012). Due to the spill of oil from heavy machinery and trucks, which transfer minerals, Haraz river receives a significant amount of oil pollution. Other sources of contamination are mountain bumps and erosion of soil and earthquake taking place in a hillside close to Haraz river, which could be classified as natural pollutants. Fish farming workshops could contaminate Haraz river through physicochemical ways (like increasing turbidity of the river by the discharge of food residual and fish drugs) and biological means (entering non-native fishes like rainbow trout). One of the destructive actions, which has a negative and direct impact on aquatic life, is the extraction of sand from the riverbed (Luo and Su et al. 2011). This action was started by the extraction of sand from the seashore and recently extended to the riverbed. This act has certain drawbacks, including widen and distortion of the riverbed, the creation of tributaries, which leads to disturbance of ecological condition and lessening the self-purification capacity of the river (Gebremicael and Mohamed et al. 2013). Currently, an immense amount of sand is extracted from the Haraz riverbed by over 15 workshops. The numbers of point and non-point sources which discharge pollutant to Haraz river have been increased in recent years which causes a lower level of dissolved oxygen in the river and especially in spring and summer, crisis condition is dominant.



Fig. 2. (a) The elevation map of the Haraz river's basin, (b) Map of significant pollutants in Haraz riverbank.

Fig. 2b expresses the location of primary pollution sources on the riverside. Also, due to the rise of TDS concentration, reduction of precipitation and consequently diminishing river flow and increasing pollutant concentration and riverbed erosion by human activity, the electrical conductivity of Haraz river has been increased in recent years. Although the discharge of urban and rural wastewater could increase water turbidity, augmentation of turbidity in several regions of the river represents high sand extraction activity around the river. Also, according to previous studies, phosphate and nitrate

concentrations have negligible changes that show discharges to Haraz river do not contain a high amount of phosphate and nitrate (Mehrdadi. 2010). Fig. 3 shows the location of sampling stations along the river. Station 1 (Plor), station 5 (Amol Bridge) and station 6 (Sorkhrood bridge) belong to the Department of Environment and stations 2 to 4 (Panjab, chelav and kore sang) belong to the regional water authority. The coordinates of these stations are represented in Table 1.



Fig. 3. Satellite map of locations of sampling sites in Haraz river.

Table 1. Coordinates of sampling stations along the Haraz river.

Stations	Coordinates				
Sorkhrood Bridge	4058924,46 m N	628923,34 m E			
Amol Bridge	4032785,00 m N	621121,00 m E			
Kore sang	4015171,00 m N	622876,00 m E			
Chelav	4011495,00 m N	622958,00 m E			
Panjab	3995278,00 m N	614182,89 m E			
Poloor	3967558,01 m N	595367,08 m E			

2.2. Qual2k model

There are several models for analysis and investigation of the deviation of dissolved oxygen concentration and organic load in rivers. Finding a suitable model depends on the aim of the study. In this regard, choosing the simplest model that has an acceptable application in desire research is the best criterion. Qual2k model is the last version of Qual models, which has developed at Tufts University and has broad application in water quality simulation of rivers. Regarding model capabilities in considering different existing phenomena, parameters and living organisms, Qual2k is the most comprehensive model. The Qual2k model can analyze uncertainties and solve relating equations in the river in both steady and semi-dynamic (For simulating qualitative parameters along the river, is dynamic but flow and point and non-point sources of pollution are considered constant). For the first time, Streeter and Phelps proposed

a mathematical equation based on the reduction of organic load or BOD or increasing dissolved oxygen concentration, which became the basis for self-purification calculation. According to their proposed equation, as organic load enters the river, due to turbulence, it absorbs oxygen of water and consequently, organic load lessened, or self-purification occurs in the river (Chapra. 2005).

Streeter–Phelps equation determines the relationship between dissolved oxygen concentration (DO) and biological oxygen demand (BOD) over time as a first-order linear differential equation (Eq. 1).

$$\frac{dD}{dt} = K_1 L_t - K_2 \tag{1}$$

This differential equation expresses oxygen deficit changes (D) as the difference between deoxygenation and reaeration rates over time. In this equation, D (g/m3) is calculated as the difference between the saturated dissolved oxygen and dissolved oxygen concentrations by the (Eq. 2):

$$D = DO_{sat} - DO$$
(2)

Also, K1 is the deoxygenation rate (d-1), K2 is the reaeration rate (d-1) and Lt is oxygen deficit over time (Brouwer and Martin-Ortega et al. 2015). The qual2k model can simulate dissolved oxygen, biological oxygen demand, temperature, acidity, suspended solids, different phosphors and nitrogen and algae in the river. This model could adequately consider other qualitative parameters including required

oxygen by precipitation along the river, precipitation of carbonaceous materials, nitrification and denitrification.

2.3 NSFWQI

National Sanitation Foundation Water Quality Index (NSFWQI) is applied to obtain the water quality level, depend on nine parameters such as DO, BOD, total solids, turbidity, nitrate, total phosphate, temperature, pH, and Fecal Coliform. Each NSFWQI parameter has its weighting factor (Wi), which describes the significance of the effect of each parameter in the calculation. The weighting factor of each parameter has been used for NSFWQI calculating. NSFWQI is obtained as (Eq. 3):

$$NSFWQI = \sum W_i I_i$$
(3)

where, li represents the corresponding quality (0-100 from proper subindex graph) for each and Wi expresses the weight factor of each parameter. The value of the NSFWQI is between 0 and 100, which rates the water quality to excellent (90-100), good (70-90), moderate (50-70), bad (25-50) and very bad (0-25) conditions (Hoseinzadeh and Khorsandi et al. 2015).

2.4 IRWQI

IRWQI is another surface water quality index that was introduced by the Iranian Environmental Protection Agency and derived from

Estuary St Caspian Sea Very High Vulnerability lamshidie TC High Vulnerability Haraz Self-Purification Power Zone High Vulnerability KareSang St High Vulnerabilit Legend If Purificat Self Purification Mediun High Very High Low Vulnerability Basin

Fig. 4. The general zoning map of the self-purification capacity of the Haraz river.

Fig. 5a shows trends of dissolved oxygen changes in the Haraz river for the spring season. In the upstream of the river owing to the low concentration of pollutants and lower saturated dissolved oxygen due to high temperature and elevation from free water level, the concentration of the observed dissolved oxygen and saturated dissolved oxygen are close. As we go downstream of the river, due to the higher discharge of point and non-point pollution sources to the river, higher temperature and decrease of elevation from free water level, there is a considerable difference between dissolved oxygen and saturated dissolved oxygen. According to Fig. 5a, around upstream stations, the river has acceptable quality, but after Panjab station, which is located 80 km from upstream of the river, there is a noticeable decrease in dissolved oxygen concentration. The main reasons for this reduction are wastewater from fish farming and sand extraction workshops as point sources of pollution and discharge of agricultural runoffs and rural sewage to the river as non-point sources. Although some of the streams which enter the Haraz river may have better quality than the main river, most of the streams entering Haraz river have a high level of pollution from rural sewage.

Between Mian dasht and Amol city stations, the number of pollution increases, which is caused by broader human activities in riverside and consequently increasing wastewater and runoff from Amol city, agriculture farms and rural areas. After a diversion dam in about 40 kilometers downstream of the river, the flow of the river considerably decreased. Reduction of river speed and flow, increasing human activity alongside river and augmentation of agricultural runoff and rural and urban sewage result in increasing pollution load in this region (after diversion dam to river estuary). Thus, the pollution load and oxygenation coefficient in the downstream of the river are increased and consequently, the self-purification capacity and accumulation of pollutants decrease in this area. The results of the model spring season depict that critical points of Haraz mostly occur in

downstream of the river and after diversion dam. The most oxygen drops relative to saturated dissolved oxygen is assessed at the downstream of the river and close to the river estuary. In this location, the lowest dissolved oxygen concentration is estimated to be 3.5 mg/L and the amount of oxygen deficiency 5.5 mg/L. The main reason for this deficiency is a sharp decline of river speed at the estuary, which almost the minimum pace throughout the river course that causes a reduction in aeration and indeed lower self-purification capacity of the river. The result of modeling revealed that from Amol Bridge station to the river estuary, the concentration of DO is critical and in spring season downstream of the river was considered a critical region. Thus, the concentration of DO after the diversion dam is not appropriate for most aquatic life. Fig. 5b represents the trend of dissolved oxygen change along the Haraz river in the summer. The concentration of dissolved oxygen in summer in the whole of river length is lower than spring and especially at the estuary of the river, it reaches its lowest amount, which is 3 mg/L. This amount shows the critical condition of the river at this location, which requires improvement. Although the amount of oxygen deficiency relative to saturated dissolved oxygen at upstream of Haraz river is about 1 to 2 mg/L, in the downstream of the river, this deficiency reaches 5 mg/L. According to the information mentioned above, Haraz river experience more critical conditions in summer rather than spring and its selfpurification capacity considerably decreased. Also, critical points take place in midstream and downstream of the river after Panjab station in the range of Amol and Chelav cities where a significant amount of pollution load enters the river. The changes in dissolved oxygen concentration during autumn are depicted in Fig. 5c. Although DO concentration is below 6 mg/L n this season, it does not fall lower than 4 mg/L and, in most of the river, is around 5 mg/L, which shows a higher self-purification capacity of Haraz river in autumn rather than summer. The decline of dissolved oxygen concentration in 30 km from



NSFWQI. Using this index is an appropriate approach for the determination of water quality due to the natural condition in Iran's water resources. IRWQI is determined according to (Eq. 4) and (Eq. 5).

$$IRWQI = \left[\prod_{i=1}^{n} I_{i}^{W_{i}}\right]^{\overline{\gamma}}$$
(4)

where;

$$\gamma = \sum_{i=1}^{n} W_i \tag{5}$$

Like NSFWQI, li and Wi are the quality and the weight factor of each parameter. The index is classified by a relative scale which indicates water quality from very bad to excellent (excellent (> 85), good (70.1-85), relatively good (55.1-70), moderate (45-55), relatively bad (30-44.9), bad (15–29.9), very bad (< 15) (Mirsaeedghazi. 2017).

3. Results and discussion

The results of the model for self-purification in different segments of the river are represented in Fig. 4. Since the hydrological and ecological condition of the river is a variant in different seasons, the result of the model is expressed distinctly for each season.

upstream of the river to the estuary is due to precipitations in autumn and increase of runoff from non-point sources of pollution such as downstream farms. More precipitation in autumn, enhance rural and urban runoff, which therefore increase dissolved oxygen concentration drop around Chelav and Amol cities. Hence, in the downstream of the Haraz river, the critical condition is dominant. Despite the pollution sources in the upstream of the river, upstream of Haraz river is not in critical condition due to the high self-purification capacity of the river and the negligible accumulation of pollutants in this area.

In Fig. 5d, the trend of dissolved oxygen changes in the length of the Haraz river during the winter season is represented. In this season, the self-purification capacity of the river is better than other seasons and approximately is similar to the spring season. In upstream of the river, DO concentration is about 7 mg/L, which is acceptable in comparison to saturated DO, but in the midstream of the

river starts to decline. After Chelav station, as a result of the discharge of pollution load from around villages and other sources, the concentration of dissolved oxygen decreases and consequently, self-purification capacity is diminished, but it is above 5 mg/L before Amol city. Between Mian Dast (Amol city) and river estuary, due to the release of agricultural runoff and wastewater from Amol city and Jamshid Abad industrial area, a decrease in the amount of dissolved oxygen is observed but it is still above 4 mg/L. According to Fig. 6, around Sorkh Roud, Jamshid Abad industrial area and Amol city critical condition are prevalent in the winter season and upstream of the river has a more favorable condition. The values of parameters of quality for all seasons and each stations are presented in Tables 2. According to these parameters NSFWQI and IRWQI index was calculated and brought to Table 2.



Fig. 5. Dissolved oxygen changes during different seasons in Haraz river, (a) Spring, (b) Summer, (c) Autumn and d) Winter.

Table 2. The values of parameters of quality for all seasons and each stations.									
Station	рН	Turbidity	N-NO₃	PO₄	BOD	DO	Temp	Fecal Coliform	TSS
Spring									
Polur	7.7	563	3.74	0.35	13.6	7.4	9.6	1743	147
Panjab	7.7	1583	6.7	0.26	14	6.3	10	1966	163
Chelav	8.1	1544	9.36	0.207	12.6	6.2	12.3	1966	276
Karesang	7.8	1544	4.96	0.3	12.6	6.22	13.1	2400	309
Pole Kamarbandi	7.7	1546	8.72	0.31	12.66	6.22	15.4	1966	438
Sorkh Roud	7.79	2160	3.57	0.62	16	5.87	16.2	2400	465
Summer									
Polur	685	504	6.92	0.34	10	7.06	16.7	1400	115
Panjab	381	529	6.73	0.19	7.3	6.3	17.9	1750	132
Chelav	606	544	5.56	0.219	8.3	6.12	21.4	1966	202
Karesang	637	543	9.26	0.22	8.3	5.9	23	1966	237
Pole Kamarbandi	614	542	5.27	0.25	7.6	5.86	24.8	1966	303
Sorkh Roud	706	546	7.35	0.73	11.6	5.9	25.7	1966	349
			Α	utumn					
Polur	8.16	834	4.9	0.1	5.6	6.7	11.3	460	180
Panjab	7.9	1013	4.06	0.14	7.6	6.2	11.6	1500	213
Chelav	7.8	1306	4.8	0.189	10.3	6.1	12.9	2400	333
Karesang	7.9	1299	3.96	0.11	10.3	6.1	13.4	2400	361
Pole Kamarbandi	8.1	1320	2.46	0.13	10	6.06	14	2400	552
Sorkh Roud	8.01	1247	1.86	0.14	12.6	6.4	16.1	2400	597
Winter									
Polur	8	399	2.38	0.34	7.8	8.1	7	1023	232
Panjab	7.7	1138	5.06	0.14	10.5	7.7	11	1733	235
Chelav	7.7	1225	3.3	0.21	10.1	7.36	8	1966	462
Karesang	7.8	1231	3.8	0.26	10.1	7.3	8.5	1966	483
Pole Kamarbandi	7.97	1200	2.32	0.3	10.1	7.43	10	1966	687
Sorkh Roud	7.9	322	2.19	0.73	7.5	7.36	8.1	1966	754

As it is clear from Table 2, river water quality in most of the sampling stations based on NSFWQI and IRWQI index was classified as "medium" and relatively bad, respectively. The higher value of NSFWQI and IRWQI for station polur is due to the low values of BOD, COD and fecal coliform, as well as higher dissolved oxygen than that

of the other stations. The results showed that as the elevation reduced along the river, the quality of water decreases. Also, during water deficit months at the end of spring and summer, when the flow of the river and the precipitation are low, the self-purification capacity and water quality of the river decrease. According to researches on water quality changes in the Takahashi and Kakioka rivers in Japan, the use of land around rivers has significant effects on the type and amount of pollution and its changes (Teraoka and Ogawa. 1984). For example, after Panjab station in the Chelav station and downstream areas as a result of the discharge of pollution load from around villages, the water quality and dissolved oxygen were decreased. Especially, due to agricultural activity and use of fertilizers, the concentration of nitrate and phosphate has increased in downstream areas. These results can be seen in the Tables 2-4.



Fig. 6. Map of the critical points and areas along the river of Haraz.

 Table 3. Results of NSFWQI values of each station for all seasons.

Station	NSFWQI						
Station	Spring	Summer	Autumn	Winter			
Polur	57	56	60	62			
Panjab	52	54	56	56			
Chelav	48	51	54	55			
Karesang	48	50	52	52			
Pole Kamarbandi	46	50	52	51			
Sorkh Roud	43	49	45	49			
Table 4. Results of IRWQI values of each station for all seasons.							
Station	IRWQI						
	Spring	Summer	Autumn	Winter			
Polur	42	44	47	47			
Paniab	41	44	44	44			

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4. Conclusions

Based on the results of the study, the water quality of Haraz river undergoes positive and negative variation, but ultimately it could be concluded that the more elevation decreased, the more the water quality deteriorated. The water quality and the self-purification capacity of the river are moderately acceptable only in the upstream stations and near Polur so that the NSFWQI value is 57-62 and the concentration of DO is higher than 6 mg/L in the whole year. As we get closer to the Caspian sea, due to the discharge of pollutants from different sources, the water quality reaches critical condition, especially near rural and urban areas. Around midstream and downstream of Haraz river, especially near Amol city, oxygen deficiency is significant and the self-purification capacity of the river diminished considerably. Also, the population growth and human activities in the watershed of Haraz river particularly development of villages, industrial areas, agricultural farms, fish farming and discharge of solid waste are the primary sources of different oxygen demand and biodegradable pollutants which alongside various chemical, mineral and hard degradable pollutants, have deteriorated the water quality of Haraz river in recent years. Among the wide range of pollution sources, human activities have the leading role and natural factors like low precipitation, seasonal precipitation, degradation of land use and soil, short duration and heavy precipitation, erosion and precipitation, which disturb natural biological activities of the river,

Chelav

Karesang Pole Kamarbandi

Sorkh Roud

intensify the destructive impacts of human activities. The implementation of a frequent monitoring program and strict environmental laws are practical approaches for sustainable development and increasing efficiency in the Haraz river.

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