

## ORIGINAL RESEARCH PAPER

# Spatio-temporal changes of water quality variables in a highly disturbed river

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**ABSTRACT:** Quality of river varies widely depending on the land use in the catchment and environmental factors. Many rivers in developing countries are unhealthy because they contain harmful physical, chemical and biological agents. Zanzanrud River, located in Zanzan Province, Iran, where recently faced human intervention needs a regular monitoring from upstream to downstream for sustainable management. Hence, the current study aimed to assess spatial and temporal variations of pollutant in Zanzanrud River in different stations from headstream to tail of the river. To achieve this goal, semi-monthly samples were collected from October 2015 to Jun 2016 at 5 stations along the river. The physicochemical variables were monitored and analysed using two-way analysis of variance. The results showed the highest values of suspended and dissolved solids and total solids ( $220.13\pm 5.57$ ,  $641.6\pm 39.63$  and  $793.6\pm 34.5$ mg/L respectively) were at the tail site in low-flow period. Nitrate-nitrogen and nitrate were also highest ( $5.39\pm 0.244$  and  $23.90\pm 10.85$  mg/L) at the middle of the river where was vicinity to farm lands. The values of pH and dissolved oxygen ranged from 6 to 8.15 and 0.5 to 4mg/L respectively with the highest values in high-flow period at most of the study sites. The maximum and minimum values of electrical conductivity (1439 and 256 $\mu$ s/cm) were recorded at tail site and headstream site respectively. Hardness had an increasing trend from upstream to downstream ( $189.60\pm 53.53$  to  $515.83\pm 64.77$ mg/L). Phosphorus was also lowest ( $0.09\pm 0.04$ mg/L) at upstream. Results illustrated the high degree of pollutant in studied river. So, an effective management of erosion, domestic waste and agricultural activities in watershed is highly recommended.

**KEYWORDS:** Hydrologic behaviour; Non-point source pollution; Physicochemical variables; Quality indicators; River management.

## INTRODUCTION

Throughout the history of human civilization, rivers have always been severely exposed to pollution owing to their easy accessibility to three major sources of pollution include industry, agriculture and domestic (AjjazBhat *et al.*, 2014). Industries, farms and cities have historically been located along rivers and discharged chemical waste into river. However,

by increasing human population, industrialization, anthropogenic activities and also uses of fertilizers and pesticides, pollutants have accumulated and reached to harmful levels in rivers and entered to the food chain (Patil *et al.*, 2012). Besides, natural processes, such as precipitation inputs, soil erosion, and weathering of rocks affect river water quality (Jarvie *et al.*, 1998). Water in rivers contains different types of floating, dissolved, suspended, microbiological and bacteriological impurities (Tiwari, 2015). Selection of variables in order to test the water quality exclusively

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depends on what purposes the water is used for and what extent is needed for its quality and purity. Some physical factors such as temperature, colour, pH, conductivity (EC), turbidity, total suspended solids (TSS), total dissolved solids (TDS) and etc. present the physical appearance of water. While, chemical tests such as alkalinity, total hardness, biochemical oxygen demand (BOD) and chemical oxygen demand (COD), dissolved oxygen (DO) and other characters are also required for monitoring the quality of water.

Rivers are heterogeneous at different spatial scale which may be attributed to a number of factors (Qadir et al., 2008). Thus, due to undesired changes in the physical, chemical and biological characteristics of rivers, monitoring river water quality is recently considered as the highest priority in environmental protection policies (Simeonov et al, 2002; Animesh and Saxena, 2011). Owing to importance of water quality rather than water quantity in the river system, many researchers have focused on throughout the globe during last two decades.

In this regards, Agbaire and Obi (2009) investigated the influence of seasonal changes on the properties of water in six different sampling points in Ethiopie River at Abraka, Nigeria. The seasonal variations of physiochemical variables of pH, temperature, conductivity, TDS, TSS, DO, BOD and heavy metals for both dry and wet seasons were assessed in six different sampling points. The results showed the differences between dry and wet seasons and the values were also within the World Health Organization (WHO) permissible limits. Bu et al. (2010) investigated the temporal and spatial variations of water quality in the Jinshui River (China) using multivariate statistical techniques and gridding methods. Two-way analysis of variance (ANOVA) showed that 25 studied water quality variables had significant temporal and spatial variability ( $p < 0.01$ ). This result confirmed the influence of domestic sewage and agricultural runoff discharged from Jinshui Town and agricultural lands from the watershed study area. Further, Eneji et al. (2012) investigated the spatial and temporal variation in 14 water quality variables at ten different locations along 0.7% of total length of River Benue, which located at Nigeria, for three seasons. They used multivariate analysis of variance in order to explore the spatial-temporal variations. They stated that there was no significant difference between the stations but there was on seasons. While,

Ogah et al. (2013) also analysed 13 physicochemical variables in 24 samples collected from six states of north central of Nigeria in wet and dry seasons. They indicated that there were significant differences between physicochemical variables in wet and dry seasons. Bassey et al. (2015) also statistically analysed quality variables of monthly collected samples along Calabar River in Nigeria from January to December. The results illustrated the usefulness of multivariate statistical techniques for analysis and interpretation of water quality assessment.

Zanjanrud River is an appropriate example of such human intervention (Shirdeli and Nasiri, 2014). Effluent and sludge discharged into this river are more than its self-cleaning capacity by recipient ecosystems and therefore ends in the accumulation of pollutants to problematic and toxic levels (Shahmoradi et al., 2013). On the other hand, quantity of the river is a seasonal phenomenon and largely affects by climate within the watershed (Davaranah and Abdi, 2007). The seasonal variation in precipitation which cause the variation in surface runoff, interflow, ground water flow, and pumped in and out flows also have a strong effect on the concentration of pollutants in this river (Shahmoradi et al., 2013). In spite of high importance of the Zanjanrud River, very few studies have tried to investigate the quality of this river. In this regards, Davaranah and Abdi (2007), based on data collection from library, stated that pasteurized milk factory and animal slaughter were the major contaminate industries which caused more than 94% of water contaminating of the Zanjanrud River. Shahmoradi et al. (2013) evaluated some variables such as pH, EC, TDS, temperature, some cations and anions in different points along the part of the Zanjanrud River. They stated that the values of cations and anions were within the WHO permission limits. Shirdeli and Nasiri (2014) also compared the water quality of the part of the Zanjanrud River with National Sanitation Foundation (NSF) index. According to their study, the quality of the Zanjanrud was classified fair to poor class.

Review of literatures demonstrated the importance of water quality monitoring in watershed scale. Due to spatial and temporal variations in river water characteristics, a comprehensive monitoring plan which includes frequent water sampling at several station from upstream to downstream can provides a typical, representative and trustworthy assessment of

the water quality for decision makers to design suitable management in the watershed (Boyacioglu *et al.*, 2005). However, no significant and regular monitoring and also spatial and temporal analysis has been ever done along the whole of the Zanjanrud River from the head to tail considering the land use effects which is a vital necessity for controlling pollutants in many seriously polluted rivers (Liu *et al.*, 2016). As pollutant loading to the Zanjanrud River is continuously increasing by anthropogenic activities, a major monitoring is essential for ecosystems of the Zanjanrud watershed. Thus, the aim of this study is to assess present status of quality of the Zanjanrud River in different stations from head to tail to present concrete measures for its sustainable management. This study has been carried out in Zanjanrud River in Zanjan Province of Iran in 2015-16.

## MATERIALS AND METHODS

### *Description of the study area*

The Zanjanrud River is one of the longest rivers in Zanjanrud watershed bounded by latitude 36° 15' N to 37° 14'S and longitude 47° 66' E to 48° 59' W with a total area of 4616 km<sup>2</sup>. The river with a total length of 127 km passes through the south of the city of Zanjan (capital of the Zanjan Province) and inflows into Qizil Ūzan River flowing in north-western and northern Iran. The Zanjanrud River which is considered as the life line of the city, drains a large area of high socioeconomic importance and provides water for both domestic and agricultural purposes. The climate of the study region is typically Mediterranean with hot and dry summer and rainy winter (Davarpanah and Abdi, 2007). So, hydrological conditions of the river during the hot and wet periods are quite different. The region has a wet season from November to March, with about 73% of the annual rain falls, with peak of the rainfall in February. The annual rainfall and temperature were about 297.1 millimetre (mm) and 11.1 centigrade degree (°C) in 2016 respectively. The last 20-year average and the peak flow in Sarcham hydrometric station (at 47° 53'E and 37° 07'N) were recorded 1.36 and 171 cubic meter per second (m<sup>3</sup>/s) respectively.

From geological point of view, this area overlap with Zanjan sub geomorphologic unit. A sequence of conglomerate, marl and sandstone somewhere with gypsum lenses incompatibly cover the Eocene pyroclastic rocks along the Zanjanrud watershed.

Geological evidences indicate that the Neogene sediments are accumulated in an inter-mountainous depression in upstream of the basin. Also, mineralization of copper, lead, zinc and kaolin are associated with hydrothermal alteration halos placed in volcano-clastic rocks of Eocene.

The area of about 45 square kilometre (km<sup>2</sup>) of the total watershed is urban region and serves as a recipient of urban sewage. Wastewater discharges from urban, industrial sources, and cultivation activities in this river is reported by Shahmoradi *et al.* (2013) as about 81191 cubic meter per day (m<sup>3</sup>/day). In recent decades, lack of precipitation, well digging and excessive pumping cause a significant reduction of water in stream. Thus, the river dries during the summer from July to September. However, the water level increases during winter and spring with peak of discharge in February (Davarpanah and Abdi, 2007).

### *Sampling Stations*

Five stations were chosen along the river from upstream to downstream based on some factors such as uniform flow in x-section, well-mixed flow, accessibility and its distance to the road, channel stability, distribution of point source pollution and land use effects. The location of study area, Zanjanrud watershed and monitoring stations are observed in Fig. 1. Moreover, geology and land use maps of Zanjanrud watershed are presented in Fig. 2. Station one (St1) located about 3.26 km downstream from the source of the river is a tourist spot with a calm and serene environment. The station is placed at Zakeer between latitude 36° 38' 50"N and longitude 48° 43' 14"E with altitude of 1894 m. It is the head station which considered as a baseline (AjjazBhat *et al.*, 2014, Bassay *et al.*, 2015). As the wastes which flow into the river from this site is insignificant, this site is assumed to be unpolluted. The water channels are clean and very little industrial and agricultural activities occurs at the river bank.

Station two (St2) is the first discharge point which receives effluents from Zanjan city. Off-loading of food product, Livestock and poultry slaughter, carwash and carpet cleaning and some other industrial wastes are also drained into the river. This station is located about 37.153 km downstream from St1 at Chiar between Latitude 36° 43' 44"N and Longitude 48° 18' 38"E at 1515 m altitude.

Station three (St3) is the second discharge point

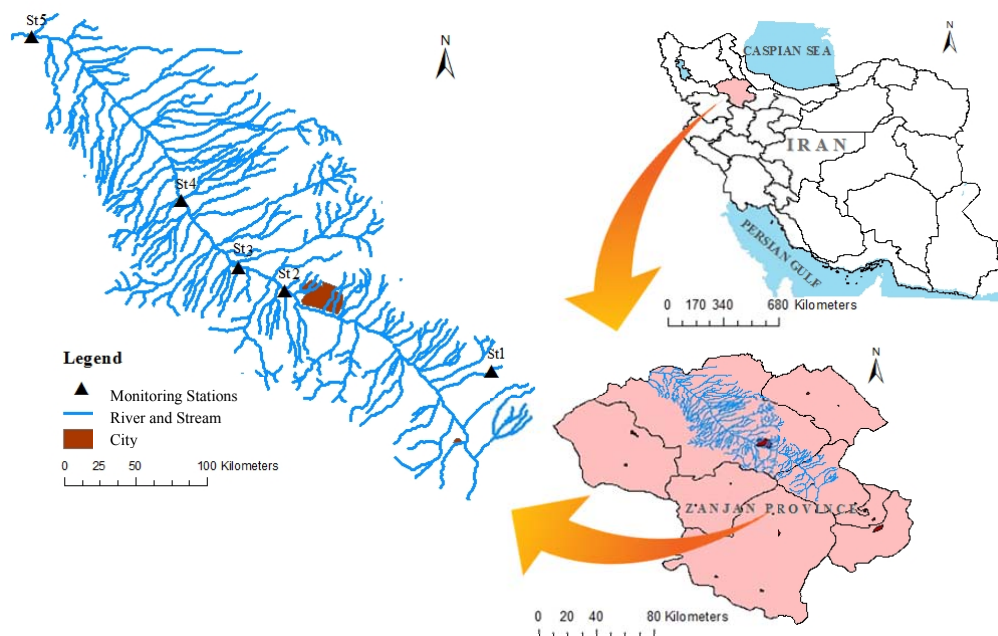


Fig. 1: Location of the study area with respect to Zanjanrud watershed and monitoring stations along the Zanjanrud River

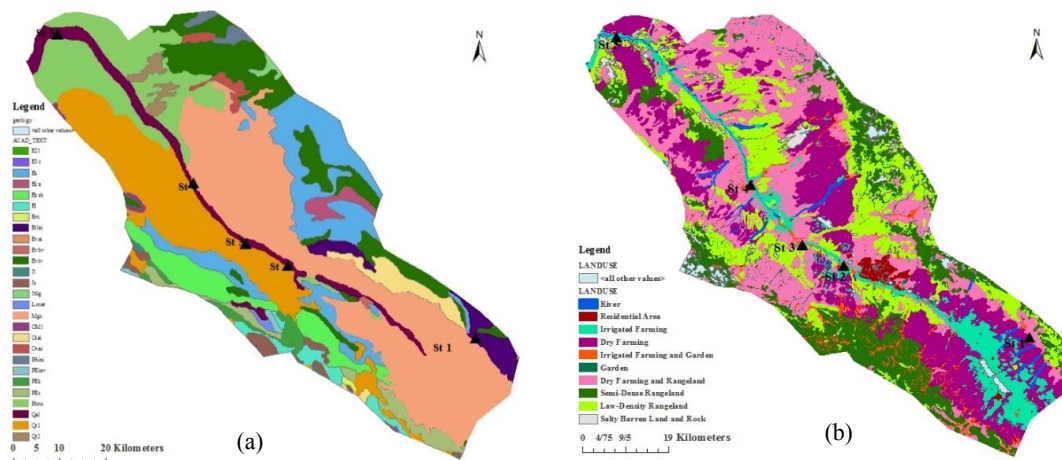


Fig. 2: Map of geology (a) and land use (b) details of Zanjanrud watershed

located at Yengeje with distance of about 8.9 km from St2, between Latitude  $36^{\circ} 45' 37''N$  and Longitude  $48^{\circ} 15' 40''E$ , where anthropogenic effluents from rural regions and agricultural and industrial wastes also empty into the river.

Station four (St4) is placed about 12.19 km downstream of St3, between Latitude  $36^{\circ} 50' 47''N$  and Longitude  $48^{\circ} 10' 36''E$  at 1388 m altitude, where the fishing activities are predominate.

Station five (St5) was chosen at the tail of the river with the distance of about 38.1 km from St4 between Latitude  $37^{\circ} 7' 26''N$  and Longitude  $47^{\circ} 53' 12''E$  at 1150 m altitude.

#### Sampling and preparation

The surface river water samples were collected semi-monthly (more frequently during high flow periods than during low flow periods) from October

2015 to Jun 2016 at five different stations between 10.00 A.M. to noon. It should be noticed that, whereas the river is generally dry during July to September period, almost one complete year of data was collected. All water samples were collected in three points over the width of each channel cross section from each of the sampling sites and from different depths using depth-integrated and equal-width increment (EWI) methods (Myers, 2006). Stopper-fitted polyethylene bottles initially labelled were used for sample collection. It was ensured that the plastic bottle used for sampling was packed by tape to make the sample free from air contact (Alam *et al.*, 2010). The water samples were kept at 4°C for laboratory investigations. Chemical tests were performed in the laboratory of Zanjan Department of the Environment. Some physical variables such as width of cross sections, depth of flow, channel discharge, flow velocity, water temperature, pH and dissolved oxygen (DO) were determined on the spot, while the variables includes total suspended solid, total solid, chemical oxygen demand, total phosphorus, nitrate-nitrogen, nitrate, chloride and total hardness were determined in the laboratory by standard methods developed by American Public Health Association (APHA, 1998). As well, the HACH AMES IOWA (DR19100) photometer was used in order to measure colour of water in this study. It can accurately determine the colour of filtered samples within a 0 to 500 PCU (Platinum Cobalt Units) range. Moreover, conductivity and total dissolved solid were measured using conductivity/TDS meter 86505. Turbidity was also recorded by The HACH 2100P Turbidimeter.

The monitoring variables were selected based on conventional variables of Iran water quality index for surface water resources (IRWQIsc).

### Statistical Analysis

Prior to investigating the seasonal effect on water quality variables, the whole observation period was divided into two different hydrological periods of high water (November, December, January, February and March) and low water (April, May, Jun, July, August, September and October).

Descriptive analyses of physicochemical variables of samples were summarized in Table 2. In order to understanding spatiotemporal variations between five stations and two periods in the study river, statistical analysis of the collected data were interpreted using two-way analysis of variance to determine the level of significance among the measured variables. Therefore, Duncan test which is more powerful than methods performing all possible pairwise comparisons in order to compare one group to each of the others was employed to separate the means for variables which had significant differences (Day and Quinn, 1989). Spearman correlation test was analysed to identify the association between pairs of variables for sampling stations and the results were presented in Table 4 (Sharma and Chhipa, 2016). For data analysis the softwares of microcomputer statistics written in C programming language (MSTAT-C) (Shokati and Zehtab-Salmasi, 2014) and statistical package for the social sciences (SPSS16.0) were used. The data was then compared with Food and Agriculture Organization (FAO) standard in order to interpret the quality of Zanjanrud water for irrigation. The Guidelines for interpretations of water quality for irrigation based on FAO Standards (Ayers and Westcott, 1994) were summarized in Table 1. In addition, an index of water quality was calculated for each station and period based on the weight of each variable in water quality and then the stations were classified into the water quality classes.

Table 1: Guidelines for interpretations of water quality for irrigation (FAO Standards)

Variable	Degree of Restriction on Use		
	None	Slight to Moderate	Severe
Total dissolved solids (mg/L)	< 450	450 – 2000	> 2000
Conductivity (µs/cm)	700	700-3000	>3000
pH	Normal Range 6.5 – 8.4	-	-
Total Hardness (mg/L)	0-460	-	-
Nitrate-Nitrogen (mg/L)	< 5	5 – 30	> 30
Phosphate-phosphorus (mg/L)	0 – 2	-	-
Chloride (mg/L)			
-surface irrigation	< 142	142 – 355	> 355
-sprinkler irrigation	< 106.5	> 106.5	



*Water Quality Index*

Water quality index of Zanjanrud River along two high-flow and low-flow periods at five stations were determined by Iran water quality index for surface water resources-conventional parameters (IRWQIsc) based on the Eq. 1.

$$IRWQIsc = \left[ \prod_{i=1}^n I_i^{w_i} \right]^{\frac{1}{\gamma}} \quad (1)$$

Where:  $\gamma = \sum_{i=1}^n w_i$

$W_i$  refers to the weight of parameter  $i$ ,  $n$  is the number of parameters,  $I_i$  also refers to the sub-index value of each parameter based on ranking curves (Sadeghi et al., 2016).

IRWQIsc is classified into seven classes of "very bad" (IRWQIsc<15), "bad" (IRWQIsc15-29.9), "rather bad" (IRWQIsc30-44.9), "medium" (IRWQIsc45-55), "rather good" (IRWQIsc55.1-70), "good" (IRWQIsc70.1-85) and "very good" (IRWQIsc>85). The classification of water quality based on IRWQIsc values was presented in Table 5.

**RESULTS AND DISCUSSION**

Annual mean and monthly average discharge of the Zanjanrud River at different stations were presented in Fig. 3.

The mean values of physicochemical variables at selected sampling stations in the Zanjanrud River during the period of October 2015 to Jun 2016 are presented in Table 2. Maximum surface water velocities were recorded in March at all the stations

and minimum values were observed at the beginning of the summer. Discharge values also were higher (3.67±0.9 m<sup>3</sup>/s) at St5 during wet season and lower at St1 (0.09±0.03 m<sup>3</sup>/s) during dry season. The highest values of Total suspended solids, total dissolved solids and total solids (220.13±5.57, 641.6±39.63 and 793.6±34.5 milligram per litre (mg/L) respectively) were recorded at the tail site (St5) in low-flow period. Total suspended solids, dissolved solids and total solids values were almost lower in high-flow period in upstream. Poor vegetation cover, high agricultural activities and inappropriate management are potential factors that cause much runoff and soil loss (Khalik et al., 2013). Consequently, more pollutants with dissolved conducting minerals are transferred from the farms to the river (Khalik et al., 2013). Thus, the concentrations of nitrate-nitrogen and nitrate were highest (5.39±0.244 and 23.90±10.85 mg/L) in low-flow period at St3 where was vicinity to farm lands and N-P-K fertilizers or chicken dung (Wan Abdullah et al., 2005) were common to apply for agricultural activities (Shirdeli and Nasiri, 2014) and lowest (1.11±0.31 and 4.91±1.40 mg/L) at St1 which were similar to results reported by Wu et al. (2009) and AijazBhat et al. (2014). Finding result was shown that present annual mean of concentration of nitrate is much higher than previous data (2.7 mg/L) as recorded by Davarpanah and Abdi (2007). The more land is converted into agricultural site, the more pollution of nitrate is expected to be increased in recent years.

Recorded data of water temperature, pH, and dissolved oxygen confirmed a seasonal cycle during the period of study. Maximum water temperature

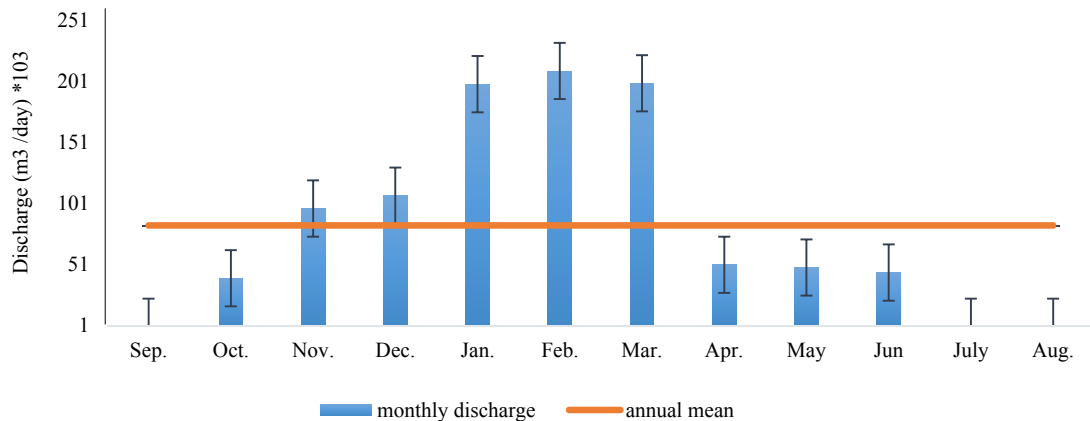


Fig. 3: Annual mean and monthly average discharge of the Zanjanrud River at different stations

Table 2: Descriptive statistics of water quality data under low-flow and high flow conditions

Variables	Periods	Station 1	Station 2	Station 3	Station 4	Station 5
Depth of Flow (m)	High flow	0.21±0.04	0.36±0.02	0.40±0.01	0.23±0.02	0.40±0.07
	(Min-Max)	(0.10-0.33)	(0.27- 0.40)	(0.35 - 0.45)	(0.16- 0.28)	(0.18- 0.55)
	Low flow	0.07±0.01	0.12±0.01	0.22±0.00	0.14±0.00	0.29±0.00
	(Min-Max)	(0.05-0.10)	(0.12- 0.14)	(0.22-0.23)	(0.14 -0.15)	(0.29- 0.30)
Flow Velocity (m/s)	High flow	0.87±0.12	1.01±0.03	1.06±0.02	0.81±0.03	1.03±0.12
	(Min-Max)	(0.54- 1.15)	(0.89- 1.08)	(1.01- 1.14)	(0.68-0.90)	(0.64- 1.26)
	Low flow	0.43±0.05	0.60±0.01	0.68±0.07	0.63±0.01	0.54±0.19
	(Min-Max)	(0.36 -0.54 )	(0.59- 0.64)	(0.54 - 0.82)	(0.61- 0.66)	(0.34-0.93)
Discharge (m <sup>3</sup> /s)	High flow	0.74±0.22	1.77±0.14	1.59±0.13	1.61±0.2	3.67±0.9
	(Min-Max)	(0.13-1.37)	(1.38-2.15)	(1.38-2.10)	(0.91-2.12)	(1.04-6.01)
	Low flow	0.09±.03	0.36±.07	0.66±.12	0.76±.03	1.05±.04
	(Min-Max)	(0.01-0.13)	(0.29-0.58)	(0.51- 1.05)	(0.67-0.83)	(0.99-1.12)
Total suspended solids(mg/L)	High flow	75.21±72.38	38.17±5.47	55.38±17.53	86.49±30.14	307.38±165.61
	(Min-Max)	(0.10-364.69)	(30.89-59.87)	(29.38-124.67)	(38.65-205.47)	(42.15-911.50)
	Low flow	2.52±1.05	106.70±72.2	100.32±49.06	93.61±19.38	220.13±5.57
	(Min-Max)	(0.94-4.53)	(21.34-322.79)	(49.89- 247.52)	(70.38-151.53)	(211.79-230.70)
Total dissolved solids (mg/L)	High flow	156.2±11.32	530.2±23.76	534±22.73	531±26.57	633.8±35.07
	(Min-Max)	(129-187)	(479-591)	(489-593)	(483-597)	(500-708)
	Low flow	229.6±1.2	549.7±18.4	521.5±20.8	535.7±21.49	641.6±39.63
	(Min-Max)	(228-232)	(513-593)	(498- 584)	(500-598)	(592-720)
Total solid (mg/L)	High flow	232.16±76.1	557.84±27.3	571.03±38.5	548.66±24.6	737.15±92.8
	(Min-Max)	(131.35-533.69)	(510.78-650.87)	(495.5-708.6)	(490.13-605.11)	(507.45-1073.89)
	Low flow	234.63±2.2	643.03±91.6	611.06±74.1	653.39±86.0	793.6±34.5
	(Min-Max)	(231.10-238.72)	(519.78-915.79)	(509.8- 831.5)	(534.17-908.86)	(727.25-843.70)
pH	High flow	6.49±0.04	6.70±0.22	6.99±0.22	7.54±0.22	7.63±0.15
	(Min-Max)	(6.41-6.62)	(6.00-7.16)	(6.56-7.72)	(7.15-8.10)	(7.35-8.15)
	Low flow	6.33±0.18	6.97±0.13	6.86±0.16	6.93±0.12	7.18±0.02
	(Min-Max)	(6.09-6.70)	(6.76-7.34)	(6.62- 7.34)	(6.58-7.15)	(7.13-7.23)
EC (µs/cm)	High flow	337.6±33.79	1070.4±43.1	1073.4±43.15	1069.6±50.4	1249.0±70.03
	(Min-Max)	(256-461)	(969-1181)	(972-1185)	(963-1193)	(1001-1415)
	Low flow	459.6±2.33	1112.7±34.0	1099.2±35.82	1122.2±29.9	1412.3±13.38
	(Min-Max)	(456-464)	(1025-1183)	(1006- 1169)	(1052-1193)	(1397-1439)
Colour	High flow	4.58±1.83	20.60±2.99	15.40±2.94	12.40±1.07	9.60±1.12
	(Min-Max)	(1.1- 10)	(14- 30)	(8- 25)	(10-15)	(6- 13)
	Low flow	4.00±2.64	63.00±12.03	46.00±11.71	23.75±5.66	12.33±1.20
	(Min-Max)	(0- 9)	(40-95)	(25- 76)	(12- 39)	(10-14)
Turbidity (NTU)	High flow	6.94±1.72	12.60±4.57	17.77±6.78	12.43±1.18	522.22±275.8
	(Min-Max)	(1.17-11.20)	(7.87- 30.90)	(5.93- 43.50)	(9.10- 15.60)	(42.10- 1000)
	Low flow	0.96±0.12	9.05±2.01	19.37±13.05	14.79±8.78	99.52±29.43
	(Min-Max)	(0.74- 1.18)	(3.97-12.40)	(4.64- 58.50)	(4.58- 41.10)	(40.76- 132.00)
Dissolved oxygen (mg/L)	High flow	3.74±0.12	1.17±0.22	2.20±0.30	2.63±0.37	2.79±0.41
	(Min-Max)	(3.40- 4.10)	(0.60- 1.73)	(1.16- 2.80)	(1.24- 3.46)	(1.32- 3.87)
	Low flow	3.05±0.21	0.86±0.26	1.81±0.46	2.15±0.60	1.75±0.35
	(Min-Max)	(2.70- 3.43)	(0.50- 1.65)	(0.90- 3.10)	(1.03- 3.80)	(1.16- 2.40)
Water temperature (°C)	High flow	6.11±1.31	9.14±0.67	12.20±1.72	13.67±1.66	14.41±1.65
	(Min-Max)	(2.40- 9.96)	(6.90- 10.65)	(8.00- 16.98)	(8.60- 16.90)	(8.90- 17.50)
	Low flow	11.64±0.29	15.77±2.15	18.71±1.05	19.87±1.39	21.77±1.46
	(Min-Max)	(11.09- 12.09)	(10.00- 20.40)	(16.00- 21.03)	(17.00- 23.60)	(19.02- 24.00)
Chemical oxygen demand (mg/L)	High flow	18.04±7.41	119.36±13.57	75.45±10.88	44.92±10.33	37.71±14.23
	(Min-Max)	(0.40 - 36.16)	(78.00- 151.87)	(37.61- 105.59)	(16.00- 78.11)	(0.90- 67.62)
	Low flow	14.83±6.50	106.61±43.28	92.63±41.06	18.59±3.86	7.99±1.52
	(Min-Max)	(4.77- 27.01)	(37.33 -217.67)	(29.54- 202.57)	(8.97- 27.80)	(5.14- 10.33)
Total hardness (mg/L)	High flow	189.60±53.53	303.20±48.62	321.40±42.61	338.20±33.97	478.10±96.57
	(Min-Max)	(89.00-354.00)	(170.00-445.00)	(183.0-393.0)	(207.00- 394.00)	(239.00- 712.50)
	Low flow	296.66±64.95	317.37±73.39	309.00±63.05	332.00±69.09	515.83±64.77
	(Min-Max)	(185.00-410.00)	(101.0-427.50)	(121.0-390.00)	(133.00- 450.00)	(429.00- 642.50)
Nitrate (mg/L)	High flow	4.91±1.40	8.09±0.70	10.13±1.36	10.78±1.69	17.19±3.99
	(Min-Max)	(0.18- 8.40)	(6.37- 10.14)	(6.59- 14.50)	(4.63- 14.40)	(3.75- 27.55)
	Low flow	6.57±2.76	8.15±2.75	23.90±10.85	11.07±3.19	18.43±2.25
	(Min-Max)	(1.09- 9.83)	(1.17- 12.99)	(1.36- 51.05)	(1.57- 15.12)	(15.36- 22.83)
Nitrate-nitrogen (mg/L)	High flow	1.11±0.31	1.82±0.15	2.08±0.43	2.43±0.38	3.88±0.90
	(Min-Max)	(0.04- 1.90)	(1.44 - 2.29)	(0.79- 3.27)	(1.05- 3.25)	(0.85- 6.22)
	Low flow	1.48±0.62	1.84±0.62	5.39±0.24	2.49±0.72	4.16±0.50
	(Min-Max)	(0.25- 2.22)	(0.27- 2.93)	(0.31 - 11.52)	(0.35- 3.41)	(3.47- 5.15)
Phosphate-phosphorus (mg/L)	High flow	0.09±0.04	1.14±0.13	1.01±0.12	0.82±0.11	0.36±0.08
	(Min-Max)	(0.05 - 0.26)	(0.79 - 1.41)	(0.67 - 1.36)	(0.57 - 1.25)	(0.21- 0.67)
	Low flow	0.10±0.04	0.25±0.03	0.75±0.14	0.38±0.05	0.15±0.01
	(Min-Max)	(0.05- 0.19)	(0.20-0.37)	(0.32 - 0.92)	(0.22-0.46)	(0.13- 0.18)
Chloride (mg/L)	High flow	35.78±3.59	117.83±6.16	118.25±6.15	125.08±8.33	142.98±8.21
	(Min-Max)	(23.43- 42.60)	(99.40-134.40)	(99.40- 134.90)	(99.40- 149.10)	(125.32- 170.70)
	Low flow	17.50±2.06	93.10±2.69	98.12±1.44	104.50±1.73	126.36±11.38
	(Min-Max)	(14.20 - 21.30)	(88.75- 100.90)	(95.67- 101.60)	(100.60- 108.20)	(113.80- 149.10)

values were recorded in the low-flow period at St5 ( $21.77 \pm 1.46^\circ\text{C}$ ) and low values were recorded in high-flow period at St1 ( $6.11 \pm 1.31^\circ\text{C}$ ). The values of pH ranged from 6 (St2) to 8.15 (St5) with the highest values in high-flow period and the lowest in low-flow period at most of the study sites (except St2). The pH values at the St4 and St5 of the stream showed a decreasing trend from high-flow to low-flow season. While upstream values were slightly high during the low-flow season rather than high-flow season. AijazBhat et al. (2014) who studied on Sukhnag stream in Kashmir Himalaya also reported similar results.

There was a progressive increase in conductivity from upstream to downstream at all the sampling sites. The maximum and minimum value of conductivity of 1439 and 256 micro Siemens per centimetre ( $\mu\text{S}/\text{cm}$ ) were recorded in low-flow season at the tail site (St5) and the headstream site (St1) respectively. The higher value of conductivity is attributed to the high degree of agricultural runoff and domestic effluent discharges. There was no defined trend in variation of mean value in turbidity among the periods, but the values slightly increased from head stream to tail of the river.

Dissolved oxygen ranged from 0.5 at St2 to 4 at St1. Although dissolved oxygen values were generally higher at the head of the river, but the lowest values of dissolved oxygen referred to St2 where effluents of Zanjan City and industrial wastes were released into the river. There was however an increasing trend

in dissolved oxygen values at all the sampling sites during the transition to rainy period as observed in Table 2. The utterances given by Khalik et al. (2013) proved the same finding. There was fluctuated variation of chemical oxygen demand observed in sampling sites. However, St2 and St3 were seen to be the most contaminated area with chemical pollutant. As observed in Table 2, total hardness were also higher in high-flow period at St1, St2 and St5 with an increasing trend from upstream to downstream (from  $189.60 \pm 53.53$  mg/L at St1 to  $515.83 \pm 64.77$  mg/L at St5).

Contrarily to nitrate status, mean concentration of phosphate in the Zanjanrud River was slightly increased during high-flow season rather than low-flow season which were similar to results reported by Khalik et al. (2013). Total phosphorus concentration was highest ( $1.14 \pm 0.13$  mg/L) in December at St2 and lowest ( $0.09 \pm 0.04$  mg/L) in January at St1. Phosphate concentrations point out the presence of anthropogenic pollutants (AijazBhat et al. 2014). According to Filik Iscen et al. (2008) and Ugwu and Wakawa (2012), domestic wastewaters and industrial discharges, particularly those containing detergents and fertilizer runoff, or changes in land use in areas where phosphorous is naturally abundant in the soil would be lead the higher levels of phosphates in the water column.

The results indicated that colour of water was highest ( $63.00 \pm 12.03$ ) at St2, where it turned to green

Table 3: Analysis of variance for physicochemical variables in the Zanjanrud River

Source	Station	Time	Error	Total	Coefficient of Variation (%)
Degree of freedom	4	1	4	9	
Flow velocity (m/s)	0.014 <sup>ns</sup>	0.363**	0.007 <sup>ns</sup>		10.73
Discharge (m <sup>3</sup> /s)	1.00 <sup>ns</sup>	4.39*	0.31 <sup>ns</sup>		45.77
Total suspended solids (mg/L)	10777.06**	1698.59 <sup>ns</sup>	337.63 <sup>ns</sup>		20.51
Total dissolved solids (mg/L)	57905.57**	867.39 <sup>ns</sup>	535.69 <sup>ns</sup>		4.76
Total solid (mg/L)	76558.15**	8345.33*	791.41 <sup>ns</sup>		5.04
pH	0.310*	0.182 <sup>ns</sup>	0.042 <sup>ns</sup>		2.97
EC ( $\mu\text{S}/\text{cm}$ )	248009.82**	16503.90*	1725.49 <sup>ns</sup>		4.15
Colour	457.52 <sup>ns</sup>	748.27 <sup>ns</sup>	171.77 <sup>ns</sup>		61.92
Turbidity	35846.41 <sup>ns</sup>	18341.94 <sup>ns</sup>	17755.99 <sup>ns</sup>		186.19
Dissolved oxygen (mg/L)	1.45**	0.83*	0.04 <sup>ns</sup>		9.33
Temperature ( $^\circ\text{C}$ )	27.30**	103.87**	0.22 <sup>ns</sup>		3.28
Chemical oxygen demand (mg/L)	3628.67**	300.62 <sup>ns</sup>	180.34 <sup>ns</sup>		25.05
Total hardness (mg/L)	17771.69*	1970.51 <sup>ns</sup>	1167.40 <sup>ns</sup>		10.05
NO <sub>3</sub> (mg/L)	57.12 <sup>ns</sup>	28.94 <sup>ns</sup>	17.01 <sup>ns</sup>		34.58
NO <sub>3</sub> -N (mg/L)	2.79 <sup>ns</sup>	1.63 <sup>ns</sup>	0.98 <sup>ns</sup>		37.21
PO <sub>4</sub> -P (mg/L)	0.20 <sup>ns</sup>	0.32 <sup>ns</sup>	0.05 <sup>ns</sup>		47.08
Cl (mg/L)	3439.05**	1006.63**	4.64 <sup>ns</sup>		2.20

\*, \*\*, <sup>ns</sup>: significant at  $p \leq 0.01$ ,  $p \leq 0.05$  and non-significant respectively.



during dry and hot season. This may be due to the fact that Algae use from the high amount of phosphate and nitrate and other substances and multiply rapidly. This massive growth of algae leads to pollution. When the algae die they are broken down by the action of the bacteria which quickly multiply, using up all the oxygen in the water (Hill, 2005). Thus, as mentioned above, the dissolved oxygen reached to the lowest level at St2 during hot and dry season. Clarke (2002) and Liu *et al.* (2016) were reported the same findings.

Results also showed that chloride was the dominant anion observed in the study river and ranged between  $17.50 \pm 2.06$  mg/L at St1 in low-flow season and  $142.98 \pm 8.21$  mg/L at St5 in high-flow season. Meanwhile, chemical oxygen demand concentrations ranged between  $7.99 \pm 1.52$  mg/L at St5 during low-flow period and  $119.36 \pm 13.57$  mg/L at St2 during high-flow period. As observed in Table 2, the concentration of chemical oxygen demand had a decreasing trend from high-flow to low-flow period. The highest values of this variables referred to St2 which showed high degree of pollutant. This condition was highly expected in this station duo to its vicinity to residential area, farm lands and industrial centres.

The results of analysis of variance for physicochemical variables in the Zanjanrud River monitored at five stations were summarized in Table 3. Multivariate analysis of variance was used to determine the significant difference between water quality variables from upstream to downstream of the river within the two hydrological periods. The results showed significant variations at P value of

0.01 for the stations and periods for two variables of water temperature and chloride (Table 3). As the sum of squares of water temperature were meaningfully different at all five stations, it was divided into five levels of St5<sup>a</sup>, St4<sup>b</sup>, St3<sup>c</sup>, St2<sup>d</sup> and St1<sup>e</sup> which "a" referred to maximum value and "e" stated for minimum value (Fig. 4). However, Duncan's test showed that the variable of chloride did not vary from St2 to St3 and both were so set into level of "c" (Fig. 4). Dadi-Mamud *et al.* (2014) also found significant difference for water temperature between different seasons and stations at value level of 0.05. Also total solid, conductivity and dissolved oxygen were significantly varied both spatially ( $P < 0.01$ ) and temporally ( $P < 0.05$ ). As observed in Table 3, the variables of total suspended solids, total dissolved solids and chemical oxygen demand had strong meaningfulness differences along the river from upstream to downstream ( $P < 0.01$ ). However, they didn't show any significant difference during the time. Results in Fig. 4 showed that the variable of total dissolved solids was statistically different at St1<sup>c</sup>, St4<sup>b</sup> and St5<sup>a</sup>. The variable of chemical oxygen demand was also divided into two levels of "a" and "b" which was implied that there was no significant difference between St1<sup>b</sup>, St4<sup>b</sup>, St5<sup>b</sup>. Moreover, pH varied along the river with interactions between stations of St5<sup>a</sup>, St4<sup>ab</sup>, St3<sup>abc</sup> and St1<sup>c</sup>, St2<sup>bc</sup>, St3<sup>abc</sup> ( $P < 0.05$ ). Total hardness also varied at tail site (St5<sup>a</sup>).

Meanwhile, by scrutinizing in Table 3 and Fig. 4 significant variation is seen for flow velocity and river discharge during the time of study which were similar

Table 4. Spearman correlation (r) test for physicochemical variables in the Zanjanrud River

Variables	TSS	Q <sub>w</sub>	TDS	TS	pH	EC	colour	turbidity	DO	T (°C)	COD	TH	NO <sub>3</sub>	PO <sub>4</sub> -P	Cl
TSS	1/00														
Q <sub>w</sub>	0/64	1/00													
TDS	0/47	0/38	1/00												
TS	0/41	0/25	0/90**	1/00											
pH	0/76*	0/66*	0/78*	0/64	1/00										
EC	0/41	0/25	0/90**	1/00*	0/64	1/00									
colour	-0/32	-0/09	0/25	0/36	0/08	0/36	1/00								
turbidity	0/60	0/56	0/65*	0/79*	0/70*	0/79*	0/19	1/00							
DO	0/28	-0/01	-0/47	-0/52	-0/09	-0/52	-0/81*	-0/26	1/00						
T (°C)	0/28	-0/08	0/71*	0/85*	0/52	0/85*	0/45	0/60	-0/49	1/00					
COD	-0/41	0/20	-0/05	-0/05	-0/03	-0/05	0/73*	0/03	-0/56	-0/15	1/00				
TH	0/70*	0/53	0/88*	0/78*	0/94**	0/78*	0/09	0/72*	-0/22	0/71*	-0/19	1/00			
NO <sub>3</sub>	0/48	0/25	0/58	0/77*	0/65*	0/77*	0/35	0/85*	-0/32	0/84*	-0/02	0/73*	1/00		
PO <sub>4</sub> -P	-0/07	0/58	0/08	0/05	0/30	0/05	0/53	0/33	-0/41	-0/02	0/72*	0/19	0/25	1/00	
Cl	0/76*	0/85*	0/71*	0/60	0/90**	0/60	-0/02	0/79*	-0/15	0/37	0/01	0/87*	0/61	0/43	1/00

\*, \*\*, ns: significant at  $p \leq 0.01$ ,  $p \leq 0.05$  and non-significant respectively.

to results reported by Dadi-Mamud *et al.* (2014). Nevertheless, there were insignificant difference for the variables of colour, turbidity, nitrate and phosphate-phosphorus within both periods and stations. The spatial variations of water quality variables and the results of comparison of means at different stations along the studied river were presented in Fig. 4

Whereas, Dadi-Mamud *et al.* (2014) found significant differences in phosphate-phosphorus and nitrate-nitrogen concentrations in both the time and stations in their study.

Statistical comparison among different selected stations using Duncan test was presented in Fig. 4. Duncan test revealed that water temperature significantly

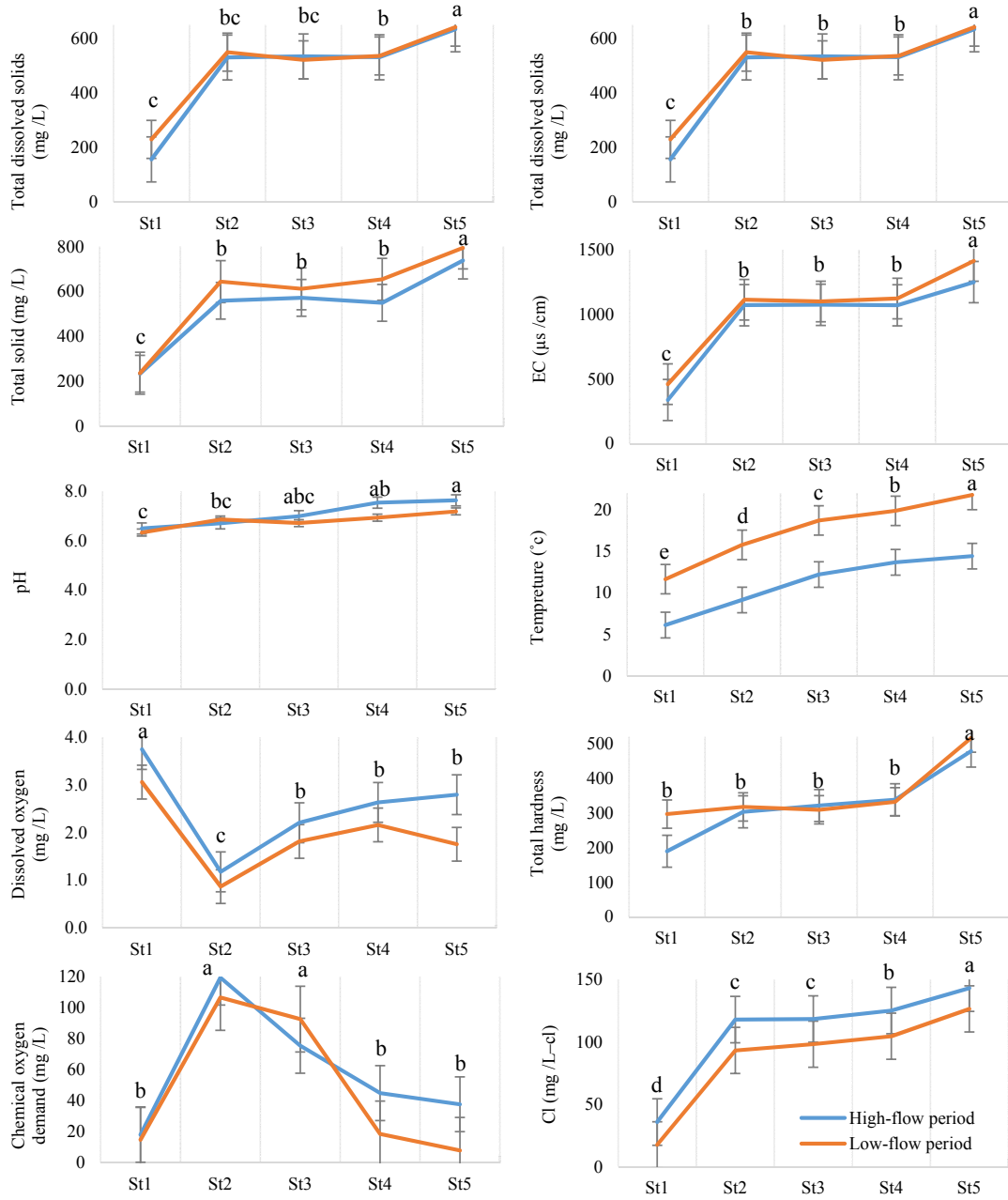


Fig. 4: Comparison of means and spation variations of physicochemical variables from upstream to downstream (the Zanjanrud River)

Table 5: The values of IRWQISC for all monitoring stations in Zanjanrud River

Station	High-flow period		Low-flow period	
	IRWQI <sub>SC</sub>	Class	IRWQI <sub>SC</sub>	Class
St1	61.62	Rather good	54.13	Medium
St2	19.19	Bad	24.11	Bad
St3	22.20	Bad	14.59	Very bad
St4	25.43	Bad	28.23	Bad
St5	15.45	Bad	20.22	Bad
Mean IRWQI <sub>SC</sub>	28.78	-	28.26	-

increased from upstream to downstream. While, total hardness from St1 to St4 didn't show any significant difference, but St5 showed meaningful difference with other stations. Means of the total dissolved solids, total solids and conductivity were respectively placed St5, St2 to St4 and St1 into class level of 'A', 'B' and 'C'. Kavian *et al.* (2016) reported the similar results. The mean values of chemical oxygen demand at St2 and St3 showed significant difference with other monitored stations. Dai *et al.* (2015) and Liu *et al.* (2016) also stated that sewage discharge from urban and rural regions is still the most important cause of water pollution. The results also indicated that the dissolved oxygen was significantly the highest at St1. Whereas, St3 to St5 showed insignificant difference in dissolved oxygen and were placed into class level of 'B'. Dissolved oxygen is in fact the most important indicator of water quality and is essential for the survival of all aquatic organisms. As well, St2 and St3 were ranked in the same class of 'C' for chloride. Other stations were significantly difference for this parameter. However, the highest and lowest ranks were referred to St5 and St1 respectively. Regarding to variables of total suspended solids and pH, St2, St3 and St4 were the sources of differences by Duncan test (Fig. 4). Overall, significant degree of spatial and temporal variations in the concentration of water quality variables was observed using two-way analysis of variance in this regards. Comparing the results with the standards of irrigation presented in Table 1 showed that the Zanjanrud River has no potential water quality problems about variable of phosphorus. However, the variables of pH was slightly lower than standard at St1 in low-flow period and at St2 in high-flow period. Likewise, Results showed a slight to moderate restriction on use for irrigation about total dissolved solids at St5 and nitrate nitrogen at St3 respectively. The variable of chloride has also moderate restriction for sprinkler irrigation at all stations except St1.

The results of calculating the values of IRWQI<sub>SC</sub> for all monitoring stations in both periods were presented in Table 5. As seen in Table 3, IRWQI<sub>SC</sub> was in the ranges from 61.62 at St1 in high-flow period to 14.59 at St3 in low-flow period.

The results showed that the water quality index of St1 and St3 decreased in low-flow period. Whereas, the water quality index of St2, St4 and St5 increased in dry season. It was implied that meteorological parameters such as rainfall has negative influenced on deterioration the water quality at the parts of the river where were near the residential area and farmlands. So, much more pollutants were carried out into the river. However, the mean water quality index in low-flow period with the value of 28.26 was slightly lower than mean water quality index for high-flow period with the value of 28.78. Generally, since the water quality index introduced the present status of Zanjanrud River as polluted river, an integrated and comprehensive management is highly recommended.

## CONCLUSION

Analysis of variance and comparison of means of physicochemical variables at different station, it could be construed that the river water quality primarily influenced by effluents of residential area, industrial centres and agricultural runoff disposed directly or indirectly into the river. The increasing level of pollution at St2 and St3 indicated progressive anthropogenic pressure to the river in these sites. Land use changes either legal or illegal, inefficient and poor management, low awareness of local community and unplanned and uncontrolled development cause that the present environmental conditions of the Zanjanrud watershed are already stressed, along the whole river. It can be also concluded that present the Zanjanrud River water quality has degraded from high-flow to low-flow period and also from headstream to tail of the river. Considering the IRWQI<sub>SC</sub> Index calculated for monitoring stations and complex

variation in water quality across time and space, an effective management of soil erosion from land use change, domestic waste and agriculture activities in the vicinity of the watershed should be planned and enforced. However, this study shall provide a scientific support for water pollution control and help in the decision making process and providing a holistic watershed management plan to survive and recover the quantity and quality of this important stream. In order to reduce the degree of pollutant of this stream, setting up of sewage treatment system in the residential and industrial areas and regulating the use of excessive fertilizers in cultivation activities are highly recommended.

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#### CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

#### ABBREVIATIONS

°C	Centigrade degree
$\mu\text{s/cm}$	Micro siemens per centimetre
A.M.	Ante meridiem
ANOVA	Analysis of variance
APHA	American Public Health Association
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
Cl	Chlorine
DO	Dissolved oxygen
E	East
EC	Electrical conductivity
Eq.	Equation
EWI	Equal-width increment
FAO	Food and Agriculture Organization
IRWQIsc	Iran water quality index for surface water resources
km	Kilometre
km <sup>2</sup>	Square kilometre
m	Meter
Max.	Maximum

<i>m/s</i>	Meter per second
<i>m<sup>3</sup>/day</i>	Cubic meter per day
<i>m<sup>3</sup>/s</i>	Cubic meter per second
<i>mg/L</i>	Milligram per litre
<i>Min.</i>	Minimum
<i>mm</i>	Millimetre
<i>MSTAT-C</i>	Microcomputer statistics written in C programming language
<i>N</i>	North
<i>NO<sub>3</sub></i>	Nitrate
<i>NPK</i>	Nitrogen phosphorus potassium
<i>ns</i>	Non-significant
<i>NSF</i>	National sanitation foundation index
<i>NTU</i>	Nephelometric turbidity units
<i>p</i>	P-value
<i>PCU</i>	Platinum cobalt units
<i>pH</i>	Potential hydrogen
<i>PO<sub>4</sub></i>	Phosphate
<i>r</i>	Correlation coefficient
<i>S</i>	South
<i>SPSS</i>	Statistical package for the social sciences
<i>St</i>	Station
<i>T</i>	Temperature
<i>TDS</i>	Total dissolved solids
<i>TH</i>	Total hardness
<i>TS</i>	Total Solid
<i>TSS</i>	Total suspended solids
<i>W</i>	West
<i>WHO</i>	World Health Organization

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