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Evaluation of Bartin river water quality index and suitability as irrigation water with physicochemical parameters

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ABSTRACT

In this study, it was aimed to determine the water quality of Bartin River and its usability as irrigation water. In order to evaluate the change of water quality according to the precipitation the samples were collected from 4 points in December and July months. pH, NO₃, SO₄, Cl⁻, total phosphorus (TP), chemical oxygen demand (COD), suspended solid (SS), turbidity, some cations and metals were analyzed in the collected samples. The assessment of physicochemical parameters was made according to the Surface Water Quality Regulation. It was determined that SS and turbidity parameters increased after precipitation and 98% of turbidity was caused by SS. Cl⁺, Na⁺, K⁺, Ca⁺², Mg⁺², SO₄⁻², TP were determined higher in the dry period. Although COD, total dissolved solid (TDS), electrical conductivity (EC), NO3 were higher in the rainy season, the difference between the two periods is not much. According to the water quality index, water quality was poor at all sampling points during the rainy season. In the dry period, good quality was also determined at only 1 sampling point. COD is the parameter with the greatest effect on effective weight and water quality. Irrigation water suitability was evaluated with the indexes sodium adsorption ratio (SAR), (EC), %Na, magnesium ratio (MR), Kelly index (KI), potential salinity (PS) and total hardness (TH). River water is suitable as irrigation water in both periods according to SAR, %Na, MR, KI indexes. However, since the potential salinity (PS) value is greater than 3 μ eq/L at the SP4 in the dry period, it is not suitable as irrigation water. Its total hardness value is >180 mg/L, so it is in the very hard water class.

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INTRODUCTION

Water resources are an important part of the ecological system and one of the natural resources necessary for the survival of humans and other living things [1, 2]. Today, as a result of rapid industrialization and rapid population growth, increasing domestic and industrial discharges and

agricultural activities cause deterioration of water quality in natural water resources [3]. Water quality is closely related to human health, and organic compounds, toxic metals, nutrients, suspended solids and pathogens in water are important parameters that affect water quality [4]. Agricultural activities (excessive use of fertilizers), industrial and domestic wastewater discharges are the main

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causes of nitrogen and phosphorus pollution in natural waters [5, 6]. Heavy metals are another type of pollutant found in natural waters and cause environmental problems by accumulating in the food chain [7]. The most important metals in terms of water pollution are zinc (Zn), arsenic (As), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), nickel (Ni) and chromium (Cr). Heavy metals enter the river system through natural and anthropogenic activities [8]. The most important anthropogenic sources are industrial discharges, domestic wastewater, metal-containing fertilizers and pesticides [9, 10]. Since heavy metals cannot be decomposed in nature, they accumulate in animals and humans and cause undesirable effects. As, Pb, Cd are highly toxic even at low concentrations [11, 12]. Protection of water quality is also important in terms of determining the usability of river water as irrigation water. Irrigation water quality affects soil structure and plant growth. Especially in arid environments, low precipitation amount, high evaporation and use of inappropriate irrigation water cause salinity problem in soils [13] and excessive salinity causes soil degradation [14]. The chemical components in the irrigation water affect the plant in different ways, such as having a direct toxic effect on the plant, causing the plant to be without nutrients, or preventing the plant from taking nutrients from the soil [15, 16]. For this reason, irrigation water quality should be determined by different indexes such as electrical conductivity (EC), potential salinity (PS), sodium adsorption rate (SAR), sodium percentage (%Na), Kelly's Index (KI), magnesium ratio (MR). In this study, it was aimed to determine the water quality of the Bartin River with physicochemical parameters. Physicochemical water quality parameters were analyzed in water samples taken from different points of the river in rainy and dry periods, and the water quality index was calculated and the water quality classes were determined. The assessment of physicochemical parameters was made according to the Surface Water Quality Regulation (SWQR) [17]. In addition, the suitability of river water as irrigation water was evaluated by using indexes defined in the literature such as sodium adsorption rate, sodium percentage, magnesium ratio, potential salinity, Kelly's index.

MATERIALS AND METHODS

Sampling Area

Bartin River is located within Bartin Province in Turkey. Bartin is located in the western Black Sea Region and has a rugged geography. Its heights are covered with mountain rows reaching 1736 meters. The mountains are very steep, steep and rocky towards the beaches, although not high. The average rainfall is 69.3 mm and 111.3 mm for the summer and winter seasons. Sampling locations are shown in (Fig. 1) [18]. SP1, SP2 (water dept ≈ 2 m) and SP3 sampling points are located in the area of the river passing through the city center. At these three points, domestic wastewater discharges are effective. SP4 sampling point is on a different tributary of the river. At this point, water depth and bed width are higher (>5 m) than other points [18].

Sample Collection and Analysis

Water samples were collected immediately after heavy rain and snowfall in winter, in December, when the water level and flow rate increased. In the summer season, the samples were collected in July, when the rains were very ineffective and the river water level and flow rate decreased. Water samples were collected in high density polyethylene bottles. Bottles were washed within a solution of 10% nitric acid followed by repeated rinsing with distilate water and finally rinsing with ultrapure water prior to sampling [18]. Details on heavy metal analyzes have been explained in detail in the author's previous work [18]. For physicochemical analyzes, water samples were collected in accordance with the ISO 5667-3: 2018 [19] method. Before the water samples were collected, the plastic bottles were rinsed 3 times with distilled water and 1 time with sample water. All physicochemical analyzes were performed in accordance with the American Public Health Association Method [20]. Nitrate and sulfate analyzes were performed by UV VIS Spectrophotometer (HACH Lange 6000 DR) device according to spectrophotometric method, and chloride and COD analyzes were performed by titrimetric method. Turbidity was determined by the turbidimeter (Hach 2100 Q Portable Turbidimeter) according to the nephelometric method, and the color was determined by the Hach Lico 620 device according to the photometric method. pH, electrical conductivity, total dissolved solids (TDS) values were measured with Hanna (HI 9812-5) multi parameter probe. Suspended solid (SS) analysis was done by gravimetric method.

Evaluation of Data

River water quality was evaluated with the water hazard index [21] and water quality indexes [22]. The usability of river water as irrigation water was evaluated by sodium adsorption rate (SAR), magnesium ratio, sodium percentage, Kelly's index (KI), potential salinity (PS), and total hardness (TH) and electrical conductivity (EC) indexes. All calculations were made with Microsoft Excel 2016 and SPSS 26 programs.

Suitability of River Water as Irrigation Water

Salinity causes deterioration of soil quality [23]. For this reason, the suitability of river water as irrigation water was evaluated with the indexes sodium adsorption ratio (SAR), electrical conductivity (EC), sodium percentage (%Na), magnesium ratio (MR), kelly's index (KI), potential salinity (PS) and total hardness (TH). The formulas of the indexes and water quality classifications are shown in Table 1.

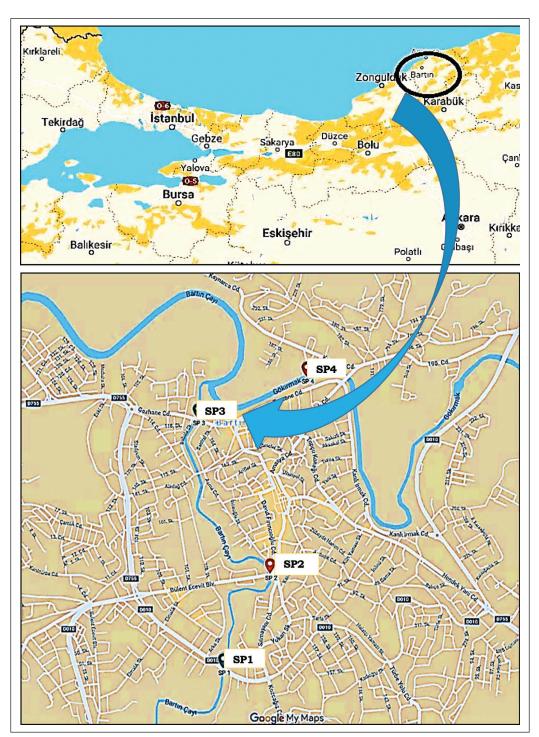


Figure 1. Location of sampling points [18].

Water Quality Index

The water quality index is used to determine and evaluate water quality. The influence of many water quality parameters is reduced to a single value. In other words, the water quality index can be defined as an indicator of the combined effect of many water quality parameters [30]. The WQI value calculated for each sampling point allows the sampling points to be classified according to different quality categories. Different water quality indexes have been used in the literature [22, 31]. In this study, WQI was calculated according to equation (1) [22]. The grading of water quality according to water quality indexes is shown in Table 2.

$$WQI = \sum SI_i \tag{1}$$

Index	Formula	Classification	Reference
Kelly Index	$KI = \frac{Na^{\pm 1}}{Ca^{\pm 2} + Mg^{\pm 2}}$	<1 safe	[24]
	$cu^{-} + My^{-}$	>1 unsafe	
Sodium adsorption ratio (SAR)	$Na^{\pm 1}$	<10 excellent	[25]
	$SAR = \frac{Na^{+1}}{\sqrt{\frac{Ca^{+2} + Mg^{+2}}{2}}}$	10–18 good	
	$\sqrt{2}$	18–26 doubtful	
		>26 unsuitable	
Sodium percentage (%Na)		<20 excellent	[26]
	$\% Na = \left(\frac{Na^{+} + K^{+}}{Ca^{+2} + Mg^{+2} + K^{+} + Na^{+}}\right)$	20-40 good	
	× 100	40-60 permissible	
		60-80 doubtful	
		>80 unsuitable	
Magnesium ratio (MR)	$MR = \frac{Mg^{+2} \times 100}{Ca^{+2} + Mg^{+2}}$	<50 suitable	[27]
	$MK = \frac{1}{Ca^{+2} + Mg^{+2}}$	>50 unsuitable	
Potential salinity (PS)	$PS = Cl^{-} + 0.5SO_4^{-2}$	<3 suitable	[28]
	$PS = Ct + 0.55O_4^{-1}$	>3 unsuitable	
Total hardness (TH)	$TH = (2.497Ca^{+2}) + (4.11Mg^{+2})$	<60 soft	[29]
	$IH = (2.497Ca^{-2}) + (4.11Mg^{-2})$	60–120 medium hard	
		120–180 hard	
		>180 very hard	
Electrical conductivity (EC)		EC<250 excellent	[25]
		250–750 good	
		750–2000 permissible	
		2000-3000 doubtful	
		>3000 unsuitable	

Table 1. Quality indexes for irrigation water (concentrations of all parameters are meq/L except EC (µs/cm) and TH (mg/L)

$$WQI = \sum SI_i \tag{2}$$

Where, W_i : the relative weight of ith parameter, w_i : the weight of ith parameter [22, 32–35] (Table 3), n: the number of parameters.

$$q_i = \frac{C_i}{S_i} \times 100 \tag{3}$$

Where, q_i : quality rating of ith parameter, C_i : concentration of each chemical parameter in each water sample in mg/l, S_i : drinking water standard for each chemical parameter in mg/L except for conductivity (μ S/cm) and pH turbidity and colour. $SL = W_i \times a_i$ (4)

$$SI_i = W_i \times q_i \tag{4}$$

SI_i: Sub-index of ith parameter;

The effective weight of each water quality parameter was calculated according to equation (5) to determine the parameter that has the greatest effect on the water quality index.

$$EW_i = \frac{SI_i}{WQI} \times 100 \tag{5}$$

Where EW_i: Effective weight of i water quality parameter, SI_i: Subindex value of i water quality parameter.

Table 2. Water quality classification according to WQI values

WQI value	Water quality
<50	Excellent
50-100	Good water
100-200	Poor water
200-300	Very poor water
>300	Water unfit for drinking

Water Hazard Index

One of the indexes used to evaluate the impact of heavy metals on water quality is the water hazard index [21]. As shown in equation (6), this index is calculated by dividing the measured concentration of the metal by the maximum allowable value for drinking water [36]. According to the hazard index, the toxicity of water is categorized into 4 classes [21, 38]: WHI <5 (low to minimal toxicity), $5 \le$ WHI ≤ 10 (slightly toxic), $10 \le$ WHI ≤ 15 (moderately toxic) and WHI >15 (extremely toxic).

	Si [36, 37]	wi (weight)	Wİ (relative weight)	EW% rainy	EW% dry	Mean EW %
pН	8.5	4	0.100	7.39	7.5	7.45
TDS	1000	4	0.100	3.09	2.85	2.97
EC	2500	1	0.025	0.62	0.57	0.6
SO ₄ ⁻²	200	4	0.100	1.35	1.86	1.6
NO ₃ -	50	5	0.125	0.3	0.14	0.22
COD	10	4	0.100	80.38	77.81	79.09
Cl	250	3	0.075	0.15	1.46	0.8
Ca ⁺²	200	2	0.05	1.26	1.85	1.55
Mg^{+2}	30	2	0.05	0.8	1.78	1.29
Na+	200	2	0.05	0.16	1.04	0.6
K+	200	2	0.05	0.04	0.13	0.08
Mn	0.05	4	0.1	4.53	3.16	3.85
Cu	1	3	0.075	0.01	0.01	0.01
		Σ wi= 40	Σ Wi= 1.0			

Table 3. Weight factors, unit weight values and effective weights (EW) of water quality parameters

Concentrations of all parameters are mg/L except for pH, EC (µs/cm).

WHI =
$$\left\{\frac{AI}{0.2} + \frac{Fe}{0.3} + \frac{Mn}{0.05} + \frac{Cu}{1} + \frac{Zn}{0.3} + \frac{Cr}{0.05}\right\}/6$$
 (6)

RESULTS AND DISCUSSION

Evaluation of Physicochemical Water Quality Parameters The results of physicochemical water quality parameters are shown in Table 4. It was determined that the suspended solid (SS) and turbidity parameters increased considerably after precipitation and 98% of the turbidity was caused by suspended solids. Suspended solid concentrations were determined to be 14.5 mg/L and 41.5 mg/L for dry and rainy periods, respectively [18]. In the previous study, although the dry period concentration was higher than the rainy period, it was determined that there was no significant difference between the two periods [39]. For this reason, it is thought that the soil particles carried from the surrounding land together with the precipitation waters increase the SS and turbidity. In addition, topographic features (slope, altitude) can partially affect the transport of pollutants from diffuse sources to the river [40]. The fact that the mountains around Bartin are quite steep and the land is quite rugged may affect the transport of materials from diffuse sources to the river during the rainy season. At the same time, the increased water flow rate after precipitation may cause resuspension of compounds from the sediment to the water column, thus increasing suspended solids and turbidity [41]. The highest values for SS and turbidity in the rainy season were determined in SP4. This point is located at a point where soil transport from the surrounding land is effective.

Electrical conductivity (EC) is a parameter directly related to dissolved solids in water. Total dissolved solids include inorganic salts (calcium, magnesium, potassium, sodium, bicarbonate, chloride, sulfates) and dissolved organic matters [42]. Salts can be of geogenic origin (decomposition of rocks) as well as anthropogenic origin (domestic/industrial wastewater discharge) [43]. EC was determined as 730 µs/ cm in the dry period and 800 µs/cm after precipitation. According to the Surface Water Quality Regulation [17], the river is in the second quality water class in terms of EC. Although the average EC value is higher for the rainy season, there is no significant difference between the two periods. The highest average EC and TDS values were determined in SP4 in the dry period and in SP3 in the rainy period (Table 4). Precipitation waters can cause soil erosion and increase in the EC and TDS values in the river, and sometimes cause a decrease in these parameters with the effect of dilution [44]. In the dry season, the concentrations of EC, TDS, Na⁺, Cl⁻, K⁺, Ca⁺², SO₄⁻² were quite high in SP4 compared to other sampling points. This situation can be explained by the geological features of the river bed at this point. The same parameters were determined higher in SP 3 during the rainy period. This situation can be explained by 2 reasons: 1) due to the high flow rate, the compounds in the sediment move back to the water column 2) the composition of the soil particles carried around the sampling point. Contrary to this study, in a previous study in the river, TDS, EC values were determined to be higher in the dry period [39]. The difference between the results of both studies can be explained by the fact that the sampling points were different in this study and the rainy period samples were taken just after the precipitation.

	Dry period			Rainy period				Irrigation ^a guideline			
	SP1	SP2	SP3	SP4	Mean	SP1	SP2	SP3	SP4	Mean	
Suspended solid	24	9	12	13	14.5	35	39	37	55	42	
Temperature	26	25	26	26	26	6.0	6.0	6.0	7.0	6.3	
Turbidity	22.90	8.39	9.62	5.16	11.5	40	33	39	85	49	
Filtrate turbidity	0.33	0.81	0.29	1.09	0.6	1.06	0.50	0.88	2.32	1.19	
pН	8.20	7.90	7.90	8.30	8.1	8.30	8.50	8.30	8.60	8.4	8.5
EC	600	530	520	1270	730	660	570	1350	620	800	3000
TDS	290	260	260	640	363	330	290	670	310	400	2000
NO3 ⁻ N	0.17	0.17	0.13	0.17	0.16	0.37	0.34	0.36	0.38	0.36	10
SO ₄ ⁻²	40	40	40	70	48	48	37	35	27	37	960
Total phosphorus (TP)	0.10	0.29	0.20	ND	0.20	ND	ND	0.08	0.06	0.07	
COD	64	192	96	96	112.0	168	84	84	126	116	
Cl	18	20	22	196	64.0	15.0	6.93	4.50	2.50	7.2	1063
Na ⁺	28	26	26	135	54	8.79	8.68	9.19	6.24	8.2	919
K ⁺	6.50	6.42	5.22	8.43	6.6	2.22	2.20	2.39	1.53	2.1	2
Ca ⁺²	113	89.2	89.6	72.8	91.2	68	68.2	70	62	67	400
Mg^{+2}	12.2	9.58	8.85	23.5	13.53	5.86	5.77	6.12	8.14	6.47	60
Al	0.112	0.019	0.027	0.013	0.043	0.24	0.303	0.365	0.567	0.369	5
Fe	0.476	0.04	0.09	ND	0.202	0.307	0.323	0.41	0.47	0.378	5
Mn	0.017	0.013	0.043	0.00445	0.019	0.025	0.027	0.03	0.04	0.031	0.2
Ni	ND	ND	ND	ND	ND	0.009	ND	0.0058	0.0083	0.008	0.2
Cu	0.0029	0.0022	0.0043	ND	0.003	0.0018	0.0016	0.0021	0.0024	0.002	0.2
Zn	0.0062	0.0052	0.0117	ND	0.008	0.0072	0.0073	0.0076	0.0066	0.007	2

Table 4. Results of physicochemical parameters

a [15], All units are mg/L except pH, turbidity (NTU) and EC (µs/cm).

Sulphate was determined to be 47 mg/L and 37 mg/L for the dry and rainy periods, respectively. The most important sources of sulfate in surface waters are atmospheric storage, bacterial oxidation of sulfur compounds, and sulfate-containing fertilizers [45]. In addition, wastewater discharges and the degradation of sediment and organic materials in the soil can cause sulfate compounds [46]. In this study, the decreasing SO₄⁻² concentration during the rainy season can be explained by the diluting effect of precipitation.

Nitrogen and phosphorus are nutrients that cause eutrophication in surface waters [47]. In this study, NO₃⁻N was determined to be 0.17 mg/L and 0.36 mg/L for dry and rainy periods, respectively. Since NO₃⁻N is <3 mg/L, the river is in I. quality water class according to SWQR [17]. The seasonal variation of NO₃⁻N depends on the amount of precipitation and the residence time of the water [48]. The water solubility of nitrate is high [49]. The transport of soil particles to the river by erosion is generally considered to be the most important nutrient source for rivers [50]. For this reason, the high concentration determined for the rainy period in this study can be explained by soil erosion from agricultural areas and the transport of animal wastes stored in open areas to the river with rainfall waters. The absence of soil erosion in the dry period when the water temperature is high and the increase in the rate of biochemical reactions may cause a decrease in NO₃-N. It has also been reported by [51] that water temperature may have an effect on the decomposition rate of NO₃⁻. Again, in the rainy period, the transition of the compounds in the sediment to the water column may cause an increase in nitrate concentration. Reference [52] reported that the NO_3^{-1} concentration is higher in the summer season, when precipitation is effective, compared to the winter season. In the previous study in the river [39], it was reported that the NO₃⁻ concentration was 0.91 mg/L and 0.96 mg/L for the rainy and dry periods, respectively. For this reason, soil erosion and resuspension from the sediment to the water column during the rainy period are considered to be important.

Since the TP concentration was determined to be 0.2 mg/L and 0.1 mg/L for dry and rainy periods, respectively. According to SWQR [17], it is in the water class in the 2th quality class. Wastewater discharges and agriculture and livestock have been reported as the most important sources of phosphates [53]. In this study, domestic wastewater discharges, animal wastes and fertilizers are considered as the most important sources of total phosphorus. TP concentration could not be detected in SP4 during the dry period. It is a far point from wastewater discharges, and the depth and amount of water is higher than other points. The highest concentration in the dry period was determined in SP2 and SP3, where domestic wastewater discharges are intense. It is thought that detergents, which are the most important source of phosphorus in domestic wastewater, cause an increase in TP concentration in the dry period. Similar results have been reported by [48], and [52] in the literature. In the rainy season, it is thought that leaks from manure and animal wastes, which are defined as diffuse sources, will cause TP in the river. In the rainy season, it is thought that leakages from manure and animal wastes, which are defined as diffuse sources, cause TP in the river.

Chemical oxygen demand (COD) is the parameter used to determine organic pollution in waters [54]. In this study, the average COD concentration was determined as 112 mg/L and 116 mg/L for dry and rainy periods. According to SWQR [17], it is in the water class in the 4th quality class. Domestic wastewater discharges and natural organic substances carried by precipitation waters are considered as the causes of organic pollution in water. During the dry period, the highest concentration was determined in SP2. Domestic wastewater discharges are effective at this sampling point, and at the same time, the water depth and flow rate decrease in summer. COD concentrations in the rainy season were arranged as SP1>SP4>SP2=SP3. It is thought that natural organic materials carried into the river from the surrounding land during the rainy season affect the COD parameter [55]. The concentration of natural organic matter varies depending on many factors such as topography, season, flood, drought, and human activity [37]. In a previous study in the Bartin River, the rainy season concentration (115 mg/L) was slightly higher [39], and close to the concentration measured in this study. In another study conducted in the Aksu River, it was reported that the average COD concentrations for the rainy and dry periods were 28.81 mg/L (13.40-157.6 mg/L) and 32.55 mg/L (15.14-178.09) mg/L, respectively [56]. The mean concentrations for Pazarsuyu Stream (Giresun) and Karasu (Aksaray) and Coruh Rivers (Bayburt) were reported as 7.07 (1.54-17.67) mg/L [57], 9.42 (<10-45.38) mg/L [58] and 3.59 mg/L [59], respectively.

It has been reported that the COD concentration in the Umguza River (Zimbabwe), where wastewater discharges are made, varies in the range of 55–381.2 mg/L [53]. In a study conducted in the Nile river, COD was reported as

Table 5. W	VQI values	and quality	v classification
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Sampling point		/QI ainy	WQI Dry		
1	193	Poor	89	Good	
2	108	Poor	214	Very poor	
3	113	Poor	124	Poor	
4	153	Poor	133	Poor	

11.8 mg/L and 9.7 mg/L in winter and summer seasons, respectively [13]. It was determined to be 114.7 mg/L and 151 mg/L in the summer (rainy period) and winter seasons, respectively in Karnaphuli River (Bangladesh) [44].

Statistical Evaluation

It was determined whether there was a statistically significant difference between the concentrations determined for the rainy and dry periods at the sampling points. According to Shapiro-Wilk normality test, it was determined that Temperature (T), EC, TDS, NO3, Mg+2, Cl, Ni, Na+, Cu and Zn did not show normal distribution (p<0.05). In addition, since the Skewness-Kurtosis coefficients for T, EC, TDS, NO_{2}^{-} , Ni, Cu varied in the range of -2 and +2 [60, 61], these parameters were considered to have a normal distribution. It was determined that suspended solid (SS), turbidity, pH, SO₄⁻², Ca⁺², Al, Fe, TP, COD, K⁺, Mn showed normal distribution (p>0.05). According to the Mann-Whitney U test, the concentration difference between rainy and dry periods for Mg^{+2} , Cl^{-} , and Na^{+} was statistically significant (p<0.05), while for Zn it was insignificant (p>0.05). Independent Sample T-Test, which is a parametric test, was applied for other parameters. According to the independent sample T-test, the concentration difference between rainy and dry periods for suspended solid, turbidity, pH, Ca⁺², Al, K⁺, temperature and NO₂⁻ is statistically significant (p<0.05). The concentration difference between the two periods for Fe, Mn, TP, COD, EC, TDS is not statistically significant (p>0.05).

Evaluation of Water Quality Index

In order to determine the suitability of river water as drinking water, the water quality index was calculated in both periods and the results are shown in Table 5. According to WQI values, water quality was determined in the poor category at all sampling points during the rainy season. It was determined that the water quality was lower in SP1 and SP4. In the dry period, it was determined that it was good only in SP1, poor in SP3 and 4, and very poor in SP2. The effective weights (EW) of water quality parameters are shown in Table 3. The parameter with the highest EW value is COD (79%). Although the nitrate relative weight is the highest parameter, the EW value is low. These results show that COD, in other words organic pollution, is the main parameter affecting the water quality of the river.

	0	1 /			1
Rainy	SP1	SP2	SP3	SP4	Mean
SAR	0.27	0.27	0.28	0.20	0.26
KI	0.10	0.10	0.10	0.07	0.09
%Na	10.20	10	10.30	7.60	9.53
MR	12	12	13	18	13.75
PS	0.34	0.34	0.36	0.24	0.32
TH	194	194	200	189	194.25
EC	660	570	1350	620	800

Table 6. Irrigation water quality index values for the rainy season

Table 7. Irrigation water quality index values for the dry season

Dry	SP1	SP2	SP3	SP4	Mean
SAR	0.68	0.69	0.70	3.52	1.40
KI	0.19	0.21	0.22	1.05	0.42
%Na	17.4	19.6	19.6	52.2	27.2
MR	15	15	14	35	19.75
PS	1.10	0.99	1.01	5.22	2.08
TH	332	262	260	278	283
EC	600	530	520	1270	730

Evaluation of the Water Hazard Index

In order to evaluate the toxicity of heavy metals in river water, the water hazard index was calculated according to the concentrations of Al, Fe, Mn, Cu, Cr, Zn [18]. Since Cr could not be detected at any sampling point during the dry period, it was not included in the calculation. The water hazard index was calculated to be 0.23 (0.03-0.5) for the dry period and 0.83 (0.46–0.88) for the rainy period. The lowest WHI value in the dry period was determined for SP4. At this point, determination of only Al and Fe may result in lower WHI value. The highest WHI was determined in SP1 (WHI=0.5) and the contribution of Fe was higher. In the rainy period, on the contrary to the dry period, the highest WHI value (0.88) was determined in SP4 and the lowest in SP1 (0.46). The elements with the highest impact at both sampling points are Al and Fe, which is thought to be related to the transported soil particles carried into the river. It was determined that metals could cause minimal toxicity since WHI <5 determined for both periods. In a study conducted in Ghana, WHI values were reported in the range of 0.68-5.9 for surface waters [38].

Evaluation of Suitability as Irrigation Water

According to the irrigation water criteria, the K⁺ concentration exceeded the limit value (2 mg/L) at all sampling points. In the dry season, the average concentration (6.6 ml/L) is approximately 3 times the limit value (2 mg/L) (Table 4). For the rainy season, the average K⁺ concentration (2.1 mg/L) is acceptable at the limit value. All other parameters are suitable for irrigation water criteria (Table 4). When the suitability of EC values in terms of irrigation water was evaluated, it was determined that 3 of the sampling points for each period were good (EC=250-750 µs/cm) and one of them was permissible (EC=750-2000 µs/cm). In another study conducted in Porsuk and Felent Streams, 3 of the surface water samples in the rainy period and 5 in the dry period were determined to be of good quality [62].

The results of the irrigation water quality indexes are shown in Table 6 and Table 7. Concentrations of all parameters were used as meq/L in calculations except EC (μ s/cm) and TH (mg/L). Sodium percentage (%Na) is an index used to deter-

mine the sodium hazard in irrigation water [63]. Excess sodium in the irrigation water is adsorbed by the ion exchange points in the soil matrix, and as a result of this process, Ca⁺² and Mg+2 ions are released into the soil. This causes a decrease in the infiltration capacity of the soil [23]. For this reason, %Na is calculated to determine the suitability of water as irrigation water [26]. In this study, the average %Na was determined to be 9.5% and 27% for the rainy and dry periods, respectively. Since the %Na values were <20% at all sampling points during the rainy season, it was determined that the river water was of excellent quality as irrigation water at all sampling points. In the dry period, it was determined to be of good quality in SP4 and other permissible sampling points. In another study, the %Na value was reported as 20% for rainy and dry periods [62]. In the study conducted at 5 sampling points in the Murat River (Euphrates basin), it was reported that the %Na values varied between 23.1 and 58.7 [64]. In another study, %Na values were reported in the range of 52.8 to 54.6 in Güllübağ irrigation pond (Uşak) [65].

As explained above, excess Na⁺ ion causes a decrease in soil permeability and deterioration of soil structure. The sodium adsorption rate (SAR) is important in determining the Na⁺ ion to be adsorbed by the soil. If the SAR ratio of the irrigation water is high, the ability of the soil to form stable aggregates will decrease [66], and its infiltration and permeability properties will decrease and cause problems with plant growth [65]. In this study, the SAR value varied between 0.68-3.52 (1.4) in the dry period and between 0.2-0.28 (0.26) in the rainy period. Since SAR<10 at all sampling points, Na⁺ does not pose a hazard in water samples. It can be said that river water is suitable for all crops and all kinds of soils [67] except for sodium sensitive crops. SAR values for Porsuk and Felent streams have been reported in the range of 0.25-0.8 in the rainy season and 0.21-0.56 in the dry season. For the Murat River, SAR values have been reported in the range of 0.68–4.19 meq/L [64]. In the study conducted in the Güllübağ Dam Pond in Uşak, it was reported that the SAR values ranged from 3.1 to 3.5 [65].

One of the indexes used to determine the suitability of irrigation water is the magnesium ratio (MR). Excess magnesium in the soil increases the salt level of the soil and negatively affects plant growth [62]. The magnesium ratio was determined to be 19.8 and 13.8 for the dry and rainy periods, respectively. Since the values for both periods were <50, it was determined that the river water was suitable as irrigation water. The highest magnesium ratio was determined in SP 3 in the dry period and in SP 1 in the rainy period. The mean MR was reported as 36 for Güllübağ Irrigation Pond [65], and between 31.52–44.68 for Porsuk and Felent Streams [62].

Kelly's Index is one of the indexes used to evaluate irrigation water quality [68]. Since Kelly index was less than 1 at all sampling points in both periods, it was determined Similarly, other researchers have reported KI in the range of 0.07–0.14 [62] and 0.94–1.0 [65] that river water was suitable as irrigation water.

The potential salinity (PS) index is calculated based on the Cl⁻ and SO₄⁻² anions. Potential salinity values varied between 0.99–5.22 meq/L and 0.24–0.36 meq/L in the dry and rainy periods, respectively. Since PS <3 at all sampling points during the rainy season, they are suitable as irrigation water. In the dry season, only the 4th sampling point is not suitable as irrigation water (PS>3 meq/L). The high Cl^{-} and SO_{4}^{-2} anions at this sampling point in the dry period caused the PS value to be high. High Cl⁻ concentration in irrigation water may cause toxicity to plants. Since Cl- is not adsorbed by the soil, it is transported with soil water and is taken up by plants and accumulated in their leaves [13] and causes toxicity. Similarly, in the study conducted in the irrigation pond, PS values were determined in the range of 4.41–5.72 meq/L, and the value in July was found to be higher than March and May [65]. In another study, mean PS values for December and June were determined as 1 meq/L and 0.79 meq/L [62].

Total hardness is related to $CaCO_3$ compounds of Ca^{+2} and Mg^{+2} in water. TH values were determined to be 283 mg/L and 194 mg/L for the dry and rainy periods, respectively. According to the classification made by [29], river water is in the very hard water class as irrigation water, since TH>180 mg/L at all sampling points in both periods. The widespread presence of dolomite (CaCO₃, MgCO₃) in the geological formation of the study area is considered to be the most important cause of water hardness.

CONCLUSION

It was determined that the increase in SS and turbidity concentrations after precipitation was significant. While the rainy season concentration of SS is about 3 times of the dry period, the turbidity is about 4 times. Considering the sampling point where these parameters are the highest, it is thought that soil transport from the surrounding land is effective. The fact that 98% of the turbidity is caused by SS also confirms this idea. It is thought that SS concentration is also effective in parameters such as bed width and water flow rate. The larger the bed width and the water depth of SP4, the higher the SS concentration may result. While dissolved salts such as Na⁺, Mg⁺², K⁺¹, Ca⁺², Cl⁻, SO₄⁻² are higher in the dry period, the higher EC and TDS concentrations in the rainy period indicate that natural organic substances are carried by precipitation waters. The higher COD concentration during the rainy season confirms this idea. According to the water quality index, it was determined that the water was of good quality at only SP1 and during the dry period. According to the water hazard index calculated for heavy metals, it has been determined that metals may cause low toxicity. When all physicochemical parameters were compared with the limit values reported for irrigation waters, it was determined that only K⁺ exceeded the limit value at all sampling points, especially in the dry period. According to the SAR, %Na, MR, Kelly Indexes related to Na⁺, K⁺, Ca⁺², Mg⁺² ions, it was determined that the river water was suitable as irrigation water. However, according to the potential salinity (PS) index related to Cl⁻ and SO₄⁻², the river is not suitable as irrigation water at the SP4 in the dry period. According to the total hardness index, the river water was categorized at the very hard water class (>180 mg/L) at all sampling points. River water, NO₃, TP, Al, Fe, Mn, Ni, Cu, Zn in terms of 1st quality water class according to the Regulation on Surface Water Quality Management. In terms of electrical conductivity, the second quality is in the water class. According to the regulation, the 1st and 2nd class waters are defined as high quality and low-contaminated waters, respectively. According to the water quality index, river water is in the 4th quality water class in terms of COD. 4th grade water is defined as very contaminated water. For this reason, organic pollution was effective in the river. It is thought that domestic wastewater discharge and spread resources (especially in rainy period) affect organic pollution in the river. Fully prevention of domestic wastewater discharge will also reduce organic pollution. According to the statistical analysis, the concentration difference between rainy and dry periods for suspended solid, turbidity, pH, Ca+2, Al, K+, Mg, Cl-, Na+, and NO₃- is statistically significant unlike Fe, Mn, Zn, TP, COD, EC, TDS (p>0.05).

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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