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Assessment of spatial and temporal water pollution patterns in Aydos River (Turkey) by using water quality index and multivariate statistical methods

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ABSTRACT

Küre National Park, which also includes the Aydos River, is Turkey's First PAN Park (Protected Area Network Parks). The monthly, seasonal, and spatial changes in physicochemical parameters and heavy metals were determined using water quality index (WQI), hierarchical cluster analysis, principal components analysis (PCA), and other statistical methods revealing the water quality characteristics and pollutants. WQI was calculated using parameters constituting the main components of water. It was determined that, according to WHO and SWQR, the water quality of this river varied between high quality and very polluted. The sodium absorption rate, % Na, residual sodium carbonate, and Kelly Ratio results did not exceed the threshold but the water was found to be dangerous in terms of magnesium hazard. In cluster analysis, winter and spring were found to be similar to each other more than autumn and summer. Moreover, with this analysis, the basin was spatially divided into an upper basin and a lower basin. Five main factors were found to be significantly affected by parameters explaining 84.65% of the total variance in PCA. It was found that temperature, anions originating from pesticides and fertilizers, and non-point pollutants originating from heavy metals were the pollution sources of this river. Monitoring is recommended in freshwater management of basins for the future of wildlife.

Keywords: Water quality index; Irrigation water quality (IWQ); Hierarchical cluster analysis (HCA); Principal components analysis (PCA); PAN Parks

1. Introduction

Clean and high-quality water is one of the most important components of all ecosystems and is necessary for the life and development of all organisms. In the 21st century, ecosystems' ability to provide the important goods and services needed by societies, meet the water, food, and energy needs, and water security has become the most important difficulties for societies. The increasing economic activities, the changes in land use, and the growth in the population increasing the climate change also increase the pressure on the quality and quantity of global water resources. These pressures threaten all the ecosystems but especially the freshwater ecosystems. The decline in water quality became a global source of concern since it affects the use of water, the health and process of the ecosystem, and the biodiversity supported by the ecosystems. The excessive pollution in water resources, besides its other irreversible effects, causes water scarcity in many countries. Water resources are contaminated by different pollutants as a result of industrialization and human activities. This pollution arises from the presence of material/energy wastes that can be monitored as negative changes in physical, bacteriologic, radioactive, and ecological characteristics of water

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and will directly/indirectly cause preventive changes in human health, water quality, and use of water for different purposes [1].

In order to maintain the rivers constituting 2% of surface water in the world and having an important function in the water cycle, the resources should be accurately managed by monitoring the pollution. Canalization waters, industrial wastes, materials transported by surface waters, heavy metals, and agents such as pesticides and fertilizers used in agricultural activities are responsible for the contamination of rivers [2].

The quantity and quality of waters can be maintained by protecting the underground and surface waters, developing monitoring programs, revealing all the factors related to water resources, improving all the waters to high-quality water (good condition) class, defining the water quality from biological, chemical, hydrological, and morphological aspects, and ensuring the participation of all governmental and non-governmental organizations in economic analyzes and river basin management plans [3,4].

In the Third Global Environment Report of United Nations Environment Programme (UNEP), it is projected that, within the next 20 y, the amount of freshwater needed for meeting the food demand increasing with the growing human population will increase by 40% and, unless the consumption habits change, the demand of water will double and, thus, two-thirds of the global population will encounter water scarcity. Irrigation has well-known importance in increasing the yield and quality of agricultural production. In modern irrigation practice, the quality of water is as important as the amount, timing, and method of irrigation are. There are many indices used for determining the quality of irrigation water. By using these indices, the pollutions problems can be solved rapidly and high-quality waters can be used for achieving healthy agricultural products [5,6].

High-quality water can be obtained by monitoring the current water resources, determining their status, collecting reliable data, assessing the spatial and seasonal quality changes, determining the sources of pollution, and controlling the pollution sources of natural waters. Since no variable can solely define the water quality accurately, the water quality is assessed by measuring a set of physicochemical parameters. Since it is easy to implement and it has simple scientific basics, the water quality index (WQI) has become a popular and useful instrument in measuring the water quality of rivers throughout the world. Since the introduction of the WQI concept, many researchers have developed various indices. In several studies aiming to determine the factor changing the water quality, the principal components analysis is employed and the weighted scores of each variable are calculated [7,8]. The main purpose of all these water quality indices is to convert a wide range of variables into numerical data and simply and understandably classify the waters by biological, chemical, and physical characteristics [9,10].

By making use of cluster analysis (CA), principal components analysis (PCA), and factor analysis among the multivariate statistical technics, which makes it possible to interpret very complex water quality datasets, and irrigation water quality parameters, the water quality can be analyzed. Besides that, they are also important in water resource management. These methods also facilitate determining the sources of water pollution and determining and interpreting the natural or anthropogenic factors affecting the water quality.

In the present study, the water samples were collected from the sampling stations representing the whole of Aydos River located within the body of Küre National Park listed in 100 Forest Hot Spots of Europe and certified as the first PAN (Protected Area Network) park of Turkey. Küre Mountains National Park is a national park located on the Küre Mountains in the west of the Black Sea Region. The Küre Mountains National Park, which makes you feel the lush nature of the Snow Sea, is located between the provinces of Bartın and Kastamonu. In the National Park, there are natural wonders, waterfalls, caves, canyons, and landscapes that you cannot take your eyes off. It was aimed to determine the monthly, seasonal, and spatial changes in specific physicochemical parameters and heavy metal concentrations in water samples, to identify the water quality class of the river, to reveal the pollutants, and to reveal the level of pollution. Besides them, it was also aimed to provide suggestions for monitoring the pollutants in future studies by making use of multivariate statistical methods and relating the water quality index to the main components of PCA analysis in order to make spatial and temporal analyses and interpret the data more simply. The water quality of the Aydos River was classified using the parameters of the World Health Organization and the general chemistry and physicochemical parameters of Turkey's Surface Water Quality Regulation (SWQR) [11,12].

2. Methods and materials

2.1. Study area

Aydos River originates from the Cide district of Kastamonu Province, located in the Black Sea Region of the Anatolian Peninsula. Emerging from the northern shoulders of İsfendiyar (Küre National Park) fold mountains coursing alongside the shore, the Aydos River creates a deep bed along a forested and locally rough area. It pours into the Black Sea in the Cide district of Kastamonu Province. Currently used for irrigation and energy purposes, the Aydos River has 60 km of total length, 11.01 km of length within the borders of the city, 523.6 km^2 of drainage area, and 6.42 m^3 s^{-1} of flow rate. On the river, there is the arc-shaped Aydos Canyon, which has a depth of 700–750 m in a north–northwestern direction, is suitable for rafting, and has 6 km of the walking road [13]. Moreover, there also is a Sand – Gravel Pit Facility, which has a physical purification system, on the river. The karstic figures in the study area have developed under an intense plant cover and a soil cover, thickness of which changes locally. With this characteristic, the study area has a covered karst appearance [14].

Küre National Park, which is one of the best wild examples of "Black Sea Moist Karstic Forests" being under threat nowadays, is listed in Europe's 100 Forest Hot Spots, which should be protected. In Küre Mountains National Park having significant importance for the region, there are 157 endemic plant species and 59 of them are plant taxa, which are under danger of extinction [14]. Besides being 9 hot spots to be protected in Turkey, Küre National Park, where Aydos River originates, is Turkey's First PAN Park certified as Europe's elite PAN. The projects conducted for protecting nature and strengthening the biodiversity and sustainable source management with the participation of national park management, local non-governmental organizations, and local people were presented as successful cases in both national and international circles and, awarded with "Best Practice", they represent Turkey in Rio+20 Conference [15].

On Aydos River, there are 1 barrage and hydroelectric plant power plant (HES) and 3 HES projects, feasibility phases of which have been completed. Having a total of 9 MW installer power, the constructed HES constitutes 0.023 of electricity generated by HES in Turkey and meets 0.007 of the total electric consumption in Turkey.

The study area has a 26 m elevation. In this region, summers are cool but winters are not that cold. It is rainy in all the seasons and the Black Sea climate is dominant. The region receives much more rain in winter when compared to the summer season. The mean annual precipitation is 948 mm. July was found to be the aridest month (39 mm), whereas December is the rainiest month (134 mm). The annual mean temperature of the region is 11.0°C; August is the hottest (20.4°C) month, whereas January was found to have the lowest mean temperature (1.7°C). Due to the rough land structure, the precipitation and temperature decrease in inner regions and the temperature difference between night and day decreases [16].

The economy in the study area depends on agriculture, forestry, animal husbandry, fisheries, and shipbuilding activities. Besides cereal production, also viticulture, fruit farming, and vegetable farming are conducted. In addition to the agricultural production, the other income sources of local people include small-scale forestry products. In animal husbandry, range animals come to the forefront.

2.2. Sample collection and analysis methodology

Surface water samples were collected between January 2019 and December 2019 from 13 stations on the Aydos River (Fig. 1). The station was determined before, after the settlements and to characterize the whole river.

Water samples were taken 15–20 cm below the water surface by using 2.5 L sampling containers. Sample bottles, containing polyethylene and screw caps, were first passed through weak acid in the laboratory, then rinsed with tap water, and finally, they were prepared for fieldwork by passing pure water.

The water samples to be used in heavy metal analyses were collected using 1 L polyethylene sampling containers washed with acid. The samples were taken to the laboratory using a large thermos and then they were kept in a refrigerator at 4°C temperature until analyses.

Dissolved oxygen (DO), water temperature (WT), electrical conductivity (EC), and salinity were measured in the field by making use of YSI 556 MPS multi-parameter device. Nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+), chemical oxygen demand (COD), biological oxygen demand (BOD), total hardness (TH), phosphate (PO_4^{-3}), total alkalinity (TA), sodium (Na^{+1}), sulfite (SO_3^{-2}), sulfate (SO_4^{-2}), magnesium (Mg^{+2}), chloride (Cl^-), calcium (Ca^{+2}), and potassium (K^+) parameters were measured using the standard method in the

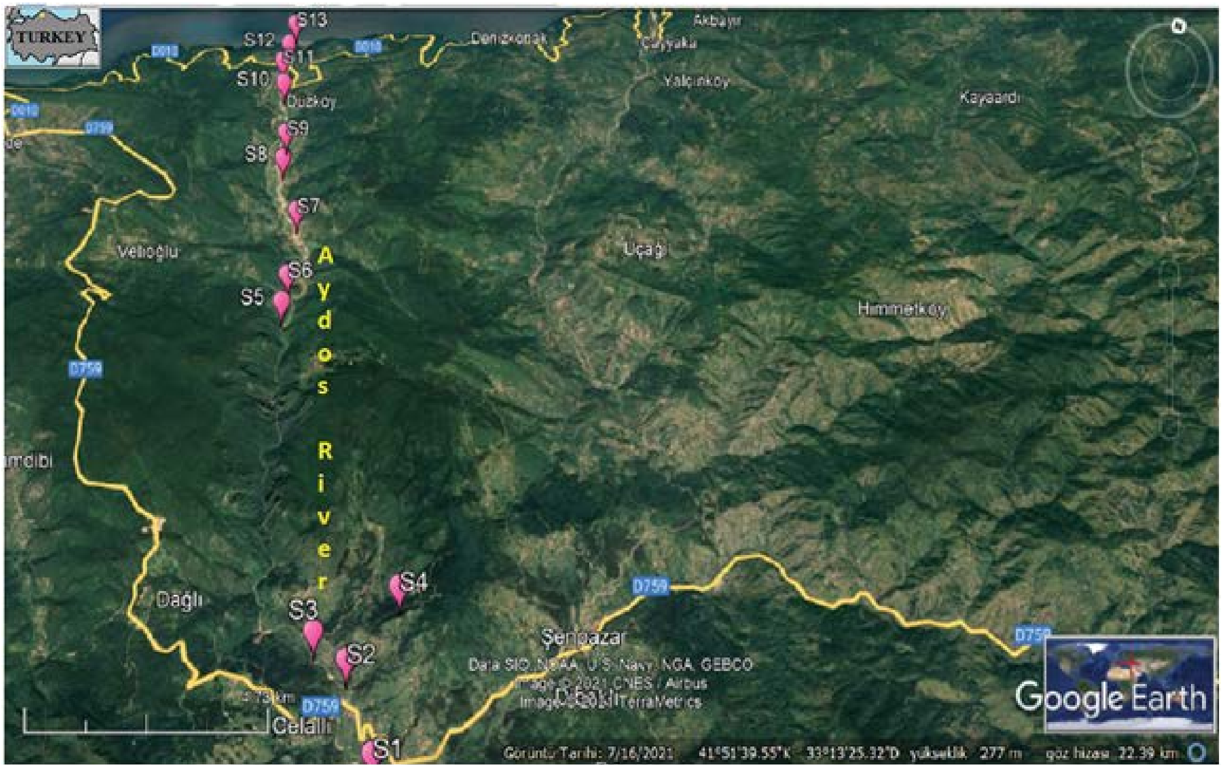

Fig. 1. Map of the study area with sampling point locations (*Source*: Google Earth).

laboratory [17]. The analyses of metals such as ferrous (Fe^{+2}), zinc (Zn^{+2}), lead (Pb^{+2}), cadmium (Cd^{+2}), nickel (Ni^{+2}), and copper (Cu^{+2}) were performed using Perkin Elmer Optima 2000 DV ICP-OES device. The creation of the calibration curve was carried out using a certified multi-element standard in triplicate and each parallel. It was analyzed by ICP-OES instrument 10 readings. Blank samples were prepared with 1% HNO_3 solution 20 times and 3 times with a standard curve obtained and LOD (limit of detection) and 10 times the LOQ (detection limit) is determined [18].

2.3. Irrigation quality parameters

The highest quality in agricultural products can be achieved only with high-quality soil, accurate agricultural practices, and high-quality irrigation water. The effect of irrigation water on the soil and plant depends on physical and chemical properties of soil, salt-resistance of plant being grown, climatic conditions of the region, irrigation method, irrigation interval, and amount of irrigation water [19]. The chemistry of irrigation water might have a direct effect on herbal products in terms of deficiency or toxicity, as well as direct effects such as nutrient availability.

In order to examine Aydos River in terms of irrigation water quality, sodium absorption rate (SAR), sodium percentage (% Na), residual sodium carbonate (RSC), magnesium hazard (MH), and Kelly Ratio (KR) values were calculated using Eqs. (1)–(5), respectively [8,20,21]. After the calculation of values, the element concentrations were converted from mg L^{-1} to meq L^{-1} [8,21].

$$\%\mathrm{Na} = \frac{\left(\mathrm{Na}^{+}_{\mathrm{meq}} + \mathrm{K}^{+}_{\mathrm{meq}}\right)\times 100}{\left(\mathrm{Na}^{+}_{\mathrm{meq}} + \mathrm{Ca}^{2+}_{\mathrm{meq}} + \mathrm{Mg}^{2+}_{\mathrm{meq}} + \mathrm{K}^{+}_{\mathrm{meq}}\right)} \tag{1}$$

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}_{\mathrm{meq}}}{\dfrac{\sqrt{\mathrm{Ca}^{2+}_{\mathrm{meq}} + \mathrm{Mg}^{2+}_{\mathrm{meq}}}}{2}} \tag{2}$$

$$\mathrm{RSC} = \left(\mathrm{Alkalinity}\times 0.0333\right) - \left(\mathrm{Ca}^{2+}_{\mathrm{meq}} + \mathrm{Mg}^{2+}_{\mathrm{meq}}\right) \tag{3}$$

$$\mathrm{MH} = \left(\frac{\mathrm{Mg}^{2+}_{\mathrm{meq}}}{\mathrm{Ca}^{2+}_{\mathrm{meq}} + \mathrm{Mg}^{2+}_{\mathrm{meq}}}\right)\times 100 \tag{4}$$

$$\mathrm{KR} = \left(\frac{\mathrm{Na}^{+}_{\mathrm{meq}}}{\mathrm{Ca}^{2+}_{\mathrm{meq}} + \mathrm{Mg}^{2+}_{\mathrm{meq}}}\right) \tag{5}$$

2.4. Water quality index

In determining the water quality of Aydos River, the WQI that is a simple but comprehensive indicator was calculated as follows [22] (6):

$$\mathrm{WQI} = \sum_{n=1}^{\infty}\left[W\times\left(\frac{C_i}{S_i}\right)\right]\times 100 \tag{6}$$

where WQI refers to the eigenvalue for each principal component in PCA, which was performed using 28 parameters indicating the relative importance of each water quality parameter, and the weight attributed to each parameter according to the factor load. C_i refers to the concentrations of parameters examined in water samples. S_i, however, is the reference value for each parameter [11,12,22]. The calculated WQI values were interpreted using 5 classes: $0 \leq \mathrm{WQI} < 50$ perfect water quality, $50 \leq \mathrm{WQI} < 100$ good water quality, $100 \leq \mathrm{WQI} < 200$ bad water quality, $200 \leq \mathrm{WQI} < 300$ very bad water quality, and $\mathrm{WQI} > 300$ water that is not suitable for drinking [23].

2.5. Statistical analysis methodology

Surface water analysis results were analyzed using IBM SPSS 25 statistical package program. Using One-Way ANOVA analysis of parameters, both descriptive statistical analysis and significance tests (0.01 and 0.05) were performed in order to determine differences between stations and also between seasons. Since the data sets showed normal distribution according to the Kolmogorov Smirnov test, ANOVA, and Pearson correlation tests could be applied. The significant differences between mean values were determined using Tukey's multiple tests. Pearson's correlation index (PCI) was used in analyzing the structure of correlations between measured water quality parameters [24]. In spatially and temporally revealing the surface water quality of Aydos River, the large datasets were subjected to multivariate hierarchical cluster analysis (HCA), a combination of technics aiming to classify the datasets in clusters based on similarities or differences [25]. Ward's method was also used as the similarity criterion for HCA [26]. For PCA used in assessing the spatial and temporal variations of water quality, the Kaiser–Meyer–Olkin (KMO) and Bartlett's tests were performed first. Since KMO value of Aydos River was found to be 0.851 and Bartlett's test to be ($P = 0$), PCA test was found to fit the purpose. In order to false classification due to important differences in datasets, the data were standardized using Z-scaled conversion and the analyses were performed using experimental image data.

3. Results and discussion

3.1. Water quality evaluation

The surface water samples monthly collected from 13 stations on Aydos River for a year were examined in terms of 28 physicochemical water quality parameters. Statistically significant differences were found between stations in terms of the annual mean values of all the parameters ($P < 0.05$). The temporal differences between seasonal mean values are expressed with different letters and the seasonal mean, standard deviation (SD), and range (minimum–maximum) values are summarized in Table 1.

The results are as follows: DO = 14.86 ± 1.61 mg L^{-1}, salinity = 0.06‰ ± 0.02‰, pH = 8.49 ± 0.29, WT = 10.44°C ± 7.08°C, EC = 346.76 ± 39.44 µS cm^{-1}, suspended solids (SS) matter = 1.98 ± 1.31 mg L^{-1}, COD = 0.82 ± 0.57 mg L^{-1}, BOD_5 = 0.45 ± 0.41 mg L^{-1}, $[Cl^-]$ = 8.18 ± 1.39 mg L^{-1}, $[PO_4^{3-}]$ = 0.017 ± 0.02 mg L^{-1}, $[SO_4^{2}]^-$ = 33.39 ± 26.47 mg L^{-1},

Table 1
Seasonal mean, standard deviation (SD), range (mean ± SD; minimum – maximum) value

	Winter	Spring	Summer	Autumn	WHO [11]	Class (SWQR, [12])
DO (mg L^{-1})	15.48 ± 0.43^{b}	15.70 ± 0.54^{b}	15.61 ± 1.24^{b}	12.64 ± 1.32^{a}		I
	14.52 – 16.07	14.76 – 16.39	12.56 – 16.59	10.79 – 15.13		
Salinity (‰)	0.04 ± 0.01^{a}	0.05 ± 0.01^{a}	0.08 ± 0.02^{b}	0.07 ± 0.02^{b}		I
	0.03 – 0.08	0.03 – 0.08	0.04 – 0.12	0.04 – 0.12		
pH	8.36 ± 0.40^{a}	8.35 ± 0.19^{a}	8.55 ± 0.16^{b}	8.69 ± 0.20^{b}	6.5 – 8.5	IV
	6.57 – 9.02	8.02 – 8.77	8.29 – 8.95	8.27 – 9.01		
WT (°C)	3.70 ± 0.84^{a}	6.45 ± 2.35^{b}	16.44 ± 4.96^{c}	15.17 ± 7.13^{c}		I
	3.00 – 6.30	3.30 – 10.50	7.50 – 24.80	5.80 – 25.30		
EC (μS cm^{-1})	322.82 ± 15.14^{a}	331.05 ± 52.53^{a}	370.06 ± 23.28^{b}	367.67 ± 28.24^{b}	1,500	II
	295.48 – 352.80	197.6 – 359.18	309.88 – 399.36	306.10 – 406.47		
SS (mg L^{-1})	1.03 ± 0.64^{a}	1.59 ± 0.97^{a}	2.70 ± 1.30^{b}	2.60 ± 1.39^{b}		I
	0.04 – 2.28	0.06 – 3.00	0.38 – 4.47	0.78 – 5.04		
COD (mg L^{-1})	0.48 ± 0.11^{a}	0.48 ± 0.28^{a}	0.93 ± 0.55^{b}	1.37 ± 0.60^{c}	10.0	I
	0.26 – 0.73	0.02 – 0.96	0.14 – 1.92	0.36 – 2.19		
BOD$_5$ (mg L^{-1})	0.19 ± 0.10^{a}	0.28 ± 0.18^{a}	0.70 ± 0.55^{b}	0.63 ± 0.39^{b}		I
	0.04 – 0.46	0.00 – 0.56	0.01 – 2.03	0.10 – 1.34		
Cl^{-} (mg L^{-1})	9.01 ± 0.21^{b}	8.72 ± 0.54^{b}	7.72 ± 2.28^{a}	7.29 ± 0.58^{a}	250	
	8.62 – 9.76	7.82 – 9.40	4.62 – 11.09	6.36 – 8.56		
PO$_4^{3-}$ (mg L^{-1})	0.008 ± 0.01^{a}	0.009 ± 0.01^{a}	0.024 ± 0.03^{b}	0.027 ± 0.02^{b}		II
	0.00 – 0.02	0.00 – 0.04	0.00 – 0.08	0.00 – 0.06		
SO$_4^{2-}$ (mg L^{-1})	7.02 ± 4.00^{a}	26.47 ± 19.26^{b}	54.67 ± 19.55^{c}	45.41 ± 26.70^{c}	250	
	0.06 – 13.03	1.80 – 52.41	4.40 – 69.55	3.29 – 76.50		
SO$_3^{-2}$ (mg L^{-1})	0.70 ± 0.47^{a}	1.39 ± 0.76^{b}	2.37 ± 0.91^{c}	2.44 ± 1.12^{c}		I
	0.00 – 1.50	0.14 – 2.63	0.42 – 3.53	0.12 – 4.11		
Na^{+} (mg L^{-1})	45.13 ± 6.65^{a}	53.50 ± 10.98^{a}	51.95 ± 15.73^{b}	42.35 ± 5.99^{b}	200	
	33.24 – 58.31	29.14 – 72.26	29.87 – 80.52	29.84 – 52.41		
K^{+} (mg L^{-1})	17.41 ± 1.96^{a}	18.73 ± 1.59^{b}	18.56 ± 1.57^{b}	18.03 ± 1.50^{a}	12	
	13.68 – 20.52	15.96 – 20.62	16.04 – 20.72	15.83 – 20.01		
TH (mg L^{-1})	230.07 ± 6.78^{a}	249.10 ± 15.89^{b}	252.81 ± 18.62^{b}	247.58 ± 9.86^{b}		
	219.76 – 242.27	224.56 – 275.51	223.66 – 286.61	223.48 – 261.00		
TA (mg L^{-1})	250.42 ± 7.37^{a}	269.06 ± 16.36^{bc}	274.32 ± 18.82^{c}	265.21 ± 10.97^{b}	200	
	240.04 – 266.53	245.17 – 297.53	244.09 – 307.74	245.97 – 285.98		
Mg^{2+} (mg L^{-1})	21.96 ± 0.88^{a}	21.98 ± 0.60^{a}	23.35 ± 1.39^{b}	25.45 ± 1.68^{c}	50	
	20.94 – 23.81	21.02 – 23.05	21.26 – 26.34	22.23 – 28.81		
Ca^{2+} (mg L^{-1})	26.36 ± 1.14^{a}	27.56 ± 1.74^{a}	28.10 ± 1.67^{b}	31.56 ± 2.06^{c}	300	
	25.09 – 28.42	25.22 – 33.06	25.26 – 31.46	28.25 – 34.98		
NO$_2^{-}$ (mg L^{-1})	0.00001 ± 0.00002^{a}	0.00004 ± 0.00003^{b}	0.00001 ± 0.00005^{d}	0.00007 ± 0.00004^{c}		I
	0.0 – 0.0001	0.0 – 0.0001	0.0 – 0.0002	0.0 – 0.0001		
NO$_3^{-}$ (mg L^{-1})	0.59 ± 0.16^{a}	0.66 ± 0.52^{a}	1.75 ± 0.88^{b}	1.92 ± 1.050^{b}	50	II
	0.30 – 0.95	0.10 – 1.88	0.20 – 3.37	0.42 – 4.02		
NH$_4^{+}$ (mg L^{-1})	0.0004 ± 0.0005^{b}	0.0002 ± 0.0003^{ab}	0.0002 ± 0.0003^{ab}	0.0002 ± 0.0001^{a}	35	
	0.0001 – 0.0014	0.0001 – 0.0018	0.0001 – 0.0020	0.0 – 0.0009		
Fe^{2+} (mg L^{-1})	0.0029 ± 0.003^{b}	0.0048 ± 0.004^{c}	0.0021 ± 0.002^{ab}	0.0011 ± 0.0007^{a}	0.300	I
	0.0001 – 0.0102	0.0002 – 0.0139	0.0002 – 0.008	0.0001 – 0.0025		
Pb^{2+} (μg L^{-1})	1.07 ± 0.491^{a}	1.64 ± 0.720^{b}	1.21 ± 0.461^{a}	1.07 ± 0.46^{a}	0.010	I
	0.30 – 2.10	0.30 – 2.60	0.30 – 2.00	0.30 – 2.00		
Cu^{2+} (μg L^{-1})	14.54 ± 5.85^{a}	20.44 ± 9.02^{b}	12.28 ± 5.69^{a}	13.77 ± 7.05^{a}	2	I
	3.0 – 24.0	3.0 – 34.0	3.0 – 24.0	3.0 – 26.0		
Cd^{2+} (μg L^{-1})	0.082 ± 0.12^{a}	0.12 ± 0.191^{a}	0.076 ± 0.129^{a}	0.54 ± 0.36^{b}		IV
	0.0 – 0.40	0.0 – 0.70	0.0 – 0.50	0.0 – 1.10		
Hg^{2+} (μg L^{-1})	0.00008 ± 0.0004^{a}	0.0017 ± 0.002^{a}	0.0010 ± 0.002^{a}	0.0037 ± 0.005^{b}		I
	0.0 – 0.002	0.0 – 0.008	0.0 – 0.007	0.00 – 0.015		
Ni^{2+} (μg L^{-1})	1.08 ± 1.83^{a}	2.67 ± 2.88^{b}	1.49 ± 2.17^{ab}	1.64 ± 2.18^{ab}		I
	0.0 – 7.0	0.0 – 9.0	0.0 – 8.0	0.0 – 7.0		
Zn^{2+} (μg L^{-1})	1.23 ± 1.95^{a}	7.59 ± 5.34^{c}	3.87 ± 3.04^{b}	2.62 ± 2.82^{ab}	0.010	I
	0.00 – 7.00	0.00 – 18.00	0.0 – 9.00	0.0 – 9.0		

^{a,b,c,d}Means with different letters in the same column are statistically significantly different ($P < 0.05$).

$[SO_3^{2-}]$ = 1.73 ± 1.11 mg L^{-1}, $[Na^+]$ = 48.23 ± 11.47 mg L^{-1}, $[K^+]$ = 18.18 ± 1.73 mg L^{-1}, TH = 244.89 ± 16.10 mg L^{-1}, TA = 264.75 ± 16.58 mg L^{-1}, $[Mg^{2+}]$ = 23.18 ± 1.87 mg L^{-1}, $[Ca^{+2}]$ = 28.40 ± 2.56 mg L^{-1}, $[NO_2^-]$ = 0.00005 ± 0.00005 mg L^{-1}, $[NO_3^-]$ = 1.23 ± 0.95 mg L^{-1}, $[NH_4^+]$ = 0.0002 ± 0.0003 mg L^{-1}, $[Fe^{2+}]$ = 0.003 ± 0.0028 mg L^{-1}, $[Pb^{2+}]$ = 1.25 ± 0.59 μg L^{-1}, $[Cu^{2+}]$ = 15.26 ± 7.62 μg L^{-1}, $[Cd^{2+}]$ = 0.21 ± 0.29 μg L^{-1}, $[Hg^{2+}]$ = 0.00164 ± 0.003 μg L^{-1}, $[Ni^{2+}]$ = 1.72 ± 2.35 μg L^{-1} and $[Zn^{2+}]$ = 3.83 ± 4.21 μg L^{-1}.

3.2. Temporal changes in water quality

Having significant importance for organisms living in the aquatic ecosystem, DO value was found to be at the highest level in July (16.59 mg L^{-1}) and at the lowest level in September (10.79 mg L^{-1}). At the statistical significance level of $P < 0.05$, DO was found to have significant negative relationship with WT, COD, $[Mg^{2+}]$, $[Ca^{2+}]$, $[NO_3^-]$, and $[Cd^{2+}]$ ($r \geq -0.5$) and significant positive relationship with $[Cl^-]$, $[Na^+]$, TA, $[Fe^{2+}]$, $[Cu^{2+}]$, and $[Zn^{2+}]$ parameters (Table 2). Aydos River poses no threat in terms of DO. From the aspect of DO, Aydos River was classified as Class I (>8 mg L^{-1}) "high-quality water" according to WHO [11] and SWQR standards [12].

It is well-known that irrigation plays an important role in increasing the yield and quality of agricultural production. In the modern irrigation approach, irrigation water quality is as important as the amount, timing, and method of irrigation. One of the parameters influencing the quality is salinity. In case of insufficient amount and quality of water, the salty waters and drainage waters not fitting the irrigation purposes are used in irrigation [27]. In parallel with seasonal conditions, the lowest level of salinity was found to be 0.03 PSU in winter months, when the level of precipitation was high, whereas the highest level was found to be 0.12 PSU in August, when the vaporization peaked. At the statistical significance level of $P < 0.05$, salinity was found to have significant positive relationships with WT, EC, SS, COD, BOD_5, $[SO_4^{2-}]$, $[SO_3^{2-}]$, $[Mg^{2+}]$, $[NO_2^-]$, and $[NO_3^-]$ ($r > 0.750$) (Table 2). From the aspect of salinity, the Aydos River poses no threat to either agriculture or aquatic life.

pH value tended to increase until November (9.02) and reached its lowest value in January (6.57). Photosynthetic activity is believed to play role in this change. Low pH values threaten the aquatic ecosystem by increasing the toxicity of heavy metals. At the statistical significance level of $P < 0.05$, this parameter was found to have significant positive relationships with salinity, water temperature, SS, COD, BOD_5, $[PO_4]$, $[SO_4^{2}]$, $[SO_3^{2-}]$, $[K^+]$, $[Mg^{2+}]$ $[Ca^{+2}]$, $[NO_2^-]$, $[NO_3^-]$, and $[Cd^{2+}]$ ($r > 0.50$) (Table 2). According to WHO criteria and SWQR's general chemical and physicochemical parameters, pH value of Aydos River was found to be Class IV (6–9), which indicates very polluted water [13,14]. Fırtına Brook and Gomti River were found to have lower pH values but be within the limits [28,29].

Water temperature was found to be at the lowest level in February (3.0°C) and at the highest level in September (25.30°C). At the statistical significance level of $P < 0.05$, water temperature was found to have significant positive relationships with EC, SS, COD, BOD_5, $[Cl^-]$, $[SO_4^{2-}]$, $[SO_3^{2-}]$, $[Mg^{2+}]$, and $[NO_3^-]$ ($r > 0.750$) (Table 2). Water temperature poses no threat for organisms living in aquatic medium.

Water's electrical conductivity depends on the solubility of rocks having contact with water. The highest level of EC in Aydos River was found in September (406.47 μS cm^{-1}) and its lowest value was observed in March (197.60 μS cm^{-1}). At the statistical significance level of $P < 0.05$, EC was found to have significant positive relationship with SS, COD, BOD_5, $[SO_4^{2-}]$, $[SO_3^{2-}]$, $[Mg^{2+}]$, and $[NO_3^-]$ ($r > 0.750$) (Table 2). According to SWQR, Aydos River was found to be Class II "slightly polluted water" in terms of EC (<1,000 μS cm^{-1}) [11,12].

SS level is influenced by the amount of water flows originating from precipitation and the phytoplankton concentration. SS level in Aydos River was found to be 0.04 in December and its highest level was observed in September (5.04 mg L^{-1}). At the statistical significance level of $P < 0.05$, SS level was found to have significant positive relationship with COD, BOD_5, $[SO_4^{2-}]$, $[SO_3^{2-}]$, $[Mg^{2+}]$, $[NO_3^-]$, and $[NO_2^-]$ ($r > 0.750$) (Table 2). COD is an important parameter for determining terrestrial-origin organic pollution. In this study, COD value was found to range between 0.02 and 2.19 mg L^{-1}. The lowest COD level was found in March and April, while the highest value was found in September. At the statistical significance level of $P < 0.05$, this parameter has significant positive relationship with salinity, pH, WT, EC, SS, BOD_5, $[SO_4^{2-}]$, $[SO_3^{2-}]$, $[Mg^{2+}]$, $[Ca^{2+}]$, and $[NO_3^-]$ ($r > 0.750$) (Table 2). This parameter didn't exceed the limit values and the water was found to be Class I "high-quality water" (<25 mg L^{-1}) [11,12].

Biological oxygen demand is accepted as an indicator of pollution level. In the Aydos River, the lowest level of BOD_5 was observed in March. Then, in parallel with the increase in water temperature, it started increasing and peaked in October (2.03 mg L^{-1}). At the statistical significance level of $P < 0.05$, BOD_5 level was found to have significant positive relationship with salinity, WT, EC, SS, COD, $[SO_4^{2-}]$, $[SO_3^{2-}]$, $[Mg^{2+}]$, and $[NO_3^-]$ ($r > 0.750$) (Table 3). According to SWQR, the BOD_5 level was found to not exceed the limit and be Class I "high-quality water" (<4 mg L^{-1}) (Table 1) [11,12].

Phosphate ions in the Aydos River course at the lowest levels throughout the year. It was found to peak in July (0.08 mg L^{-1}) and, started decreasing again, it reached an undetectable level in March and started increasing again. The phosphate level of Aydos River was found to be Class II (<0.16 mg L^{-1}), which indicates slightly polluter water quality [11,12]. Kuruçay Brook was found to have a lower level of phosphate concentration in comparison to Aydos River but within the limits [30].

The acceptable sulfate limit in natural waters is 90 mg L^{-1} and the sulfate concentration in Aydos River was found to range between 0.06 mg L^{-1} (February) and 76.50 mg L^{-1} (September). At the statistical significance level of $P < 0.05$, sulfate ion has significant positive relationship with salinity, WT, EC, SS, COD, BOD_5, $[SO_3^{2-}]$, $[NO_3^-]$, and $[NO_2^-]$ ($r > 0.750$) (Table 2). The sulfite ion concentration of Aydos River ranged between 0.0 (February) and 4.11 mg L^{-1} (September). The sulfite level of the river was found to be suitable for aquatic life and does not pose a threat for irrigation. The sulfite ion concentration of Aydos River was found to be Class I (≤2 mg L^{-1}) "high-quality water" [11,12].

Table 2
Pearson's correlation matrix among the variables

	DO	Salinity	pH	WT	EC	SS	COD	BOD_5	Cl^-	PO_4^{3-}	SO_4^{2-}	SO_3^{2-}	Na^+	K^+
DO	1													
S	–0.478**	1												
pH	–0.483**	0.647**	1											
WT	–0.544**	0.756**	0.466**	1										
EC	–0.463**	0.785**	0.456**	0.832**	1									
SS	–0.484**	0.889**	0.666**	0.753**	0.807**	1								
COD	–0.788**	0.771**	0.577**	0.846**	0.802**	0.813**	1							
BOD_5	–0.445**	0.768**	0.551**	0.793**	0.771**	0.862**	0.762**	1						
Cl^-	0.550**	–0.399**	–0.244**	–0.720**	–0.510**	–0.391**	–0.693**	–0.528**	1					
PO_4^{3-}	–0.217**	0.576**	0.524**	0.280**	0.450**	0.588**	0.339**	0.586**	–0.108	1				
SO_4^{2-}	–0.374**	0.819**	0.529**	0.866**	0.874**	0.878**	0.789**	0.798**	–0.433**	0.437**	1			
SO_3^{2-}	–0.527**	0.872**	0.643**	0.840**	0.858**	0.941**	0.865**	0.826**	–0.509**	0.527**	0.924**	1		
Na^+	0.303**	0.310**	0.243**	–0.073	0.152	0.350**	–0.015	0.024	0.432**	0.190*	0.320**	0.312**	1	
K^+	–0.126	0.563**	0.526**	0.192*	0.351**	0.702**	0.314**	0.465**	0.095	0.526**	0.479**	0.581**	0.652**	1
TH	–0.010	0.603**	0.456**	0.348**	0.512**	0.612**	0.317**	0.345**	0.153	0.411**	0.686**	0.614**	0.788**	0.606**
TA	0.060	0.591**	0.465**	0.306**	0.473**	0.605**	0.268**	0.346**	0.171*	0.451**	0.652**	0.581**	0.818**	0.660**
Mg^{2+}	–0.840**	0.794**	0.717**	0.752**	0.736**	0.816**	0.904**	0.761**	–0.544**	0.541**	0.707**	0.821**	–0.005	0.415**
Ca^{2+}	–0.786**	0.701**	0.615**	0.680**	0.661**	0.714**	0.830**	0.602**	–0.483**	0.385**	0.665**	0.732**	0.047	0.403**
NO_2^-	–0.228**	0.747**	0.570**	0.593**	0.659**	0.815**	0.576**	0.771**	–0.241**	0.679**	0.784**	0.794**	0.362**	0.644**
NO_3^-	–0.647**	0.868**	0.590**	0.873**	0.840**	0.886**	0.930**	0.775**	–0.570**	0.364**	0.853**	0.920**	0.180*	0.420**
NH_4^+	–0.019	0.165*	0.365**	–0.044	–0.067	0.166*	0.051	0.102	0.026	0.071	–0.005	0.108	0.276**	0.284**
Fe^{+2}	0.240**	0.150	0.036	–0.174*	0.038	0.268**	–0.017	0.058	0.251**	0.105	0.134	0.166*	0.634**	0.494**
Pb^{+2}	0.101	0.389**	0.158*	0.114	0.367**	0.544**	0.238**	0.328**	0.166*	0.222**	0.481**	0.468**	0.665**	0.624**
Cu^{+2}	0.126	0.243**	0.210**	–0.212**	0.120	0.351**	0.058	0.085	0.285**	0.360**	0.192*	0.255**	0.702**	0.666**
Cd^{2+}	–0.843**	0.617**	0.501**	0.440**	0.477**	0.619**	0.734**	0.485**	–0.324**	0.396**	0.434**	0.604**	–0.019	0.386**
Hg^{2+}	–0.385**	0.434**	0.412**	0.188*	0.342**	0.440**	0.408**	0.273**	0.025	0.420**	0.404**	0.363**	0.260**	0.433**
Ni^{+2}	–0.081	0.485**	0.243**	0.053	0.237**	0.499**	0.234**	0.253**	0.239**	0.263**	0.330**	0.354**	0.548**	0.611**
Zn^{+2}	0.080	0.371**	0.208**	0.130	0.299**	0.512**	0.223**	0.293**	0.082	0.239**	0.461**	0.438**	0.690**	0.638**

(Continued)

Table 2 Continued

	TH	TA	Mg^{2+}	Ca^{2+}	NO_2^-	NO_3^-	NH_4^+	Fe^{+2}	Pb^{+2}	Cu^{+2}	Cd^{+2}	Hg^{+2}	Ni^{+2}	Zn^{+2}
DO														
S														
pH														
WT														
EC														
SS														
COD														
BOD_5														
Cl^-														
PO_4^{3-}														
SO_4^{2-}														
SO_3^{2-}														
Na^+														
K^+														
TH	1													
TA	0.978**	1												
Mg^{2+}	0.372**	0.343**	1											
Ca^{2+}	0.445**	0.406**	0.892**	1										
NO_2^-	0.610**	0.612**	0.596**	0.498**	1									
NO_3^-	0.462**	0.418**	0.848**	0.750**	0.659**	1								
NH_4^+	0.103	0.146	0.123	0.016	0.070	0.071	1							
Fe^{+2}	0.438**	0.450**	–0.099	–0.012	0.261**	0.057	0.205*	1						
Pb^{+2}	0.653**	0.623**	0.143	0.218**	0.478**	0.318**	0.058	0.803**	1					
Cu^{+2}	0.582**	0.606**	0.073	0.168*	0.350**	0.072	0.157	0.788**	0.829**	1				
Cd^{2+}	0.232**	0.163*	0.794**	0.737**	0.417**	0.655**	0.018	0.049	0.232**	0.202*	1			
Hg^{2+}	0.519**	0.539**	0.514**	0.595**	0.416**	0.310**	–0.039	0.204*	0.303**	0.469**	0.531**	1		
Ni^{+2}	0.559**	0.542**	0.243**	0.318**	0.435**	0.311**	0.072	0.734**	0.754**	0.711**	0.454**	0.562**	1	
Zn^{+2}	0.712**	0.726**	0.166*	0.281**	0.495**	0.293**	0.082	0.816**	0.852**	0.801**	0.188*	0.479**	0.755**	1

*Correlation is significant at the 0.05 level (2-tailed), **Correlation is significant at the 0.01 level (2-tailed).

Table 3
Standard and calculated Na(%), SAR, RSC, Mg hazard, and KR values of water (meq L^{-1})

Na(%)		SAR		RSC		Mg hazard		KR	
Water class		Water class		Water class		Water class		Water class	
<20	Excellent	0–10	Excellent	<1.25	Safe/good	<50	Suitable	<1	Suitable
20–40	Good	10–18	Good	1.25–2.50	Doubtful	>50	Unsuitable	>1	Unsuitable
40–60	Permissible	18–26	Fair	>2.50	Unsuitable				
60–80	Doubtful	>26	Poor						
>80	Unsuitable								

The chloride concentration of Aydos River was found to be at the lowest level in August (4.62 mg L^{-1}) and at the highest level in June (11.09 mg L^{-1}). At the statistical significance level of $P < 0.05$, chloride level has significant negative relationship with COD, BOD$_5$, WT, [SO$_3$], [Mg^{2+}], [Ca^{2+}], and EC and positive relationship with DO and [Na^{+}] (Table 2). Found to be at its lowest levels in spring months, sodium peaked in summer and then started decreasing again. Sodium-ion levels ranged between 29.12 and 80.52 mg L^{-1}. At the statistical significance level of $P < 0.05$, sodium concentration was found to have a significant relationship with TH and TA ($r > 0.750$) (Table 2). A potassium ion is one of the salts giving the water its taste. In the Aydos River, potassium ion concentration was found to be at its lowest level (13.68 mg L^{-1}) in January and at its highest level (20.72 mg L^{-1}) in June.

In natural waters, TH varies depending on calcium and magnesium chloride, nitrate bicarbonate compounds, and slight amounts of strontium, ferrous, and aluminum concentrations. In this study, the lowest level of TH (219.76 CaCO$_3$ mg L^{-1}) was found in February and the highest value was found in June (286.61 CaCO$_3$ mg L^{-1}). At the statistical significance level of $P < 0.05$, TH has a significant and positive relationship with [Na^{+}] and TA ($r > 0.750$) (Table 2). TA of the river was found to range between 240.04 and 307.74 CaCO$_3$ mg L^{-1} in parallel with the changes in TA. At the statistical significance level of $P < 0.05$, TA parameter has significant positive relationship with TH ($r = 0.978$) and [Na^{+}] (r = 0.788) (Table 2).

Since the presence of calcium and magnesium in water increases the water permeability of the soil, they are important for river water's suitability for irrigation. The magnesium concentration of Aydos River ranged between 20.94 and 28.81 mg L^{-1}. At the statistical significance level of $P < 0.05$, [Mg^{2+}] parameter has significant positive relationship with salinity, WT, SS, COD, BOD$_5$, [SO$_3^{2-}$], [NO$_3^{-}$], [Cd^{2+}], and [Hg^{2+}] ($r > 0.750$) (Table 2). In this study, the lowest level of calcium was found in February (25.09 mg L^{-1}) and the highest level in October (34.98 mg L^{-1}).

Chemical fertilizers used in agricultural activities, microbiological activities of nitrogenous organic matters, and industrial and domestic wastewaters constitute the sources of nitrogenous compounds in water. In this study, nitrite level of Aydos River ranged between 0 and 0.002 mg L^{-1} and peaked in July. As a result of Pearson's correlation analysis, it was found to have a significant relationship with [NO$_3^{-}$], salinity, SS, BOD$_5$, and [SO$_3^{2-}$] (Table 2). Nitrate concentration of Aydos River ranged between 0.0 and 4.02 mg L^{-1}. In this river, nitrite concentration was found to be Class I (≤0.01 mg L^{-1}) and nitrate concentration to be Class II (<10 mg L^{-1}), which indicates "slightly polluted water" [11,12]. Zerveli Creek's nitrate concentration was reported to be lower than the concentration found in the present study [31]. Ammonium might become toxic for fishes and other organisms due to high levels of pH and temperature changes and it was found to not be highly toxic to organisms living in aquatic ecosystems [32]. Ammonium concentration of Aydos River was found to range between 0 and 0.002 mg L^{-1}. In this study, ammonium concentration was found to be Class I (<0.2 mg L^{-1}) indicating "high-quality water" [11,12].

In an aquatic medium, ferrous is a necessity for the secretion of many enzymes by autotroph bacteria. Ferrous concentration in Aydos River ranged between 0.0001 and 0.0139 mg L^{-1}. At the statistical significance level of $P < 0.05$, [Fe^{2+}] has significant positive relationship with [Na^{2+}], [Cu^{2+}], [Pb^{2+}], [Zn^{2+}], and [Ni^{2+}] (Table 2). In this study, ferrous concentration was found to not be at a dangerous level (36–101 mg L^{-1}) [11,12].

[Cu^{2+}], [Cd^{2+}], [Zn^{2+}], and [Pb^{2+}] heavy metals having anthropogenic origins may accumulate in the liver, kidney, and muscular tissues of organisms living in aquatic media. In this study, lead concentration was found to range between 0.30 and 2.60 μg L^{-1} and peaked in July. At the statistical significance level of $P < 0.05$, lead concentration has significant positive relationship with [Cu^{2+}], [Zn^{2+}], and [Ni^{2+}] ($r > 0.750$) (Table 2). The river was found to not be dangerous in terms of lead concentration (1.2–14 μg L^{-1}) [14]. Copper levels in the Aydos River ranged between 3 and 34 μg L^{-1} and peaked in July. At the statistical significance level of $P < 0.05$, it has significant positive relationship with [Fe^{2+}], [Pb^{2+}], [Nİ$^{2+}$], [Zn^{2+}], and [NO$_2^{-}$] parameters ($r > 0.750$) (Table 2). According to the inland water quality criteria of SWQR, the Aydos River was found to be very dangerous in terms of copper concentration (1.3–5.7 μg L^{-1}) [12]. Yağlıdere Creek was found to have a high copper concentration as in the present study, whereas Karasu and Sarmısaklı Creeks and Kizilirmak River were found to have lower concentrations [33,34].

Cadmium concentration in the Aydos River ranged between 0.0 and 1.1 μg L^{-1} and peaked in September and October. According to the results of Pearson's correlation analysis, [Cd^{2+}] has a significant relationship with [Mg^{2+}] and a negative relationship with DO (Table 2). According to the inland water quality criteria of SWQR, the Aydos River was found to be dangerous and Class IV (<1.5 μg L^{-1}) "very polluted water" in terms of cadmium [11,12]. The cadmium concentration of Yağlıdere Creek was found to be high as in the present study [33].

In this study, the level of mercury ranged between 0.0 and 0.0150 μg L^{-1} and peaked in October. At the statistical significance level of $P < 0.05$, mercury was found to have significant positive relationship with [Cd^{2+}], TH, TA, and [Mg^{2+}] ($r > 0.50$) (Table 2). According to surface water quality criteria, the Aydos River was found to be not dangerous in terms of mercury (<0.07 μg L^{-1}) [11,12]. Nickel concentration in the Aydos River ranged between 0.0 and 9.0 μg L^{-1} and peaked in April. The river poses no threat in terms of nickel concentration [11,12]. The zinc concentration of Aydos River ranged between 0.0 and 18.00 μg L^{-1} and peaked in May. At the statistical significance level of $P < 0.05$ in Pearson's correlation analysis, zinc concentration was found to have significant positive relationship with [Fe^{2+}], [Pb^{2+}] [Cu^{2+}], [Ni^{2+}], [Na^+], [K^+], and TA ($r > 0.50$). According to surface water quality criteria, the zinc concentration in this river poses no threat for aquatic medium (5.33–76 μg L^{-1}) [11,12].

3.3. Evaluation of irrigation water quality

Since Aydos River is used for irrigation in the study area, water quality parameters of % Na, SAR, RSC, MH, and KR values were calculated and results are interpreted using Table 3 [8,20,35].

% Na is one of the parameters used for determining the potential sodium hazard of irrigation waters. In the Aydos River, mean % Na value was found to be 35.19; the lowest value was found in the first station in October (24.54 % Na) and the highest value in the 13th station in June (54.44 % Na). Aydos River was found to be "good" (20–40 % Na) in terms of %Na (Table 3) [8,35].

Used for expressing the potential sodium hazard of water, the mean SAR value of Aydos River was found to be 1.63 meq L^{-1}; the lowest value was found in the first station in October (0.97 meq L^{-1}) and the highest value in the 13th station in June (3.19 meq L^{-1}). Aydos River was found to be "excellent" in terms of SAR (0–6 meq L^{-1}) (Table 3) [8,35]. Since the RSC value was found to be negative, the Aydos River poses no possible sodium hazard for irrigation. High magnesium concentration in water salinizes the soil and negatively affects plant growth and yield [21]. MH value of Aydos River was found to range between 52.15 and 80.59 and not suitable for irrigation (MH > 50) (Table 3). KR is calculated as the ratio of sodium (Na^+) to calcium (Ca^{2+}) and magnesium (Mg^{2+}). KR higher than 1 indicates excessive sodium concentration in water. KR of Aydos River was found to be higher than 1 only in 7th–13th stations and it is generally suitable for use as irrigation water [20].

3.4. Assessing the water quality index

Water quality parameters of Aydos River were interpreted using WQI. Index was calculated by determining the weight loads by considering the distribution of PCA's principal components by their loads (Table 4) and the calculations were made using SWQR [12] and WHO [11] limits [12,36]. According to PCA analysis result, the index was calculated using WT, [SO_4^{2-}], [SO_3^{2-}], [NO_3^-], BOD_5, COD, SS, [NO_2^-], EC, salinity, [Fe^{2+}], [Pb^{2+}], [Zn^{2+}], [Cu^{2+}], [Ni^{2+}], [Cd^{2+}], TH, TA, [PO_4^{3-}], and [NH_4^+] parameters [36]. Given the annual mean values, Aydos River's water quality index (WQI) (81.73) was found to be in "good water quality" (50 ≤ WQI < 100) class.

The lowest WQI value of Aydos River was found to be 55.6 in December and the highest value to be 114.3 in October (Fig. 2). Given these results, it can be stated that river is in "good water quality" class in terms of potable water. High values are believed to arise from the fertilizers, which are used in agricultural activities and reach the river through precipitation.

Huge amount of complex data, which were obtained from 28 parameters examined using water samples monthly

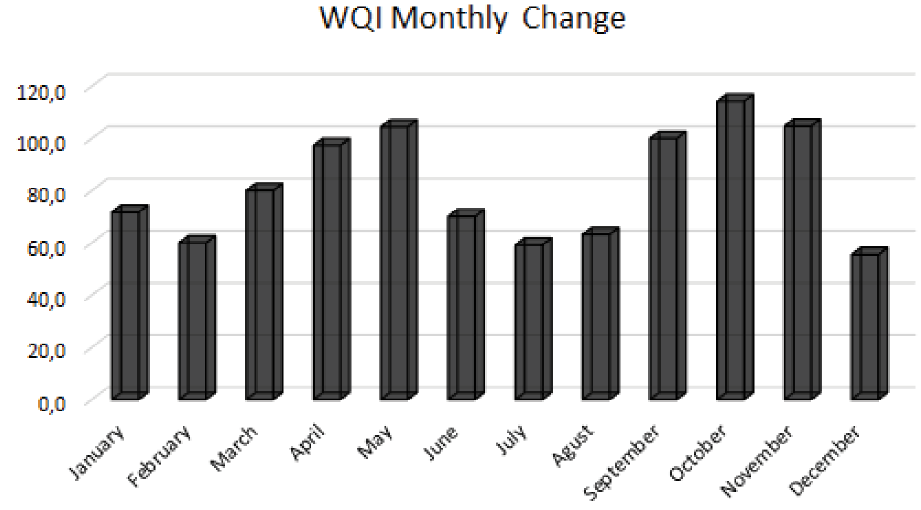

Fig. 2. Monthly change of Aydos River's water quality index (WQI).

Table 4
Weights for the 19 variables in the water samples from the Aydos River

PC	Eigenvalue	Relative eigenvalue	Variable	Loading value	Relative loading value on same PC	Weight (relative eigenvalue × relative loading value)
1	9.01	0.380	WT	0.949	0.114	0.043
			$[SO_4^{2-}]$	0.895	0.108	0.041
			$[SO_3^{2-}]$	0.871	0.105	0.040
			$[NO_3^-]$	0.87	0.105	0.040
			BOD_5	0.82	0.099	0.038
			COD	0.791	0.095	0.036
			SS	0.791	0.095	0.036
			$[NO_2^-]$	0.777	0.094	0.036
			EC	0.77	0.093	0.035
			Salinity	0.764	0.092	0.035
			Total	8.298	1.000	
2	6.51	0.275	$[Fe^{2+}]$	0.92	0.205	0.056
			$[Pb^{2+}]$	0.918	0.205	0.056
			$[Zn^{2+}]$	0.912	0.204	0.056
			$[Cu^{2+}]$	0.89	0.199	0.055
			$[Ni^{2+}]$	0.837	0.187	0.051
			Total	4.477	1.000	
3	3.91	0.165	$[Cd^{2+}]$	0.841	1.00	0.165
4	2.86	0.121	$[PO_4^{3-}]$	0.663	1.00	0.121
5	1.42	0.060	$[NH_4^+]$	0.897	1.00	0.060
	23.701					

collected from 13 stations for a year, were spatially and temporally analyzed.

HCA was used in revealing the temporal and spatial differences/similarities and to identify the groups. HCA analyses were performed on seasonal mean values and station mean values. During the analyses, Euclidian Distance and Wart method showing the relationship between distances and correlation at best were used. According to the results of HCA performed using station mean values of Aydos River, the similarities/differences of stations clustered as seen in Fig. 3. The similarity rate of Cluster A is stronger than Cluster B. Given these results, Aydos River can be considered as upper basin (stations 1–7) and lower basin (stations 8–13). Cluster A (upper basin) is the portion, where the river water is under the effect of its source. Cluster B (lower basin) is the region, where the river water reaches the seawater and where the effects of changes in many factors such as climate, soil structure, and plant cover are clearly felt (Fig. 3).

Given the results of HCA performed using seasonal mean values, the seasonal differences clustered as seen in Fig. 4. Among two main clusters arising from analysis, the similarity rate of Cluster A is higher than Cluster B. Cluster A includes winter and spring seasons, whereas Cluster B includes summer and autumn. In HCA analyses, rather than 4 seasons, the discrimination can be clearly seen in 2 seasons. However, it is not possible to state a wet and dry season because the climate changes create any weather event in any season. The results of this analysis are in corroboration with ANOVA test results.

Before the principal components analysis/factor analysis, KMO and Bartlett tests were applied to datasets and the fitness of PCA was confirmed. While selecting the number of principal components, the confirmation was performed using the number of principal components passing through 1 before a clear break in the scree plot (Fig. 5) [37,38]. As a result of PCA test, it was determined that 5 principal components could represent the data of Aydos River (Table 5). Using the eigenvalues summarizing 84.65% of the total variance in datasets, these principal components with eigenvalue >1 were obtained (Table 5, Fig. 6). The PCA factor loads >0.75, between 0.75 and 0.50, and between 0.50 and 0.30 were classified as "strong", "moderate", and "weak" corresponding to the absolute load values [39].

PC1 explaining 32.18% of total variance has strong positive load on WT, $[SO_4^{2-}]$, $[SO_3^{2-}]$, $[NO_3^-]$, BOD_5, COD, SS, $[NO_2^-]$, EC, and salinity ($r > 0.75$) parameters. This component can be stated to represent the non-point pollution sources and salinity sources. Surficial water flow occurring as a result of atmospheric precipitation in the basin brings soil and rocks and constitutes this non-point pollution source [29,39,40]. Moreover, the nitrogenous fertilizers and pesticides, which are used in the agricultural activities in the basin of Aydos River, might be the pollution loads of the river.

PC2 explaining 23.23% of total variance has strong positive load on $[Fe^{2+}]$, $[Pb^{2+}]$, $[Zn^{2+}]$, $[Cu^{2+}]$, and $[Ni^{2+}]$. This component arises from the combination of heavy metal content, which originates from soil or rock structure, with water [41].

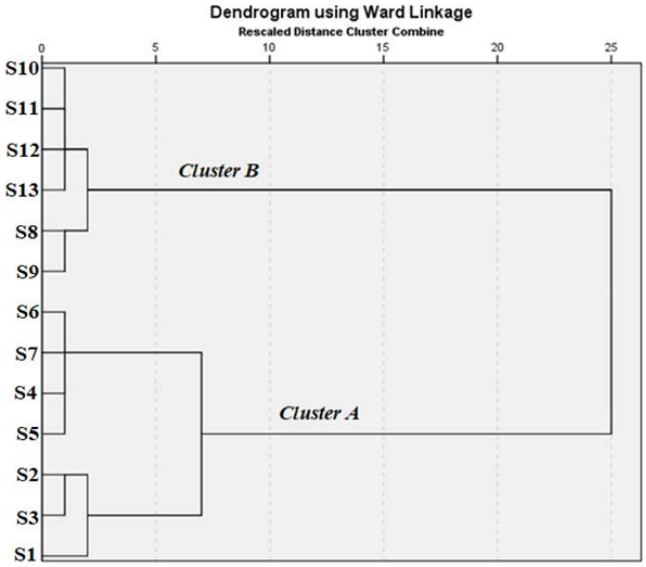

Fig. 3. Dendrogram (Using Ward Method) shows clusters of variables (S: Station).

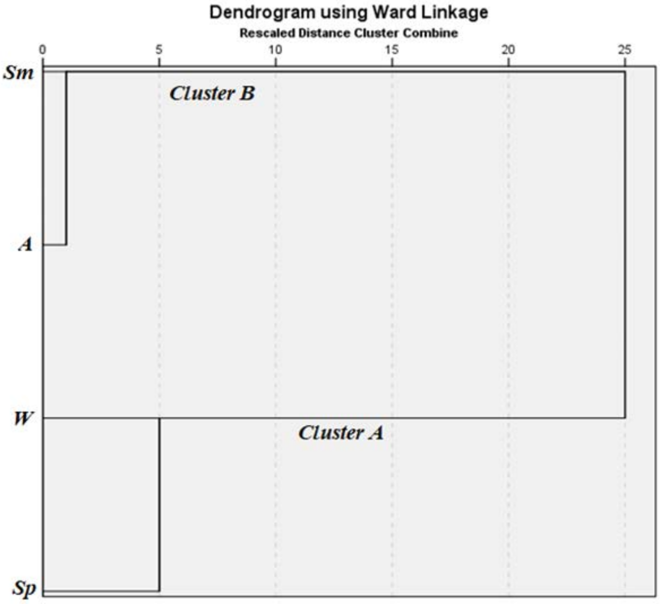

Fig. 4. Dendrogram (Using Ward Method) shows clusters of variables (A: Autumn, Sm: Summer, Sp: Spring and W: Winter).

PC3 explaining 13.95% of total variance has a strong positive load on TH, TA, and [Cd^{2+}] and a negative load on DO. Cadmium is a heavy metal, which dissolves in water and dissolubility of which is increases in parallel with temperature. There is no industrial facility in the basin. Thus, cadmium source can only be the fertilization in the basin. Since the water of river is used in agricultural activity, cadmium poses risk not only for the organisms living in this basin but also for human health. On the other hand, the total hardness and total alkalinity in water are related with dissoluble soil or rock and atmospheric precipitation and basin geology [42]. The negative load of DO for this principal component arises from the reverse relationship between these parameters and it is an expected result.

PC4 explaining 10.20% of total variance has a positive load for [PO_4^{3-}]. It is thought that the phosphorous fertilizers used in agricultural activities in the basin reach Aydos Water through the brook water and precipitation and they constitute a non-point pollution source. This non-point pollution is constituted by phosphate or phosphate-rich rocks, which release phosphor with erosion, degradation, and extraction, by combining with water reservoir after precipitation. Human-origin phosphor sources include

Table 5
Varimax rotated factor matrix for the whole dataset

Variable factor loadings (varimax normalized)	PC1	PC2	PC3	PC4	PC5
Eigenvalues	9.01	6.51	3.91	2.86	1.42
Variance (%)	32.18	23.23	13.95	10.21	5.08
Cumulative (%)	32.18	55.42	69.36	79.57	***84.65***
WT	***0.949***	–0.111	0.191	0.018	–0.058
SO_4^{2-}	***0.895***	0.266	0.091	0.239	–0.089
SO_3^{2}	***0.871***	0.269	0.261	0.213	0.108
NO_3	***0.870***	0.143	0.350	0.085	0.076
BOD_5	***0.820***	0.094	0.250	0.149	0.144
COD	***0.791***	0.065	0.563	0.000	0.036
SS	***0.791***	0.369	0.298	0.269	0.170
NO_2^-	***0.777***	0.304	0.071	0.418	0.138
EC	***0.770***	0.058	0.088	0.141	–0.162
Salinity	***0.764***	0.247	0.274	0.349	0.142
Mg^{2+}	0.665	–0.007	0.649	0.295	0.121
Cl^-	–0.662	0.300	–0.343	0.364	–0.047
Fe^{2+}	–0.050	***0.920***	–0.061	–0.137	0.150
Pb^{2+}	0.255	***0.918***	–0.021	–0.006	–0.027
Zn^{2+}	0.216	***0.912***	0.016	0.084	–0.049
Cu^{2+}	–0.091	***0.890***	0.105	0.219	0.081
Ni^{2+}	0.071	***0.837***	0.273	0.164	–0.021
Na^+	0.080	0.745	–0.319	0.384	0.171
K^+	0.270	0.619	0.145	0.424	0.328
TH	0.415	0.612	–0.112	0.551	–0.077
TA	0.382	0.611	–0.155	0.602	–0.023
DO	–0.378	0.181	***–0.856***	–0.012	–0.044
Cd^{2+}	0.319	0.164	***0.841***	0.157	0.029
Ca^{2+}	0.387	–0.031	0.652	–0.004	–0.013
PO_4^{3-}	0.309	0.105	0.224	***0.663***	0.147
Hg^{2+}	0.072	0.378	0.534	0.541	–0.253
pH	0.433	0.068	0.353	0.513	0.437
NH_4^+	0.012	0.123	–0.015	0.059	***0.897***

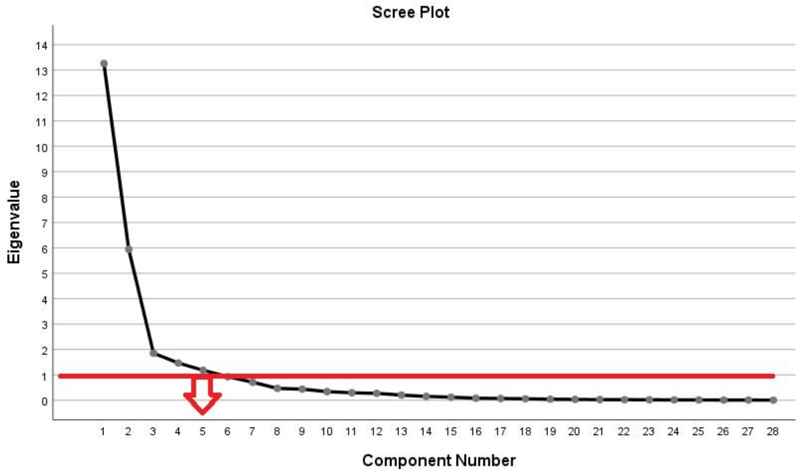

Fig. 5. Scree plot for the principal component model of the monitoring data.

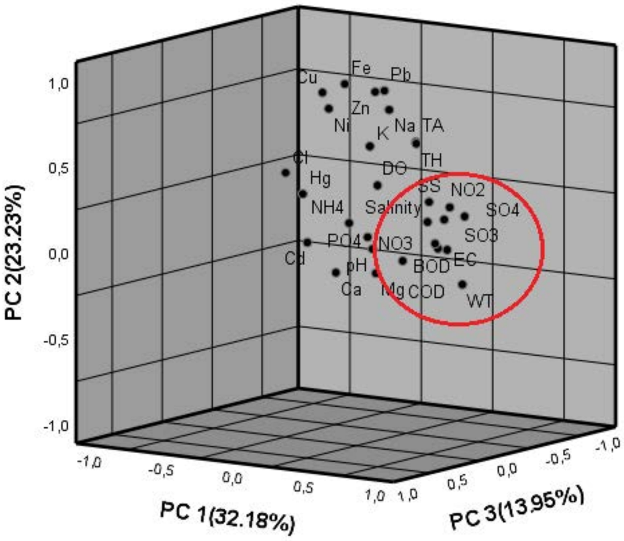

Fig. 6. The component plot in the rotated space.

phosphor mining lands, agricultural lands, and urban/residential areas exposed to precipitation [43,44].

PC5 explaining 5.08% of total variance has a significant positive load for [NH_4]. Rainwater, which is the strongest solvent in the world, partially dissolves the nitrogenous matters in soil and the nitrogenous compounds reach the water. For this reason, the presence of nitrogenous compounds in waters obtained from under or above the ground. The disintegration and degradation of many organic matters and herbal proteins in nature create ammonium. Human and animal bodies excrete ammonium through urine. Dangerous amounts of NH_4^+ ion might be seen in wells located in agricultural regions or it can be stated that nitrogenous artificial fertilizers pass underground through rainwaters and make the quality of well waters risky [45].

4. Conclusions

In the 21st century, the protection of existing water resources became one of the most important challenges. Even if the measure is taken immediately, the rehabilitation of degraded freshwater ecosystems would take years. For this reason, immediate actions are required.

In this study, water samples were monthly collected from 13 stations on Aydos River, which is very important for the biodiversity in Turkey's First PAN Park, for a year. The data obtained were used for determining the water quality, fitness of Aydos River for irrigation purposes, calculating the water quality index based on the principal components of PCA analyses, and spatially and temporally analyzing the data.

Aydos River was found to be very risky in terms of heavy metal because the water is used for agricultural purposes and the organisms living in Aydos River are involved in food chain and reach even humans. It is recommended to continue the sampling as a monitoring process.

The basin should be monitored also for phosphate and nitrate since fertilizers and pesticides are uncontrolledly used in agricultural activities. The water quality can be protected and improved only through supporting and teaching the "best environment practice" principle. pH and EC values of river can be explained with irregular contact between water and minerals existing in river basin or soil and rocks, sudden changes in climate of sensitive aquatic ecosystems due to climate change, and the presence of a hydroelectric power plant on the river.

In this study, Aydos River was classified according to WHO and SWQR criteria and regulations. Even though the water was classified as "clean water" according to general chemical and physical parameters for inland surface waters, phosphate, nitrate, pH, EC, copper, and cadmium concentrations were found to be beyond the limits desired for agricultural and drinking purposes and it was concluded that agricultural products might pose a health risk.

From the aspect of irrigation, Aydos River was found to be suitable in terms of SAR, % Na, MH, and KR parameters but the magnesium hazard results indicate that this water might have negative effects on the soil. Thus, it is not suitable for irrigation purposes.

Statistical analyses (ANOVA, Pearson's correlation, HCA, and PCA) applied to datasets yielded similar results. Using HCA, the river basin can be spatially divided as upper basin and lower basin. Winter and spring seasons were found to be similar to each other more than summer and autumn seasons were.

It was concluded that, in order to protect and improve the water quality of Aydos River, measures should be taken in accordance with WHO and SWQR regulations (Class I–V).

PCA analysis on the water quality data of Aydos River showed that the water mass is represented by 5 principal components. Temperature that is one of the most important indicators of global climate change, anions originating from fertilizers and pesticides used in agricultural activities, and non-point heavy metal pollutants are the pollution sources of Aydos River. According to annual mean values, WQI was found generally to be high-quality water. However, in future freshwater management of basin, monitoring is recommended for the continuity of wildlife.

In this basin, which has been certified as the First PAN Park of Turkey, water quality is of inarguable importance for the purest wildlife and the use of agricultural, recreation, and touristic use of region. In order to prevent agricultural-origin pollution, the fertilizers and pesticides should be used consciously, and animal wastes should prevent from reaching the water. Since they offer time and cost advantages, statistical models should be used in further studies and regular monitoring should be performed.

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