RESEARCH ARTICLE

Comprehensive assessment of water quality and associated health risk by using physicochemical quality indices and multivariate analysis in Terme River, Turkey

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Abstract

The ecosystem and water quality of Terme River, an essential drinking and irrigation water source in the region, are at risk due to anthropogenic pressures. Therefore, the present study aim to present a comprehensive overview of the water quality state and pollution sources of the river. Some physicochemical water quality parameters were analyzed by standard methods along the surface water of river spatiotemporally. The concentrations of major elements and heavy metals (Na, Mg, K, Ca, Al, Cr, Fe, Co, Mn, Ni, Zn, Cd, Cu, Pb, As) were measured in water samples. Relationships between physicochemical data were assessed by using multivariate statistical analysis (MSA) methods. The order of the mean values of cations were as follow: $Ca^{2+} > Mg^{2+} > Na^+ > K^+ > NH_4^+$ (32.66, 26.82, 13.29, 6.45, 0.305; mg/L), and order of anions: $SO_4^{2-} > NO_3^- > F^- > NO_2^-$ (7.88, 3.988, 1.01, 0.0316; mg/L). Increases in ion concentrations in the downstream zone have been monitored in the summer and autumn months. Average water quality index (WQI) 22, heavy metal pollution index (HPI) 15.61, heavy metal evaluation index (HEI) 0.78, and nutrient pollution index (NPI) 0.404 values indicated that the general water quality of Terme River was fine. All hazard quotient (HQ) and hazard index (HI) values in this study were calculated below the risk threshold (<1). HI-total values (2.48E-01) in children were higher than in adults (2.14E-01). This suggests that children's health is at higher risk than adults. Principal component analysis (PCA) data formed four principal components (PCs) explaining 85.22% of the total variance. These PCs revealed that the significant changes in water quality occurred from point and diffuse sources, including rock types of the basin, soil erosion, domestic wastewater discharges, and agricultural flow of inorganic fertilizers.

Keywords Water management · Irrigation water usage · Nutrient pollution index · Water-quality indices · Health hazard index · Heavy metal pollution

Introduction

Freshwater, the most important natural resource on earth, is a prerequisite for life as well as all life forms and basic requirement of ecological diversity and sustainable development (Taş et al. 2019). However, the water crisis has come to be a global problem in last decade (Ustaoğlu et al. 2020a). Rapid increase in human population, urbanization, and industrialization have led to excessive water use from freshwater sources (e.g., rivers, lakes) for various purposes of daily needs (Kamrani et al. 2016; Tepe and Aydın 2017). As a result, the discharge of untreated water containing organic and inorganic compounds into water bodies from domestic wastes, industry and agricultural runoff, has caused water quality deterioration and threatens public health by restricting the use of water as a water resource for humans (Amiri et al. 2015; Sohrabi et al. 2020; Tokatlı and Varol 2021). Approximately, 70% of surface water sources are used in irrigation and agriculture, while only 10% is used for domestic purposes. Around 850 million people on a global basis lack access to safe and clean water. Nearly 80% of the illnesses in these people are caused by polluted water (Amiri et al. 2021a). One in five deaths in infants is caused by contaminated water consumption. Five

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hundred thousand people die of diarrhea due to approximately two billion people consuming contaminated drinking water in the world (Amiri et al. 2021b).

Rivers are the most exposed resources to both anthropogenic and natural contamination. They are naturally affected by precipitation, weather conditions, and sediment transport. However, anthropogenic effects could exacerbate the negative effects on the ecological character of the stream (Gao et al. 2020). Heavy metals (HMs) in particular are among the most dangerous pollutants in aquatic environments due to their long-lasting, high bioaccumulation potential and toxicity (Amiri et al. 2021b). Collecting reliable data on rivers' water quality, assessing its spatial and temporal fluctuations, identifying the contamination sources, determining the state of water quality, and monitoring water pollution in rivers are critical points for effective water management (Varol 2020).

Considerable spatial and temporal variations occur in water quality of surface water. It is essential to understand the influences affecting the spatiotemporal variability in water quality to determine the quality of streams' water passing through city centers and develop improvement strategies. Physicochemical water quality indices are auxiliary tools used for water quality evaluation. These index values are administered to determine water quality status and sometimes specific water uses (drinking, irrigation, recreation, domestic, and industrial purposes). Multivariate statistical analysis (MSA), WQI, heavy metal pollution index (HPI), heavy metal evaluation index (HEI), HQ, HI, CR, sodium percentage (% Na), sodium absorption ratio (SAR), magnesium hazard (MH), and residual sodium carbonate (RSC) are broadly used to assess drinking/irrigation water quality of rivers. Therefore, they play a significant role in the management of water resources for decision makers (Sohrabi et al. 2017).

The water quality assessment has become a vital issue in last decade due to rapid deterioration in high quality freshwater resources in Turkey (Ustaoğlu and Tepe 2019; Ustaoğlu et al. 2020a, b; Yılmaz et al. 2020). Located in the north of Turkey, Terme River is a main river in Central Black Sea which forms the alluvial Terme Plain. It reaches the Black Sea by passing through Salıpazarı town on the plateau and through the center of Terme town in the plain (Fig. 1). Hazelnuts are grown in more than 50% of the fertile Terme Plain. The population of Terme district (10-m altitude) is 71,492, and the population of Salıpazarı (75-m altitude) is 19,990 people. The districts' drinking water is supplied from the borehole and caisson wells on the banks of Terme River. However, in recent years, serious problems have been experienced in drinking and irrigation water supply during dry seasons due to global warming.

The lack of drinking water treatment plant and infrastructure of the region, inadequate wastewater treatment facilities, and deficiencies in sewage and rainwater lines negatively affect public health. Terme River is under the pressure of both basin and flood pollution factors. A comprehensive study focused on determining the possible factors causing the spatial-temporal change in the water quality of Terme Stream was needed. The aim of the present study is to (i) evaluate the spatial and seasonal changes of some parameters affecting the water quality of Terme River by comparing them with national as well as international guidelines, (ii) classify anthropogenic and natural resources/factors that affect the water quality of the river, (iii) estimate the drinking water quality of the river using WQI, HPI, and HEI indexes, (iv) calculate the irrigation water quality of the river with SAR, MH, Na%, and RSC indexes, and (v) determine the heavy metal values in the water with THQ, HI, and CR indexes to evaluate in terms of public health. This study is the first to present a comprehensive overview of the water quality state and pollution sources of the Terme River, and will be a reference study for possible future research.

Materials and methods

Description of the study area

The present study was conducted in the Terme River located in the Black Sea region, north of Turkey. The Terme River joins the Black Sea 5 km downstream of Terme district center (Fig. 1). Typical Black Sea climate with precipitation prevails in Terme every season. The mean annual rainfall is 964.8 mm. Hazelnut farming is widespread in the Terme River Basin. Paddy, maize, and poplar are produced in the lower parts of the basin. Terme River's annual mean of flow rate is 10.51 m^3/s. Terme River is under the pressure of agricultural fertilizers, pesticides, and household wastes.

Seasonal water samples were collected from four different stations to assess spatiotemporal water quality along the riverbed of Terme River between April 2019 and January 2020 (Fig. 1). Site 1 (T1: 41° 04′33″ N–36° 49′33″ E), selected from the highland part of the stream, has the least possible anthropogenic impact with pebble stone geological structure. The project of Salıpazarı Dam has been planned in this area. The geological structure of the rest of three stations was similar and all located on alluvion basin. Site 2 (T2: 41° 07′13″ N–36° 50′59″ E), located approximately 5 km north of Salıpazarı district (after passing through the district center), is also exposed to the domestic wastewater of this district. Site 3 (T3: 41° 11′18″ N–36° 56′33″ E), which is selected approximately 4 km south of Terme district, is affected by agricultural activities (hazelnut, paddy, corn, bean, poplar, etc.). Site 4 (T4: 41° 12′59″ N–36° 59′53″ E), selected after passing through Terme district center in the lower basin of the stream, is in a position to represent the entire pollution load of the basin.
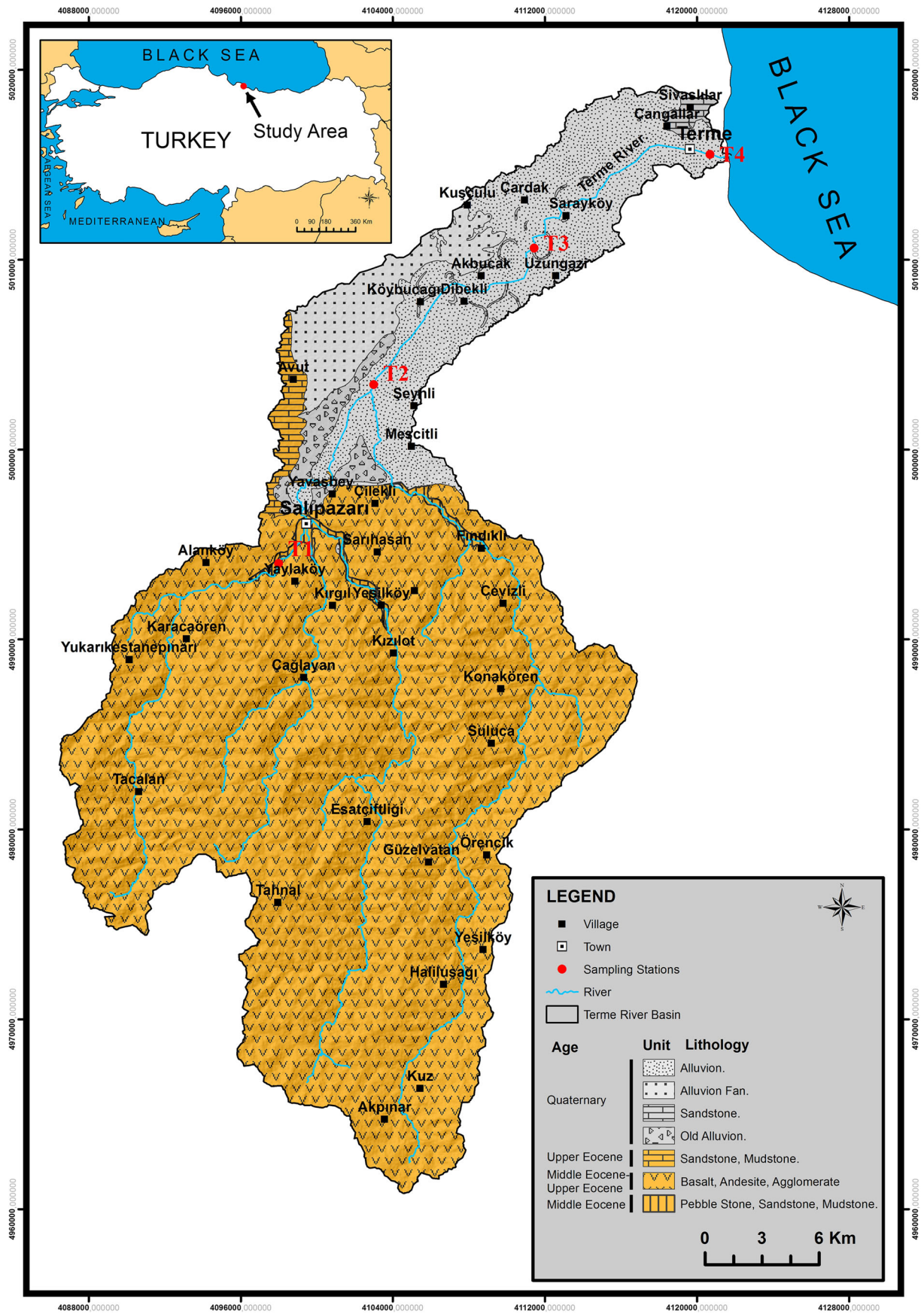
Fig. 1 Location of sampling stations in the study area

Water sampling and analytical procedure

A total of 48 representative water samples were taken from 10 to 20 cm underneath the water surface from the determined stations. Plastic bottles (2.5 L), washed initially with 4% HCl and then rinsed with deionized water, were used for this purpose (Ustaoğlu et al. 2017). The collected water samples were stored in an ice chest and transported immediately to the laboratory through the cold chain in the dark environment, and water analyses were performed on the same day. Water temperature (WT), pH, dissolved oxygen (DO), total dissolved solids (TDS), electrical conductivity (EC), oxidation reduction potential (ORP), and salinity were measured on site by Hach HQ 40d (Hach Company, Loveland, CO, USA) and YSI Pro1030 multianalyzer (YSI Incorporated, Yellow Springs, OH, USA). The turbidity of the samples was determined in the field using a Hach 2100Q portable turbidimeter (Hach Co., USA). This instrument provides a direct readout in nephelometric turbidity units (NT). Total suspended solids (TSS), total alkalinity (TA), total hardness (TH), and biological oxygen demand (BOD_5) were measured in the laboratory following standard procedures (Tepe et al. 2006). Samples were analyzed for ammonia nitrogen (NH_4-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), total phosphorus (TP), sulfate (SO_4), free chlorine (Cl_2), anionic surfactant (AS), fluoride (F^-), and silicate (SiO_2) using Hach test kits and a spectrophotometer (Hach DR 2800™, Hach Co., USA) following the manufacturer's instructions. Water samples were vacuum filtered through 0.45-μm filter paper, then acidified to pH below 2 with concentrated HNO_3 for metal analysis (Ca, Mg, K, Na, Cr, Al, Co, Mn, Ni, Cu, Fe, Zn, Pb, Cd, As). Metal analysis in water was performed in triplicate by means of ICP-MS (Agilent® 7700x, Agilent Technologies, USA) (Yüksel and Arıca 2018; Amiri et al. 2021a).

Analysis of water quality indices

Water quality assessment by WQI

WQI is a simple, useful, and convenient approach to determine the overall quality of surface/groundwater and its suitability as drinking water (Aydın et al. 2021). For this reason, it has been broadly used in studies that evaluate the water quality in last decade (Wang et al. 2017; Varol 2020; Ustaoğlu et al. 2020b). WQI was calculated using the formula below (1);

$$WQI = \sum \left[W_i \times \left(\frac{C_i}{S_i} \right) \times 100 \right] \tag{1}$$

where $W_i = w_i/\Sigma w_i$ is the relative weight (Table 1). The W_i value is assigned to 5 as maximum and 1 as minimum, with regards to the relative significant effects of the parameters on

Table 1 Relative weight of each water quality parameters

Parameters	WHO (2011)	Weight (w_i)	Relative weight (W_i)
pH	8	5	0.054
EC (μS/cm)	1500	4	0.043
TDS (mg/L)	600	4	0.043
TH (mg/L $CaCO_3$)	100	1	0.011
BOD_5 (mg/L)	5	5	0.054
NO_2-N (mg/L)	0.15	5	0.054
NO_3-N (mg/L)	11.3	5	0.054
SO_4 (mg/L)	250	5	0.054
F (mg/L)	1.5	5	0.054
Ca (mg/L)	75	2	0.022
K (mg/L)	12	2	0.022
Mg (mg/L)	50	2	0.022
Na (mg/L)	200	3	0.032
Al (μg/L)	200	4	0.043
Cr (μg/L)	50	5	0.054
Mn (μg/L)	400	5	0.054
Fe (μg/L)	300	4	0.043
Co (μg/L)	50	2	0.022
Ni (μg/L)	70	5	0.054
Cu (μg/L)	2000	2	0.022
Zn (μg/L)	3000	3	0.032
As (μg/L)	10	5	0.054
Cd (μg/L)	3	5	0.054
Pb (μg/L)	10	5	0.054

human health and their significance in water quality (Ustaoğlu and Aydın 2020). C_i is the concentrations of the parameters included in the calculation, and S_i is the standard values determined by WHO (2011) in drinking water. In this study, 24 water quality parameters (pH, EC, TDS, TH, BOD_5, NO_2-N, NO_3-N, SO_4, F^-, Ca, K, Mg, Na, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, and Pb) were included in the WQI calculation. Water quality is evaluated in five different classes according to WQI values. Accordingly, WQI < 25 is excellent; 26 ≤ WQI < 50 is good; 51 WQI < 75 is poor; 76 ≤ WQI < 100 is very poor; WQI ≥ 100 is undrinkable (Yadav et al. 2010).

Heavy metal pollution index

The HPI is a useful method for assessing the combined effect of individual heavy metal indicators on the general water quality. For this reason, researchers use the HPI value as a comprehensive instrument to find general water quality derived from heavy metals (Tokatlı and Ustaoğlu 2020). HPI was calculated using the following formulas (2–4) (Mohan et al. 1996).

$$HPI = \frac{\sum_{i=1}^{n}(Q_i W_i)}{\sum_{i=1}^{n} W_i} \quad (2)$$

$$Q_i = \frac{C_i}{S_i} x 100 \quad (3)$$

$$W_i = \frac{k}{S_i} \quad (4)$$

Q_i represents the subindex of each metal, C_i represents the detected concentration value of metals, the standard values of S_i parameters permitted by WHO (2011) as drinking water, W_i represents the unit weight of metals, and k represents a fixed value of "1". If HPI is <100, it indicates a slight level of heavy metal contamination and no adverse related health effects. HPI = 100 indicates threshold risk as well as potential adverse health effects. If HPI is > 100, water is not usable for drinking and also not suitable for consumption (Saleh et al. 2018).

Heavy metal evaluation index

The index of HEI was used as an indicator of heavy metal contamination in water. Hence, it helps the easy interpretation of the water pollution level (Edet and Offiong 2002). HEI was computed according to the formula below.

$$HEI = \sum_{i=1}^{n} \frac{H_C}{H_{MAC}} \quad (5)$$

here HC stands for the value determined for each metal and H_{MAC} stands for the maximum allowed concentration value (MAC) of each metal (WHO 2011). If HEI <10, it is interpreted as "low pollution"; if 10 <HEI <20, "medium pollution"; if HEI> 20, it is interpreted as "high pollution" (Saleh et al. 2018).

Nutrient pollution index (NPI)

Nutrients such as phosphate and nitrate enter the river water mostly through agricultural activities, synthetic fertilizers, fish farms, barn leachate, domestic wastes/sewage waters, surface waters, and flood waters. NPI can be a good method to understand nutrient load in waters where water flow is slow, such as urban plain streams. NPI was computed to find out the pollution in the surface water. NPI was calculated using the below expression in Eq. 6 (Isiuku and Enyoh 2020).

$$NPI = \frac{C_N}{MAC_N} + \frac{C_P}{MAC_P} \quad (6)$$

where $C_{N/P}$ is the mean nitrate and phosphate concentration in the riverine surface water, $MAC_{N/P}$ is maximum allowable concentration established by WHO to be 50 mg/L and 5 mg/L for nitrate and phosphate in surface water, respectively. The water quality was categorized into four types based on the NPI

values: <1 (no pollution), $1 \leq 3$ (moderate polluted), $>3 \leq 6$ (considerable polluted), and >6 (very high polluted).

In order to prevent eutrophication, monitoring of nitrate contamination is a serious issue as important as monitoring of phosphate contamination (Amiri et al. 2015). Nitrate index (NI) was calculated to evaluate the effects of fertilizers used in agricultural activities as well as wastewaters on the stream in Terme Plain. For the determination of nitrate pollution, NI, a particular parameter WQI, can be used as an indicator of nitrate pollution in streams due to anthropogenic activity. The below formula is applied to calculate the NI (7):

$$NI = \frac{Cs-HAV}{HAV} \quad (7)$$

where Cs is the analytical concentration of nitrate in the sample, HAV (human affected value) is the threshold value of anthropogenic source, taken as 20 mg/L. The water quality was categorized into five groups based on the NI values: <0 (unpolluted-clean), 0–1 (light pollution), 1–2 (moderate pollution), 2–3 (significant pollution), and>3 (very significant pollution) (Panneerselvam et al. 2020).

Health risks assessments

Heavy metals from freshwater are taken the human body through ingestion or skin contact. Noncarcinogenic and carcinogenic health effects from oral intake and skin contact may be estimated by experimental models. In the present study, the health risk evaluation method recommended by USEPA (2004) was used, and the toxicological parameters of metals are shown in Table 2 (Wang et al. 2017). The average daily dose (ADD) by direct digestion (ADD ingestion) and skin absorption (ADD dermal) was calculated using the formulas (8 and 9) below (Zeng et al. 2015; Amiri et al. 2021b).

$$ADD_{ingestion} = \frac{C_{water} \times IR \times ABS_g \times EF \times ED}{BW \times AT} \quad (8)$$

$$ADD_{dermal} = \frac{C_{water} \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \quad (9)$$

where $ADD_{ingestion}$ expresses average daily dose by ingestion and ADD_{dermal} reveals average daily dose by dermal, μg/kg/d; C_{water} shows level of the heavy metals in freshwater, μg/L; IR indicates ingestion rate (L/d), 2 for adult, 0.64 for children in this study; EF reveals exposure frequency 365 days/year in this study; ED stands for exposure duration (in years), 70 for adults and 6 for children in this study; K_p represents dermal permeability coefficient in water (cm/h); ET is the exposure time during bathing and shower, 0.6 h/day in this study; CF shows the unit conversion factor, 1 L/1000 cm^3; BW represents average body weight (kg), 70 for adults and 20

Table 2 Toxicological parameters of the investigated metals used for health risk assessment (USEPA 2004; Wang et al. 2017)

	K_p	RfD$_{ingestion}$ (μg/kg/day)	RfD$_{dermal}$ (μg/kg/day)	ABS$_g$ (%)
Al	1×10^{-3}	1000	200	95
Cr	1×10^{-3}	3	0.075	1.3
Mn	1×10^{-3}	24	0.96	6
Fe	1×10^{-3}	700	140	1.4
Co	4×10^{-4}	0.3	0.06	nd
Ni	2×10^{-4}	20	0.8	4
Cu	1×10^{-3}	40	8	57
Zn	6×10^{-4}	300	60	20
As	1×10^{-3}	0.3	0.285	95
Cd	1×10^{-3}	0.5	0.025	5
Pb	1×10^{-4}	1.4	0.42	11.7

for children in this study; *AT* indicates averaging time (day), 25,550 for adults and 2190 for children in this study; SA expresses exposed skin area (cm^2), 18,000 for adults and 6600 for children in this study; *ABS$_g$*, which is dimensionless, was the gastrointestinal absorption factor (Xiao et al. 2019).

Hazard quotient (HQ) and hazard index (HI), representing the possible noncarcinogenic effects of heavy metals taken with digestion and skin, were calculated by the following formulas (10–12).

$$HQ_{ingestion} = \frac{ADD_{ingestion}}{RfD_{ingestion}} \qquad (10)$$

$$HQ_{dermal} = \frac{ADD_{dermal}}{RfD_{dermal}} \qquad (11)$$

$$HI = \sum_{i=1}^{n} \left(ADD_{ingestion} + ADD_{dermal} \right) \qquad (12)$$

HQ <1 represents that exposure to any adverse health effects is not likely, while a HI > 1 value indicates that there may be noncarcinogenic effects from heavy metals contact. Carcinogenic risk (CR) describes an individual's risk of cancer due to lifetime contact to potential carcinogens and is calculated by the formula (13) below.

$$CR = ADD \times CSF \qquad (13)$$

here *CSF* is cancer slope factor. Cancer risk was calculated for arsenic only in this study. *CSF* values are 0.0015 and 0.00366 μg/kg/day for digestion and skin, respectively (Gao et al. 2019).

Water quality evaluation of irrigation water

Highly salty water is toxic to plants and creates a salinity hazard. Therefore, the quality of water to be used for irrigation

is critical as it affects the soil, plant, and human health. SAR is generally considered to be a major index for irrigation water assessment. The high sodium content in irrigation water leads to an alkali hazard and reduces soil permeability (Singh et al. 2020). The negative value of RSC shows the incomplete precipitation of Ca^{2+} and Mg^{2+}. Irrigation water quality of the Terme River was assessed with the SAR, %Na, RSC, and MH parameters which calculated as the following formulas (14–17), respectively (Ravikumar et al. 2013).

$$SAR = \frac{\left[Na_{meq}^+ \right]}{\sqrt{\dfrac{\left[Ca_{meq}^{2+} \right] + \left[Mg_{meq}^{2+} \right]}{2}}} \qquad (14)$$

$$Na\% = \frac{\left(Na_{meq}^+ + K_{meq}^+ \right) \times 100}{Na_{meq}^+ + Ca_{meq}^{2+} + Mg_{meq}^{2+} + K_{meq}^+} \qquad (15)$$

$$RSC = (Alkalinity \times 0.0333) - \left(Ca_{meq}^{2+} + Mg_{meq}^{2+} \right) \qquad (16)$$

$$MH = \left(\frac{Mg_{meq}^{2+}}{Ca_{meq}^{2+} + Mg_{meq}^{2+}} \right) \times 100 \qquad (17)$$

Data analysis

MSA enables to reduce, consolidate, and categorize data. Thus, convenient meanings are derived from the large number of data. MSAs such as cluster analysis (CA), principal component analysis (PCA), and Pearson correlation index (PCI) are widely used worldwide to identify sources and factors affecting water quality chemistry (Amiri et al. 2021a; Gao et al. 2020; Ustaoğlu 2020a, b; Amiri and Berndtsson 2020; Amiri et al. 2021c). In this study, descriptive statistical analysis of water quality parameters and whether there is a significant difference between stations was calculated by one-way variance of analysis (ANOVA) (p<0.05). PCI was applied to determine the direction and amount of relationship between parameters and CA to investigate similarities and differences. PCA was used to reduce the dataset and reveal new factors. All these statistical analyses were carried out with the SPSS 22 statistical program. In addition, PAST4.x software was used in the production of box plot and heat map graphics.

Results and discussion

Physical and chemical features of surface water

The results of the analysis performed to determine the spatio-temporal physicochemical properties of the Terme River surface water are given in Table 3. Descriptive statistical information of water quality parameters is also presented in the

table. In addition, seasonal changes are shown with the boxplot graph (Fig. 2).

According to annual mean values, Terme River water is warm (≤25 °C, mean 17.63 °C), alkaline character (pH> 8), less salty (EC, 100–250 μS/cm), medium hard (TH, 75–100-mg/L CaCO$_3$), and freshwater (TDS, <1000 mg/L). Waters with high pH value show negative ORP value because they have higher amount of reducing agent (Ustaoğlu et al. 2020a).

The spatiotemporal trend of Terme River water varied across sites and seasonally. ORP value was measured as −139.4 mV on site 1 (July) and −44.5 mV on site 4 (April). The mean ORP value of the stream is −76.43 mV. Terme River water has antioxidant power (especially in upstream zone) and anticorrosion properties due to ORP results measured at negative values. Similar results were obtained in Melet and Turnasuyu rivers, which are drinking water basins in the

Table 3 Physicochemical parameters of Terme River's stations (mean ± st dev)

	Site 1	Site 2	Site 3	Site 4	Mean	Min.	Max.	WHO Guideline (2011)	Turkish Guideline (2012) class*
pH	8.69	8.61	8.25	8.06	8.40 ± 0.41	7.85	9.46	7.5	I
WT (°C)	16.65	16.88	18.58	18.4	17.63 ± 7.68	6.5	29.2		I
DO (mg/L)	10.65	9.79	10.16	9.04	9.91 ± 1.43	7.17	12.12		I
EC (μS/cm)	125.88	159.93	190.85	242.48	179.78 ± 71.05	93.5	350	2500	I
TDS (mg/L)	60.13	76.55	91.95	102.85	82.87 ± 26.49	43.7	125	600	I
TA (mg/L)	37	35	48	48	42 ± 13	17	63	600	-
TH (mg/L)	61	72	91	126	87 ± 42	50	220	100	✓
TSS (mg/L)	2.74	3.63	6.63	12.38	6.34 ± 8.41	0.9	30		✓
Salinity (ppt)	0.07	0.08	0.09	0.12	0.09 ± 0.04	0.05	0.21		-
ORP (mV)	−92.53	−88.23	−67.98	−56.98	−76.43 ± 23.42	−139.4	−44.5		-
BOD$_5$ (mg/L)	1.7	2.26	2.56	2.89	2.35 ± 0.74	1.2	3.57		I
Turbidity (NT)	3.46	7.33	10.42	15.52	9.18 ± 10.57	1.69	38.5		✓
NO$_2$-N (mg/L)	0.013	0.009	0.01	0.007	0.01 ± 0.06	0.004	0.025	0.9	I
NO$_3$-N (mg/L)	0.83	0.88	0.8	1.13	0.91 ± .53	0.3	2.5	11.3	I
NH$_4$-N (mg/L)	0.10[a]	0.11[a]	0.17[a]	0.32[b]	0.17 ± .12	0.04	0.44		I
SO$_4$(mg/L)	1.75	6.75	8	15	7.88 ± 7.90	1	35	250	I
AS (mg/L)	0.19[a]	0.58[b]	0.57[b]	0.72[b]	0.51 ± .26	0.09	0.96		III
Cl$_2$ (mg/L)	0.04[a]	0.04[ab]	0.04[ab]	0.12[b]	0.06 ± 0.05	0.01	0.22	5	I
F$^-$ (mg/L)	1.07	0.94	1.05	0.99	1.01 ± 1.26	0.01	3.1	1.5	I
SiO$_2$ (mg/L)	18.6	17.08	16.3	18.05	17.51 ± 2.25	11.7	21.2		-
TP (mg/L)	0.49	0.06	0.52	0.15	0.3 ± 0.57	0.01	1.75		III
Ca (mg/L)	13.6	20.55	29.57	66.9	32.65 ± 35.49	11.31	158.97	75	✓
K (mg/L)	0.8	1.36	1.7	21.96	6.45 ± 20.16	0.49	82	12	✓
Mg (mg/L)	4.06	5.4	7.91	89.91	26.82 ± 81.18	3.07	331.07	50	✓
Na (mg/L)	7.25	8.81	12.47	24.63	13.29 ± 10.27	5.95	48.37	200	I
Al (μg/L)	16.9	97.53	61.65	22.64	49.68 ± 88.91	2.11	337.62	200	I
Cr (μg/L)	0.99	1.06	0.95	1.03	1.01 ± 0.15	0.84	1.27	50	I
Mn (μg/L)	1.34	2.21	2.72	2.71	2.25 ± 1.39	0.98	4.73	400	I
Fe (μg/L)	7.85	46.21	32.13	11.85	24.51 ± 41.59	1.37	152.98	300	I
Co (μg/L)	1.21	1.25	1.28	1.26	1.25 ± 0.04	1.19	1.32	50	I
Ni (μg/L)	2.43	2.44	2.11	1.9	2.22 ± 0.68	1.38	3.54	70	I
Cu (μg/L)	1.77	2.26	2.4	2.5	2.23 ± 0.74	1.19	3.68	2000	I
Zn (μg/L)	22.98	8.67	35.77	12.98	20.10 ± 27.29	4.04	115.07	3000	I
As (μg/L)	0.41	0.49	0.47	0.61	0.49 ± 0.7	0.28	1.02	10	I
Cd (μg/L)	0.7	0.68	0.7	0.76	0.70 ± 0.08	0.66	0.98	3	I
Pb (μg/L)	0.72	1.06	0.73	0.63	0.79 ± 0.04	0.29	2.15	10	I

[a,b] Means with different letters in the same row are statistically significant ($p < 0.05$)

✓: Acceptable according to TS 266 standard of the Turkish Standard Institute

*: "I", very good water; "II", good water; "III", moderate water; "IV", poor water (presented as a supplemented material)
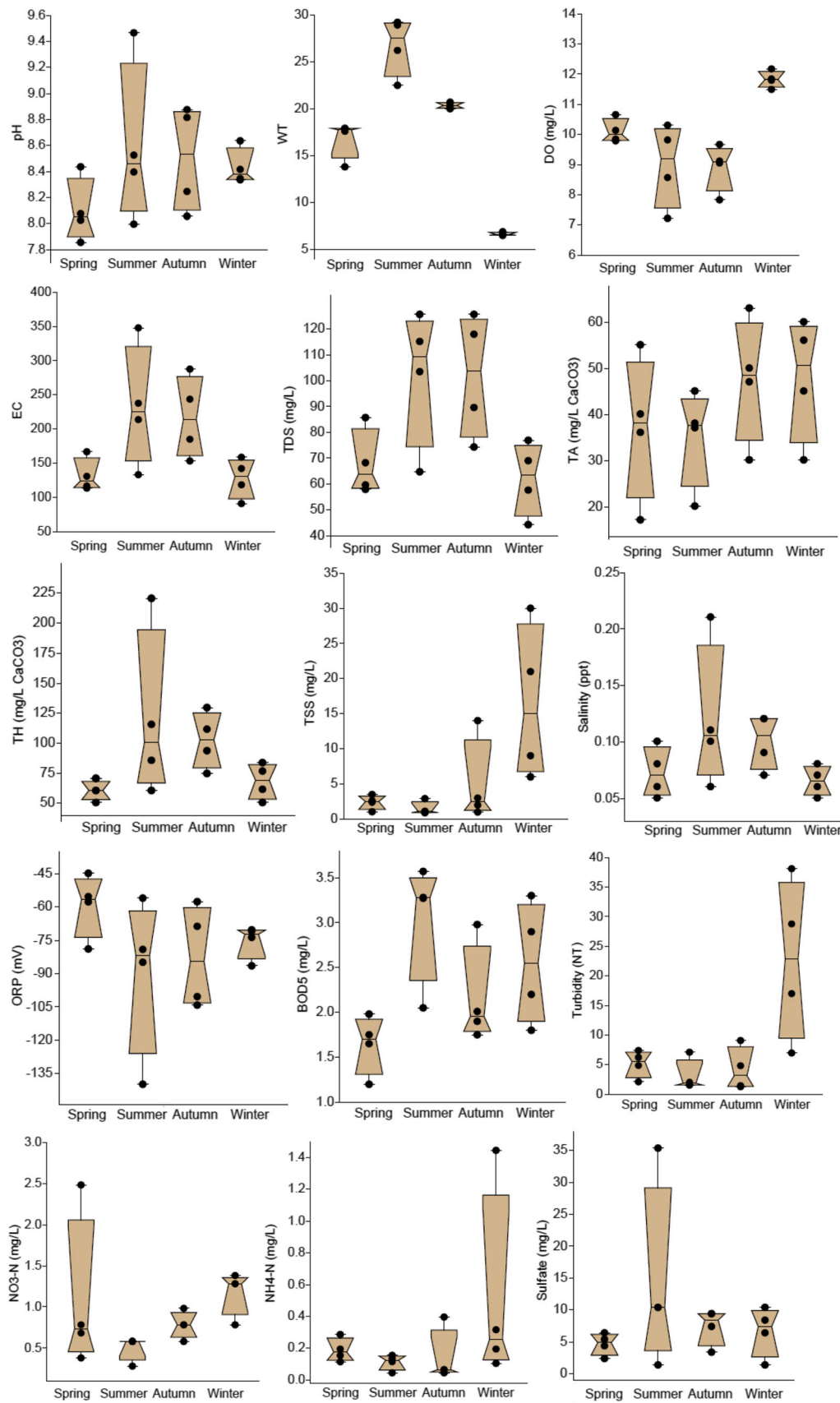
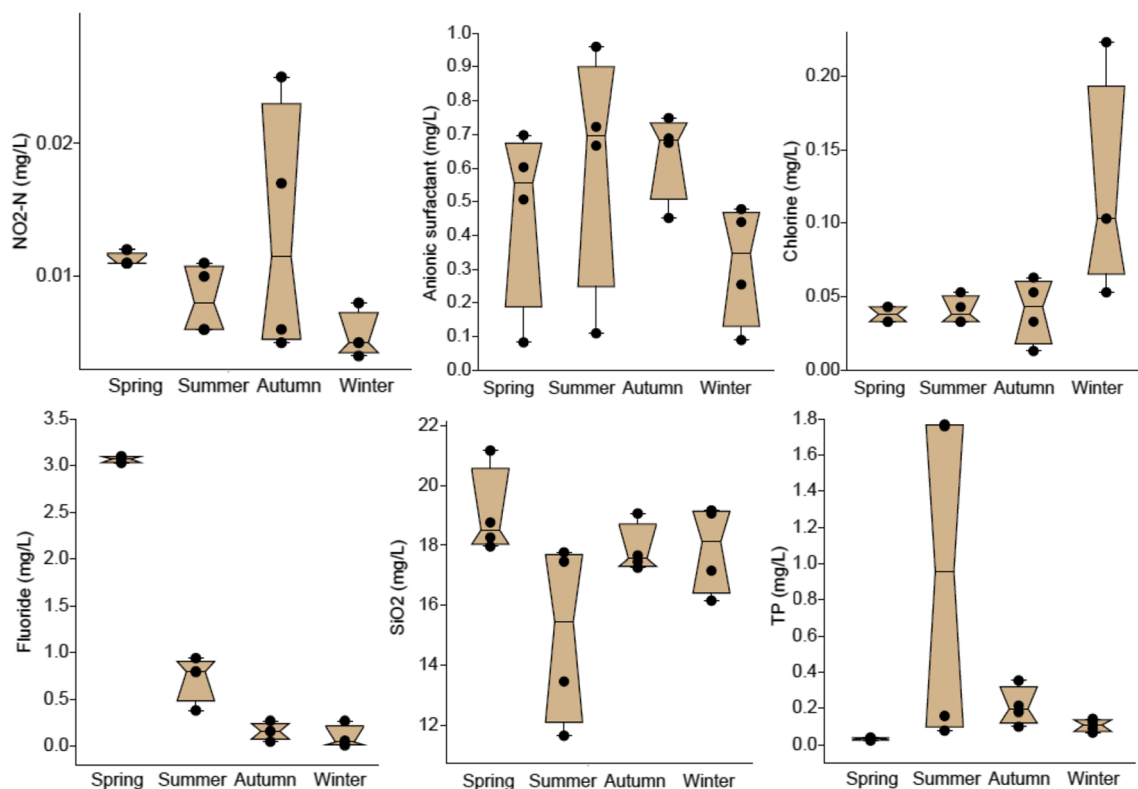**Fig. 2** Boxplot graph for hydrochemical parameters at different seasons of the Terme River

Fig. 2 (continued)

Black Sea Region (Ustaoğlu et al. 2017; Ustaoğlu et al. 2020a). During the study, no abnormal changes in taste, odor, and color were observed in the stream except during flood times. A similar situation was observed in surveys of water quality recently conducted in the riverbeds which located in the temperate zone of northern Turkey (Tepe and Aydın 2017; Taş et al. 2019; Ustaoğlu and Tepe 2019; Aydın et al. 2021; Ustaoğlu et al. 2020a).

The water quality in terms of oxygenation parameters (DO and BOD_5) is class I, that is, high quality water. Class I refers to "very good" water condition. The highest concentration of DO was measured upstream (site 1, 12.12 mg/L) in the winter season and the lowest downstream (site 4, 7.17 mg/L) in the summer season. DO determines metabolism and is a critical index in water quality. BOD_5 concentration, which is a general indicator of pollution load in water, indicates that the upstream zone is oligosaprobic (1.2 mg/L, site 1, spring), and the downstream zone is the β-mesosaprobic zone (BOD_5, 3–5 mg/L) (3.57 mg/L and 3.28 mg/L, sites 3 and 4; July) (Taş et al. 2021). Numerous organic substances found naturally in surface waters or reaching water from pollutant sources decompose as anaerobes or aerobes as a result of the activities of microorganisms in the environment and affect the oxygen balance of the water in this process. Oxygenation analysis performed in Terme River shows that the organic pollution load has increased in downstream. Lowland urban streams often produce anaerobic phenomena due to scarcity of

water supply and slow movement of water in the river (Taş et al. 2021).

River water quality is in class I according to the concentration of nitrogenous compounds from the nutrient parameters, while it is in class III in terms of total phosphorus (TP) concentration (contaminated water). Class III refers to the "medium" water state. The NH_4-N concentration differed from the other stations in site 4 as seen in the descriptive statistics of the analyzed parameters (Table 3). The highest value was recorded at this station (1.44 mg/L, max.; 0.565 mg/L, mean). Seasonally, the winter season differed from other seasons (0.51 mg/L). The elevated concentration of NH_4-N in the river water is caused by the trout farm on the river, domestic wastewater mixed with water from the district centers, and agricultural activities in the Terme Plain. Though, there is no pollution in the stream due to highly nitrogenous compounds. However, the concentration of phosphate compounds in the stream was high due to overfertilization for agricultural production and detergents in domestic wastewater. As seen in Fig. 1, both agricultural waters coming from the plain and domestic wastewater in the upstream are mixed in site 3. The highest TP value in spatiotemporal evaluation was recorded on site 3 in summer season (max. 1.75 mg/L; mean 0.923 mg/L).

When seasonal trend was examined, it was observed that AS concentration varied as autumn > summer > spring > winter. According to the Turkish Guideline criteria (2012)

which presented in the Supplementary Section (Table S1), Terme River water is class III in terms of AS parameter, that is, contaminated water. It is seen that detergents (AS) containing anionic surfactants in site 1 are different from other sampling stations (Table 3). As said by the mean values, the lowest AS value was measured at 0.187 mg/L upstream and increased along the stream at sites 2, 3, and 4 as 0.575 mg/L, 0.571 mg/L, and 0.725 mg/L, respectively. This situation indicates that domestic wastewater is mixed with river water. AS value, which is one of the aesthetic parameters in Turkish Standard TS 266 (2005), is 0.2 mg/L. In this case, the upper basin of the stream (site 1) may be used for drinking/potable water, but the downstream basin is not suitable due to pollution.

Terme River water is high quality water (class I) according to the trace elements (metals) and inorganic pollution parameters (Turkish Guideline 2012). It is very important to investigate the concentration, distribution, and sources of HMs in order to understand the health risks of heavy metals (HMs) in water. Spatial properties of major ions and HMs are presented in Table 1. In addition, spatiotemporal changes are shown with hotmaps graph (Fig. 3). Major ions and HMs in the study area are listed according to their average concentration values as follows: Ca (32.65 mg/L)> Mg (26.82 mg/L) > Na (13.29 mg/L) > K (6.45 mg/L) >Al (49.68 μg/L) > Fe (24.51 μg/L) > Zn (20.10 μg/L) > Mn (2.25 μg/L) > Cu (2.23 μg/L) > Ni (2.22 μg/L) > Co (1.25 μg/L) > Cr (1.1 μg/L) > Pb (0.79 μg/L) > Cd (0.7 μg/L) > As (0.49 μg/L). The river water that does not exceed the HM limit values has a "very good" water condition. The absence of industrial factories in our study area is very important for basin water quality, because pollution of urban river is a major concern associated to water quality for ecosystems and human health. Once heavy metals in urban rivers exceed standards, they may cause a long-term health threat to river organisms as well as humans (Töre et al. 2021). Since the urban and agricultural drainage systems are connected to the stream in the Terme River basin, there is an increasing pollution in the downstream zone. Apart from these pollution parameters, downstream zone have increased levels

of EC, TDS, TSS, turbidity, sulfate, calcium, magnesium, and potassium. The geological structure of uphill station with pebble stone is different than alluvion-structured downstream zone. This specific geological structures of the stations might have caused all aforementioned parameters to increase.

Hydrochemical indices

Drinking water quality assessment—WQI

Spatial and temporal WQI was calculated based on 24 water quality variables in Terme River (Fig. 4). The station averages of the WQI values from upstream to downstream are 17.39, 20.67, 20.92, and 29.13, respectively. According to these results, sites 1, 2, and 3 have excellent (WQI <25), and site 4 has good (25 ≤ WQI <50) water quality (Fig. 4). The mean WQI values were calculated as 23.68, 25.4, 16.28, and 16.87 in spring, summer, autumn, and winter, respectively. These results presented that the water quality was "excellent" in all seasons except summer. Terme River is a "good" quality water according to the WQI value in the summer season. Calculated overall average WQI value (WQI = 22, <25) showed that Terme River has "perfect" water quality (Yadav et al. 2010). WQI is widely applied in the monitoring and management of water resources, especially in rivers. For instance, Turnasuyu River, which is not affected much by human effects, has "perfect" water quality according to its average WQI value (18.97; 16.94–21.30). It has been reported that the WQI value is between 33.52 and 43.3 in Çömlekci Creek and the water quality of the stream is at a "good" level (Ustaoğlu et al. 2020a). In the study conducted on the Büyük Menderes River (Yılmaz et al. 2020), it was reported that the WQI value was calculated in a wide range (37.27–85.96), so the river water quality varied between "good" and "very poor" quality. "Very poor" quality waters were recorded at stations with high rural and urban concentration. While the water quality of Terme River, which is both a plain and an urban stream, was excellent in the upper basin, it changed to
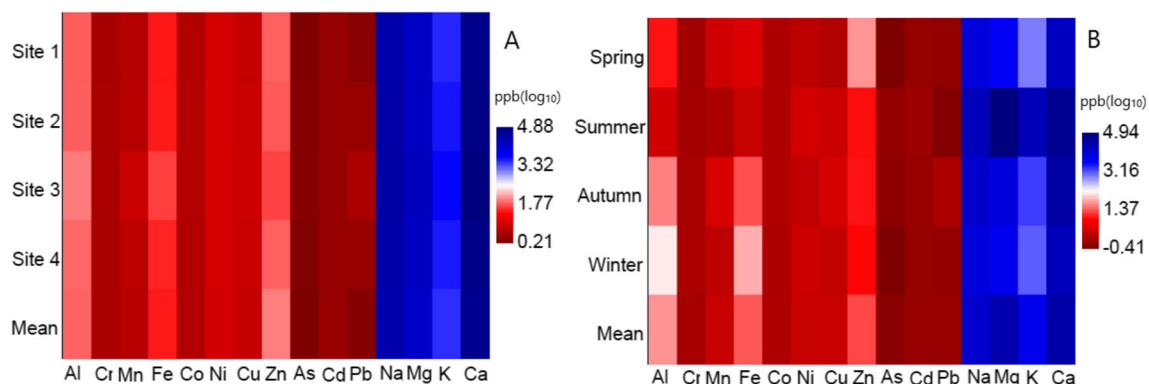

Fig. 3 Spatial and temporal heat map graphic of major ions and HMs in Terme River
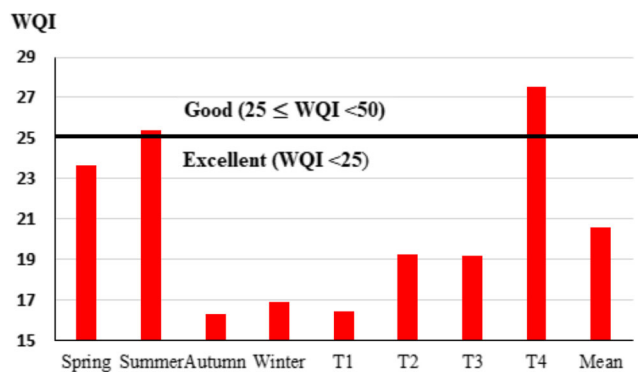
WQI

Fig. 4 Temporal and spatial change of WQI values in Terme River

good water quality in the lower basin (T4) and in the summer season after passing through the district centers.

Assessment of nutrients pollution—NPI

During the present study, the NPI value was recorded in the range of 0.038–1.124 (NPI mean, 0.404). The highest value was noted in the summer and the lowest in the spring season on site 1. Fertilization activities in rice and corn cultivation around the midstream region in the Terme Plain are carried out intensively starting the middle of spring. Indeed, the highest NPI values in these areas were recorded after the fertilization season: on site 1: 1.119, summer; 1.085, winter; on site 3: 1.097, summer; 1.123 on site 4, winter. In these three stations where maximum NPI values are calculated, water can be evaluated as "moderate polluted" (NPI of $1 \leq 3$). The average NPI result of the sampling stations was as follows: 0.592 (T1)> 0.394 (T4)> 0.357 (T3)> 0.275 (T2). In seasonal evaluation, the average NPI values areas follow respectively; winter

(0.802)> summer (0.61)> spring (0.107)> autumn (0.0989). According to the average NPI values, it is seen that there is no nutrient pollution in Terme River (NPI <1, no pollution) (Isiuku and Enyoh 2020). Tepe and Boyd (2001) recommended that TP and TN levels in eutrophic streams and rivers are greater than 0.075 mg/L and 1.5 mg/L, respectively. In the present study, the average TP value was measured above the recommended value in all areas (0.058–0.518 mg/L, TP) except for site 2 downstream of Salıpazarı. The highest TP concentrations (1.74 mg/L, T1; 1.75 mg/L, T3) were recorded in the localities where hazelnut and rice farming were carried out intensively.

Nitrate pollution index values, which we also used to evaluate the nitrate pollution in Terme River, showed a range between −0.94 and −0.97. Since the nitrate pollution index is <0, Terme River is spatiotemporally included in the "clean" water class (Bahrami et al. 2020). As a result of NPI, we can mention that there is a moderate nutrient pollution caused by phosphate fertilizers in our study area.

Assessment of heavy metals—HPI, HEI

The integrated effect of heavy metals (Cr, Co, Cd, Mn, Ni, Cu, Fe, Zn, Pb, Al, As) on stream quality was determined by HEI and HPI. Global standard values were used when calculating HPI and HEI results (WHO 2011). The average HPI values according to the stations were close to each other, and the HPI values were calculated as 14.71, 15.93, 15.40, and 16.41 from the upstream to the downstream, respectively, while the HEI values were 0.52, 1.11, 0.86, and 0.61. Similarly, average HPI values were 14.93, 16.84, 17.57, and 20.56 in spring, summer, autumn, and winter, respectively, while HEI values were 0.48, 0.49, 0.76, and 1.38. Both all HPI values (<100) and all HEI values (<10) showed that there was no significant heavy metal contamination in the Terme River (Saleh et al. 2018). In fact, lower values were recorded in our study than other studies conducted in streams discharging into the Black Sea. It was reported that the lowest HPI values calculated from nearby rivers in the region were 59.68 in Gelevera Stream, and the highest was 69.43 in Yağlıdere Stream. HEI values have also been reported in the range of 1.94 (Yağlıdere Stream) to 2.76 (Aksu Stream) (Ustaoğlu and Aydın 2020). It has been observed that the maximum values of the metals we analyzed in Terme River are also suitable for drinking-potable water according to Turkish (TS 266 2005; Turkish Guideline 2012), World Health Organization (WHO 2011) and Council of the European Union directives (EU 1998). There is no public health risk arising from heavy metal contamination in the drinking water sources at the upper basin due to the lowland area of our study, the low population density at the upper basin, and the undeveloped industry in the Terme River basin.

Table 4 The health risk assessment for metals in water for adults and child via ingestion and dermal routes

Metals	Adult	Child	Adult	Child	Adult	Child
	HQ$_{ingestion}$		HQ$_{dermal}$		HI	
Cr	1.20E-04	1.34E-04	1.93E-03	4.26E-03	2.05E-03	4.40E-03
Ni	1.22E-04	1.36E-04	7.94E-05	1.76E-04	2.01E-04	3.12E-04
Cu	8.71E-04	9.75E-04	3.99E-05	8.82E-05	9.10E-04	1.06E-03
Zn	3.67E-04	4.11E-04	2.87E-05	6.36E-05	3.96E-04	4.75E-04
As	4.25E-02	4.76E-02	2.46E-04	5.44E-04	4.28E-02	4.82E-02
Cd	1.95E-03	2.18E-03	4.06E-03	8.99E-03	6.01E-03	1.12E-02
Pb	1.76E-03	1.97E-03	2.62E-05	5.80E-05	1.79E-03	2.03E-03
Mn	1.53E-02	1.72E-02	3.34E-04	7.38E-04	1.57E-02	1.79E-02
Fe	1.51E-03	1.69E-03	2.81E-05	6.22E-05	1.54E-03	1.75E-03
Al	2.72E-02	3.05E-02	3.55E-05	7.86E-05	2.73E-02	3.06E-02
Co	1.14E-01	1.28E-01	1.19E-03	2.64E-03	1.15E-01	1.30E-01
HI$_{total}$					2.14E-01	2.48E-01
	CR$_{ingestion}$		CR$_{dermal}$		CR	
As	1.91E-05	2.14E-05	2.56E-07	5.68E-07	1.94E-05	2.20E-05

Environ Sci Pollut Res (2021) 28:62736–62754

Table 5 Classification of irrigation water based on electrical conductivity (EC, μS/cm) (Ravikumar et al. 2013)

Class	Conductivity range in water	Suitability for irrigation
C1	100–250 (low salinity water)	Suitable for all types of crops and all kinds of soil.
C2	250–750 (medium salinity water)	Can be used, if a moderate amount of leaching occurs. Normal salt-tolerant plants can be grown without much salinity control
C3	750–2250 (high salinity water)	Unsuitable for soil with restricted drainage. Only highly salt tolerant plants can be grown
C4	>2250 (very high salinity water)	Unsuitable for irrigation

Human health risk assessment

Heavy metals in drinking water are risky to health and can be source to various types of cancer and noncarcinogenic conditions. In the present study, the noncarcinogenic/carcinogenic health risk properties of heavy metals for children and adults were investigated. ADD (dermal, ingestion), HQ (dermal, ingestion), CR, and HI values were calculated by means of the toxicological values of each metal (Table 4) (USEPA 2004; Wang et al. 2017). According to HQ standards, when the HQ value is > 1, adverse health effects (noncarcinogenic risk) may occur in humans. Co (1.14E-01, 1.28E-01) and As (4.25E-02, 4.76E-02) showed the highest HQ ingestion value in adults and children, respectively. Co (1.15E-01, 1.30E-01) and As (4.28E-02, 4.82E-02) showed the highest HI value. In the present study, all HQ and HI values were less than the risk threshold (<1). Similarly, HI total values are less than 1 in adults (2.14E-01) and children (2.48E-01). As a result, Terme River water is safe for public health in terms of residential uses. These values are also compatible with the results of Turnasuyu Stream in the same region (Ustaoğlu et al. 2020a). Cancer risk (CR) is accepted as the lifetime probability of any type of cancer occurring due to exposure to carcinogens. In this study, CR for adults and children was calculated for arsenic only using the cancer slope factor (CSF) (Table 4). The arsenic concentrations taken through the skin and digestion were included in the calculation.

CR values calculated for children (2.20E-05) are higher than adults (1.94E-05). This indicates that when children are exposed to the same environment as adults, they are relatively more susceptible than adults (Xiao et al. 2019). CR results are in the acceptable range (1.00E-06 <CR <1.00E-04) recommended by USEPA (2004). Therefore, if somehow the arsenic

in Terme River water is exposed through digestion and skin, there will be no significant cancer risk. The CR values determined as a result of two different studies conducted in Keban Dam are within the acceptable range as in this study (Canpolat et al. 2020). It has been reported that if surface waters are used in regions exposed to urbanization, industrialization, and agricultural pressures, there may be high cancer risks related to arsenic (Sohrabi et al. 2020). The USEPA (2004) has recommended an acceptable range of carcinogenic risk as 10^{-6} to 10^{-4}. However, when the CR is $\geq 10^{-4}$, the risk of harmful effects for human health is high (Canpolat et al. 2020). Certain essential heavy metals may lead to various health problems in humans if found in levels exceeding allowable limits.

Assessment of water quality for irrigation

In situ measurements of the salinity of the river water were recorded in the range of 0.05–0.21‰. The salinity of water is also typically measured with TDS or EC. TDS values of Terme River were measured between 43.7–125 mg/L and EC 93.5–350 μS/cm. In spatial and temporal evaluation, salinity, TDS, and EC values tended to increase downstream. The lowest values were measured in site 1 in the rainy season (January), when the temperature is low, and the highest values in site 4 (downstream) in the dry season (July) when the temperature is high. The anthropogenic impact sites (downstream zone) showed high levels of salinity, TDS, and EC, reflecting the inverse effect of different wastes on the branch water. A similar situation has been reported in streams flowing into the Black Sea (Ustaoğlu et al. 2020a; Ustaoğlu and Aydın 2020). When we evaluate the irrigation water quality according to EC values (Table 5); sites 1, 2, and 3 were grouped as excellent/

Table 6 Temporal and spatial variation values of the irrigation water quality indices of Terme River

Season	MH	Na%	SAR	RSC	Site	MH	Na%	SAR	RSC
Spring	45.86	35.86	0.62	1.00	T1	48.90	35.84	0.54	0.55
Summer	83.32	23.67	0.43	−7.23	T2	45.74	33.74	0.55	0.19
Autumn	44.44	31.72	0.66	−0.15	T3	47.05	34.62	0.54	0.77
Winter	47.83	33.30	0.57	−0.23	T4	81.18	24.00	0.50	−7.52
Mean	55.72	32.05	0.53	−1.50	Mean	55.72	32.05	0.53	−1.50

Table 7 Water quality levels (WQL) based on Na%, SAR, RSC, and MH (Ravikumar et al. 2013)

MH (meq/L)	WQL	Na%	WQL	SAR (meq/L)	WQL	RSC (meq/L)	WQL
< 50	Suitable	< 20	Excellent	0–6	Good	< 1.25	Good
> 50	Unsuitable	20–40	Good	6–9	Doubtful	1.25–2.5	Doubtful
		40–60	Permissible	> 9	Unsuitable	> 2.5	Unsuitable
		60–80	Doubtful				
		> 80	Unsuitable				

low salinity water (C1), site 4 as good/medium salinity water (C2) (Ravikumar et al. 2013).

The Black Sea climate, which has been rainy and mild in all seasons, has changed in recent years. The dry summer season continues until midautumn. As a matter of fact, the TDS value in October was recorded the same as the TDS value in midsummer (site 4, 125 mg/L). We can express the concentrations of inorganic ions that increase both in dry seasons and in the flow direction. Order of the mean cations' values is Ca^{2+} > Mg^{2+} > Na^+ > K^+ > NH_4^+ (32.66, 26.82, 13.29, 6.45, 0.305; mg/L); order of anions is SO_4^{2-} > NO_3^- > F^- > NO_2^- (7.88, 3.988, 1.01, 0.0316; mg/L). Increases in ion concentrations in the downstream zone may be due to severe drought and anthropogenic activity during the summer and autumn months.

Na%, SAR, RSC, and MH indices were calculated based on Na, K, Ca, Mg, and TA variables in order to determine the potential usability of Terme River as irrigation water (Table 6). In Table 6, the mean values of the seasons are presented in the first column and the mean values of the stations in the second column. The detected values then were evaluated according to scale in Table 7 (Ravikumar et al. 2013). In the present study, the spatial-temporal SAR values vary between 0.43 and 0.66, and the average SAR value is 0.53. Since all SAR values are lower than 6, Terme River can be considered as "good quality" for irrigation purposes according to this index. Terme rice is the product commonly produced in the river basin during the irrigation season (dry season). The quality of irrigation water used in the cultivation of this famous rice will be important for public health.

Na% values in the study area were evaluated as spatiotemporal and were calculated between 24.00 and 35.86 with the mean Na% value of 32.05 (Table 6). According to all Na% values, Terme River irrigation water is included in the "good" (20 <Na <40) water quality class (Table 7). The measured RSC values in this study are in the range of −7.23–1.00 spatially and temporally, and all parameters are involved in the "good water quality" (RSC <1.25) class in terms of irrigation water. In most of the waters, calcium and magnesium are generally equal. However, high Mg disrupts this balance and affects the growth of plants by converting the water into more alkaline. Water with MH> 50 is not suitable as irrigation water. In this study, spatial and temporal values fluctuated between 44.44 and 83.32 (Table 6). In terms of MH, it is not

appropriate to use Terme River T4 station (MH = 81.18) for irrigation water in summer season (MH = 83.32). In a study conducted on Sakarya River, one of the rivers of the Western Black Sea Region, the irrigation water for all stations; it has been reported to be excellent, good and suitable in terms of SAR, Na%, and MH, respectively (Özer and Köklü 2019).

When the water quality of Terme River was assessed for irrigation purposes according to FAO Directive (Ayers and Westcot 1985); seasonal averages were calculated as EC <0.7 (0.1798 dS/m), SAR <3 (0.53), and NO_3^- <5 (3.988 mg/L). According to these results, it can be reported that there will be no problems in using the stream for irrigation. However, it is necessary to take into account the trend of increasing ion concentrations downstream. Gradual increase from slight to moderate precaution in selection of crop and management strategies is necessary if full yield potential is to be reached (Ayers and Westcot 1985). The properties of the irrigation water may have a key function in the augmentation or appearance of secondary soil salinization and in the increase of destructive effects of soil salinity on crop production, especially under climatic adverse conditions (Tomaz et al. 2020). In the Black Sea Region (between October 1st and September 30th), reported rainfall by the Ministry of Agriculture and Forestry was 711 mm in 2018–2019 and was 634 mm in 2019–2020. Therefore, a 10.8% reduction in precipitation in the temperate Black Sea climate zone has had a significant impact on river discharge and pollutant levels.

## Appraisal of contamination sources between physicochemical parameters of Terme River

Pearson correlation analysis was performed to determine the trend and correlation between physicochemical parameters as presented in Table 8. When the parameters with strong correlations (r>0.8) are evaluated; the highest correlation was between ORP and pH in the negative direction ($r = -0.99$, p<0.01). Potential hydrogen (pH) value affects ORP and ORP value of waters with high pH value is negative. In Terme River, pH is greater than 8, and ORP is −76.43. The relationship between these two parameters has been verified by correlation analysis. In our study, there is a significant positive relationship between the basic parameters (TDS-EC, TH-Salinity, EC-Salinity, TH-EC, TH-SO$_4$) ($r = 0.91$–0.96;

Table 8 Pearson correlation matrix between physicochemical parameters in Terme River

Correlations

	pH	WT	DO	EC	TDS	TSS	Sal	ORP	BOD$_5$	Turb	NO$_2$-N	NO$_3$-N	NH$_4$-N	SO$_4$	AS	Cl$_2$	F	SiO$_2$	TP	TA	TH
pH	1																				
WT	.12	1																			
DO	.19	**−.80****	1																		
EC	−.31	.64**	**−.83****	1																	
TDS	−.30	.66**	**−.82****	**.96****	1																
TSS	−.14	−.63**	.40	−.06	−.09	1															
Sal	−.39	.55*	**−.74****	**.91****	**.81****	−.12	1														
ORP	**−.99****	−.21	−.12	.26	.24	.19	.34	1													
BOD$_5$	−.12	.23	−.27	.63**	.62**	.42	.49	.10	1												
Turb	−.15	**−.68****	.50*	−.14	−.18	**.95****	−.14	.20	.38	1											
NO$_2$-N	.18	.23	−.15	−.12	−.05	−.41	−.14	−.19	−.47	−.40	1										
NO$_3$-N	−.21	−.44	.33	−.30	−.29	.12	−.33	.26	−.23	.21	.08	1									
NH$_4$-N	−.38	−.42	.19	.04	.02	**.83****	−.04	.41	.36	**.76****	−.42	.26	1								
SO4	−.37	.40	−.59*	**.81****	.66**	.05	**.89****	.33	.61*	.10	−.27	−.18	.09	1							
AS	−.40	.55*	**−.77****	**.80****	**.82****	−.13	.64**	.35	.49	−.14	−.01	−.04	.04	.68**	1						
Cl$_2$	−.46	.37	−.64**	.69**	.52*	−.03	**.77****	.42	.30	−.03	−.11	.06	.20	**.83****	.58*	1					
F	−.40	.11	−.01	−.30	−.28	−.40	−.16	.38	−.50*	−.31	.16	.13	−.04	−.19	−.04	.06	1				
SiO$_2$	−.11	−.39	.21	−.39	−.48	−.05	−.28	.15	**−.72****	−.01	.28	.64**	.12	−.24	−.26	.18	.31	1			
TP	.49	.53*	−.03	.13	.18	−.19	.02	−.53*	.30	−.24	−.07	−.36	−.11	−.07	−.08	−.20	−.13	−.49*	1		
TA	−.49	.54*	−.55*	.34	.42	−.36	.30	.43	−.09	−.42	.21	−.12	.07	.10	.42	.30	.66**	.01	.09	1	
TH	−.32	.55*	**−.72****	**.94****	**.82****	−.02	**.95****	.27	.59*	−.05	−.20	−.29	.04	**.93****	**.71****	**.79****	−.29	−.29	.08	.20	1

**Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed), *Turb* Turbidity, Strong relationships (r> ±0.70) are shown in boldface

Fig. 5 Dendrogram for the surface water grouping with respect to the physicochemical parameters
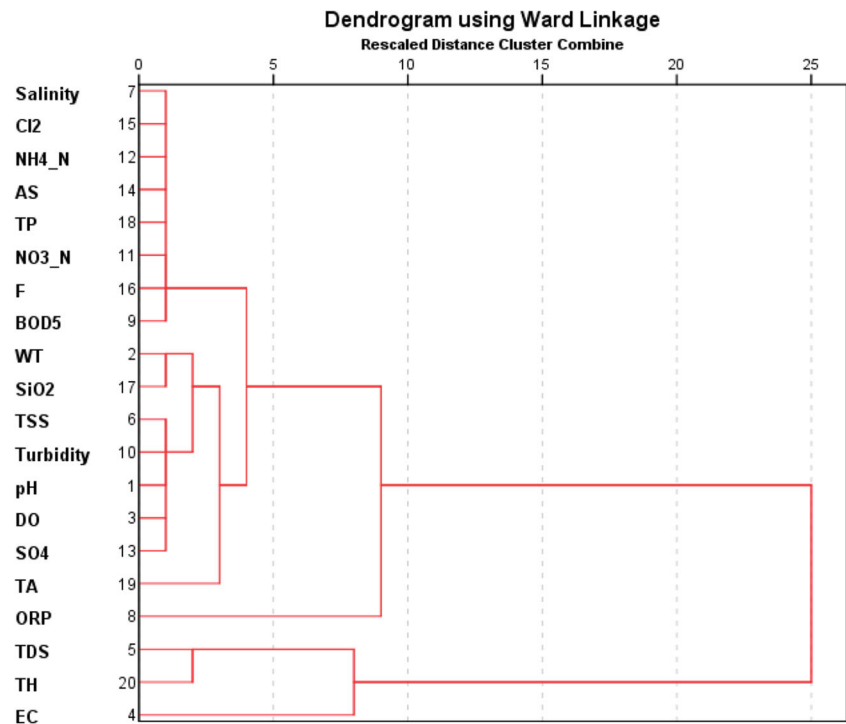
$p<0.01$). The concentrations of all these parameters gradually increased along the stream flow, especially in the arid season, because the EC value of the waters increases with the increase in temperature. The EC increase can be caused by wastewater discharge in areas where the streams cross, as well as drainage water returning from agricultural irrigation along the stream. Because Terme River is both an urban and a plain river, it is exposed to all these effects. Therefore, the anions and cations that impart salinity to the water are likely to mix into the water from similar sources. Again, there is a positive strong relationship between water turbidity and TSS ($r = 0.95$; $p<0.01$) (Table 8). In the downstream zone, high turbidity is observed with nutrient contamination in the water. Turbidity, which may arise from organic or inorganic substances or a combination of both, can be observed with the naked eye over about 4.0 NTU (WHO 2011). In our study area, turbidity measured in the range of 1.69 (site 2)–38.5 (site 4) (mean 10.39 NTU) was recorded the lowest in dry season and the highest in rainy season (winter). Similarly, in the same seasons, TSS values were measured at lowest (0.9 mg/L) in the upstream zone and the highest (30 mg/L) in the downstream zone. In the study conducted in Elekçi Stream, it was reported that turbidity has a very high correlation ($p<0.01$) with ammonia, ammonium, iron, and free chlorine (Taş et al. 2021). In the present study, there is a positive strong correlation between NH_4-N and TSS ($r = 0.83$; $p<0.01$). Nitrogenous compounds, which are among inorganic pollution parameters, which are indicators of organic pollution, are also nutrient parameters. The contamination of these pollutants into the water may be caused by agricultural activities, domestic wastewater, and aquaculture activities. Other correlations indicating that domestic wastewater is mixed with water is a positive strong correlation between AS–TDS ($r = 0.82$) and AS–EC ($r = 0.80$) ($p<0.01$). DO was significantly and negatively correlated with WT ($r = -0.80$; $p<0.01$), as the cooler the water the more oxygen is soluble (Varol 2020).

Cluster analysis

In our study, CA was performed to group twenty different physicochemical parameters of river water samples (Fig. 5). As a result of CA, Terme River surface water samples were divided into three subgroups. Cluster 1 covered 80% of water quality parameters. It was evaluated that this subgroup included general conditions, oxygenation parameters, nutrient parameters, and inorganic pollution parameters and was associated with ORP. The highest correlation was also recorded in the correlation analysis between pH in cluster 1 and ORP in cluster 2 (Table 8). Cluster 3 consisted of TDS, EC, and TH parameters, which are closely related to each other and form the indicators of mineral content of water. The relationship between pH, WT, and DO in cluster 1 and EC and TDS in cluster 3 draws attention. It has been reported in a study that the highest similarity in terms of total hardness and phosphate compounds is between Terme River and Yeşilırmak River. Again, the highest EC and TDS values were observed in Terme River (Taş and Kolören 2017). A strong positive correlation was determined between Ca and Mg ions, which are important parameters affecting total hardness, and EC in Sürgü Stream (Varol 2020).

Table 9 Varimax rotated component matrix for some analyzed variables

| Variable | Components | | | |
	PC1	PC2	PC3	PC4
TH	*0.967*	0.025	0.119	−0.045
TA	*0.865*	−0.274	0.169	0.241
EC	*0.951*	−0.012	0.255	0.052
Salinity	*0.935*	−0.056	0.093	0.069
SO$_4$	*0.922*	0.129	−0.021	−0.051
TDS	*0.856*	−0.023	0.366	0.135
Cl$_2$	*0.838*	−0.002	−0.317	0.149
BOD$_5$	0.569	0.526	0.516	−0.159
TSS	−0.054	*0.954*	−0.027	−0.163
Turbidity	−0.081	*0.939*	−0.119	−0.178
NH$_4$-N	0.041	*0.848*	−0.068	0.248
WT	0.533	*−0.615*	0.503	0.151
AS	0.088	−0.035	*0.810*	0.240
TP	−0.075	−0.193	*0.791*	−0.126
NO$_3$-N	−0.170	0.168	*0.683*	0.059
DO	−0.172	0.405	*−0.798*	−0.205
SiO$_2$	−0.224	−0.142	0.80	*0.864*
F	−0.256	−0.297	−0.188	*0.812*
pH	−0.386	−0.341	0.332	*−0.718*
ORP	0.338	0.387	−0.377	*0.689*
Eigenvalues	7.95	4.15	3.40	1.52
% of variance	39.79	20.76	17.04	7.62
Cumulative %	39.79	60.55	77.60	85.22

Extraction method: principal component analysis

Rotation method: Varimax with Kaiser normalization

Bold values represent strong and moderate loadings, respectively

Principal component analysis

PCA is calculated to convert the raw variables into original, unrelated variables, named the principal components, which are combinations of the original raw variables. PCA converts the original raw variables into some integrated variables named elementary components (PCs) and can revealed PCs with eigenvalues higher than one (Varol et al. 2012; Ustaoğlu and Islam 2020). Principal components (PCs) are formed by subjecting PCs to varimax rotation (Tokatlı and Varol 2021). PCA was performed to find potential factors/sources affecting the water quality of the stream. Bartlett's test and Kaiser-Meyer-Olkin (KMO) were applied to check the suitability of the data before analysis. Bartlett and KMO analyzes were $p = 0.00$ (<0.001) and (> 0.5), respectively, and the data were found to be suitable for PCA (Ustaoğlu 2020a).

Four PCs with an eigenvalue greater than 1 were defined with Varimax rotation PCA, explaining 85.22% of the total variance (Table 9 and Fig. 6). TH, TA, EC, salinity, SO$_4$,

TDS, and Cl$_2$ in PC1 representing 39.79% of the total variance are strongly positively charged (> 0.75). TDS, TH, and EC are grouped together as seen in the cluster analysis dendrogram in Fig. 5. In addition, there are strong relationships between these three parameters (Table 8). When MSAs are assessed together, it can be said that soluble salts forming PC1 are of natural origin due to the rock/soil structure of the basin and spread from the same sources (Varol 2020).

In PC2, which represents 20.76% of the total variance, turbidity, TSS, and NH$_4$-N have strong positively charged, WT moderate (0.75–0.50) negatively loaded (Table 9). Turbidity, TSS, and WT are in the same group in the cluster analysis. The presence of a strong correlation between TSS, which is one of the main causes of turbidity, supports this PC. TSS can be of both natural and anthropogenic origin (Varol 2020). According to PC2, it can be understood that erosion effect and surface flows are effective on the water quality of Terme River (Ustaoğlu et al. 2020a). In PC3 (17.04% of total variance), AS and TP showed strong positive, NO$_3$-N moderate positive, and DO showed strong negative loads. In cluster analysis, AS, TP, and NO$_3$-N were collected in the same cluster (Fig. 5). Herbicides, pesticides, and fertilizers used in agricultural activities in order to obtain high-yielding crops have been the essential pollutants of river basins recently. Huge amounts of nitrate and phosphate fertilizers are used in agricultural activities in the Terme River basin. Nutrients are mixed into streams by runoff from both domestic wastewater and agricultural land (anthropogenic activities). Since Terme River is the urban plain river, it can be said that PC3 is typically directly related to agricultural activities and domestic wastes (Tokatlı and Varol 2021). Additionally, DO's negative contribution to this PC is as a result of the consumption of DO required for the decomposition of organic matter (Varol 2020). In PC4, SiO$_2$, and F showed strong positive, ORP moderate positive, and pH moderate negative load. Reflecting 7.62% of the total variance, this PC can represent the physicochemical source of the variables. In the present study, PCA helped to identify the responsible sources and factors of water quality change of Terme River. The results showed that edaphic factors (dissolution of minerals in rock/soil), anthropogenic factors (domestic waste/wastewater and nutrients), and climatic factors are effective on water quality.

Conclusion

The water quality of Terme River has been evaluated in "very good" water condition except TP and AS (class I). The Terme River, which is an urban plain stream, is especially under the pressure of anthropogenic activities. As can be understood from the analysis results, nutrients such as phosphorus from agricultural activities and detergents from domestic

Fig. 6 PCA of measured parameters by (a) scree plot of the characteristic roots (Eigen values) and (b) component plot in rotated space
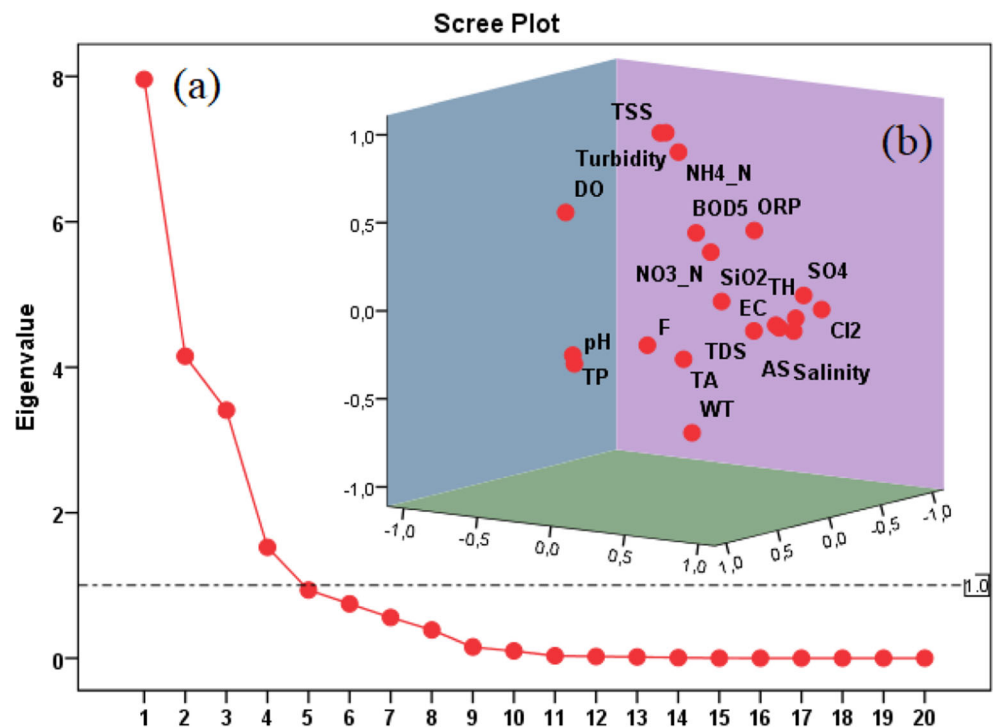
wastewater contaminated the stream and expressed the "moderate" water state (Class III). The stream has first class water according to general hydrochemical parameters, and it can be used for drinking purpose and agricultural irrigation. A variety of multivariate statistical methods was performed to evaluate spatiotemporal changes in surface water quality. WQI, HPI, and HEI values were calculated as 16.28–29.13, 14.71–20.56, and 0.48–1.38, respectively. $HQ_{ingestion}$, HQ_{dermal}, and HI results were calculated as less than the threshold value of 1. CR results in both children (2.20E-05) and adults (1.94E-05) were slightly above the limit values for arsenic alone. These indexes (WQI, HPI, HEI, HI, HQ, CR), in which the effects of heavy metal contents on water quality and human health are evaluated together, were applied for the first time in Terme River. Analysis results showed that metal contamination in Terme River surface water poses a low risk for residents. In the water quality assessment made according to nutrient pollution, the NPI value was recorded in the range of 0.038–1.124. Water is moderately polluted according to the maximum value and clean according to the seasonal average value (NPI mean = 0.404).

Terme River was evaluated in terms of irrigation water (SAR, Na%, RSC) and showed good quality water characteristics. In the spatial and temporal evaluation, it was observed that the water quality in the downstream region decreased in parallel with the increase in the pollutant concentration in the flow direction. Farmers should be made aware of good agricultural practices both for improving this situation and for sustainable basin management, and mixing of sewage water with rivers should be prevented by establishing infrastructure facilities.

Declarations

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