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The assessment of health risk from heavy metals with water indices for irrigation and the portability of Munzur Stream: A case study of the Ovacık area (Ramsar site), Türkiye

by

Banu Kutlu (ORCID:0000-0001-6348-2754)*,
Ali Sarıgül

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Faculty of Aquaculture, Department of Basic Sciences, Munzur University, Türkiye

Abstract

Surface water samples from the area of Munzur Stream in Türkiye (a Ramsar site) were evaluated for their suitability for irrigation and drinking purposes using different water quality indices. The human health risks were assessed as well. The study was conducted over a period of 24 months from January 2019 to December 2021 by taking samples from nine stations every month in order to determine the water quality of Munzur Stream, located in Tunceli. According to the results, Munzur Stream is in good condition in terms of the quality of drinking water and irrigation water. The concentrations of heavy metals such as Cu, Ni, Fe and Hg were high, though the water quality parameter according to Türkiye Ministry of Forestry and Water Affairs Surface Water Quality Regulations (TSWQR) was significantly lower than the permitted limits. In Munzur Stream, the irrigation water for all stations was reported to be excellent, good and suitable in terms of SAR, Na% and MH, respectively. The principal component analysis data formed the four principal components, explaining 98.22% of the total variance. The sources of pollution in this area include the rock types of the basin, soil erosion, domestic waste water discharge and agricultural flow of inorganic fertilisers.

Key words: Drinking and irrigation water quality Munzur Stream, water quality, water quality index, surface water

* Corresponding author: kutlubanu@gmail.com

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1. Introduction

Wetlands are a major source of freshwater and an essential part of human life, primarily for drinking and domestic purposes. The rapid increase in the human population and overindustrialisation has created problems regarding the disposal of wastewater products. River water is very vulnerable to pollution, as it is exposed to a large number of pollutants from natural and human activities. Along with a global industrial revolution, rapid increase in human population and developing industry, the need for freshwater has increased drastically (Kutlu et al. 2017). Lotic systems are the most vulnerable sources of pollution because of their role in water flow from domestic, industrial and agricultural areas.

The pollutants directly affect surface waters (Fatima et al. 2022, Gao et al. 2020). As a result, the use of water is restricted since it threatens public health (Adeleke et al. 2019, Oyekanmi et al. 2017, Rosli et al. 2019, Tokatlı et al. 2021). The natural pollutants directly affect a single area. Meanwhile, the anthropogenic sources disperse and affect the entire area. Heavy metals are among the most hazardous pollutants in aquatic environments because of their toxicity and high bioaccumulation potential (Amiri 2021b).

To collect reliable data on river waters, it is important to evaluate the quality and the spatial and temporal waves as well as to monitor the sources of pollution and the water condition and quality. To determine these parameters, many indices have been developed. Several indices are used to measure water used for drinking, irrigation, recreation and domestic and industrial purposes. Multivariate statistical analysis, WOI, heavy metal pollution index (HPI), sodium percentage (Na %), sodium absorption rate (SAR) and magnesium hazard (MH) are usually used on the surface waters of rivers (Uddin et al. 2021).

Munzur Stream, located in Tunceli's Ovacık region, is the most important source of drinking water in the East Anatolia region of Türkiye. It lies between an organic farming area and a Ramsar sensitive water resource. The water quality should be monitored periodically and important factors affecting pollution change should be identified to protect and control the ecosystems that feed many water resources and dams in order to maintain the ecological balance and to make efficient use of water resources; appropriate measures should also be taken (Cüce et al. 2022). The aim of the study was to determine the quality of water and drinking water properties using physicochemical parameters, heavy metal content, multivariate statistical analysis and WOI. The HPI indices were used to determine the surface water quality of Munzur Stream, which is of great importance for the region and is used to irrigate agricultural areas. The study aims to effectively interpret the data obtained using these indices. It helps in determining the factors that affect the system, classifying the basin in sensitive areas by water quality, revealing the water quality of the sensitive area in comparison with the data obtained through various national and international criteria and creating a resource for future studies in the region.

2. Materials and methods

The field studies were carried out for 24 months, with monthly samplings between February 2019 and January 2021. In this study, three sampling stations (S1–S9) were selected on Munzur Stream (Fig. 1). The sampling points of the study are presented in Figure 1. Station 1 was located in the upper course of the stream (39°19′53″N, 39°03′17″E). There are no point sources of pollution (industrial and domestic wastewater) in this region, but there are non-point sources of pollution (septic pits and animal manure storage areas). Stations 2 and 9 were located at 39°20′33″N, 39°28′25″E. In these regions, the stream receives farming area effluent and domestic wastewater from Ovacık. In addition, Stations S2 and S9 are affected by runoff from urban and agricultural activities.

The samples were collected from the nine different stations on Munzur Stream. Stream water samples were collected 0.5 m below the water surface in pre-cleaned 2.5-l plastic bottles. The samples were taken according to the "Sampling and Analysis Methods Communication of the Regulation of Water Pollution Control" and were transported to the laboratory, kept away from light in glass bottles at a temperature of +4°C. Temperature, pH, salinity, ORV, TH, EC, conductivity and dissolved oxygen content were quantified and recorded with a YSI Professional Plus Portable Multi-Parameter device at the time of sampling. Nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), ammonia nitrogen (NH_4-N), phosphorus (PO_4) and TS4956 were measured volumetrically. The total hardness (mg l^{-1}) was determined by the EDTA titrimetric method (WHO/M/26.R1,1999). The water to which the Eriochrome Black T indicator was added was titrated with a standard EDTA solution at a pH of 10, from wine red to blue. The volume of the standard EDTA solution used was recorded, and the total hardness of the water was calculated as $CaCO_3$ mg l^{-1} (Egemen and Sunlu, 1999). Heavy metal analyses (As, Cd, Cu, Mn, Ni, Pb and Zn) were performed with inductively coupled plasma optical emission spectrometry (ICP-OES) in three repetitions.

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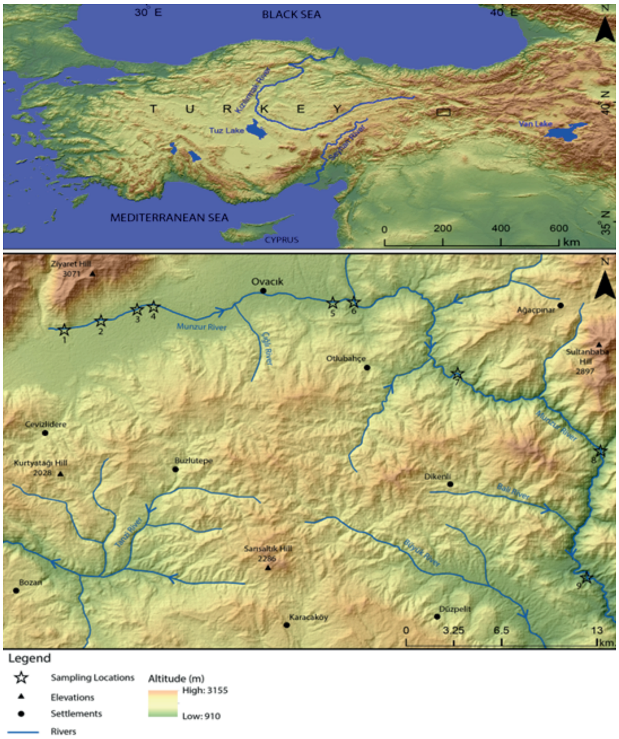

Figure 1

The location of stations on Munzur Stream

2.1. Water quality assessment by WQI

WQI is a simple and convenient approach to determining the overall quality of surface or groundwater and its potability. Assuming that $Wi = wi/\sum wi$ is the relative weight, Wi values (minimum 1 and maximum 5) were assigned to each parameter by considering the significant relative effect of heavy metals on human health and their significance in terms of portability. Table 1 shows that the highest weight applied to Mn, Hg, As, Pb, Cr and Cd, which have the most harmful effects on water quality (Gao et al. 2019).

$$WQI = \sum\left[Wi \times \left(\frac{Ci}{Si}\right) \times 100\right]$$

$$IWQI \frac{1}{N} \sum_{i=1}^{N} WQI$$

Ci is the trace element concentration measured in the water. Si refers to the standard values determined by the WHO (2011) for drinking water. This was evaluated in accordance with WQI by Ramakrishnaiah et al. (2009), in which I (excellent) is an IWQI of ≤ 1.96, II (good) is 1.96 ≤ IWQI ≤ 5.88, III (average) is 5.88 < IWQI ≤ 9.80 and IV (poor) is > 9.80 (Maia and Rodrigues, 2012).

2.2. Assessment of heavy metals (HPI)

The heavy metal pollution index (HPI) proposed by Mohan et al. (1996) was used to estimate the overall pollution status of the water concerning heavy metals and metalloid elements. This method of indexing is based on the weighted arithmetic quality mean. The heavy metal pollution index (HPI) of Kumar and Singh (2018) is calculated with the following equation:

$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} Qi = \frac{Ci}{Si} \times 100$$

Here, Qi represents the sub-index of each metal, C represents the detected concentration value of metals, Si represents the standard values of parameters permitted by the WHO (2011) as drinking water, Wi represents the unit weight of metals and k represents the fixed value of '1'. Generally, pollution indices are developed for classifying water qualities for a specific purpose. The HPI was proposed to classify drinking water. The critical or permissible value was set as 100 (Mohan et al. 1996).

2.3. Heavy metal evaluation index (HEI)

The indicator HEI measures contamination of water by heavy metals. Therefore, it helps in the easy interpretation of water pollution levels (Edet and Offiong, 2002). The HEI is computed using the formula below.

$$HEI = \sum_{i=0}^{n} \frac{HC}{HMAC}$$

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, it is interpreted as medium pollution; and if HEI > 20, it is interpreted as high pollution (Saleh et al. 2018).

2.4. Health risk assessment

Heavy metals from freshwater are taken into 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. This study used the health risk evaluation method recommended by the USEPA (2004), and the toxicological parameters of metals are shown in Table 1 (Wang et al. 2017). The average daily dose (ADD) by direct digestion ($ADD_{ingestion}$) and skin absorption (ADD_{dermal}) were computed using the formulas below (Zeng et al. 2015, Amiri et al. 2012b).

$$ADD_{ingestion} = \frac{C_{water} \times IR \times EF \times ED}{BW \times AT}$$

$$ADD_{dermal} = \frac{C_{water} \times SA \times KP \times ET \times EF \times ED \times CF}{BW \times AT}$$

$ADD_{ingestion}$ is the average digestive and dermal ingestion dose (μg kg^{-1} day^{-1}); ADD_{dermal} is the daily average dose from digestion and through the skin (μg kg^{-1} day^{-1}), C_{water} is the concentration of metals detected in the water (μg l^{-1}), IR is the ratio (2 for adults and 0.64 for children) (l day^{-1}), EF is the frequency of exposure (in this study, 365 days year^{-1}), ED is the exposure time (in this study, 70 days year^{-1} for adults and 6 for children), BW is the average body weight (70 kg for adults and 20 for children in this study), AT is the average life expectancy (in this study, 25,550 days for adults and 2190 for children), SA is the skin area exposed (in this study, 18,000 cm^2 for adults and 6600 for children), ABS_g is the gastrointestinal absorption factor, KP is the dermal permeability coefficient in water (cm h^{-1}), ET is the exposure time during baths and showers (in this study, 0.6 hours day^{-1}) and CF is the unit conversion factor (1 l 1000 cm^{-3}) (Saleem et al. 2019, Xiao et al. 2019).

Ingestion and skin ingestion of heavy metals are both possible carcinogenic and non-carcinogenic risks for children and adults. The non-carcinogenic risk ratio (hazard quotient [HQ]) of the ADD to the reference dose (RfD) was calculated. The hazard index (HI) is equal to the sum of the HQ values and represents all potential non-carcinogenic risks from heavy metals. HQ and HI were calculated with the following formulas.

$$HQ_{ingestion} = \frac{ADD_{ingestion}}{RF_{ingestion}}$$

$$HQ_{dermal} = \frac{ADD_{dermal}}{RF_{dermal}}$$

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

A HQ of < 1 suggests that exposure to any adverse health effects is not likely, while an HI of > 1 indicates that there may be non-carcinogenic effects from heavy metal contact.

Table 1

Toxicological parameters of selected metals used for health risk assessment (USEPA 2004, Wang et al. 2017)

	Kp	$RfD_{ingestion}$ (μg kg^{-1} day^{-1})	RfD_{dermal}	ABSg (%)
Al	1 × 10^{-3}	1000	200	95
Cr		3	0.075	1.3
Mn		24	0.96	6
Fe		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		0.5	0.025	5
Pb	1 × 10^{-4}	1.4	0.42	11.7

2.5. Water quality evaluation of irrigation water

Excessively salty water is toxic to plants and creates a salinity hazard. Therefore, the quality of water used for irrigation is critical, since it affects the soil, plant and human health. SAR is generally considered to be a major index for assessing irrigation water. High sodium content in irrigation water leads to an alkali hazard and reduced soil permeability (Singh et al. 2020). A negative value of residual sodium carbonate (RSC) suggests the incomplete precipitation of Ca and Mg^2. The quality of irrigation water at Munzur Stream was assessed using the parameters SAR, %Na, RSC and MH, which were calculated with the following formulas (Ravikumar et al. 2013).

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

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

$$RSC = \left(CO_3^{2-} + HCO_3 \right) - \left(Ca^{2+} + Mg^{2+} \right)$$

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

2.6. Permeability index (PI)

If mineral-rich water is regularly used for irrigation, the earth's transmittance will diminish. The permeability index is calculated as follows (Falowo et al. 2017):

$$PI = \left(\frac{Na^{+} + \sqrt{HCO_3}}{Ca^{2} + Mg^{2} + Na^{+}} \right) \times 100$$

Factor, correlation and clustering analyses were performed in order to determine the processes occurring in the ecosystem identify the relationship between the calculated values and relate the sources. All stations are excellent according to the IWQI index.

2.7. Data analysis

In the study, descriptive statistical analysis of water quality parameters and whether there is a significant difference between stations was calculated using one-way analysis of variance (ANOVA) ($p < 0.05$). PCI was applied to determine the direction and degree of correlation between parameters, while CA was used to investigate the similarities and differences. PCA was used to reduce the dataset and reveal new factors. All these statistical analyses were carried out with the statistical software programme statgraphics (XVI).

3. Results and discussion

3.1. Physical and chemical features of surface water

Table 2

Toxicological parameters of selected metals used for health risk assessment (USEPA 2004, Wang et al. 2017)

	Units	Mean	Min.	Max	WHO (2011)	TSWQR*
pH		9.01 ± 0.38	8.27	9.45	7.5	III
T	°C	9.15 ± 2.05	5.2	14.8		I
DO		8.33 ± 0.55	8	9.67		I
EC	µS c^{-1}	324 ± 79.5	202.4	467	2500	I
TDS	mg l^{-1}	80.7 ± 44.75	20.3	138.4	600	I
TH		26.6 ± 584	19	34.87	100	I
Salinity		0.16 ± 0.09	0.07	0.34		-
ORP		324 ± 79	202.4	467		-
NO_2-N		0.14 ± 0.0.11	0.002	0.035	0.9	IV
NO_3-N	mg l^{-1}	0.12 ± 0.1	0.03	0.34		I
Si_2		2430 ± 1449	4437	520		I
TP		0.718 ± 0.5	1.87	0.13		III
Ca		142.2 ± 57.6	218.5	54.75	75	
Mg	mg l^{-1}	125.7 ± 39.2	184.2	69.9	50	
Na		4.04	1.85	6.74	200	I
Al		50.5 ± 122.6	4	372	200	I
Cr		9 ± 4.08	2.8	6.6	50	I
Mn		0.04 ± 0.012	0.02	0.04	400	I
Fe		31.55 ± 63.54	10	201	300	I
Co		0.04 ± 0.04	0.02	0.16	50	I
Ni	µg l^{-1}	0.75 ± 0.1	0.2	3	70	I
Cu		0.9 ± 0.72	0.4	2.8	2000	I
Zn		2.07 ± 1.53	0.5	6.0	3000	I
As		0.68 ± 0.65	0.2	2.3	10	I
Cd		6.88 ± 0.60	6.0	8.0	3	III
Hg		0.07 ± 0.02	0.06	0.1		I
Pb		12.44 ± 5.81	2.2	21.5	10	II

* "I" – very good water; "II" – good water; "III" – moderate water; "IV" – poor water (presented as a supplemental material)

The physicochemical parameters of drinking water and irrigation water reveal the natural quality of the water. Table 2 shows the results of the evaluation of the general physicochemical parameters of Munzur Stream, a sensitive water body area, following the WHO (2011) and Turkish guidelines (2016). The change wasn't observed in the colour, smell or taste. The pH value was higher than the values determined as the limits (6.8 and 8.5) by the WHO (2011) and the TSWQR (Rasol et al. 2017, Ali et al. 2017, Arshad and Imran 2017). The pH value was in the 3rd Class according to TSWQR (2016) (Table 1). S5 had the highest pH, while S6 had the lowest value. Munzur Stream is classified as alkaline water. The fact that the river basin has a karstic structure has contributed to this. Surface water temperature and atmospheric temperature changes occur simultaneously with each other. As a result, it was concluded that aquatic life did not reach a temperature beyond dangerous limits in any month of the year. In terms of temperature, S1 was the lowest, while S9 was the highest. In terms of temperature, it has features of Class I water (Kutlu et al. 2017).

EC is an indicator of water salinity. Pollutants may raise the EC value of surface waters (Şener et al. 2017). If the EC value rises, when this water is used as irrigation water, the plants will not be able to compete with the ions in the soil solution, which may lead to a physiological drought (Naseem et al. 2010). High EC values are associated with animal farms, agricultural waste and sewage and discharge waste (Kanhabam et al. 2017). The EC values of Munzur Stream were within the acceptable limit range, according to the WHO (2011). While the lowest EC value was at S1, the highest was found at S7. Additionally, in the study, there was an increase in the EC values along with increased temperature. The EC rises as a result of higher salinity with evaporation (Jiang et al. 2015, Zhang et al. 2016).

In regard to the total dissolved solids, it has been reported that the main difference between the characteristics of lakes and streams is related to the distribution, composition and relative concentration of the substances along the stream. It has also been reported that the geochemical structure of the drainage basin and the seasonal changes in runoff and falling precipitation influence the composition of the streams (Reid 1961, Jain 2002). While the TDS value was the lowest at S1, the highest was detected at S5. According to the WHO and TSWQR, this is in Class I. In this study, it was determined that the sodium concentration (Na) values of Munzur Stream were within the WHO (2011) limits. The highest value in the sampling area was detected at S3, while the lowest one was detected at S1. Cation change is related to the geological characteristics of the solution of lithogenic sodium (Guo et al. 2007, Rafigue et al. 2008). The magnesium concentration was within the WHO (2011) concentration limits. The highest value was observed at the end station of the stream (Station 9), and the lowest value was observed at the origin of the water. Magnesium is the most abundant element in the earth's crust. It is normally found in mineral rocks and enters waters by natural or anthropogenic means. High amounts of magnesium negatively affect the health of humans (Daud et al. 2017, Rasol et al. 2017). According to the SWOR (2016), it has been said that phosphate values do not exceed the limits given in TSWQR Class III. While the phosphate value was the lowest at S8, the highest was found at S3. It is thought to be high as a consequence of the direct delivery of domestic waste without water treatment, along with the fact that the fertilisers used in agricultural areas are phosphate-based.

The main sources delivering nitrites to surface and ground waters are degraded plant and animal waste, domestic wastewater, fertilisers used in agriculture, industrial wastewater and leaching of nitrogen from the atmosphere. In sufficiently nitrified domestic wastewater, when added to the environment it causes high nitrite values. The lowest nitrite amount was (0.005) in the Munzur Stream region. Meanwhile, the highest amount (0.029 mg l^{-1}) at S5 can be attributed to the degradation of organic matter, the sewage waters mixed with the stream in the lower stream region and the domestic waste from the villages in the region. Munzur Stream is a Class 3 at S5 and S6, while it is Class 2 at other stations in terms of the nitrite value according to the classes of intra-continental water resources. On the other hand, according to the WHO, S3, S5 and S6 were higher than the WHO values, and the others were below the upper limit (Belal et al. 2016). Additionally, methemoglobinemia, blue baby syndrome, stomach cancer, abnormal pain, central nervous system disorders and diabetes in animals and humans are caused by a high concentration of nitrates in drinking water (Belal et al. 2016). In the study area, the nitrate level in the water was much lower than the nitrate values of drinking water in many places (Soomro et al. 2017). Additionally, since it is below the WHO (2016) values, it does not pose a danger to the health of humans.

Ammonium, on the other hand, is highly toxic to fish along with pH and temperature (Debels et al. 2005). Ammonium, which is an organic biodegradation product, is a nitrogen product that is directly used by plants. Farmers commonly use ammonium sulphate fertilisers as organic and inorganic fertilisers in agricultural fields (Vega et al. 1998). Irrigation water carries the fertilisers into lakes and ponds. While the ammonium value was the lowest at S1, the highest was found at S3. This results in an excessive increase in the level of nitrogen and phosphorus in the rivers. It also causes excessive proliferation of phytoplankton at the first level of the food chain. The sources of heavy metals of lotic ecosystems can be natural or anthropogenic. The natural sources are generally controlled by the geology and lithology of the region through which the river passes, and include processes such as bedrock weathering and erosion, soil leaching, volcanic eruption and atmospheric precipitation. Anthropogenic sources of these pollutants include mining, metal smelting and refining, landfill leachates, agricultural runoff and industrial and domestic effluent (Ustaoğlu et al. 2020a, b).

According to trace metals and inorganic parameters, Munzur Stream is in the high-quality class except for Cr and Pb (TSWQR, 2016). In terms of concentration, its sources and distribution and whether the heavy metal in the water poses a health risk are very important. The average concentrations of major ions and heavy metals were Ca > Mg > Al > Fe > Pb > Cr > Cd > Na > Zn > Cu > Ni > As > Mn > Co. With the exception of lead and chromium, it is quite good in terms of metals. The water quality of the basin is also in very good condition owing to the absence of factories in the study area, which can lead to industrial pollution. The high level of lead may be due to the geomorphological structure of the Ovacık region and pesticides (Önal et al. 2020). However, all sewage of Ovacık Province flows into the river, and agricultural waste flowing into the river cause pollution, especially during dry periods.

On the other hand, chromium may originate from solid waste leachates other than mining operations. It may mix with water sources and can be found in drinking water due to galvanised pipes. Drainage water and runoff from paddy fields may have possibly resulted in a major increase in Cd and Pb concentrations at some stations (Tokatli and Varol 2022). Agricultural runoff is likely to have increased Cd concentration in places. While the cadmium value was the lowest at Station 1, the highest was found at Station 2. Phosphate fertilisers used in agricultural fields are a major source of Cd (Rutigliano et al. 2019). It is believed that the reason for the high level of these metals may be the agricultural and surrounding mineral deposits, along with anthropogenic waste and rocks (Kumar et al. 2017). Parallels can be seen in the results of this study and other studies (Fatmi et al. 2009, Podgorski et al. 2016). If heavy metal pollution in rivers is not addressed at the right time, it will affect the freshwater ecosystem and human health in the future (Töre et al. 2021). The high level of cadmium in this region may be due to the fault line, as the sampling site is on the Ovacık fault line (Sancar et al. 2019).

3.2. Drinking water quality assessment (WQI)

The Water Quality Index (WQI) was used to determine the water quality of Munzur Stream. To compute the index, the concentrations of pH, EC, Tds, Alk, Th, Cl, DO, Ca, Mg, Mn, Cu, Cd, Pb, Ni, Zn, Cd, Pb, Ni, Zn and As were determined. The WHO (2011) limits were used, as shown in Table 2. The WQI values found in the stream were between 36.61 and 50.14. The water quality parameters did not exceed the recommended limits in any month and or any station. According to these values, Munzur Stream falls into the excellent and good categories in terms of the quality of drinking water. The lowest value was found at Station 1, whereas the highest value was found at Station 3. It has the ideal water feature according to the drinking water quality (Table 4).

3.3. Assessment of heavy metals (HPI and HEI)

The combined effect of the heavy metals in the river was determined by the HPI and the HEI. Global standard values were used in the calculations (WHO, 2011). It was determined that the HPI value exceeded 100 at S1 and S2. The maximum values of HPI were 114.56 and 111.40, which were found at S1 and S2. They may be attributed to gold mine sand domestic waste complex effluents. The HPI at this station was higher than the critical index value of 100, indicating critical contamination with heavy metals. At the other station, the value was calculated as greater than 100, particularly in the downstream parts. This includes S1, S2 and S3. The overall pollution level was low (Saleh et al., 2018). In this study, heavy metal analysis and quality assessment of the drinking water of Munzur Stream in Türkiye were performed. The results show that the HPI values in all samples was less than 100, and thus the drinking water quality was good in terms of heavy metal content (Fig. 2).

Similarly, the HEI values were also calculated to determine the metal (-loid) pollution load in the stream water. The HEI values ranged from 1.81 to 3.90 at the stations. All the values of HEI in both seasons were less than 10, which indicates low metal (-loid) pollution (Fig. 2) (Prasanna et al. 2012, Bodrud-Doza et al. 2016).

Table 3

Health risk assessment for metals in water, for adults and children via ingestion and dermal intake

Metal	Adult	Child	Adult	Child	Adult	Child
	HQIngestion		HQdermal		HI	
Pb	0.029704	0.02970367	0.02970367	0.02970367	0.059407	0.059407
Cd	0.019657	0.000736	0.00137211	0.003036	0.021029	0.003772
Fe	1.8E-05	1.2032E-06	2.0028E-06	4.4317E-06	2E-05	5.63E-06
Cu	0.000366	0.00218424	8.9299E-05	0.000199759	0.000456	0.002382
Zn	3.94E-05	0.00022229	1.5541E-05	3.4386E-05	5.5E-05	0.000257
Ni	4.29E-05	0.000288	0.00016779	3.7125E-05	0.000211	0.000325
Hg	0.000533	3.7333E-05	3.551E-05	7.857E-05	0.000569	0.000116
Total	1.8E-05	1.2032E-06	2.0028E-06	4.4314E-06	0.031368	0.027927

3.4. Human Health Risk Assessment (HQ)

Heavy metals in drinking water are a danger to health and can cause various types of cancers and noncarcinogenic conditions. In this study, the noncarcinogenic/carcinogenic health risk of heavy metals in children and adults was investigated. The ADD (dermal and ingestion), HQ (dermal and ingestion), and HI values were calculated by means of the toxicological values of each metal (Table 3) (USEPA, 2004, Wang et al. 2017). According to the HQ standards, when the HQ value is greater than 1, adverse health effects (noncarcinogenic risk) may occur in humans. Pb level had the highest HQ ingestion values in adults and children (0.029×10^{-6}; 0.029×10^{-5}, respectively) and had the highest HI values (0.05; 0.05, respectively). In the present study, all HQ and HI values were less than 1 in adults and children. As a result, Munzur Stream is safe for public health for residential uses.

Table 4

Temporal and spatial variation values of the irrigation water quality indices of Munzur Stream

Station	WQI	MH	Na%	SAR	PI	RSC	IWQI
S1	37	26.16	43.71	0.01	5.49	-216.22	2.28
S2	46	23.37	51.11	0.01	5.23	251.17	2.86
S3	50	24.48	50.60	0.01	5.29	251.75	3.13
S4	38	26.77	45.96	0.01	5.44	238.75	2.38
S5	37	25.14	49.13	0.02	4.98	-334.89	2.31
S6	36	22.48	53.87	0.03	6.84	-229.35	2.25
S7	40	23.54	52.07	0.02	5.95	-264.60	2.47
S8	40	22.48	53.78	0.04	6.60	-278.37	2.47
S9	44	25.01	48.75	0.04	7.32	-24914	2.75
Mean	40.8	24.38	49.88	0.02	5.91	-257.14	2.25

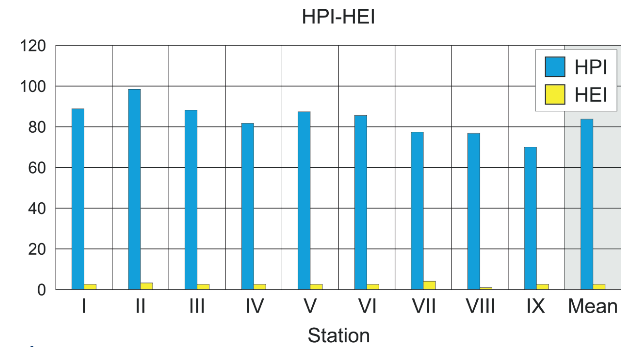

Figure 2

Temporal and spatial change of HPI and HEI values in Munzur Stream

The health risks of surface waters of Munzur Stream were calculated using the USEPA risk assessment models. The intake and skin absorption of seven heavy metals were computed using the HQ (Fig. 2). It is appropriate that these values are not greater than 1. In this study, the HI values for children were greater than those for adults. However, the exposure value for both adults and children was less than 1. The total metal pollution HI is as follows: Pb > Cu > Cd > Pb > Ni > Hg > Fe.

3.5. Assessment of water quality for irrigation

Sodium absorption ratio (SAR): The values of EC and SAR were used to determine the quality of irrigation water. The SAR value of Karaca Dam was 0.05 mEq l^{-1} (Table 4). If the SAR value is > 9, the sodium level is hazardous and the water cannot be used for irrigation (Awais et al. 2017). In this study, the SAR

Table 5

Correlation coefficient matrix

	pH	EC	TDS	Alk	TH	Cl	DO	Ca	Mg	Mn	Cu	Cd	Pb	Ni	Zn	As
pH	1															
EC	0.13															
TDS	0.09	**0.76****														
Alk	0.62*	0.06	**0.88****													
TH	-0.46	**0.88****	0.18	**0.68**												
Cl	-0.07	-0.29	-0.57*	-0.54*	-0.48											
DO	0.18	-0.24	-0.16	-0.18	-0.31	0.65*										
Ca	0.58	0.32	**0.60***	**0.97****	0.24	0.23	0.00									
Mg	0.46	0.29	0.36	0.59*	0.14	**0.88****	**0.67****	0.20								
Mn	**0.89****	**0.76****	0.47	0.50*	0.46	0.52*	0.16	0.34	0.51*							
Cu	0.44	**0.85****	0.11	0.63*	0.49	**0.86****	0.53*	0.56*	0.34	0.01						
Cd	**0.90****	**0.65****	0.03	0.6	0.17	0.08	0.10	0.05	0.13	0.55*	0.32					
Pb	**0.89****	**0.83****	0.12	0.59	0.54	0.36	0.40	0.33	**0.68****	0.23	0.15	0.33				
Ni	0.48	0.48	0.23	0.22	0.26	**0.86****	**0.72**	**0.84****	0.49	0.00	0.00	0.39	0.65*			
Zn	0.51*	0.52*	**0.74****	**0.99****	**0.83****	0.64*	0.63*	0.41	**0.75****	0.25	0.01	**0.85****	**0.91****	0.08		
As	0.50*	**0.99****	0.09	0.38	0.40	**0.67****	0.30	0.29	0.51	0.01	0.0	0.4	0.01	0.02	0.10	1

value was within the prescribed limits. High SAR values might lead to lower salinity values, which would result in a decrease in the calcium and magnesium levels. These are essential elements for the growth of plants (Vasantvigar et al. 2010, Rasool et al. 2016). The study shows that Munzur Stream is suitable for irrigation (Table 5).

Sodium percentage (%): Several researchers have classified water on the basis of the sodium percentage (Srinivas et al. 2017; El Aziz, 2017; Islam et al., 2017). In this study, the average percentage of sodium was found to be 50% (Table 4). According to Table 4, the dam water was in the permissible water quality category. The use of fertilisers in agriculture might result in the presence of a high proportion of sodium in the water. A high level of sodium (9%) in the land has adverse effects on the tightness, ventilation and texture of the soil (Singara et al. 2014). Plants that are subjected to water containing high amounts of sodium show a low fertility rate because sodium affects the osmotic pressure between the soil and the plant. Therefore, it blocks the plant's mineral uptake from the soil (Nasseem et al. 2010).

Permeability index (PI): The presence of excess minerals such as Ca, Mg, Na and HCO_3 in water affects the permeability of the soil. The long-term agricultural productivity is also greatly affected by this (Sing et al. 2008). The PI has a negative effect on the fertility of the soil (Obiefuna and Sheriff 2011). The use of water rich in minerals inhibits the growth of seedlings by blocking ventilation in the soil. The Permeability Index was developed by Doneen (1975) to classify water. According to this index, water that has a PI of > 75 is in the first class, a PI of 25–75 denotes second-class water and a PI of < 25 is in the third class (Doneen 1975, Raju et al. 2011). In this study, the PI was found to be 5.73. Thus, the region has first-class water (Table 4).

To determine the risk, the value of RSC was calculated; the indicator was in the range of -21.6 to 33. All the spatial and temporal parameters contribute to good water quality (RSC < 1.25) of irrigation water. In a study conducted on Munzur Stream, the irrigation water for all stations was reported to be excellent, good and suitable in terms of SAR, Na% and MH, respectively (Özer and Köklü 2019). The IWQI index of all stations was calculated, and the water can be used as irrigation water.

Assessment of contamination sources between physicochemical parameters of Munzur Stream: Pearson's correlation analysis was performed to determine the trend and correlation between the physicochemical parameters, as presented in Table 6. In this study, there was a significant positive relationship between the basic parameters (pH, EC, TS, Alk, TH, Cl and DO). The TDS value and alkalinity in Munzur Stream were in a negative direction. Manganese, cadmium and lead showed a strong positive correlation. The contamination of these pollutants in the water may be the result of agricultural activities, domestic wastewater and aquaculture activities.

Principal Component Analysis (PCA) is helpful, as it contracts the dimensions of multivariate data to help in understanding the problems and their contributing factors. The size of the data matrix of PCA was 9 samples and 15 variables. In this study, only five principal components (PCs) were found to describe 92.28% of the total variance in Munzur Stream (Tables 5 and 6). In Munzur Stream, 33.17% of the variance of the total dataset is explained by PC1, 26.27% of the variance by PC2 and 14.58%, 10.14% and 8.11% by PC3, PC4 and PC5, respectively. The factor loadings are generally grouped on the basis of their absolute loading values. Absolute loading values of > 0.75 are considered 'strong', values of 0.75–0.50 are considered 'moderate' and the range of 0.50–0.30 is considered 'weak' (Liu et al. 2003, Wang et al. 2017, Kumar et al. 2018). PCA was carried out to trace the origins of heavy metals and element concentrations in natural waters.

Table 6

Varimax rotated component matrix for selected variables

	PC1	PC2	PC3	PC4	PC5
pH	0.07	0.21	-0.43	-0.14	0.28
EC	0.10	-0.31	0.42	-0.02	0.03
TDS	0.30	-0.05	-0.42	-0.07	-0.08
Alk	0.19	-0.17	0.29	-0.47	0.27
TH	0.24	-0.32	0.29	-0.01	-0.04
Cl	-0.15	0.31	0.23	0.40	-0.05
DO	0.031	0.40	0.22	-0.04	-0.28
Ca	-0.01	-0.42	-0.18	0.27	0.12
Mg	0.19	-0.18	0.01	0.54	-0.29
Mn	0.33	0.17	0.21	0.11	-0.05
Cu	0.39	0.15	-0.04	0.13	0.09
Cd	0.25	-0.28	-0.27	0.11	-0.14
Pb	-0.27	-0.07	0.07	0.29	0.54
Ni	0.36	0.06	0.10	0.10	0.36
Zn	0.20	0.23	0.00	0.24	0.41
As	0.40	0.16	0.01	-0.08	-0.09
Eigenvalues	5.30	4.20	2.33	1.62	1.29
% of variance	33.17	26.27	14.52	10.14	8.11
Cumulative	33.17	59.44	74.03	84.17	92.28

4. Conclusion

To determine the water quality of Munzur Stream, which provides drinking water and irrigation water to the area, samples were taken over 24 months from nine stations and water quality analysis was carried out. The water quality in Munzur Stream was assessed with the water quality index and principal component analysis. In this research, the WQI indicated excellent water quality of the stream. The PCA revealed that the factors explained 92.2% of the total variance. The water quality was found to be very good according to TSWQR standards in terms of T, DO, EC, TDS, TH and NO_3, but medium class in terms of pH, NO_2 and TP. This suggests that there are nutrient inputs from the surrounding domestic and agricultural areas that could damage the health of the ecosystem. The limit values for Cd and Pb were exceeded. The concentrations of cadmium in the surface water along the sampling sites in Munzur Stream change seasonally, yielding higher concentrations during wet events due to stormwater runoff. Elevated concentrations of cadmium in the rainy season may be due to agricultural and mining runoff. The values of the stream basin were investigated to clarify whether these high concentrations of heavy metals are due to natural geological structure or anthropogenic factors, Heavy metal pollution index (HPI) and heavy metal evaluation index (HEI) were used for these. According to these results, they were found to be risk-free toxic substances. According to the HQ or HI results, no dangerous toxic substance was found in the Ovacık area (Ramsar site). Munzur Stream was recorded as the most risk-free habitat for the basin. The results of the present study reveal that the water quality parameters are within the WHO limits as well as national limits. Additionally, the study is expected to be a pioneer for further research on the risk assessment of heavy metals in the aquatic environment of Tunceli Province, where there is very limited information. Clean freshwater resources are an important environmental phenomenon. They need to be protected in terms of human consumption and the availability of quality water for future generations. The stream is located within the borders of Tunceli Province and is used commercially as drinking water and for mines, agriculture and livestock operations. The quality of this water was analysed with the water quality index and multivariate statistical approaches.

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